UDC 662.87

Effect of Mechanochemical Activation on Coal Combustion in Torch

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(Received April 17, 2009; revised August 4, 2009)

Abstract

Thermooxidative destruction and torch combustion of fine coal obtained by mechanochemical treatment in high-strain activator mills of different kinds was studied. Activation in mills causes a decrease in the size of coal particles, increase in the reactivity of fine coal, and acceleration of combustion in torch. The effect of combustion acceleration is essentially dependent on the type of mechanochemical treatment. In the case of the close particle size distribution, activation under the free shock conditions is more efficient: the combustion torch turns out to be close to the combustion torch of gas fuel. In comparison with coal prepared under the conditions of constrained shock, fine coal prepared under the free shock conditions burnt immediately after preparation is characterized by higher (by 20 %) oxidation rate under non-isothermal conditions, while the maximal temperature of the process changes from 560 to 780 °C. The effect is reversible; within 2 h it remains essential for the interaction of coal particles with atmospheric oxygen under non-isothermal conditions.

Key words: coal, combustion, torch, activation

INTRODUCTION

Enhancement of the role of coal in the energy balance of the country and the world puts forward the problem to improve the existing technologies and develop new ones in power engineering. Because of the drop of the quality of mined coal, much attention is paid to the new technologies of its combustion and gasification. Coal combustion in coal-dust flame is most widespread in power engineering in Russia. Coal of relatively high quality is usually used, for example coal from the Kuznetsky and Kansk-Achinsk deposits. The use of low-quality non-coking coal brings about the problems connected with the necessity to stabilize the torch combustion.

An increase in the reactivity of coal and improvement of its consumer merits (up to the level of gas or black oil) is urgent for innovations of different scales. For example, the ignition of coal-dust boilers is usually performed using a torch of gas or black oil. The use of activated coal for ignition can be implemented with available mechanochemical equipment with the productivity of 0.1–1.0 t of product per hour.

The kinetic characteristics of the heterogeneous reaction of coal dust with oxygen

$C + O_2 = CO_2$

to a substantial extent determine the rate of ignition and combustion of coal-dust torch, which is important for the construction of combustion chambers in boiler units. The kinetics characteristics of combustion are strongly dependent on the type of coal and on the method of its grinding.

Deformation causes changes in the structure of the high-molecular component of coal, which is accompanied by weakening of intra- and intermolecular bonds and the corresponding increase in the free energy of the solid substance. A decrease in the energy barrier of the reactions participated by deformed substances is observed. It is known that the mechanical action on the complicated structure of coal causes the rupture of some chemical bonds with the formation of free radicals that accelerate the development of various chemical reactions [1].

Mechanical actions of different types may lead to diverse effects. The action of uniaxial pressure causes orientation of graphite networks in coal. The action of changing mechanical load, for example during grinding high-molecular organic substances, leads to chemical transformations with bond rupture and destruction of macromolecules. Fine (1–10 μm) grinding causes changes in the composition and the number of functional groups detected in the structure of coal, as well as the composition of evolved gaseous products, the solubility in organic solvents increases, the degree of the transformation of the organic mass of coal into liquid products during hydrogenation increases [2].

The consequences of the mechanical treatment of coal in the majority of cases were studied using laboratory vibratory mills with periodic action, low intensity and long time of mechanical treatment, while the investigation of the chemical activity of mechanically activated coal was carried out for reactions in liquid medium. The authors of [3] studied the effect of vibratory grinding on the physicochemical properties of coal, its reactivity in alkaline medium with respect to the oxidizer – $KMnO_4$. A substantial increase in the reactivity of treated coal in comparison with the initial samples was established, especially for brown coal. The authors of [4] studied the effect of the conditions of vibratory grinding on the products of oxidation of brown coal. It was shown that vibratory grinding involves destruction of humic acid, which is accompanied by the changes of their fractional and elemental composition, a decrease in the average molecular mass and changes of the content of oxygenated functional groups.

The conditions of coal oxidation in torch embodied in the present work are substantially different from the conditions under which previous investigations were performed: fine activated product enters the combustion zone immediately after the treatment, within less than 1 s. The goal of the work was to determine the features of oxidation of mechanochemically activated coal under the conditions of combustion in torch directly after mechanical activation, and the use of the effect in the technology of coal combustion.

