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Influence of wood component on physical and chemical transformations during high temperature heating of composite fuel based on bituminous coal

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Abstract. Experimental studies of ignition delay time for mixtures of dispersed hard coal of two types and milled wood over a wide temperature range have been performed. Time of total completion of organic part pyrolysis of both components at different concentrations have been established in order to assess the prospects for such fuels application in large- and small-scale power engineering (combustion in boiler furnaces of different capacities). It has been established that simultaneous thermal decomposition of mixture of coal and wood particles leads to a significant change of pyrolysis temperature range and release of anthropogenic gases (sulfur and nitrogen oxides) in case of high-temperature heating of the mixture based on lean coal. The same effect, but in much smaller scale, has been recorded for a mixture based on long-flame coal. A hypothesis has been formulated on the mechanism of sulfur and nitrogen oxides precipitation during thermal decomposition of the mixture of lean coal and wood particles as a result of interaction between transitory gaseous and solid pyrolysis products of coal and wood in the temperature range up to 1000°C. Prospects of applying the milled coal and wood mixtures as fuel for steam and hot water boilers have been substantiated. With a small decrease of energy characteristics of such fuels, compared to homogeneous coals, significant improvement of ecological and economic characteristics of the fuel combustion processes can be achieved. It has been shown that vital synergistic effect of co-combustion of coal and wood particles is achieved only with certain coals.

Introduction

About a third of the world's electricity is produced by coal-fired thermal power plants [1]. Tendencies of the last decade show that the replacement of coal being the main fuel at TPPs is not possible in the near future, despite the release of combustion products with high content of sulfur and nitrogen oxides [2]. In this regard, active attempts are being made in advanced countries (China, India, USA, Japan, Germany, Denmark, Finland, etc.) to develop technologies for coal combustion in steam and waterheating boilers combined with other combustible substances and non-flammable components (various kinds of mixed fuels based on coals) [3]. These include coal-water and organic coal-water fuels, as well as mixtures of coals with biomass. The latter are the simplest ones for combustion. However, out of numerous attempts to implement this type of fuel (more than 230), only sixteen stations use composite fuel as primary source of energy [1-6]. Experimental data are also insufficient to develop combustion technologies for mixtures of dispersed coal with milled biomass. Mathematical models as in [7] describing a complex of physicochemical and heat-mass exchange processes during ignition and combustion of essentially structurally inhomogeneous media and materials, taking into account possible change in a large set of significant factors, have not yet been developed. Therefore, experimental studies of the main regularities of physical and chemical transformations in mixtures of dispersed coal with biomass under conditions of high temperatures of external environment are relevant.

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1. Experimental section

1.1. Characteristic of researched samples

Researched coal samples (D - "Listvyazhnoe" deposit, T - "Alardinskoe" deposit) were grounded in a ball drum mill to a finely dispersed state. Then, coal was screened with sieves (GOST R 51568-99) and samples with an average particle size of less than 80 µm were prepared.

Lumber waste was in advance cleaned from various impurities (bark, knots, branches) formed during sawing. Then, sieving was conducted using sieves with a mesh size of 200 µm. Preparation of mixed fuels was performed using wood of the same origin (waste of one shift of lumbering).

Specimens of the particles passing through the sieves were formed into mixed fuels at different volume concentrations of wood mixed with coals in a component ratio: 10%/90%; 25%/75%; 50%/50%. The obtained mixture was placed in a galvanized drum of Pulverisette 6 planetary mill with spherical grinding bodies with 5 mm diameter in a weight ratio of 1:1. Mixing process was performed for seven minutes with rotation speed of 500 rpm [8].

Analysis of elemental composition, shape and structure of mixture fuels was conducted by energy dispersive X-ray spectroscopy (EDX) using JSM 6000C scanning electron microscope (SEM) (JEOL, Japan) [8]. The device allows studying structures of mixed fuels surface with magnification of 10-60 000. Results of elemental composition study of initial fuels are presented in Table 1.

Cample	Measurement	Mass fraction of the element, % wt.										
Sample	method	С	Н	N	S	О	Al	Ca	Fe	Mg	Ti	Zr
D grade bituminous coal	CHNS analysis	50.20	3.60	1.60	0.11	20.48	0.45	0.04	0.60	0.10	0.10	0.01
T grade bituminous coal	CHNS analysis	58.04	6.37	2.90	0.42	5.99	0.90	1.10	0.10	0.09	0.10	0.10
Wood	CHNS analysis	53.30	6.90	_	_	34.16	_	_	-	-	-	-

Table 1. Elemental composition of researched composite solid fuel components

Analysis of Table 1 allows estimating the probability of sequestering of sulfur oxides formed during coal combustion due to interaction with water vapor (sulfuric acid is obtained) and subsequent reactions of metals and interactions of their oxides contained in coals during high-temperature decomposition of mixed fuels.

Technical characteristics of fuels (calorific value, ash content, moisture content and volatile content) are used traditionally to justify the possibility of their effective application for combustion at thermal power plants and small-scale power engineering. Experimental studies have been conducted in accordance with developed methods for numerical evaluation of these characteristics of the researched fuels [9].

