Influence of wood biomass on physical and chemical transformations during its joint high-temperature pyrolysis with coals

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Abstract. The article deals with a comparative analysis of the influence of wood biomass on the pyrolysis processes of three grades of coal, namely, "lean" (T), "long-flame" (D), and "lignite" (3B). The composition of the ash residue of the main components of fuels and mixtures based on them was determined experimentally using X-Supreme 8000 element analysis device. Fuel mixture samples were used with a percentage of wood/coal equal to 0/100, 10/90, 25/75, 50/50 wt.%. The experiments were performed in an inert gas (argon) environment within the temperature range from 400 to 800 °C. It was established that during pyrolysis of two-component fuels based on three different coals (T, D, and 3B) in a mixture with dispersed wood biomass (sawmill waste), the effect of the growth of calcium and aluminum sulfates was achieved in the ash of the thermal decomposition products of such mixtures due to a complex of reactions between pyrolysis products of coals and wood where the concentration of the wood component in the mixture changed from 10 to 50%. The results of experimental studies allow substantiating the previously formulated hypothesis about the sequestering mechanism of sulfur oxides formed during the pyrolysis of coals, as a result of the interaction of water vapor with gaseous products of thermal decomposition of wood and solid products of pyrolysis of three coals of different grades.

1. Introduction

Coal combustion in large and small power boilers leads to contamination of the earth's atmosphere with anthropogenic oxides [1]. Even the use of modern filtering devices for cleaning flue gases does not lead to a drastic improvement of the ecosystem in the world. Solving this environmental problem is an important and urgent task for power engineers in many developed countries (China, USA, India, and Australia) [2,3]. The main anthropogenic oxides formed during the combustion of coal are oxides of sulfur, nitrogen, and carbon [4, 5]. In this regard, the task of improving fuel combustion technologies at coal-fired power plants to reduce the mass of pollutants emitted into the atmosphere with flue gases, which are formed during coal combustion in the furnaces of power boilers, is one of the most important challenges [6,7].

Studies conducted by a research team (for example, [8]) have shown that one of the most promising solutions to this environmental problem of modern energy is the combustion of coal in a mixture with biomass. In the global community, biomass is considered to be a carbon-neutral fuel, and thus the most promising renewable energy source. In this regard, biomass can be considered as an essentially inexhaustible energy resource. The results of numerous experiments (for example, [9]) have shown that the addition of biomass to coal reduces concentrations of anthropogenic oxides in the pyrolysis products...
of the mixture. It was found [10] that biomass mixed with coal reduces the concentration of emissions of sulfur and nitrogen oxides due to the low content of these elements in the biomass. According to the hypothesis proposed by the authors [10], a significant decrease in the concentration of sulfur oxides in the gaseous products of coal and wood mixtures combustion (flue gases of thermal power plants) occurs as a result of the interaction of these oxides with water vapors formed during heating and thermal decomposition of wood, as well as the subsequent reactions of sulfuric acid vapors with metal oxides of the mineral part of coals occurring at high temperatures.

The purpose of this work is to experimentally establish regularities of salts formation of two main metals (calcium and aluminum) present in the mineral part of coals of T, D, 3B grades, and in the biomass (calcium) as a result of total completion of the pyrolysis of both mixture components of various types of coals with fine wood.

2. Experimental section

The schematic diagram of the experimental unit used in the study of pyrolysis of wood-coal fuel mixtures in an inert medium (argon) is shown in Fig.1.

Sample of the fuel mixture weighing 15 g. ±0.1 g. was placed in a crucible located in a specialized chamber blown by an inert gas. The heating of the crucible with the sample was carried out within a temperature range from 400 to 800 °C. The gas analysis was performed continuously during the experiment to control the lack of oxygen. Temperature recording in the temperature-controlled chamber was performed continuously by two thermocouples (platinorodium-platinum thermoelectric converters, operating within a temperature range of 0-1350°C) throughout the experiment with a methodological error of no more than ±1%.

Mixtures of crushed coals of D, T, 3B grades, and fine pine sawmill waste were studied at medium temperatures of 400, 600, and 800 °C.