MECHANOCHEMICAL ACTIVATION OF COAL FOR INTENSIFICATION OF COMBUSTION

Investigation of the changes in physicochemical characteristics of coal treated in the mills with increased intensity of mechanical action (planetary, vibratory mills, or disintegrators) was carried out using brown coal of 2B grade from the Kansk-Achinsk deposit. Anthracite of ASSh grade from the Listvyanskoye deposit (Novosibirsk Region) was used in some experiments for comparison.

Under intense mechanical action on coal substance in high-energy devices, not only rapid decrease in particle size and increase in specific surface occur but also enhancement of the reactivity of brown coal in the processes of subsequent thermooxidative destruction in the air under non-isothermal conditions.

The experimental thermogravimetric curves obtained at different heating rates (5 to 20 °C/min) were processed with the help of the Model free software. This allowed us to represent the kinetics of oxidation as a set of activation energy values (E) for each experimental point (2 to 98 % transformation).

The data on activation energy for different values of the degree of decomposition (α) of coal substance (Fig. 1) provide evidence of substantial differences in the kinetics of thermooxidative destruction of the initial and activated samples of brown coal. All the curves of the dependence $E = f(\alpha)$ for activated samples shifted to smaller E values; the largest decrease was detected for the low-temperature part of decomposition (to the degree of transformation of $\alpha = 0.5$, 260–400 °C).

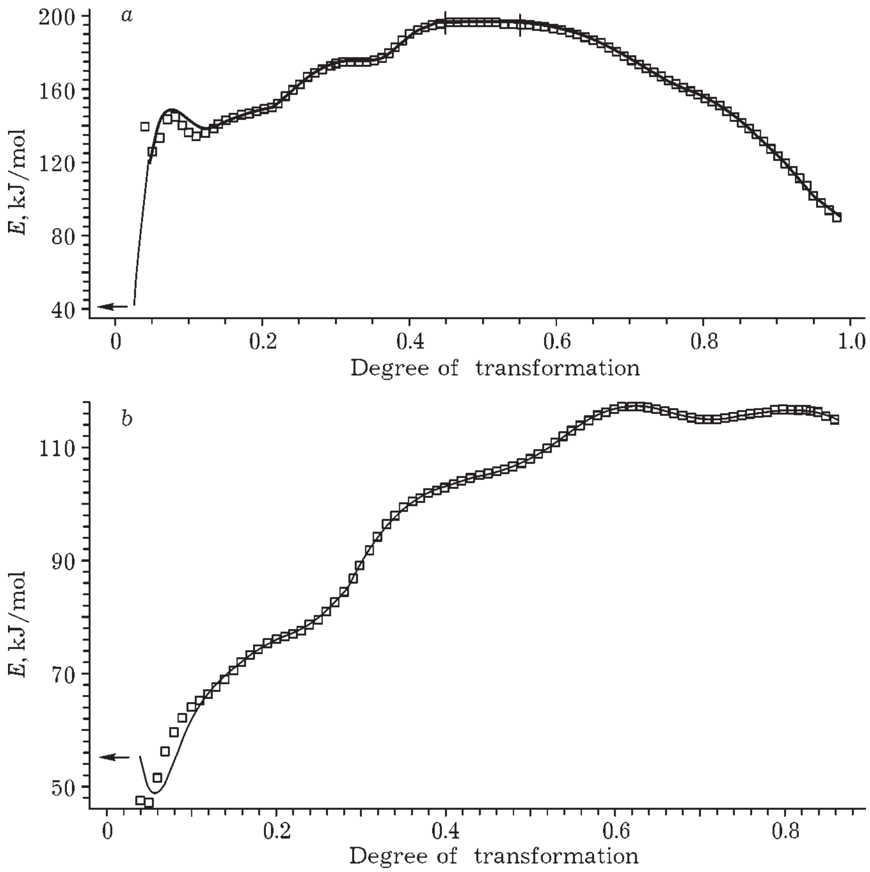

Fig. 1. Changes of the activation energy of thermooxidative destruction of brown (*a*) and mechanochemically activated (*b*) brown coal.

According to the data shown in Table 1, within the range of α values up to 0.5 $\Delta E_1 = 70$–90 kJ/mol, and the value of ΔE gradually decreases with further increase in degree of transformation. So, mechanical activation of brown coal under the conditions of intense mechanical action leads to an increase in its reactivity, which is exhibited as a substantial decrease in the activation energy of the process of thermooxidative destruction.

