Research of thermal destruction dynamics of coal particles in oxidizing medium with copper nitrate

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Abstract. Oxidation of brown coal containing 5% by weight of (Cu(NO₃)₂) initiation additive has been studied. The experiment was conducted using thermogravimetric analysis at a heating rate of 2.5°C/min up to a maximum temperature of 600°C in air. Based on DTA results, the oxidation characteristics were analytically evaluated. It has been discovered that addition of (Cu(NO₃)₂) initiation agent leads to a significant decrease of initial temperature of oxidation, which serves to shift the reaction to the low-temperature region. The effect of the initiation additive also manifested in significant reduction of sample residence time within sublimation of volatile compounds. Mass-spectrometric analysis has revealed the presence of NOₓ (intense peak at 180°C) in oxidation products of the modified sample, which is explained by decomposition of copper nitrate. SEM results for the coal partially oxidized in the muffle furnace indicate significant change of surface and internal structure of the modified sample particles.

1. Introduction
Coal is one of the most common types of fuel and plays an important role in the world power engineering. In 2016, Russia produced about 385 million tons of coal, which is almost one and a half times more than in the year 2000 [1]. More than half of all produced coal is used as the main raw material at power engineering facilities. At the same time, combustion of coal is associated with emission of flue gases, with which a lot of solid and gaseous pollutants enter the air basin [2-3]. Other significant disadvantages of burning coal are incomplete combustion of fuel and inertia of combustion process [3]. One of the modern ways to increase efficiency of coal application is catalytic combustion [4]. The peculiarity of this technology is intensification of combustion process due to active interaction of fuel with catalyst. As a rule, oxides of various metals that can accelerate oxidation process are used as a catalytic additive [4-6]. In [5], the mechanism of catalytic combustion of coal is explained by activation of fuel reactivity, resulting from close contact of coal particles with the catalyst surface. In turn, application of inorganic salts as initiation additives for coals oxidation allows achieving a higher effect on a decrease of thermal decomposition temperature of the reaction [7]. In [8], the mechanism of these additives action is explained by step-by-step promotion, which is manifested in intensified release of volatile compounds and subsequent activation of coke residue oxidation. Results of the research [7] indicate that the main effect of initiation additives application (inorganic salts) is concentrated in the region of sublimation and oxidation of volatile compounds, with parallel decomposition of inorganic salts. This fact is most likely associated with a decrease of diffusion resistance between the substrate and oxidizing medium as a result of initiation of thermal destruction of carbon particles, containing a large number of micro- and macropores. This paper
presents results of experimental research of the evolution of structural characteristics of coal samples modified by copper nitrate during their partial oxidation under conditions of thermally programmed heating.

2. Experimental part

2.1. Characteristics of researched samples

Samples of 2B brown coal from Borodinskoe deposit of Kansk-Achinsk coal mine (BC) were used in this paper. Initial sample (5-10 mm) was ground in a ball mill for 9 hours with an equal ratio of the mass of grinding bodies and the material. After milling, the samples were fractionated on sieves with a mesh size of less than 80 μm. Selected coal powders were dried in a drying furnace at 105°C to constant weight, after which their physical characteristics were determined using standard methods [9]. Results are shown in Table 1.

| Characteristics          | Value |
|--------------------------|-------|
| Ash content, %wt.        | 4.5   |
| Moisture content, %wt.   | 1.0   |
| Volatile compounds, %wt. | 39.8  |
| Carbon, %wt.             | 54.7  |
| Humidity ratio, ml/g     | 3.4   |

*Measured for water-alcohol mixture (H₂O/C₂H₅OH = 50/50).

As can be seen from Table 2, the sample has high content of volatile compounds with a relatively small value of ash and carbon, which is explained by low stage of its metamorphism. Morphology of researched coal particles is presented in micrograph (Fig. 1) made with SEM JSM-6460LV scanning electron microscope (JEOL, Japan) with an ion focused beam.

**Figure 1.** SEM image of brown coal sample (x10000)

Particles in researched sample have polyhedral spherical shape with amorphous structure and multitude of surface deepening and cracks.