Sample number	Fuel sample	Heat of combustion, Q, MJ/kg	Moisture content, W,%	Ash content, A,%	Volatile content, Vdaf, %
1	D grade bituminous coal	26.20	6.96	15.76	12.36
2	10 % − Wood, 90 % − D	24.92	5.42	14.00	14.55
3	25 % – Wood, 75 % – D	24.31	5.23	11.91	38.89
4	50 % – Wood, 50 % – D	23.84	5.35	10.44	40.96
5	T grade bituminous coal	25.72	5.52	18.37	25.56
6	10 % − Wood, 90 % − T	25.6	5.42	14.24	26.46
7	25 % – Wood, 75 % – T	25.22	5.34	13.65	28.33
8	50 % – Wood, 50 % – T	24.79	5.41	11.08	39.95
9	Wood	21.73	5.35	0.29	80.25

Table 2. Technical characteristics of composite fuels and their basic components

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Results of the research presented in Table 2 allow estimating a decrease of ash content of studied fuels as a function of wood concentration. Increase of wood fraction to 50% leads to ash content decrease to 10.44% (for mixed fuels based on D grade coal ash content is 15.76%) and to 11.08% (for fuels based on T grade coal ash content is 18.37%). Values of ash content for composite fuels show that these characteristics are not additive to ash content of the corresponding coals and wood. If processes of thermal decomposition of milled coal and wood occurred independently from one another, yield of ash would be noticeably less (8.03% for mixed fuel based on D grade coal and 9.34% for fuel based on T grade coal).

Comparison of theoretical and experimental values of ash content indicates that their differences are substantially greater than the error of recording devices used for ash content determination and random errors.

Results of experimental analysis of anthropogenic gases concentrations in products of thermal decomposition of mixed fuels based on D and T coals are shown in Figure 1.

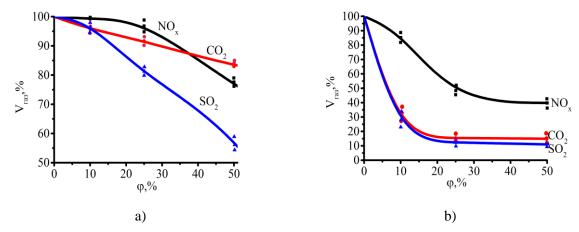


Figure 1. Concentrations of the main released harmful emissions during thermal decomposition of composite fuels based on coals of grades: a) D, b) T; $(\phi - \text{fraction of wood in fuel})$

Figure 1 shows that wood concentration increase to 50% in mixed fuels leads to a decrease of basic anthropogenic oxides release: based on D grade coal – NO_x by 23.8%, CO_2 by 17.1%, SO_2 by 38.7%; based on T grade coal – NO_x by 60.2%, CO_2 by 85.1%, SO_2 by 89.0%.

The obtained results show the possibility of a significant (up to 90%) decrease of negative impact of such TPP gases on the environment using mixed fuels based on coal and wood. On the basis of obtained results, a hypothesis has been formulated on the mechanism for reducing content of anthropogenic gases in combustion products of mixed solid fuels.

Reduction of sulfur oxides yield occurs due to their interaction with water vapor (resulting in formation of sulfuric acid) and subsequent reactions of metals and their oxides contained in coals at high temperatures with sulfuric acid:

$$\begin{aligned} Fe + H_2SO_4 &\rightarrow FeSO_4 + H_2 \\ Fe_2O_3 + 3H_2SO_4 &\rightarrow Fe_2(SO_4)_3 + 3H_2O \\ Al_2O_3 + 3H_2SO_4 &\rightarrow Al_2(SO_4)_3 + 3H_2O \\ Mg + H_2SO_4 &\rightarrow MgSO_4 + H_2 \\ 2Ti + 3H_2SO_4 &\rightarrow Ti_2(SO_4)_3 + 3H_2 \\ ZrO_2 + 2H_2SO_4 &\rightarrow Zr(SO_4)_2 + 2H_2O \end{aligned}$$

In this case, salts (sulfates), which are part of ash, water vapor (which may be later involved in carbon oxidation reactions to produce hydrogen) and hydrogen are formed. Hydrogen, in turn, can interact with sulfur oxides to form sulfuric acid, etc.

In the last years, foreign researchers established possibility (at temperatures over 900°C) of reactions:

$$NO_2 + 2H_2 \rightarrow N_2 + 2H_2O$$

 $SO_2 + CaO + O_2 \rightarrow 2CaSO_4$

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These reactions also lead to sequestration of sulfur and nitrogen oxides when they interact with hydrogen or oxygen.

Dependences established in the experiments demonstrate a synergetic effect of mixed fuels combustion and the need for detailed research not only of coals that are the basis of such fuels but directly of the mixed fuel itself at the stage of their formation. In this case, the maximum positive effect of fuels application based on coal and wood can be achieved.

Conclusion

As a result of conducted experimental studies it has been established that when thermal decomposition of lean coal and wood particles is combined, coal pyrolysis process shifts to the lower temperatures region. In addition, significant reduction of up to 90% in comparison with homogeneous coal emissions of sulfur and nitrogen oxides in the joint pyrolysis of coal and wood has been established. A hypothesis has been formulated on the mechanism of oxide sequestration during joint thermal decomposition of coal and wood as a result of thermochemical interaction of transitory pyrolysis products (sulfur oxides, water vapor, metal oxides) with formation of metal salts in solid products.

It has been shown that this effect also appears during pyrolysis of long-flame coal and wood mixture, but in much smaller amount. The obtained results illustrate the reasonability of experimental study of joint thermal decomposition of dispersed coal and milled wood at the stage of determining compositions of composite fuels. The obtained experimental are valuable in many respects including the prospects for experimental development work.

The experimental results may also serve as a basis for the development of mathematical models of combustion of a mixture of coal and wood biomass in terms of describing thermal processes occurring at the stage of thermal decomposition of a mixture of these two fuels.

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