Influence of inorganic salt on the characteristics of oxidation, ignition and combustion of bituminous coal

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Abstract. The processes of oxidation, ignition and combustion of bituminous coal containing 5 wt.% of activating agent (Cu(NO₃)₂) was studied. The experiment was performed using high-speed video recording of the combustion process of the researched coals in combustion chamber at a temperature of 700°C in the air at atmospheric pressure. Analytical assessment of the characteristics of ignition and combustion processes of the researched coals was carried out based on the obtained results. It was established that addition of Cu(NO₃)₂ promoter leads to a significant decrease of the time characterizing the delay in the beginning of coal ignition (in 2 times). Effect of the activating additive was also expressed in formation of flame during coal combustion at the stage of volatile substances separation with periodic formation of characteristic flashes formed as a result of decomposition of copper nitrate in the pores of the carbon matrix. This contributed to intensification of the release process of relatively large volume of combustible gases. The obtained results were compared with previously obtained data of the oxidation process of these coals with activating additives of copper salts by thermogravimetric analysis.

1. Introduction

Existing experience of research in the field of catalytic combustion of coal is mainly focused on application of oxides of transition, rare earth, alkaline and alkaline earth metals [1-2]. Earlier [3-4] we have established that application of salts (CuSO₄ and Cu(CH₃COO)₂) as activating additives for thermal coals leads to intensification of oxidation process, which reduces initial temperature of volatile compounds yield and their ignition. In [5] the mechanism of action of Cu(NO₃)₂ additive is explained by step-by-step promotion, expressed in intensification of volatile compounds release and subsequent activation of oxidation of the resulting carbon residue by catalytically active metal oxide. Results of the study [6] indicate that the main effect of activating additive application 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 formation of gas-phase oxidation products released during decomposition of the additive and with decrease of diffusion resistance between the substrate and oxidizing medium as a result of activation of thermal destruction of coal particles containing a large number of micro- and macropores. This paper presents results of experimental study of the characteristics of oxidation, ignition and combustion of bituminous coal modified by inorganic salt Cu(NO₃)₂ in the amount of 5 wt.%. 
2. Experimental part
Sample of bituminous coal of T grade from Alardinskaya mine of Kuzbass coal basin (BC) was used in this study. Initial sample (5-10 mm) was ground in a ball mill for 9 hours at an equal ratio of the mass of grinding media to the mass of the material. After grinding, the samples were fractionated using sieves with a cell size less than 80 microns. Particle size distribution was determined using Analysette 22 laser diffraction analyzer (Fritsch, Germany). The measurement results are presented in Table 1.

| X10 | X50 | X90 |
|-----|-----|-----|
| 4.6 | 20.4| 57.6|

The selected coal powders were dried in a drying oven at a temperature of 105°C to a constant mass, after which their physical characteristics were determined using standard methods [7]. The results are presented in Table 2.

| Sample | W<sub>r</sub> | A<sub>r</sub> | V<sub>r</sub> | C<sub>daf</sub> | H<sub>daf</sub> | N<sub>daf</sub> | S<sub>daf</sub> | O<sub>daf</sub> | Moisture capacity* |
|--------|--------------|--------------|--------------|---------------|---------------|---------------|---------------|---------------|-------------------|
| BC | 0.3 | 16.5 | 13.1 | 80.0 | 2.2 | 2.7 | 0.8 | 14.3 | 2.6 |

* – measured for water-alcohol mixture (H<sub>2</sub>O/C<sub>2</sub>H<sub>5</sub>OH = 50/50), r – as-received basis fuel, daf – dry ashless state of fuel.

As can be seen from table 2, the sample has low volatile content with relatively high ash and carbon content due to its high degree of carbonization.

2.1. Application of initiating additive
Cu(NO<sub>3</sub>)<sub>2</sub> promoting additive was introduced into the coal sample by the incipient wetness impregnation method [8]. Content of copper nitrate in the prepared sample was 5 wt.%. Water-alcohol solution in the ratio H<sub>2</sub>O/C<sub>2</sub>H<sub>5</sub>OH = 50:50 was used for impregnation. The solution was applied capillary to the pre-prepared coal powder using mechanical dispenser upon reaching complete dissolution of the salt. Further, the obtained suspensions were kept in a drying oven at a temperature of 105°C for 20 hours. The agglomerated samples were ground into powder in a mortar after drying. The modified coal sample was designated as BC/Cu.

