Studies of coal and coke ignition intensified by copper salt additives

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Abstract. Process of coal and semi-coke ignition modified with copper salts (Cu(NO₃)₂, Cu(CH₃COO)₂ and CuSO₄) in amount of 5 wt.% was studied. Application of additives to coal and semi-coke samples was carried out by incipient wetness impregnation method with preliminary dissolution of the additive in an aqueous-alcohol solution with a volume ratio of C₂H₅OH/H₂O = 50/50. Combustion of coal samples has been conducted in combustion chamber at temperatures of the heating medium 500-700 °C. Ignition time was recorded using high-speed video recording. Application of copper-salt additives helped to reduce ignition delay time for samples of BC and SC series by 1.9 and 2.2 times, respectively. The maximum change in the minimum ignition temperature for samples of BC and SC series was 70 °C and 135 °C, respectively.

1. Introduction
Catalytic combustion of solid fuel is a modern method of thermal conversion of chemical energy into thermal energy, characterized by a high conversion depth due to the intensification of the combustion process at relatively low temperatures [1-2]. It was found in [3] that application of activating salt additives allows for a wider range of regulation of the oxidation process parameters, expressed in increase of the degree of coal conversion, reduction of the initial temperature of intensive oxidation, activation energy and total time of thermal conversion process of fuel as a whole. This paper presents the results of experimental study of the effect of copper salts (Cu(NO₃)₂, Cu(CH₃COO)₂ and CuSO₄) activating additives on CO release reduction in the products of coals combustion and decrease of their underburning in the ash residue.

2. Experimental section

2.1. Experimental section
Bituminous coal of the “Alardinskaya” mine of the Kemerovo region (BC sample) and semi-coke (SC) obtained after pyrolytic treatment [4] of the same fuel were used as initial samples. Raw coal sample (size d=5-10 mm) was preliminary crushed in a drum mill in the following mode of grinding: the mass ratio of grinding bodies to the material 1:1, milling time of 8 hours, followed by a screening of fraction with d < 80 µm size. Then part of the obtained coal powder was subjected to pyrolytic heating in a rotating reactor with constant purging with an inert gas (argon) at a temperature of 650 °C (heating rate of 10 °C/min) for 3 hours. The physical and chemical characteristics of the samples are shown in table...
1. Description of the methodological support for parameters determination presented in Table 1, as well as their comparison, is given in our previous work [5].

| Sample | W<sup>r</sup> | A<sup>r</sup> | V<sup>r</sup> | C<sup>r</sup> | C<sup>daf</sup> | H<sup>daf</sup> | N<sup>daf</sup> | S<sup>da</sup> | O<sup>da</sup> |
|--------|---------------|---------------|---------------|-------------|----------------|----------------|----------------|----------------|----------------|
| BC     | 4.4           | 15.5          | 13.0          | 67.1        | 66.9           | 3.0            | 1.6            | 0.3            | 12.8           |
| SC     | 1.5           | 20.3          | 3.5           | 74.7        | 72.6           | 1.4            | 1.5            | 0.4            | 3.8            |

Table 1 shows that the studied samples of coal and semi-coke are characterized by high value of ash residue (15.5 and 20.3 wt.%). The content of volatile substances in the initial sample is 13.0 wt.%, which is typical for bituminous coals of high degree of metamorphism [6]. Analysis of the morphology and particle structure of the coal sample under study was presented in our previous work [5]. The content of volatile substances decreased to a value of 3.5 wt.% after pyrolytic treatment of coal. At the same time, the particle size distribution is practically unchanged.

2.2. Application of activating additive
Activating additives (Cu(NO<sub>3</sub>)<sub>2</sub>, Cu(CH<sub>3</sub>COO)<sub>2</sub> and CuSO<sub>4</sub>) were applied to the samples by the method of incipient wetness impregnation [7]. Aqueous-alcohol solution with a volume ratio of C<sub>2</sub>H<sub>5</sub>OH/H<sub>2</sub>O = 50/50 was used to overcome the hydrophobicity of the coal powder. Then the prepared solution was applied to previously prepared coal powders using mechanical dispenser. The impregnated coal powders were kept in a drying cabinet for 20 hours at a temperature of 105 °C. The mass fraction of additives in modified samples (in terms of dry salt) was 5 %. Reference sample was also prepared (without additives) for comparative analysis, which was subjected to exactly the same processing procedures. Coal and semi-coke samples modified with Cu(NO<sub>3</sub>)<sub>2</sub>, Cu(CH<sub>3</sub>COO)<sub>2</sub> and CuSO<sub>4</sub> additives were designated as BC/1-BC/3 and SC/1-SC/3, respectively.

2.3. Research of the ignition process
Study of ignition and subsequent combustion processes was carried out using experimental stand, the concept and detailed description of which are presented in [8]. The samples were ignited at temperatures of 500, 600 and 700 °C. Samples of coal and semi-coke weighing ~0.1±0.01 g were used for the study. They were placed in a cylindrical vessel before being fed to the combustion chamber. Ignition delay time was considered to be the time from the moment when the holder with the fuel sample entered the camera focus to the beginning of the visible glow of the fuel pellet surface corresponding to the beginning of the combustion process.