The observed change of the activation energy of oxidation can be due either with the change of coal particle size or with the mechanochemical activation of coal. Comparative investigation of the distribution of coal particle over sizes and a comparative analysis of the results of combustion of the samples obtained under different conditions but possessing close particle size distribution were carried out. Analysis of particle size was performed with the

TABLE 1

Data on the difference between the values of activation energy for initial and activated coal and fractions (d < 1.4 g/cm^3) in thermooxidative destruction

ΔE	Degree of transformation (α)																			
	0.01	0.02	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.45	0.50	0.55	0.60	0.65	0.70	0.75	0.80	0.85	0.90
ΔE_1	–	–	79	73	72	73	84	76	76	88	91	89	83	76	70	61	49	39	27	13
ΔE_2	81	68	54	48	79	66	43	36	35	27	19	21	25	16	11	11	17	7	–	–

Note. $\Delta E_1 = E(\alpha) - E^*(\alpha)$, where $E(\alpha)$ and $E^*(\alpha)$ are activation energies for the initial and activated coal samples for definite degree of decomposition (α), respectively; ΔE_2 – the same for the lightweight coal fraction (d < 1.4 g/cm^3).

TABLE 2

Content of the particles of different sizes after the mechanical treatment of coal under different conditions, %

Grinding conditions	Particle size, μm				
	<2	2–20	20–50	50–100	>100
Initial sample	7.6	9.2	9.3	73.9	
Vibrocentrifugal mill (VTsM-7), 90 s	2.3	28.5	27.4	21.9	19.9
Disintegrator	6.2	45.9	39.6	7.5	0.8
Planetary mill (TsPM), 45 s	17.0	66.4	13.9	2.7	
The same, 5 min	14.6	55.9	23.2	5.1	1.2
The same, 15 min	10.1	48.7	29.7	8.0	3.5
The same, 30 min	12.7	53.3	27.8	5.3	0.9
Lightweight fraction of initial coal (d < 1.4 g/cm^3)	2.1	19.3	16.0	19.8	42.8
Lightweight fraction, ground (TsPM), 45 s	15.0	47.9	25.9	8.5	2.7

help of Microsizer 201 instrument (Nauchnye Pribory Co., St. Petersburg) (Table 2).

INVESTIGATION OF THE COMBUSTION OF DISPERSED COAL AT THE STAND WITH THE THERMAL POWER UP TO 1 MW

To carry out mechanical activation of coal, the stand was supplemented with a vibrocentrifugal activator mill (VTsM-7) with constrained collisions (acceleration of milling bodies – balls – was 120 m/s^2, the diameter of steel balls was 12 mm) or with a disintegrator type mill with free collisions (the frequency of disc rotation 6000 rpm). Coal combustion was studied in the non-isothermal mode during combustion in torch.

The stand was constructed to embody the entire technological cycle of the combustion of dust-gas fuel (Fig. 2). It includes a precombustion chamber with furnace extension, the shaft of coal afterburning, and a system of dust and gas purification. The stand is equipped with photometric, multicomponent gas analyzing and temperature devices allowing one to perform real-time diagnostics of the process status.