2.2. Application of initiation additive

Cu(NO₃)₂ promotion additive was applied to the coal sample (BC/Cu(NO₃)₂) by incipient wetness impregnation [10]. Content of copper nitrate in the prepared sample was 5% by weight. Water-alcohol solution (H₂O/C₂H₅OH) was used for impregnation in the ratio of 50:50. After complete salt dissolution, the solution was applied to previously prepared coal powder by mechanical dispenser. Then, the obtained slurries were kept in an oven at 105°C for 20 hours. After drying, the agglomerated samples were ground in a mortar until reaching powdery appearance.

2.3. DTA and MS analyses
Thermal decomposition (oxidation) of coal samples (modified and initial samples) was studied by means of STA 449 C Jupiter synchronous thermal analyzer (Netzsch, Germany). Experiments were conducted under the same conditions, at a heating rate of 2.5°C/min in a corundum crucible with perforated cover (sample mass of ~ 25 mg) in the temperature range of 45-600°C. Mixture of air (60 ml/min) and nitrogen (10 ml/min) was used as oxidizing medium. In this case, nitrogen served as a shielding gas to ensure reliable operation of the analyzer and correct registration of obtained data. Qualitative determination of oxidation products composition was performed using STA attachment, i.e. QMS 403 D Aeolos quadrupole mass spectrometer (Netzsch, Germany). All experiments were conducted at atmospheric pressure.

2.4. Partial oxidation of samples
Partial oxidation of the samples (BC and BC/Cu(NO₃)₂) was realized in air-blown muffle furnace at 190°C in identical ceramic crucibles for one hour (sample weight of 1 g). Temperature regime of the experiment was chosen on the basis of previously obtained characteristics, calculated from the DTA data. After partial sample oxidation in the muffle furnace, crucibles were removed and cooled in a desiccator for 30 minutes. Then, samples of partially oxidized upper layer were taken for analysis.

3. Results and discussion

3.1. Effect of initiation additive on coal oxidation and pyrolysis
Figure 2 shows experimental TG- and DTG-curves of researched coal samples oxidation. They demonstrate that the sample modified by Cu(NO₃)₂ promotion additive has a different nature of the process compared with the reference sample. Analysis of obtained results (Figure 2) allows us to distinguish four stages of initial sample mass change: loss of moisture (up to 100°C); thermal destruction of particles with release of volatile compounds (100-260°C); oxidation of volatile compounds after their sublimation (260-360°C) and decomposition of coke residue (in the range of 360-520°C). It can be seen from the data in Figure 3 that the sample mass loss at the first stage of the process does not exceed 2%, which is explained by the application of previously dried samples in the experiment. As mentioned above, during the second stage, endothermic process of brown coal destruction occurs and is completed by ignition of volatile substances (stage 3). Oxidation process is accompanied by further internal destruction of particles, which facilitates the release of volatile compounds from the volume. Thus, as a result of stages 1-3, the reacting part of fuel significantly changes in structure with expansion of internal cracks and pores (Figure 4), which leads to intensification of surface interaction with oxidizing medium. It should be noted that it is impossible to distinguish transition between the third and the fourth stages in DTG-curve of the modified coal sample, since oxidation of formed coke residue occurs in parallel with afterburning of released volatile components (Fig. 2). In this case, active mass loss of the modified sample takes place in the temperature range of 190-210°C, which is due to decomposition of applied copper nitrate. Decomposition of nitrates on the surface of coal particles contributes to a significant shift of the initial temperature of active oxidation to the low-temperature region. In addition, for the modified sample at the first stages of the reaction, an increase of reaction rate is noted along with a decrease of the initial temperature (Fig. 5). In [6], this effect is explained by relatively smaller number of longitudinal and cross oxygen-containing bonds in molecular structure of high-carbon coals. It is important to note that the greatest intensity of change of mass loss rate coincides with stages of oxidation and release of volatile substances. Decrease of active oxidation onset temperature leads to a corresponding decrease of sample’s residence time in the region of sublimation and oxidation of volatile substances. It should be also noted that application of the additive reduces total residence time of the sample from the start of volatiles ignition to formation of mineral residue τᵣ, which increases the average process rate. The observed temperature effects are most likely due to the weakening of oxygen-containing molecular bonds in the structure of coals, which leads to more active release of volatile substances.
3.2. **MS-analysis**

Figure 3 shows mass-spectrometric curves corresponding to the main oxidation products (CO₂ (m/z=44) and NOₓ (m/z=30)). Release of carbon dioxide (m/z=44), the main product of combustible substance oxidation, is characterized by bimodal curve for the sample that does not contain additives (BC). The first maximum (320°C) is associated with oxidation of desorbed volatile substances, and the second (380°C) – with subsequent oxidation of coke residue. Application of promotion additive results in reduction of sublimation and oxidation temperatures of volatile substances. Concentration curves for CO₂ take a monomodal form.