2.4. Determination of the minimum ignition temperature
The minimum ignition temperature of the samples was determined T<sub>i min</sub> by setting the desired temperature in the muffle furnace, where the sample was placed using a coordinate device. The main condition for determination T<sub>i min</sub> was the time of the sample residence in the combustion chamber (5 minutes). When a visible glow appeared on the surface and in the bulk of the coal and semi-coke powder, the corresponding temperature was recorded in the specified time period. Selection of the temperature in the muffle furnace to determine this parameter was carried out by the method of half division.

3. Results and discussion
Figure 1 shows the results of measuring the ignition delay time for initial and modified samples of coal and semi-coke with various additives of copper salts in the temperature range of 500-700 °C.
Figure 1. Dependence of the ignition delay time of the initial and modified samples of coal (A) and semi-coke (B) on the temperature of the heating medium 500-700 °C.

The highest value of the ignition delay time $T_i$ of the test samples is observed at $T_g=500$ °C. The value of $T_i$ was 6.8 s for the BC sample and 19.1 s for the SC sample. Difference in the values of $T_i$ is due to the content of volatile substances and degree of carbonification of the samples under consideration (table 1). The ignition delay time is reduced for all the samples under consideration (for the BC sample by 3.7 times, for the SC by 8.8 times) with increase in the temperature of the heating medium (500→700 °C). Change of $T_i$ with increase in $T_g$ temperature has a similar nature for samples modified with copper-salt additives. It should also be added that difference in the values of $T_i$ between the considered initial samples (BC and SC) becomes insignificant with increase of $T_g$ and is 0.4 s. According to figure 1, application of additives reduces the ignition delay time. At the same time, the largest change in $T_i$ (in physical terms) is observed at a temperature of $T_g=500$ °C, which was 2.7-3.4 s and 8.0-10.4 s for BC and SC samples respectively. Change in the value of $T_i$ (at a temperature of 500 °C) allows to determine the following "activity series" of additives: Cu(NO$_3$)$_2$ > CuSO$_4$ > Cu(CH$_3$COO)$_2$. Activity of the additive, which is manifested in a relative change in the ignition delay time between the initial and modified samples, does not change with increase in the heating temperature (up to 700 °C) and on average is about 40% for a series of BC samples, and 44% for SC samples. It is also important to note that change in the "activity series" of the additives in question is observed for a series of samples at $T_g=700$ °C: CuSO$_4$ > Cu(NO$_3$)$_2$ > Cu(CH$_3$COO)$_2$. "Activity series" of promoters is preserved at all considered heating temperatures for SC samples.

Activation of the coal combustion process with introduction of copper-salt additives is most likely associated with their phase transformation and participation in the process of gas-phase oxidation products (corresponding to the nature of the additives presented), released during thermal decomposition, as well as the resulting copper oxide. More detailed mechanism of activation of carbon oxidation process during combined thermal decomposition of copper-salt additives is presented in our previous work [9].

Figure 2 shows a summary diagram showing the effect of activating additives on the minimum ignition temperature of $T_i^{\text{min}}$ bituminous coal and semi-coke. SC sample has the largest value of the ignition temperature, as expected ($T_i^{\text{min}} = 377$ °C). It is 286 °C for BC sample. Temperature difference (between the initial and modified sample) for the BC series was from 54 to 70 °C, for the SC - from 93 to 135 °C. It can be seen that the highest values of $\Delta T_i^{\text{min}}$ (70 °C and 135 °C) were observed for samples modified with copper nitrate (BC/1 and SC/1, respectively). The obtained result is also consistent with the literature data [10], where it was shown that the positive effect of the activating additive increases with increase of carbon content in the sample. Molecular structure of coal has the presence of active O-containing functional groups [10]. Concentration of functional groups decreases with increase in the degree of carbonification and promoting additives affect mainly the kinetics of the chain reaction of oxidation during thermal heating.
Figure 2. Minimum ignition temperature of bituminous coal and semi-coke modified with copper salt additives.

A good correlation is observed comparing the obtained results of determining $T_{i\text{min}}$ temperature (figure 3) and ignition delay time (figure 2), expressed in the activity of the additives used. It is also important to add that correlation can be found with the characteristic decomposition temperature of the studied additives for obtained determination results of $T_{i\text{min}}$ [9].

4. Conclusion

Results of the study showed that application of activating additives in the form of copper salts contributed to reduction of the minimum temperature and ignition delay time. The greatest change in the ignition delay time ($\Delta T_i = 10.4$ s) was recorded in the case of using copper nitrate additive for semi-coke sample at the temperature of the heating medium $T_g = 500$ °C. $\Delta T_i$ was 3.2 s for the sample of bituminous coal under the same conditions. In addition, it was found that the additives contribute to reduction of the minimum ignition temperature of coals $T_s$, the change of which in the conditions under consideration was from 54 to 135 °C. The following "activity series" of additives in the low-temperature region of the combustion process can be built using this parameter: $\text{Cu(NO}_3)_2 > \text{Cu(CH}_3\text{COO)}_2 > \text{CuSO}_4$.

5. References

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Acknowledgments

This work was supported by a grant from the President of the Russian Federation No. NSh-2513.2020.8.