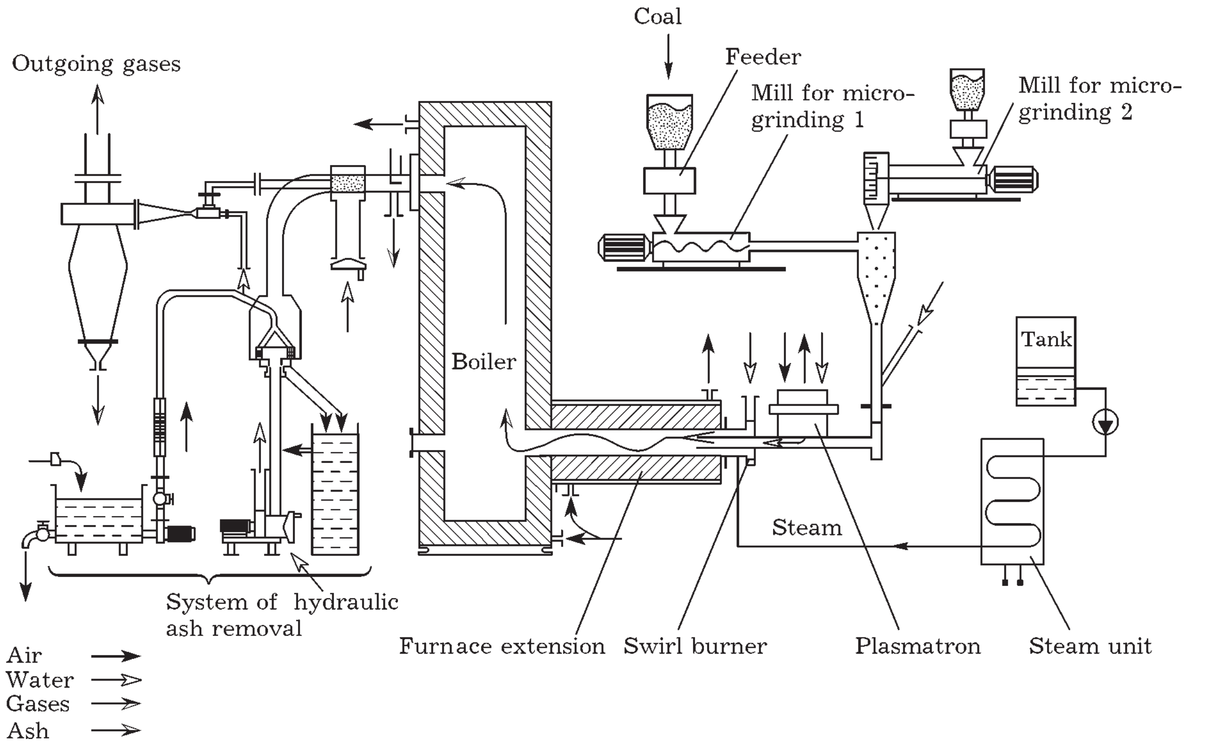

Fig. 2. Test stand for the investigation of combustion of dispersed coal.

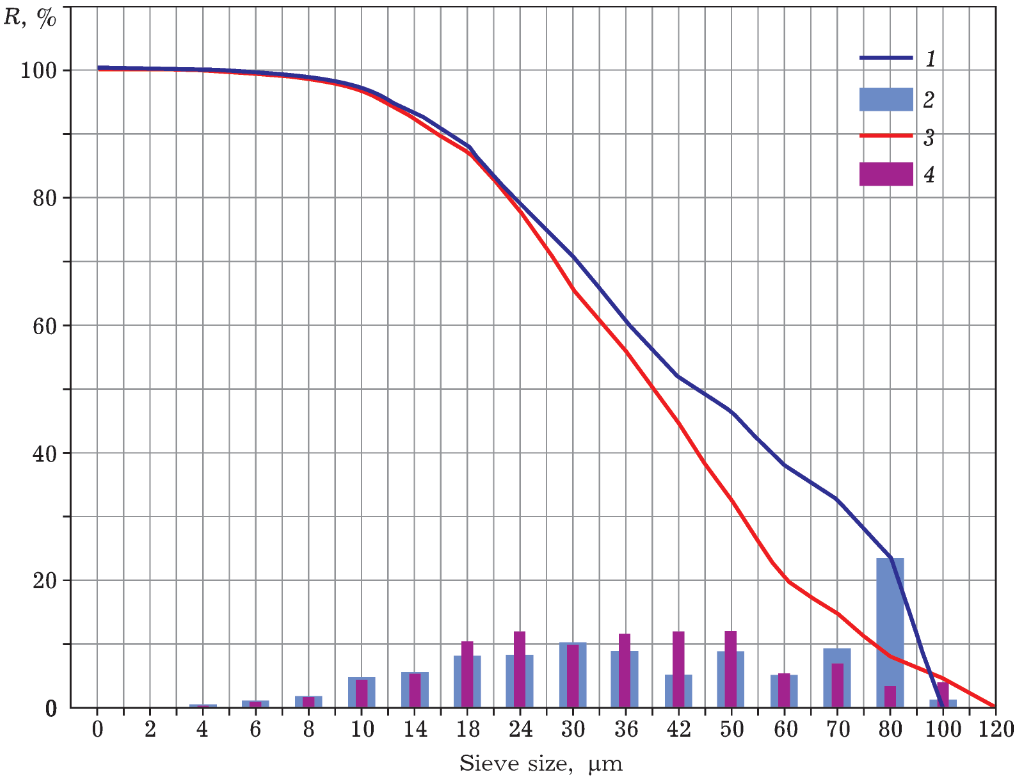

Fig. 3. Sizes of the particles of brown coal of B-2 grade and the residue at the sieve after grinding with VTsM mill and the mill of disintegrator type: *1* – R_{VTsM}, *2* – VTsM, *3* – R_{dis}, *4* – disintegrator.

