Influence of wood additives on pyrolysis products composition of mixed fuels based on 3B grade lignite

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Abstract. Experimental analysis of the influence of wood biomass on the composition of pyrolysis products of mixtures based on crushed coal ("Lignite" (3B)) and fine wood (lumber sawing waste) has been performed. Ash residue composition of the main components of fuels and mixtures based on them has been determined experimentally using X-Supreme 8000 element analysis device. Fuel mixture samples were used with a percentage of coal / wood – 100 % / 0 %, 90 % / 10 %, 75 % / 25 %, 50 % / 50 by weight. The experiments have been performed in an inert gas (Argon) environment at temperatures of 400 °C, 600 °C, and 800 °C. It has been established that during pyrolysis of two-component fuels based on 3B grade coal and dispersed wood biomass, there is growth of calcium and aluminum sulfates in the solid products of thermal decomposition of such mixtures (ash) due to a complex of reactions between pyrolysis products of coals and wood when the concentration of the wood component in the mixture changes from 10% to 50 %. Results of experimental studies allow substantiating previously formulated hypothesis about the mechanism of sequestering of sulfur oxides formed during coal pyrolysis as a result of interaction with gaseous products of thermal decomposition of wood and solid products of coal pyrolysis.

1. Introduction
Emissions of coal-fired thermal power plants lead to air pollution of territories located near them [1-2]. The scientific energy community has been searching for alternative solutions to the problems of coal application for many decades [3-8]. Research by a group of scientists (for example, [9]) has shown that one of the most promising solutions to this environmental problem of modern energy is combustion of coal in a mixture with biomass. Biomass is considered to be a carbon-neutral fuel and the most promising renewable energy source (biomass is considered to be an inexhaustible energy source). The results of numerous experiments (for example, [10]) have shown that addition of up to 10% of biomass to coal reduces concentrations of anthropogenic oxides in the pyrolysis products of the mixture. It was found [11] that biomass mixed with coal reduces concentration of emissions of sulfur and nitrogen oxides due to the low content of these elements in the biomass. Based on the hypothesis proposed by the authors [11], significant decrease in the concentration of sulfur oxides in the gaseous products of combustion of coal and wood mixtures (flue gases of thermal power plants) occurs because of the interaction of these oxides with water vapors formed during heating and thermal decomposition of wood, and subsequent reactions of sulfuric acid vapors with metal oxides of the inorganic part of coals at high temperatures.

However, mechanisms for sequestering of sulfur, nitrogen and carbon dioxides formed during joint high-temperature decomposition of coals in a mixture with dispersed wood have not yet been established despite numerous attempts (including successful ones) to co-incinerate various types of biomass with coal.

The aim of the research is to experimentally study the processes that lead to sequestering of sulfur oxides formed during high-temperature pyrolysis of coals as a result of their interaction with water vapor released during thermal decomposition of wood at high temperatures. Sulfuric acid vapors further interact with metal oxides of the inorganic part of coals. The resulting calcium and aluminum salts fall into the ash residue, which is not carried away by the flue gases of power boilers into the atmosphere.
2. Experimental section

2.1. Experimental section

Lignite of 3B grade (Balakhtinskoye field) was selected as the initial component of the studied mixed solid fuels, which is used in boilers of large- and small-scale power generation. The second component of the studied mixed fuels was crushed wood from pine processing waste (LLC Dzerzhinskiy LPK, Tomsk).

A series of experiments with mixtures of crushed coal of 3B grade and dispersed wood in the temperature range from 400 °C to 800 °C with analysis of the elemental composition of the initial mixtures, coal and wood components and their ash residue was carried out at the experimental installation for the study of thermal decomposition of fuels and mixtures based on them.

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. Gas analysis was performed continuously during the experiment in order to control the lack of oxygen. Temperature recording in the temperature-controlled chamber was performed by two thermocouples (platinorodium-platinum thermoelectric converters, operating temperature range 0 - 1350°C) continuously throughout the experiment with a methodological error of no more than ±1%.

Experiments were conducted in an inert gas environment to minimize ignition possibility of a mixture of volatile pyrolysis products and air. 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 coal of 3B grade and wood.

