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Coal-Water Systems: Conversions of the Organic Constituent of Brown Coal, Combustion Characteristics

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Abstract

The composition of the products of mechanical treatment (MT) of a mixture of brown coal and water (1 : 1) at MT temperature of 80, 120, 160, 200 °C was investigated. Mechanical treatment of the water – coal system was carried out with the help of AGO-2 installation in the atmosphere of argon. Mechanical treatment at increased temperatures promotes the destruction of the organic component of brown coal. It is demonstrated that an increase in MT temperature causes a decrease in methane yield and an increase in the yield of bitumoid. The content of resins and asphaltenes in bitumoids was determined to increase with an increase in MT temperature. The ignition and combustion characteristics of the products of mechanically treated coal-water mixture were studied.

Keywords: brown coal, coal-water systems, mechanical treatment, temperature, composition, combustion

INTRODUCTION

The strategy of energy development in Russia [1] implies extensive use of solid fuel in the production of energy through direct combustion at thermal stations (TS). The majority of thermal and heat-and-power complexes both in Russia and abroad use powdered coal as the fuel raw material. The production of coal requires substantial energy consumption and the application of expensive equipment.

The efficiency of TS may be enhanced using water-coal fuel (WCF) instead of coal. The heating value of WCF is 15.5–19.7 MJ/kg. This is substantially lower than the corresponding values for black coal and anthracite (27–28 MJ/kg) [1] but higher than the value for brown coal (13 MJ/kg). However, in comparison with coal, WCF is cheaper and more ecologically friendly as a fuel. The technologies of production, transportation and direct combustion of coal-water suspensions without coal dehydration and drying are a relevant and modern direction in the development of heat and power engineering [2]. The basis for the suspension fuel may be non-energy brown coal, wastes from coal mining and processing, the residual products of petroleum processing. Water-coal fuel possesses all characteristics of liquid fuel and may replace mazut in small boiler houses [3]. To prepare WCF, it is necessary to use high-voltage installations (mechanically activating mills, cavitators of different design, rotor grinders, *etc.*), which allow obtaining stable suspensions containing micrometer-sized coal particles. Mechanochemical destruction of coal particles in the aqueous phase is accompanied by the formation of a binary system characterized by increased surface energy due to the presence of a large number of atoms in the excited states keeping not less than one unpaired electron at the external energy level [2]. Mechanical treatment (MT) changes the rheological properties of WCF. It was revealed [4] that the application of a rotor apparatus of flow modulation causes a decrease in the viscosity of WCF and an increase in its sedimentation stability.

The conditions of MT, in particular the medium in which grinding is carried out and the process temperature, affect the yield and composition of the soluble fractions of coal. Coal grinding in a solvent directly in the cylinders of a vibratory mill causes an increase in the yield of extractable substances [4]. For example, for gas coal, the total yield of benzene extract increases by a factor of 7.9, while vibrational grinding of this coal in the air followed by extraction with benzene causes an increase in the yield of the extract by a factor of 2.4 [5]. It was demonstrated [6] that the yield of bitumoids increases with an increase in the temperature of MT of coal.

Investigation of the mechanism of ignition and combustion of WCF has been considered in many works [7–9]. It was established [7, 8] that the kind and mark of coal have a substantial effect on the dynamics of fuel ignition. For instance, the drops of WCF from brown coal ignites 2 times faster than the drops of WCF from black coal. This is connected with the higher content of volatile substances in brown coal. Temperature-time characteristics of ignition and combustion of WCF were studied in [8]. The major factors defining the efficiency of WCF combustion were revealed. The regularities of the effect of the content of water phase and mineral admixtures were studied along with the effect of the size of fuel drops [9].

It is assumed that MT of a mixture of coal with water at increased temperature would substantially enhance the yield of extractable substances, change the composition of the resulting suspension and affect the nature of ignition and combustion of WCF. In this connection, the goal of the work was to study mechanochemical transformations in a mixture of brown coal and water during MT at different temperatures (80–200 °C) and the characteristics of the combustion of resulting products.

EXPERIMENTAL

The object of investigation

The object of investigation was brown coal from the Barandat deposit in the Kuznetsk coal basin, which is typical humus, vitrinite coal with a dull lustre, high density (coalification degree R_0 0.4 %, ash content A^d 7.32 %, the yield of volatile substances V^{daf} 46.2 %).

