Influence of metal nitrates on the process of coal oxidation of various metamorphism stages

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Abstract. The process of oxidation of lignite and bituminous coal modified with metal nitrates (Cu, Ce, Na, Co, Fe) in the amount of 5 wt.% is studied. Application of additives to the coal samples is carried out by the method of incipient wetness impregnation with preliminary dissolution of the additive in an aqueous-alcohol solution with a volume ratio of C2H5OH/H2O=50/50. Reactivity of the samples is studied by thermogravimetric analysis in the oxidation mode at a heating rate of 2.5 °C/min in the temperature range 25–600°C at atmospheric pressure. It has been found that application of activating additives contributes to reduction of the initial temperature of intensive oxidation (Δt_i=5–97°C) and to a shift of the process to the low-temperature region as a whole. According to the results obtained, the greatest activity is specific for addition of Cu(NO3)2. It is manifested in a decrease in the temperature of the beginning of intensive oxidation t_i and an increase in the average reaction rate w_avg. The Coats-Redfern method is used to calculate activation energy of the oxidation process in the presence of activating additives. Maximum decrease in E_a is observed for a copper nitrate-modified coal sample.

1. Introduction

Coal is the dominant type of energy source used as primary fuel for electricity generation according to International Energy Agency [1]. The share of coal consumption in the total amount of energy sources was about 39% according to 2017 data. Despite the generally accepted energy policy aimed at reducing the share of coal use and switching to renewable energy sources, coal, as the main fuel, will occupy a leading position in the structure of energy generation. Given these facts, development of technologies for thermal conversion of coal, in particular its combustion, is a priority for coal power engineering in order to ensure efficient and environmentally sustainable production. One of the technical solutions to improve efficiency of coal combustion is application of catalytically active agents to intensify combustion process [2]. Most of the research in the field of catalytic combustion is focused on the use of various metal oxides [3-5]. At the same time, a number of studies [6-7] found that metal oxide precursors can have more significant effect on the process of carbon oxidation, which is expressed in a decrease in the initial temperature of intensive oxidation and an increase in the reaction rate. This paper presents results of experimental study of nitrates effect of various metals (Cu, Ce, Na, Co, Fe) on oxidation of coals of various metamorphism stages.
2. Experimental section

2.1. Experimental section

The following materials were used as initial samples: lignite of 2B grade (L) and bituminous coal of T grade (BC) of Borodinsky and Allardinsky deposits, respectively. Coarse samples of initial coals (5-10 mm) were crushed in a drum mill for 8 hours with an equal ratio of the mass of the grinding bodies and the mass of the crushed material. After grinding, the samples were fractionated on sieves with a cell size of 80 microns. 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 [6].

Table 1. Characteristics of the studied coal samples.

| Sample | W<sub>daf</sub> | A<sub>daf</sub> | V<sub>daf</sub> | C<sub>daf</sub> | H<sub>daf</sub> | N<sub>daf</sub> | S<sub>daf</sub> | O<sub>daf</sub> | Moisture content, ml/g |
|--------|----------------|---------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------------|
| L      | 1.0            | 4.5           | 39.8           | 54.7           | 59.4           | 5.3            | 1.7            | 0.9             | 32.7                 | 3.4                  |
| BC     | 0.3            | 16.5          | 13.1           | 70.1           | 80.0           | 2.8            | 2.5            | 0.4             | 14.3                 | 2.6                  |

2.2. Application of activating additive

Activating additives (Cu(NO<sub>3</sub>)<sub>2</sub>, Fe(NO<sub>3</sub>)<sub>2</sub>, Ce(NO<sub>3</sub>)<sub>3</sub>, NaN<sub>3</sub>, Co(NO<sub>3</sub>)<sub>2</sub>) were applied to the composition of samples by the method of incipient wetness impregnation [8]. 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. Moisture content of the dried coal samples (in ml/g) was determined immediately before applying the impregnation solution (Table 1). 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. Mass fraction of additives in modified samples (in terms of dry salt) was 5 %. Reference samples were also prepared (without additives) for comparative analysis and were subjected to exactly the same processing procedures. Modified coal samples were designated as follows: L/Me - lignite, and BC/Me - bituminous coal.

2.3. STA analysis

The oxidation process of the modified coal samples was studied using STA 449 C Jupiter simultaneous thermal analyzer (Netzsch, Germany). The experiments were conducted under the same conditions at atmospheric pressure. A sample weighing of ~15 mg was heated in a corundum crucible with a perforated lid in the temperature range of 25-600 °C at a heating rate of 2.5 °C/min. Mixture of air (60 ml/min) and nitrogen (10 ml/min) was used as the oxidizing medium. Nitrogen was used as a protective gas to ensure reliable operation of the analyzer and correct data recording.

