

# Influence of $\text{Cu}(\text{CH}_3\text{COO})_2$ promoting additive on bituminous coal oxidation process

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**Abstract.** The process of coal oxidation with applied  $\text{Cu}(\text{CH}_3\text{COO})_2$  additive was studied by the capillary incipient wetness impregnation method with 5% mass concentration. The experiment was conducted by thermogravimetric analysis at a heating rate of  $2.5^\circ\text{C}/\text{min}$  to a maximum temperature of  $600^\circ\text{C}$  in atmospheric air. It was established that application of the initiation additive leads to a significant reduction in the initial temperature of sublimation and active oxidation of volatile compounds ( $\Delta T_i = 78^\circ\text{C}$ ) and the oxidation end temperature ( $\Delta T_f = 64^\circ\text{C}$ ). It was established that in the presence of copper acetate the nature of coal oxidation reaction significantly changes (DTG data). The parameters of the coals oxidation process in the presence of copper acetate were determined, and an assumption was made about the presence of a composite catalytic effect.

## 1 Introduction

Coal is one of the most common types of fuel in the Russian energy industry [1]. The most simple and widely used method of its transformation is direct combustion in boiler furnaces [2]. Combustion of coal is associated with a number of serious problems: the emission of flue gases, the inertia of burning fuel, the incompleteness of its combustion [2]. It is possible to increase the coefficient of fuel use due to application of catalytic combustion technology, which has a significant effect on the kinetics of the combustion process [3]. As a catalytic additive, as a rule, oxides of alkali and rare-earth metals are used, which accelerate the oxidation process [3-4]. In turn, a comparative analysis of the effect of oxide additives and their precursors in the form of metal nitrates and metal chlorides on the process of coal oxidation showed that the precursors contribute to a greater decrease in the initial temperature of active oxidation of volatile substances and an increase of the reaction rate, shortening the residence time of the sample in its active oxidation area [4]. The mechanism of coal catalytic combustion is explained by the fuel reactivity activation, resulting from the close contact of the coal particles with the catalyst surface [2]. The paper presents the results of an experimental study of the coal oxidation process with  $\text{Cu}(\text{CH}_3\text{COO})_2$  initiation additive.

## 2 Experimental setup and study technique

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The coal of the Allardinskoye deposit of the Kuzbass coal basin was taken as the initial sample. The large-dispersed sample of the initial coal (particle diameter  $d = 5 \div 10$  mm) was ground in a drum mill with an equal ratio of the mass of the milling bodies and the material for 8 hours. After grinding, the sample was fractionated on sieves with a mesh size of not more than 80  $\mu\text{m}$ . The obtained micro-dispersed coal powders were previously dried at a temperature of 105°C to a constant weight. The physical and chemical characteristics of the prepared samples were determined using standard techniques [5] and are presented in Table 1.

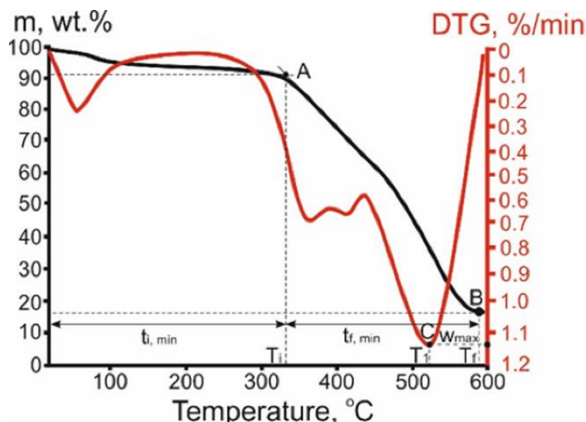
**Table 1.** Physical and chemical characteristics of a coal sample and initiation additive.

<b>Characteristics of bituminous coal sample</b>	
Ash content, %wt.	17.0
Moisture content, %wt.	0.5
Volatile compounds, %wt.	14.0
Carbon, %wt.	68.5
Humidity ratio, ml/g	2.9
<b>Characteristics of <math>\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}</math> initiation additive</b>	
Molar mass, g/mol	181.63
Decomposition temperature, °C	~290
Solubility in water, g/ml	0.10

Application of the initiation additive was conducted by the incipient wetness impregnation method [6]. To overcome the hydrophobicity of the coal powder, a water-alcohol solution with a volume ratio of  $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O} = 50/50$  was used. The prepared solution was applied to the previously prepared coal powder by means of a mechanical dispenser. The impregnated coal powder was kept in a drying oven at a temperature of 105°C for 20 hours. The mass fraction of  $\text{Cu}(\text{CH}_3\text{COO})_2$  in the modified sample (in terms of dry salt) was 5%. For comparative analysis, a reference sample containing no initiation additive was prepared which was subjected to exactly the same treatment procedures. The prepared samples had the following designation: the reference sample was BC, the modified sample was BC/Cu.