![Figure 3](image)

**Figure 3.** MS-curves of CO₂ (A) and NOₓ (B) emission in oxidation products of researched coal samples

Figure 3B compares mass-spectrometric data for nitrogen oxides NOₓ (m/z=30). It can be seen that application of copper nitrate leads to significant changes of MS-curves. First of all, appearance of intense wide peak should be noted in the low-temperature region (130-223°C), which is obviously connected with decomposition of applied nitrate. Nature of NOₓ release indicates that decomposition of Cu(NO₃)₂ begins at ~130°C, which suggests a certain degree of carrier’s (coal) participation in this process. The second less intense NOₓ release wave is connected with formation of nitrogen oxides due to involvement of molecular nitrogen N₂ in the oxidation process (Figure 4). It is important that this process is accompanied by a marked decrease of NOₓ formation intensity, which follows from comparison of the data in Figure 3B. Thus, nitrogen oxides NOₓ, formed as a result of applied nitrates decomposition, contribute to significant acceleration of coals oxidation process, initiating early sublimation of volatile compounds and their subsequent ignition. Comparison of the results of DTG and MS analysis allows us to conclude that the shift in the initial temperature of active oxidation ΔTᵢ is in direct correlation with decomposition temperature of the corresponding metal nitrate.
3.3. Change of structural characteristics after partial oxidation of researched samples

Measuring the coal mass after partial oxidation (Figure 4) indicates significant loss of the modified sample’s mass, which also agrees with obtained DTA results (Fig. 4). For BC/Cu(NO₃)₂ sample mass change was 14%, and for BC sample – 4%.

![Figure 4. Change of mass of researched coal samples after their partial oxidation](image)

Figure 4. Change of mass of researched coal samples after their partial oxidation

Figure 5 shows photographs of scanning electron microscopy of researched samples obtained with SEM JSM-6460LV (JEOL, Japan).

![Figure 5. Microphotographs of researched coal samples](image)

Figure 5. Microphotographs of researched coal samples: A – brown coal sample, B – brown coal/Cu(NO₃)₂ sample (x3000)

SEM data (Fig. 5) evidence that addition of Cu(NO₃)₂ during thermal decomposition of BC sample has contributed to a significant change of surface and internal structure of particles of brown coal sample. Thus, the modified sample, after partial oxidation, has more friable and heterogeneous surface with pronounced open porous structure (Fig. 5B). Comparing obtained results with DTA and MS data (Fig. 2), it can be concluded that significant change of morphological characteristics is due to destruction of active O-containing functional groups by molecular structure of coal. As mentioned above, intensification of molecular structure destruction and early release of volatile compounds (as evidenced by SEM data (Figure 4)) occurs as a result of coal interaction with formed NOₓ during thermal decomposition of applied copper nitrate in the volume of reducing substrate.

4. Conclusion

As a result of the research it has been shown that application of Cu(NO₃)₂ initiation addition (5% by weight) to brown coal sample has positive effect on the nature of oxidation process. The presence of
copper nitrate promotion additive is shown to lead to the following effects: 1) temperature corresponding to the onset of release and oxidation of volatile compounds decreases; 2) time of preparatory stage of samples heating is shortened before active interaction begins; 3) the process in general shifts to the region of lower temperatures. According to mass-spectrometric and thermogravimetric analysis, temperature range of volatile compounds oxidation for modified samples corresponds to the beginning of decomposition process of Cu(NO\textsubscript{3})\textsubscript{2} initiation additive. Copper oxide (II), formed as a result of copper nitrate decomposition, catalyzes further process of complete oxidation of coals. It has been also found that during the promoter decomposition, the surface and internal structure of coal particles change significantly, which contributes to reduction of diffusion resistance between substrate and oxidizing medium. The shift of coal oxidation process to the low-temperature region is found to go along with a marked decrease of concentration of undesirable nitrogen oxides NO\textsubscript{x}.

5. References

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