Conditions of mechanical treatment

Mechanical treatment of water-coal composition was carried out with the help of AGO-2 installation in the medium of argon at the cylinder rotation frequency of 2220 min^{-1} (the acceleration of milling bodies was 1000 m/s^2), the time of MT 5 min. The required temperature was maintained with a VT8-2 thermostat (heat carrier was siloxane oil PMS-100). A portion of dry coal (10 g) was placed in the reactor, and 10 cm^3 of water was added. The chosen mass ratio of coal to water (1 : 1) allowed us to carry out MT of coal in saturated water vapour. The free space in the reactors was filled with argon. To heat the reactors to the necessary temperature, we used a VT8-2 thermostat (Russia), polysiloxane oil PMS-100 was used as a heat carrier. After reaching the required temperature by the heat carrier, the reactor was kept in the thermostat for 15 min, and then MT was carried out.

Coal with particle size 3–5 mm was used in experiments. The granulometric composition (sieving) of coal after grinding during MT was as follows: fraction <0.1 mm – 86 %, fraction 0.1–0.5 mm – 13 %, fraction 0.5–1 mm – 1 %. Deviation of the composition of fractions for the resulting samples did not exceed 15 %.

Chromatographic analysis of gases

Analysis of gas composition was carried out with the help of Kristall 5000.2 (Russia) equipped with thermal conductivity detectors (TCD) and a flame ionization detector (FID), columns with molecular sieves 13X (carrier gas Ar) and Porapak R sorbent (carrier gas He).

Determination of the component composition of bitumoid

Bitumoid from mechanically treated mixture was extracted with chloroform. The content of asphaltenes, resins and oils in the bitumoid was determined. To determine asphaltene content, bitumoid was treated with hexane in 40-fold excess according to the procedure described in [10]. Maltenes obtained after deasphalting were deposited on ASK silica gel, which was then loaded into Soxhlet apparatus. At first, oils were extracted with a non-polar solvent (n-hexane), then resins were extracted with a mixture of polar solvents (benzene/ethanol = 1 : 1).

IR Fourier spectrometric analysis

Infrared (IR) spectra of resins and asphaltenes were recorded in the region 4000–400 cm^{-1} with the help of an FT-IR spectrometer Nicolet 5700 (Thermo Electron Corporation, USA).

To compare the data of IR spectra of resins and asphaltenes of MT products, characteristic absorption bands were used: 1710 cm^{-1} (vibrations of the bond of carbonyl group C=O); 1600 cm^{-1} (vibrations of C=C– bond of aromatic fragments); 720, 1480 cm^{-1} (vibrations of CH_2– and CH_3– methyl and methylene groups in paraffin hydrocarbons). Using the relations between optical densities D in the maxima of these bands, we calculated spectral coefficients of aromaticity ($C_{ar} = D_{1600}/D_{720}$) and degree of oxidation ($C_{ox} = D_{1710}/D_{1480}$), which conventionally depict the relations between aromatic and paraffin structures and the content of carbonyl groups, respectively. Coefficients C_{ar} and C_{ox} allow us to estimate the degrees of aromaticity and oxidation for resins and asphaltenes formed during MT.

Combustion characteristics

To determine combustion characteristics, the cups made of tantalum foil with the portions of samples (1.00±0.05 g) – products of MT of coal – water mixture – were placed in a muffle furnace heated to 800 °C. The time of the start of combustion and the time of complete burning out of the fuel were measured with the help of a stopwatch. Combustion behavior was evaluated visually. The ash content of the fuel was determined after its combustion.

RESULTS AND DISCUSSION

Mechanical treatment provides ultrafine grinding of solid coal particles, which causes a change of its physical and chemical properties.

The formation of gaseous products is one of the signs of chemical transformations during MT of a mixture of coal and water. The dynamics of change in the composition of gaseous products depending on MT temperature may be traced in the data shown in Table 1.

The largest amount of hydrogen is evolved at 80 °C (82.5 vol. %). With further increase in MT temperature, the amount of the formed hydrogen decreases and accounts for 60.5 vol. % at 200 ºC. Hydrogen is formed as a result of the reaction of water with the material of milling bodies according to reaction $Fe + 2H_2O \rightarrow Fe(OH)_2 + H_2$ [11], and maybe through incomplete oxidation of methane formed in the destruction of the organic matter of coal during MT. The presence of hydrogen in the reaction mixture promotes the formation of methane and ethane. However, the amount of methane decreases with an increase in temperature, which is evidently due to the possibility of methane conversion in water vapour.

TABLE 1

Composition of gaseous products of MT of coal – water mixture

Temperature of MT, °C	Content, vol. %					
	H_2	CO_2	N_2	O_2	CH_4	C_2H_6
80	82.5	5.0	8.8	2.3	1.2	0.1
120	75.6	19.9	3.0	1.0	0.3	0.1
160	61.7	32.9	4.1	1.0	0.1	0.1
200	60.5	34.3	4.0	1.0	0.1	0.1

An increase in CO_2 content with an increase in MT temperature to 200 °C is likely to be due to the destruction of the organic component of coal, in which the content of carboxyl and carbonyl groups is high, and decomposition of mineral components.