Lighting is performed within 1 min with a standard ignition spark methane device or plasmatron with a power up to 15 kW. Then the ignition device is switched off, and combustion of dust-coal fuel is performed in the autothermal mode. The time within which particles get into the flame after mechanical treatment is about 1 s.

Figure 3 shows the results obtained in the measurements of the size of brown coal particles after milling with two types of mills. One can see that the average size of particles is approximately the same and is equal to 40–42 μm. The surface available for reaction is almost identical in both cases. Therefore, the rates of ignition and combustion of dust coal torch must be identical. However, it was established as a result of experiments that the rate of ignition and combustion of the dust suspension after the treatment in disintegrator mill with free collisions is substantially higher than that after grinding in a vibrocentrifugal mill with constrained collisions (Figs. 4, 5).

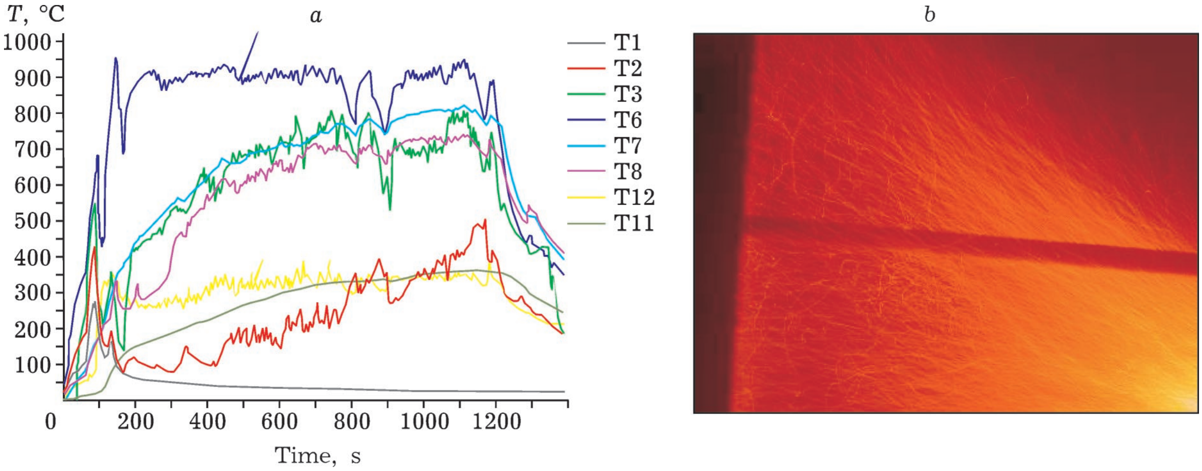

Fig. 4. Temperature dynamics of the combustion of brown coal (*a*) and its torch combustion (*b*) after grinding in the vibrocentrifugal mill with the achievement of the autothermal model of combustion. Here and in Fig. 5: T1–T12 – temperature curves for the corresponding thermocouple; thermocouples are numbered in the order of increasing distance from the beginning of the torch.

