Influence of $Cu(NO_3)_2$ initiation additive in two-stage mode conditions of coal pyrolytic decomposition

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Abstract. Two-stage process (pyrolysis and oxidation) of brown coal sample with $Cu(NO_3)_2$ additive pyrolytic decomposition was studied. Additive was introduced by using capillary wetness impregnation method with 5% mass concentration. Sample reactivity was studied by thermogravimetric analysis with staged gaseous medium supply (argon and air) at heating rate 10 °C/min and intermediate isothermal soaking. The initiative additive introduction was found to significantly reduce volatile release temperature and accelerate thermal decomposition of sample. Mass-spectral analysis results reveal that significant difference in process characteristics is connected to volatile matter release stage which is initiated by nitrous oxide produced during copper nitrate decomposition.

1 Introduction

Catalytic fuel combustion is promising technology which allows to sustain low-temperature combustion regime with minimal antropogenic impact [1]. The oxides of rare-earth, transitional and alkaline metals are known to be the most widespread among catalytic agents. The main effect appearing during application of such promoters is reducing of initial temperature of volatile matter release as well as shifting fuel oxidation into low-temperature area [2-4] which has a favorable effect on the efficiency of the energy equipment [5-8]. Scientific studies reported that activation of metal-based catalytic additives during fuel oxidation appears to be most effective only at high temperatures (above 500 °C) [9-11]. In our previous studies [12] it was found that additives of metal oxide precursors in form of mineral salts are able to provide sufficient initiative impact on coal oxidation process. During discussion on possible mechanism of fuel and initiative additive interaction the hypothesis about composite observation effect was proposed. The first one is connected to release of oxide gaseous phase in the result of additive decomposition. The second one is connected to formation of disperse non-stoichiometric metal oxide which plays role of catalyst and accelerates oxidation process. To prove composite effect of initiated combustion with salts and their bases the process was proposed to be divided into two parts: volatile matter release during additive decomposition and

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further carbon oxidation at the presence of formed non-stoichiometric metal oxide. In current study, the results of research on kinetic characteristics of two-stage thermal decomposition of modified by $Cu(NO_3)_2$ additive brown coal were presented.

2 Experimental setup and study technique

The brown coal of Borodinskoe deposit from Cansk-Achinsk coal-basin was used as initial fuel. Rough-disperse samples (d=5:10 mm) was taken and ground using ball mill at following conditions: milling bodies to material mass ratio was 1:1, milling time was 9 hours. Later samples were undergo fractionation. Physical properties of obtained sample were defined using known methodic and given in table 1.

Table 1. Physical properties of studied sample

Index	Unit of measure	Value
Ash content	wt.%	5.2
Moisture content		3.0
Volatile compounds		38.8
Carbon		55.0
Humidity ratio	ml/g	3.2

As it can be seen from table 1, studied sample has a high content of volatile substances and a low content of the mineral residue, which is explained by its stage of metamorphism [13, 14].

The initiating additive $Cu(NO_3)_2$ was dissolved in a water-alcohol solution in a volume ratio H_2O / C_2H_5OH = 50:50 and applied to the obtained sample by capillary impregnation method with respect to the moisture capacity. The content of the additive into the modified sample was 5 wt.%. Resulting sample was dried into a drying oven at 105 °C temperature for 20 hours.

For comparative analysis, a reference sample with no initiating additive was prepared and subjected to exactly same treatment procedures.

The study of the stepwise process of thermal decomposition of coal was carried out using a synchronous thermal analyzer STA 449 C Jupiter (Netzsch, Germany). The experimental regime is schematically shown in figure 1.

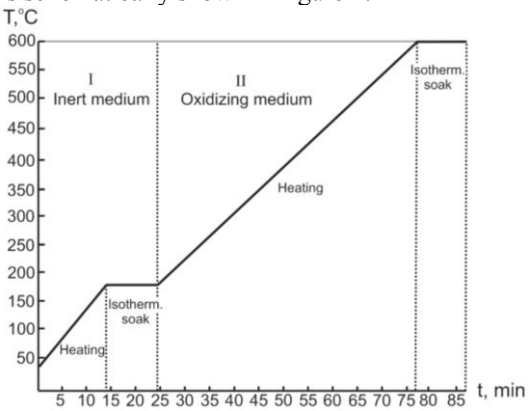

Fig. 1. Scheme of the experimental regime of synchronous thermal analyzer.

Stage I was characterized by decomposition of copper nitrate and the active release of volatiles from coal (pyrolysis). It was carried out in an inert atmosphere (argon) with a 60 ml/min gas flow rate at 10 °C/min heating rate in temperature range from 40 °C to 180 °C

(it is temperature corresponding to the decomposition of copper nitrate) and was followed by isothermal soaking for 10 minutes. Stage II includes heating with the subsequent oxidation of the samples in stream of air (60 ml / min) and argon (10 ml / min) with same heating rate (10 °C/min) to 600 °C. After reaching the maximum temperature, the samples were kept in isothermal soaking mode for 10 minutes. All experiments were carried out under ambient pressure. The sample weight was about 8 mg.