![Figure 1. Schematic diagram of the experimental unit.](image)

Experiments were conducted in an inert gas environment to minimize ignition possibility of a mixture of volatile pyrolysis products and air. The composition of solid products of thermal decomposition and concentrations of calcium and aluminum salts was determined after completion of the thermal decomposition process of mixed fuels based on coals of T, D, 3B grades, and wood.
Analysis of the elemental composition of ash residues of all studied fuel mixtures based on coals of D, T, 3B grades, and pine sawdust was carried out using X-Supreme 8000 elemental analysis device (chemical composition analyzer). Modern equipment does not allow determining the elemental composition of fuel in the process of its direct thermal decomposition, so the detection of changes in the elemental composition of fuel mixtures was carried out after the end of pyrolysis. The X-Supreme 8000 analyzer is a high-precision instrument that allows determining the content of chemical elements from sodium Na (11) to uranium U (92) in solid samples, liquids, powders, granules, etc. within the concentration range from 1 % to 100%.

The purpose of the experiments was to substantiate the hypothesis formulated earlier [11] about the mechanism of sequestering of sulfur oxides during combined thermal decomposition of coal and wood. Therefore, the main tasks of the analysis of solid pyrolysis products (after its completion) were to determine concentrations of the main components of interest (within the framework of substantiating the basic hypothesis), i.e. calcium, aluminum, and sulfur. Concentrations of calcium and aluminum sulfates should increase in comparison with pyrolysis products of homogeneous coals of D, T, 3B grades, and homogeneous wood when gaseous and solid products of pyrolysis of coal and wood interact with each other in the ash of the mixture. It is important to analyze the studied processes within a temperature range corresponding to the range of intensive pyrolysis of coal and wood components that is $400^\circ C \leq T \leq 800^\circ C$.

3. Results and discussion
The analysis was performed to detect changes in the content of calcium and aluminum sulfates in the ash of coal mixtures of D, T, 3B grades, and wood with an increase in the share of the latter component (wood) in the mixture of each coal to 50 %. The results of experimental studies are shown in Figures 2, 3.

![Figure 2](image-url)

**Figure 2.** Changes in the content of calcium sulfate with an increase in the proportion of wood in the ash of T, D, 3B coals, wood, and two-component mixtures based on T, D, 3B coals, and wood during pyrolysis in an inert environment.

Analysis of Fig. 2 allows concluding that increase in the concentration of wood components up to 50 % in mixed fuels based on coals of T, D, 3B grades leads to a significant (by 54.8 % for T grade coal, for example) increase in the proportion of calcium sulfate in the ash at a temperature of $800^\circ C$. Because there is practically no sulfur in pinewood, it can be stated, based on the results of experiments that when calcium sulfate is formed in the ash of the mixture after pyrolysis, the sulfur present in the original coal binds. The effect illustrated in Fig. 2 is significant for all studied grades of coal.

It was also experimentally established (Fig. 3) that the concentration of aluminum sulfate in the ash of mixed fuels based on coals of T, D, 3B grades, and wood waste is significantly higher compared to the ash of homogeneous coals of T, D, 3B grades. An increase in the concentration of aluminum sulfate was detected over the entire range of temperatures studied, and, for example, at $T=800^\circ C$ it was about 46.4 % for 3B coal.
Figure 3. Change in the content of aluminum sulfate in the ash of T, D, 3B coals, wood, and two-component mixtures based on T, D, 3B coals and wood during pyrolysis in an inert environment caused by the increase in the proportion of wood.

Analysis of Figure 3 allows stating that the interaction of pyrolysis products of different grades of coal with sawmill waste occurs with different intensity under identical conditions while increasing the proportion of the wood up to 50%. At the same time, there is an increase in the concentration of aluminum sulfate in the ash of coal and wood mixtures in a lower temperature range from 400 to 600°C.

Conclusions
As a result of experimental studies, it was found that combined thermal decomposition of two-component fuel mixtures based on coals of T, D, 3B grades, and wood during pyrolysis in an inert environment increases the concentration of calcium and aluminum sulfates in the ash of the mixtures with the increase in the proportion of the wood component relative to homogeneous coal. The obtained results of experimental studies allow substantiating the previously formulated hypothesis on the mechanism of sequestering of sulfur oxides formed during thermal decomposition of coals of different grades, as a result of interaction with gaseous products of heating and pyrolysis of wood.

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