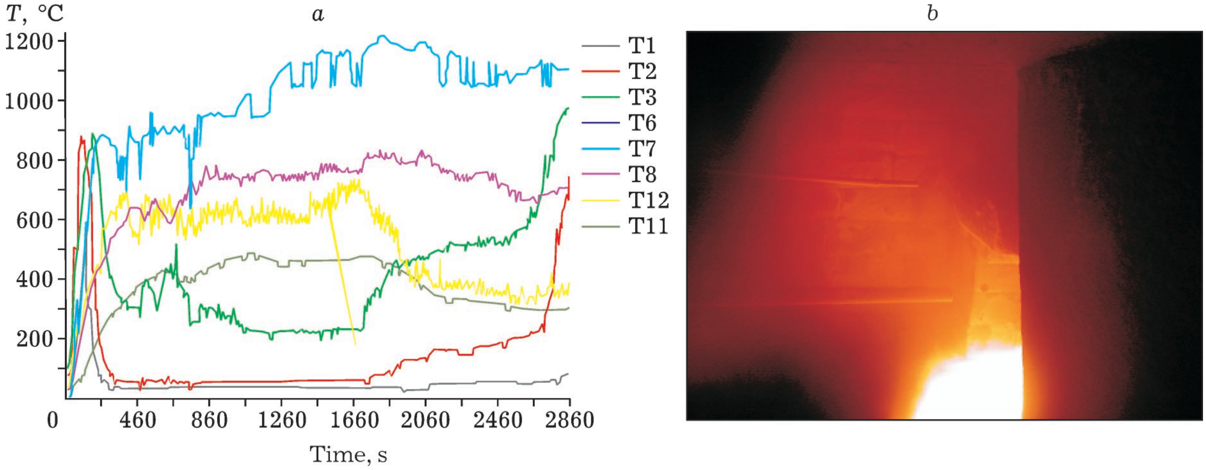

Fig. 5. Temperature dynamics of the combustion of brown coal (*a*) and its torch combustion (*b*) after grinding in the mill of disintegrator type with the achievement of the autothermal combustion mode. For designations, see Fig. 4.

It was discovered in the investigation of the combustion of mechanochemically treated coal samples that, for other parameters kept constant, the torch parameters, namely the size and distribution of temperature zones, are strongly dependent on the type of equipment used to perform mechanical treatment. In particular, for treatment to approximately the same dispersion degree in activator mills with constrained collisions (VTsM) and in the mills with free collisions (disintegrator) the torch parameters turned out to be different. In the case of grinding with free collisions, combustion in torch proceeds in a substantially stronger localized region of the torch.

So, it was demonstrated that mechanochemical activation in the mill with free collisions leads to obtaining a more reactive product than the treatment in the mill with constrained collisions.

Torch parameters are the major characteristics determining the design of heat generators. In this connection, the investigation of the physicochemical reasons of the discovered phenomenon is urgent. On the other hand, the development of the method to govern the torch parameters on the basis of the discovered phenomenon opens novel technological outlooks.

REASONS OF THE EFFECT OF MECHANICAL ACTIVATION ON THE NON-ISOTHERMAL KINETICS OF COAL COMBUSTION

Earlier, an increase in the chemical activity of coal under mechanical load was thought to be due to dispersion, the formation of new pores and opening of formerly unavailable ones. In addition to an increase in the specific surface, a number of other physicochemical phenomena are observed: rupture of chemical bonds in the organic substance of coal, change of the molar mass distribution, the formation of soluble products and volatile substances, free radicals, as well as the appearance of intense electr5ic fields, electron emission [5]. The major practically significant phenomena during the mechanical treatment of coal are considered to be connected with chemical transformations [6–8].

Experimental studies of the effect of the type of mechanical treatment on the interaction of coal with atmospheric oxygen under non-isothermal conditions were performed with STA 449C thermoanalyzer (Netzsch, Germany) in air flow. Temperature was raised from 28 to 800 °C at a rate of 10 °C/min. With an increase in heating time, we recorded the temperature of the reactor, the loss of sample mass (TG), heat flow (DSC). The heat flow from the sample is expressed in microvolts per milligramme, which is determined by the design of the measuring cell of the standard set-up for thermal analysis. The walls of the measuring cell are equipped with thermocouples measuring thermoelectromotive force arising with heat absorption by the sample or heat emission from it.

The samples were preliminarily treated using the equipment incorporated into the stand, under the above-indicated conditions. Coal was ground to the average particle size of about

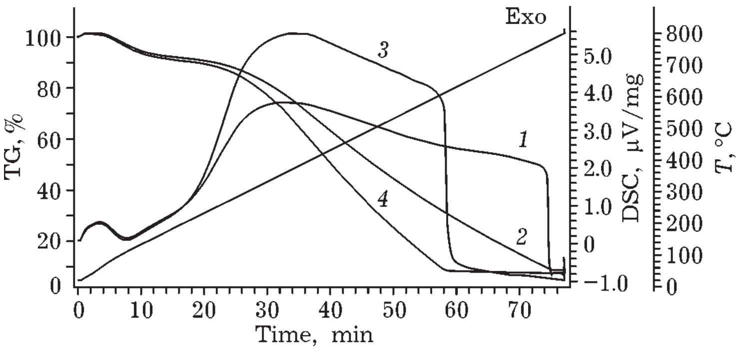

Fig. 6. Thermoanalytical data (TG, DSC) for brown coal samples: *1*, *2* – 2 h after mechanical treatment; *3*, *4* – after 48 h; the straight line: temperature change, changing rate: 10 °C/min.