2.4. Determining parameters of the oxidation process and kinetic analysis

The following characteristics of the coal oxidation process were evaluated in the experiment: temperature of the beginning (t<sub>i</sub>) and end (t<sub>f</sub>) of intensive oxidation; maximum reaction rate (w<sub>max</sub>) at the corresponding temperature (t<sub>max</sub>); time of sample heating before oxidation (ϕ<sub>e</sub>); total time of oxidation (ϕ<sub>f</sub>); and maximum rate of the oxidation reaction (ϕ<sub>max</sub>). The mentioned parameters were calculated by the STA data using graphical method, which is described in detail in our previous works [7]. In addition, values of activation energy E<sub>a</sub> of samples oxidation were calculated using the Coats – Redfern method [9] based on the obtained data of thermogravimetric analysis.

This method is based on the following ratio:

\[
\ln\left[\frac{\beta}{T_2^2} \frac{\ln(1-a)}{T_2} \right] = \ln\left[\frac{AR}{bE_a} \right] - \frac{E_a}{RT},
\]

here \(\beta\) is the degree of coal conversion; T is the temperature, °K; R is the universal gas constant, J/(mol·K); A is the pre-exponential multiplier, 1/min; E<sub>a</sub> is the activation energy, J/mol; and \(a\) is the
heating rate, °K/min. Solution of this equation and determination of the main kinetic parameters were realized by approximating the experimental dependence in ln(-ln(1-b)/T²) vs 1/T coordinates.

3. Results and discussion
Figures 1 and 2 show the results of the study of samples oxidation process by the STA method. It can be seen that all the applied additives have positive effect on the temperature of the beginning of the intensive coals oxidation t_i. In this case, the process has different nature depending on the type of researched coal. Thus, Ce(NO₃)₃ and NaNO₃ additives have different effects on the release temperature of volatile compounds and the oxidation process in general. Reduction of the initial temperature of intensive oxidation of released volatile compounds Δt_i in the case of NaNO₃ additive application for lignite is 30 °C, and for bituminous coal it is 8 °C. In turn, different nature of influence of the same additive is observed for further stages of oxidation of the considered coal types. Oxidation reaction slows down for the L/Na sample in the temperature range of 260-340 °C, after which the nature of TG curve becomes steeper, which symbolizes intensification of the process (Fig. 1). The increase in the oxidation reaction rate may be associated with formation of sodium oxide in the volume and on the surface of coal particles. In case of the BC/NaNO₃ sample, the main influence of the additive is concentrated in the area of carbon residue oxidation, for which the decrease in the completion temperature of the process Δt_f was 43°C.

![Figure 1](image1.png)
**Figure 1.** TG data for oxidation process of coals modified with nitrates of various metals. A – samples of the L series; B – samples of the BC series. Medium – air (60 ml/min), heating rate – 2.5°C/min.

![Figure 2](image2.png)
**Figure 2.** DTG data for oxidation process of coals modified with nitrates of various metals. A – samples of the L series; B – samples of the BC series. Medium – air (60 ml/min), heating rate – 2.5°C/min.
Cu(NO$_3$)$_2$ has the greatest effect on changing the nature of the carbon oxidation process out of all the considered activating additives. The following sequence is presented according to the analysis of the additives activity by $t_i$ parameter for lignite:

$$\text{Cu(NO}_3)_2 > \text{Fe(NO}_3)_2 > \text{Co(NO}_3)_2 > \text{NaNO}_3 > \text{Ce(NO}_3)_3$$

For bituminous coal:

$$\text{Cu(NO}_3)_2 > \text{Fe(NO}_3)_2 > \text{Co(NO}_3)_2 > \text{Ce(NO}_3)_3 > \text{NaNO}_3$$

Cobalt and sodium nitrates additives also affect the nature of DTG curves along with Ce(NO$_3$)$_3$ and Cu(NO$_3$)$_2$. In addition, NaNO$_3$ additive has different effect on $t_{\text{max}}$ parameter change depending on the type of studied coal. Thus, narrowing of the width of bimodal curve is observed (Fig. 2) for L/Na sample during its thermal decomposition, which is due to intensification of the oxidation reaction of the carbon residue under the influence of the formed non-stoichiometric alkali metal oxide [10]. Despite the known activity of cobalt oxide (formed after decomposition of Co(NO$_3$)$_2$) [11], oxidation process in the high-temperature region (over 350 °C) for all types of coals has similar nature, as in the case of converted CeO$_2$ after decomposition of the corresponding additive (Fig.1 and 2).