2.2. Investigation of ignition and combustion processes
Preparation of fuel pellets by cold pressing by hydraulic manual press was carried out before studying ignition and combustion of the coals [9]. Samples (weight ~0.75±0.02 grams) of coal were placed in matrix with a through hole with a diameter of 8 mm with thrust cup fixed to the base. Pressing was performed by a punch of the corresponding diameter fixed on the hydraulic mechanism of the press with force of 2 tons of metric system of units. Study of ignition and subsequent combustion processes was carried out using experimental stand, schematic diagram of which is shown in Figure 1.
The main elements of the stand (Fig. 1) are: TSMP Ltd R14-U temperature controlled furnace with digital temperature controller (measurement inaccuracy of ± 1°C) with a volume of 0.012 m³; FASTCAM CA4 5 high-speed video camera (Photon, USA) with 1024x1024 pixels images format, shooting frequency of 105 fps; platform of coordinate mechanism intended for pellets input into the furnace with inaccuracy of movement less than 1 mm. Method of studying the processes of ignition and combustion of fuel pellets based on bituminous coal included several stages. The required heating temperature (700°C) was set in the temperature-controlled furnace (4). Deviations of air temperatures in the combustion chamber from average values by volume did not exceed 1 - 3 °C. The fuel pellet (3) was placed on the holder of the coordinate mechanism (2), the course of which was calibrated at a given coordinate to the center of the combustion chamber and was actuated by the workstation (1). Video recording (5) was carried out simultaneously with the beginning of the rod movement with the pellet towards the combustion chamber. Further, the resulting gas-phase combustion products went along the supply ventilation path (6). The experiment was conducted at atmospheric pressure. Comparative evaluation of the ignition process characteristics was performed using ignition delay times of fuel pellet samples. Ignition delay time was the time from the moment the holder with the fuel pellet entered the focus of the camera until the beginning of visible glow formation of the fuel pellet surface corresponding to the beginning of the combustion process. At least 5 experiments were conducted under similar conditions for each sample to improve accuracy of the results.

3. Results and discussion
Figure 2 shows footage of high-speed video fragment illustrating the process of ignition and subsequent combustion of the researched coal samples. Process of thermal transformation of the reference sample was accompanied by flameless combustion (smolder). In turn, formation of increasing flame near the fuel pellet after 10 seconds of heating was observed for the sample modified by copper nitrate. The difference in combustion of the studied samples may be due to intensification of volatile substances release from the surface and the internal volume of coal during decomposition of copper nitrate.
Figure 2. Ignition and subsequent combustion of coal samples at a temperature of 700°C (A – fuel pellet of the initial sample of T grade coal, B – pellet of the modified sample of T grade coal).

Flame shape is oblong and spherical at the base of the pellet for the modified sample, the volumetric size of which exceeds the sample approximately two times. Uniformity of the flame is due to the lack of intense air movement in the immediate vicinity of the pellet. It is possible to distinguish several stages of physical and chemical transformation of the modified sample according to the results and reference data [10]: heating; evaporation of moisture; parallel decomposition of copper nitrate and thermal degradation of coal with subsequent release of volatile substances; mixing of combustible gases with oxidizing medium; ignition and combustion of the gas mixture; thermal decomposition of carbon residue in flameless combustion mode in the presence of catalytically active metal oxide [1] (this stage is not presented in Figure 2). Flameless combustion of the initial sample at the stage of volatile compounds release can be explained by the lack of reaching the threshold concentrations of the released mixture of combustible gases near the sample [11]. Also note that periodic flashes were observed at the time of stable flame formation (time interval 10-12 s) for the modified sample, the epicenter of which is located in the inner part of the pellet (Fig. 3).

Figure 3. Fragment of the flame combustion of the modified sample in a time interval of 10–12 seconds.

This effect can be associated with thermal deformation and subsequent expansion of the pore structure of coal, as a result of which a relatively large amount of combustible gases is released. Similar effects were also observed in time intervals of 18-20, 21-22, 28-30 and 171-173 seconds. Intensity of
periodic release of gas-phase products decreased with time; height of the combustion flame of the modified coal sample decreased along with it. Figure 4 shows dependence of ignition delay time of coal samples at a heating temperature of 700°C.

![Graph showing ignition delay time dependence](image)

**Figure 4.** Dependence of ignition delay time of fuel pellets (heating temperature of 700 °C. Mass of the pellet ~0.75 g ±0.02 g).

Modification of T grade coal by copper nitrate by incipient wetness impregnation helped to reduce ignition delay time of the sample 2 times. The obtained values are comparable with the results of our previous work [3-4], in which the influence of copper sulfate and acetate on thermal oxidation of identical coal samples was evaluated by thermogravimetric analysis. According to the previously obtained data application of copper-salt additives (CuSO₄ and Cu(CH₃COO)₂) leads to 1.2 and 1.4 times reduction of heating time of coal before its ignition, respectively.

**Conclusion**
The study has shown that introduction of Cu(NO₃)₂ activating additive (5 wt.%) in composition of coal sample by incipient wetness impregnation reduces the time corresponding to the beginning of coal ignition 2 times. It has been established that combustion process of the modified coal, in contrast to the initial one, is accompanied by formation of flame near the sample, the size of which exceeds the fuel granule 2 times. This observation is explained by intensification of volatile substances release from the surface and the internal volume of coal during decomposition of copper nitrate. This is also confirmed by formation of periodic flashes, the epicenter of which is located in the inner part of the fuel pellet. This effect may be associated with destruction of the activating additive in the pores of the carbon matrix, which contributes to intensification of mass and heat transfer processes, thereby accelerating the overall process of volatile substances release.

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