Analysis of the elemental composition of ash residues of all studied fuel mixtures based on coal of 3B grade 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 registration of changes in the elemental
composition of fuel mixtures was carried out after pyrolysis finished. X-Supreme 8000 analyzer is a high-precision instrument that allows to determine the content of chemical elements from sodium Na (11) to uranium U (92) in solid samples, liquids, powders, granules, etc. in the concentration range from 1 ppm 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): calcium, aluminum and sulfur. Concentrations of calcium and aluminum sulfates should increase in the ash of the mixture in comparison with pyrolysis products of homogeneous 3B grade coal and homogeneous wood when gaseous and solid pyrolysis products of lignite and wood interact with each other. It is important to analyze the studied processes in the temperature range corresponding to the range (400 °C ≤ T ≤ 800 °C) of intensive pyrolysis of coal and wood components.

3. Results and discussion

Analysis was performed to determine changes in the content of calcium and aluminum sulfates in the ash of mixtures based on 3B grade coal and wood with increase in the share of the latter component (wood) in the mixture to 50 %. Results of experimental studies are shown in Figures 2, 3.

Figure 2. Changes in the content of calcium sulfate in the ash of 3B grade coal, wood and two-component mixtures based on them with increase in the proportion of 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 the mixture leads to a significant (46.2 %) increase in the proportion of calcium sulfate in the ash at a temperature of 800 °C. Due to the fact that there is practically no sulfur in pine wood, it can be stated based on the results of experiments that sulfur present in the original coal binds when calcium sulfate is formed in the mixture ash after pyrolysis. The established effect (Fig. 2) is also significant for other (lower) temperatures.

It was also experimentally established (Fig. 3) that concentration of aluminum sulfate in the ash of the same mixed fuels is significantly higher in comparison with the ash of homogeneous 3B grade coal. Increase in the concentration of aluminum sulfate was registered over the entire range of the studied temperatures and amounted 36.26 % at 800 °C. Decrease in temperature did not affect the change in the intensity of aluminum sulfate formation in the ash of the studied fuel mixtures.
Figure 3. Changes in the content of aluminium sulfate in the ash of 3B grade coal, wood and two-component mixtures based on them with increase in the proportion of wood during pyrolysis in an inert environment.

Analysis of Figure 3 allows to state that interaction of pyrolysis products of 3B grade coal with sawmill waste occurs with different intensity under identical conditions with increase in the share of the wood up to 50%. At the same time, there is an increase in the concentration of aluminum sulfate in the ash of mixtures of 3B grade coal and wood over the entire temperature range.

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

5. References
[1] Ribeiro A., Soares M., Castro C., Vilarinho C., Carvalho J. // Lecture Notes in Electrical Engineering. 2019. V. 505. P. 641-647.
[2] Key World energy statistics / Dr. Fatih Birol // International Energy Agency (IEA), 2019. URL: https://www.connaissancedesenergies.org/ (date of the application: 06.12.2019).
[3] Nyashina // Environmental Research.2019, V. 176.
[4] Nobre C., Alves O., Longo A., Vilarinho C., Gonçalves M. // Bioresour. Technol. 2019. V. 285. 121325.
[5] Ren X, Sun R, Meng X, Vorobiev N, Schiemann M and Levendis A. Carbon, sulfur and nitrogen oxide emissions from combustion of pulverized raw and torrefied biomass // Fuel, 188 (2017), 310–323.
[6] Growing Power - Advanced solutions for bioenergy technology from Finland, Tekes & VTT Processes & Teonsana Oy. Lahti 2002. 34 p.
[7] TUBITAK. Energy-Fossil Fuel: Coal Call for proposal 2016:3. http://www.tubitak.gov.tr.
[8] Munir S // Fuel. 2011, V. 90, P.126 – 135.
[9] Li, G., Wang, B., Wang, Z., Li, Z., Sun, Q., Xu, W.Q., Li, Y. Reaction Mechanism of Low-Temperature Selective Catalytic Reduction of NOx over Fe-Mn Oxides Supported on Fly-Ash-Derived SBA-15 Molecular Sieves: Structure-Activity Relationships and in Situ DRIFT Analysis // J. Phys. Chem. 2018. V. 122 (35). P. 20210 – 20231.
[10] Syrodoi, S.V., Kuznetsov, G.V., Zakharevich, A.V., Salomatov, V.V. // Solid Fuel Chem. 2017. V. 51. P. 160 – 165 DOI: 10.3103/S0361521917030107.
[11] Kuznetsov, G.V., Yankovskii, S.A. // Thermal Engineering. 2019. V. 66(2), P. 133 - 137.

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