Tables 2 and 3 present the main parameters of the oxidation process of the studied samples calculated by the obtained STA data (Fig. 1 and 2).

**Table 2.** Characteristics of oxidation process of the studied lignite samples.

| Parameter                                      | Samples               |
|------------------------------------------------|-----------------------|
| Temperature of the beginning of intensive oxidation, $t_i$ (°C) | L 260  L/Ce 255  L/Cu 217  L/Co 225  L/Na 230  L/Fe 220 |
| Sample heating time before the beginning of intensive oxidation, $\phi_e$ (min) | 86  84  68  72  74  70 |
| Temperature of the end of oxidation process, $t_f$ (°C) | 500  460  420  420  460  420 |
| Time of intensive oxidation of the sample, $\phi_f$ (min) | 96  82  82  78  92  80 |
| Temperature at the maximum rate of oxidation reaction, $t_{\text{max}}$ (°C) | 380/-  360  280  362  380  360 |
| Maximum rate of oxidation reaction, $w_{\text{max}}$ (wt%/min) | 3.1  2.3  2.0  2.4  2.5  2.3 |
| Time to reach the maximum rate of oxidation reaction $T_{\text{max}}$ (min) | 48  42  24  54.8  60  32 |
| Activation energy of oxidation process, $E_a$ (kJ/mol) | 68.6  64.1  57.5  58.2  60.3  57.7 |

**Table 3.** Characteristics of oxidation process of the studied bituminous coal samples.

| Parameter                                      | Samples               |
|------------------------------------------------|-----------------------|
| Temperature of the beginning of intensive oxidation, $t_i$ (°C) | BC 340  BC/ Ce 294  BC/Cu 243  BC/Co 282  BC/Na 332  BC/Fe 263 |
| Sample heating time before the beginning of intensive oxidation, $\phi_e$ (min) | 118  99.6  79.2  94.8  114.8  82.5 |
| Temperature of the end of oxidation process, $t_f$ (°C) | 578  574  516  528  533  520 |
| Time of intensive oxidation of the sample, $\phi_f$ (min) | 95.2  112  109.2  98.4  80.4  102.3 |
| Temperature at the maximum rate of oxidation reaction, $T_{\text{max}}$ (min) | 361/497  331/502  291/447  341/480  388/423  320/475 |
The observed difference in the values of Δtᵢ for the studied series of L and BC samples is most likely related to different physical and chemical characteristics of coals (Table 1), decomposition temperatures of nitrate additives, and activity of the studied types of metals. An important factor affecting the change in the ignition temperature of coals is pyrolysis rate of volatile compounds. Metal cations contained in the high-molecular structure of coal contribute to slowing the rate of release of volatile compounds according to some articles [12-13]. Thus, the higher is the yield of volatile substances, the lower is the catalytic effect of the used additives. There is a shift of oxidation process towards the low-temperature region for all modified samples, as evidenced by a decrease in the value of tᵢ parameter. At the same time, the decrease in the intensive oxidation time tᵢ is observed only for lignite samples (with exception of the BC/Na sample), which is connected to the high yield of volatile compounds of lignite (Table 1). The main effect of the studied types of activating additives for bituminous coal samples is concentrated in the area of release and oxidation of volatile compounds. The reaction rate slows down at the oxidation stage of carbon residue in conditions of the process transition to a low-temperature region, as evidenced by an increase in the width of the DTG curves peaks (Fig. 2). Results of calculations using the Coats-Redfern method have shown that activation of samples with additives Co(NO₃)₂, Fe(NO₃)₂ and NaNO₃ for all types of coals leads to a decrease in the activation energy Eₐ of the process (Table 2 and 3), as in the case of Ce(NO₃)₃ and Cu(NO₃)₂ additives. Thus, the most active additive from the studied series of samples modified with various metal nitrates is Cu(NO₃)₂, which contributes to a significant change in the characteristics of oxidation process of energy coals.

Conclusions
Results of the study have shown that application of activating additives in the form of nitrates of various metals to the composition of lignite and bituminous coal samples in the amount of 5 wt.% has an accelerating effect on their oxidation process. The presence of activating additives in the samples is shown to lead to the following effects: 1) reduction of the temperature corresponding to the beginning of release and oxidation of volatile compounds; 2) reduction of the time of preparatory stage of samples heating before the active interaction begins; and 3) shift of the oxidation process to a lower temperature region. It has been found according to thermal analysis that Cu(NO₃)₂ additive has the greatest activity manifested in a decrease in the temperature of the beginning of intensive oxidation tᵢ.

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