Study of the coal samples oxidation (modified and initial samples) was conducted using STA 449 C Jupiter synchronous thermal analyzer (Netzsch, Germany). The experiments were performed under the same conditions, at a heating rate of 2.5°C/min in a corundum crucible with a perforated cover (sample mass ~ 15 mg) in the temperature range 45-600°C. A mixture of air (60 ml / min) and nitrogen (10 ml / min) was used as an oxidizing medium. Nitrogen was used as a shielding gas to ensure reliable operation of the analyzer and correct registration of the obtained data. A qualitative determination of the oxidation products composition was also performed using the STA attachment in the form of QMS 403 D Aeolos quadrupole mass spectrometer (Netzsch, Germany). All experiments were conducted at atmospheric pressure.

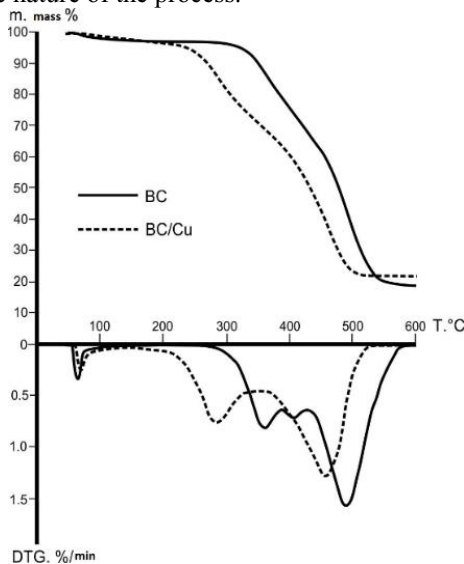
Parameters of the coal oxidation process were determined graphically (Fig. 1) with the help of the obtained TG and DTG curves. The points A and B on the TG curve characterize the onset temperature of the released volatiles active oxidation ( $T_i$ ) and the end temperature of the combustible mass loss of the sample ( $T_f$ ). The characteristic point C, lying on the DTG curve, reflects the maximum value of the reaction rate ( $w_{\text{max}}$ ) and the temperature at a certain moment ( $T_1$ ).



**Fig. 1.** TG- and DTG-curves for oxidation process of the initial (unmodified) sample of bituminous coal.

### 3 Experimental results

The TG and DTG curves for oxidation process of the researched coal samples are presented in Fig. 2. It can be seen that application of  $\text{Cu}(\text{CH}_3\text{COO})_2$  initiation additive leads to a significant change in the nature of the process.



**Fig. 2.** TG- and DTG-curves for oxidation process of the researched coal samples.

Four main stages can be distinguished for the process of the reference sample oxidation. Moisture evaporates in the first stage (up to 100°C). In the second - coal particles undergo thermal destruction, which is accompanied by sublimation of volatile compounds (140-360°C). The third and fourth stages are characterized by active oxidation of the released volatile compounds and the obtained coke residue (360-600°C).

The main parameters of the oxidation process of the researched coal samples were calculated based on the TGA data. The results of the calculations are presented in Table 2.

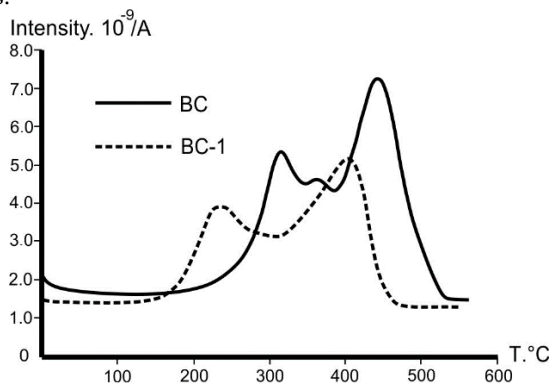
**Table 2.** Parameters of oxidation process of the researched coal samples.