40 μm as a result of treatment in the vibrocentrifugal mill or in the disintegrator.

It was discovered that the thermal data for the samples with close particle size distribution, analyzed after they were kept for 48 h after mechanical treatment, were close to each other in all the cases.

Substantial differences are observed for the samples analyzed within a short time after mechanical treatment. The results of the analysis of brown coal after treatment in VTsM and storage for 2 and 48 h are shown in Fig. 6. One can see that the sample freshly treated under the constrained collision conditions looses its mass during heating in the air slower than the sample stored for 48 h after treatment; the limiting minimal mass is achieved within 75 and 59 min, respectively. Combustion rate decreased from 1 to 0.79 rel. units. The limiting mass of the samples corresponds to the content of ash (inorganic substances). The maximal temperature of samples after treatment in VTsM with subsequent storage for 2 and 48 h during oxidation with atmospheric oxygen is 560 and 780 °C, respectively.

The general appearance of the TG curves provides evidence that decomposition proceeds in two main stages. Low-temperature decomposition characterized by heat absorption and endoeffect with the minimum at the eighth minute of decomposition at a temperature about 140 °C and high-temperature decomposition with stronger pronounced exoeffect at the 34th minute are distinguished. Low-temperature endoeffects are usually related to the evolution of various gases from coal, while the exoeffect at high temperatures – with coal oxidation.

So, we discovered that, unlike for treatment in disintegrator (mill with free collisions), the treatment of brown coal in the ball planetary mill with constrained collisions leads to an increase in the time of combustion and a decrease in the maximal temperature of combustion of the sample. However, this phenomenon is temporary, and it is not observed in the case when the coal samples were kept for 48 h after treatment. In the case of anthracite, the phenomenon is exhibited substantially weaker.

The physicochemical reasons of an increase in combustion time for coal after mechanochemical treatment in the mills with constrained collisions may be considered on the basis of the notions of coal structure [9]. The treatment of coal leads to the formation of a denser, less reactive framework composed of aromatic nuclei and weakly bound low-molecular substances. The recovery of the thermochemical properties of coal with time, observed within 48 h after mechanical treatment, points to the fact that the transformations occurring during the mechanical treatment of coal in the mill with constrained collisions are reversible. These transformations may be desorption and adsorption of low-molecular volatile substances. Under the action of mechanical strain, the molecules of volatile substances may migrate into the closed pores of coal; after mechanical treatment they may diffuse to previously left adsorption centres on the surface of aromatic nuclei. An alternative explanation of the effect may be connected with the formation of radical defects in the mineral part of coal, their relaxation and the effect of the defects of radical nature on coal combustion.

The discovered phenomenon must be taken into account when designing the devices for gasification and combustion of fine coal, in particular devices for mazut-free ignition of thermal boilers.

CONCLUSIONS

1. Mechanical treatment of coal in high-strain activator mills of different types leads to a decrease in coal particle size and acceleration of the combustion of fine coal in torch; the effect is essentially dependent on the type of mechanical treatment.

2. In the case of the close particle size distribution, mechanochemical activation under the conditions of free collisions is more efficient: combustion torch turns out to be close to the torch of the combustion of gas fuel.

3. Comparative thermal studies of coal samples treated in the devices of different types shows that in comparison with the fuel obtained under the conditions of constrained collisions, the fuel obtained under the conditions of free collisions when burnt immediately after treatment is characterized by the higher (by 20 %) oxidation rate under non-isothermal conditions, and the maximal temperature of the process increases from 560 to 780 °C.

4. The effect is reversible; during 2 h it remains essential for the interaction of the particles with atmospheric oxygen under non-isothermal conditions; this effect disappears within 48 h.

5. The discovered effect must be taken into account when designing modern power engineering devices for the combustion of dispersed fuel in which the particles get into the torch within 1–3 s after mechanical treatment.

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