The effect of the temperature of MT of coal – water mixture on the transformation of the organic component of brown coal was evaluated relying on the analysis of the dynamics of bitumoid yield (Fig. 1) and its component composition (Table 2). An increase in MT temperature to 160 °C promotes acceleration of the destruction of the organic component of coal. Further increase in MT temperature to 200 °C leads to some decrease in the yield of bitumoid. More profound destruction of the fragments of the organic matter of coal with the high yield of gaseous products may occur at this temperature.

One can see in Table 2 that bitumoids extracted after MT of coal – water mixture at 80 and 120 °C contain mainly oils. The fraction of resins and asphaltenes becomes prevailing at MT temperature above 120 °C. With resins prevailing in the products of MT at 80 and 120 °C, asphaltenes dominate with further temperature rise. Tem-

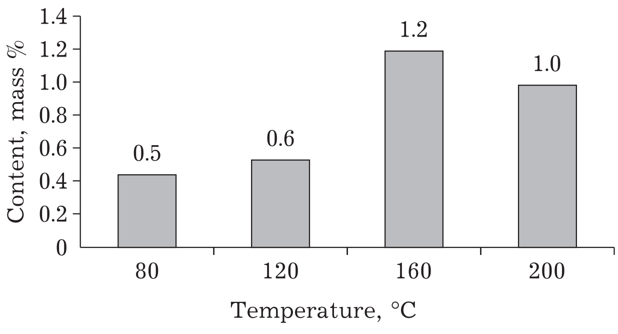

Fig. 1. Effect of the temperature of MT of coal – water mixture on the yield of bitumoid.

TABLE 2

Component composition of bitumoids in the products of MT of coal – water mixture

Temperature of MT, °C	Content, mass %		
	Oils	Asphaltenes	Resins
80	79.6	9.0	11.4
120	69.6	11.5	18.9
160	21.4	45.6	33.0
200	12.9	47.2	39.9

TABLE 3

Characteristics of IR spectra of the products of MT (resins and asphaltenes) in coal – water mixture

Temperature of MT, °C	Resins		Asphaltenes	
	C_{ox}	C_{ar}	C_{ox}	C_{ar}
Initial coal	0.92	0.66	1.28	0.56
80	2.09	0.65	3.73	0.73
120	1.23	0.6	2.16	0.75
160	1.82	0.86	3.4	0.87
200	1.25	0.87	1.63	1.0

Note. Oxidation degree $C_{ox} = D_{1710}/D_{1480}$; aromaticity degree $C_{ar} = D_{1600}/D_{720}$ [12].

perature rise may involve an increase in the rates of condensation of the formed radicals, which leads to an increase in the content of asphaltenes, which are highly condensed structures.

According to the data of IR spectroscopy, the degree of oxidation (C_{ox}) of resins and asphaltenes formed during the MT of a mixture of coal with water decreases with temperature rise, and their aromaticity degree (C_{ar}) increases, which is connected with condensation reactions (Table 3).

Ignition and combustion characteristics for coal and water mixtures obtained as a result of MT at different temperatures are presented in Table 4. The time of combustion of volatile substances during the combustion of samples was measured from the moment of their inflammation till the complete disappearance of the flame. At the stage of coal – water mixture heating and at the stage of the emission of volatile substances, determinant processes are heat exchange processes that depend on the content of the aqueous phase and mineral admixtures [9]. The content of the combustible component per unit mass of the fuel is the dominating factor in the combustion of WCF.

TABLE 4

Characteristics of ignition and combustion of the products of MT in coal – water mixture

Temperature of MT, °C	Time, s		Ash content, %
	before inflammation	combustion	
80	130	115	7.9
160	150	118	8.1
200	165	110	8.3

In general, the nature of the combustion of samples obtained at different MT temperatures is the same. Combustion is not accompanied by the escape of coal particles into the gas phase. The shortest delay before the inflammation is observed for the coal-water mixture prepared at 80 °C, which may be due to the higher content of oil fractions in that sample (see Table 2). The duration of combustion of the studied samples reveals some differences and is determined by both the physical parameters of fuel and the kinetics of chemical reactions [9].

CONCLUSION

It is demonstrated that the MT of a mixture of coal with water (1 : 1) at increased temperature (80–200 °C) promotes the destruction of the organic component of brown coal, which leads to an increase in the yield of bitumoid. With an increase in the temperature of MT, the formed bitumoids are enriched with resins and asphaltenes. Their aromaticity degree increases, which may be due to condensation reactions.

The temperature of MT of coal-water mixtures does not affect the nature of combustion of the resulting samples. The shortest delay of inflammation for the sample prepared at 80 °C may be due to the higher content of oily fractions in it.

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