Parameter	BC	BC/Cu
Active oxidation onset temperature of volatile compounds, $T_i$ (°C)	361	283
Time of the sample heating to the active oxidation onset of volatile compounds, $t_e$ (min)	126	94
Oxidation end temperature of the combustible mass of the sample, $T_f$ (°C)	583	519
Temperature at the point of maximum oxidation rate, $T_1$ (°C)	527	493
Maximum oxidation rate, $w_{max}$ (%wt./min)	0.49	0.40

As can be seen from Table 2, modification of a coal sample by addition of  $\text{Cu}(\text{CH}_3\text{COO})_2$  leads to a significant decrease in the onset temperature of active coal oxidation ( $\Delta T_i = 78^\circ\text{C}$ ), a decrease in the oxidation end temperature ( $\Delta T_f = 64^\circ\text{C}$ ), and a reduction of the sample warm-up time before the start of volatile compounds oxidation ( $\Delta t_e = 32$  min).

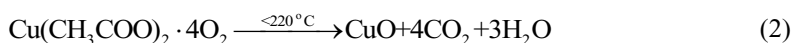
The decrease of the onset temperature of active oxidation is accompanied with an increase of the average process flow rate ( $\Delta w = 0.023\%/min$ ) and a decrease in the maximum reaction rate ( $\Delta w_{max} = 0.09\%/min$ ). At the same time, the temperature corresponding to the maximum oxidation reaction rate of the sample decreases ( $\Delta T_{max} = 34^\circ\text{C}$ ).

The mass spectrometric curves corresponding to the appearance of  $\text{CO}_2$  ( $m/z=44$ ) in the composition of gas phase oxidation products of the researched coal samples are presented in Fig. 3. It can be seen that in the presence of  $\text{Cu}(\text{CH}_3\text{COO})_2$  initiation additive, a considerable shift of the emission peaks to the low-temperature region is observed, which agrees well with the data of DTG (Fig. 2). In this case, a significant change in the shape of the curves also occurs.



**Fig. 3.** MS-curves of  $\text{CO}_2$  emission in the composition of oxidation products of the researched coal samples.

Thermal destruction of  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  copper acetate monohydrate in an oxygen-containing medium is accompanied by a loss of water at  $\sim 130^\circ\text{C}$  (stage 1), followed by salt decomposition in the  $220\text{-}300^\circ\text{C}$  range [7]. The primary gas-phase decomposition products of  $\text{Cu}(\text{CH}_3\text{COO})_2$  (acetone, acetaldehyde and acetic acid vapor) are oxidized to carbon dioxide and water (step 2) when reacted with air oxygen. Despite the complex mechanism of destruction and a large set of intermediate products of copper acetate decomposition [7], the main reaction (stage 2) can be presented in a simplified form:



The oxidation reactions of the gas-phase decomposition products of copper acetate are exothermic, as a result of which additional heat is released contributing to the earlier thermal destruction of the carbon particles, which initiates the process of volatile compounds sublimation.

It is important to note that the solid phase product formed as a result of  $\text{Cu}(\text{CH}_3\text{COO})_2$  salt decomposition can be presented by a set of different oxide phases:  $\text{CuO}$ ,  $\text{Cu}_2\text{O}$  and  $\text{Cu}_4\text{O}_3$  [7]. Nevertheless, with a further rise of the temperature to  $400^\circ\text{C}$  and higher in oxygen-containing atmosphere leads to stabilization of the only phase of copper oxide (II). At the same time, it is known [8] that the copper oxide formed as a result of the reaction is an active catalyst of the complete oxidation processes in heterogeneous catalysis. Thus, the appearance of dispersed  $\text{CuO}$  particles on the surface of the samples, apparently, contributes to the further acceleration of the coals oxidation process.

## 4 Conclusion

The results of the study showed that application of  $\text{Cu}(\text{CH}_3\text{COO})_2$  initiation additive in the composition of coal in an amount of 5% by weight has a positive effect on the oxidation process nature. The presence of the copper acetate promoter in the coal sample leads to a decrease of the temperature corresponding to the onset of release and active oxidation of the volatile compounds, a reduction of the sample warm-up time prior to the active interaction onset of the volatile compounds and the blown medium, and also to a shift to the lower temperature region of the process in general. The temperature range of volatile compounds oxidation for the modified sample corresponds to the decomposition process beginning of  $\text{Cu}(\text{CH}_3\text{COO})_2$  initiation additive. Copper oxide (II) formed as a result of copper acetate decomposition catalyzes the further process of complete coal oxidation. The revealed patterns of the initiated coals oxidation in the presence of copper acetate can be further used in the development of more efficient methods for solid fuels combustion.

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