To determine the qualitative composition of the gaseous products (NO_x m / z = 30) of sample pyrolysis and oxidation at the outlet of thermal analyzer the mass spectrometric analysis was performed using a QMS 403 D Aeolos (Netzsch, Germany) interfacing quadrupole mass spectrometer.

3 Experimental results

The TG and DTG-curves for pyrolysis (figure 2a) and oxidation (figure 2b) stages are given in figure 2.

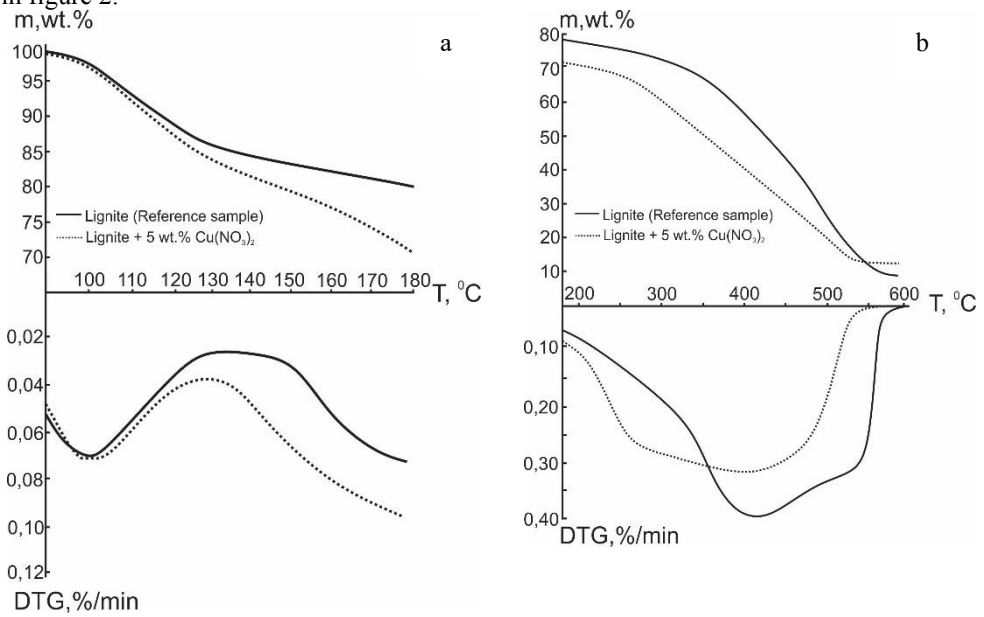

Fig. 2. TG and DTG-curves of pyrolysis (a) and oxidation (b) processes for studied samples.

From the obtained results it could be seen that the introduction of $Cu(NO_3)_2$ initiating additive into the coal sample resulted into decreasing og the initial temperature of volatile matter release (figure 2a) and an increasing of the average reaction rate of oxidation process (figure 2b). Comparing the obtained results of mass-spectrometric analysis of NO_x emission (m/z=30) (figure 3), it can be seen that the main effect of the initiating additive appears during pyrolysis process. It is accompanied by the release of nitric oxide as a result of the copper nitrate decomposition in the temperature range of 140-180 ° C (figure 3a)

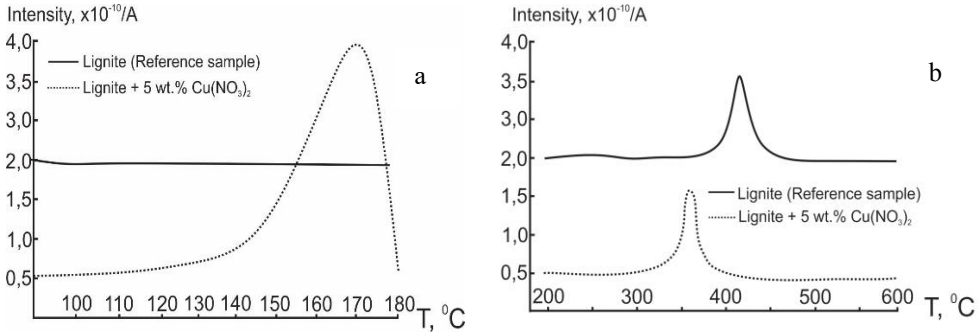

Fig. 3. MS-profiles of NO_x release for pyrolysis (a) and oxidation (b) processes.

The second peak of NO_x release is less intense and connected to formation of nitrogen oxides in the flame regime due to the involvement of molecular nitrogen N_2 in the combustion process.

Considering the possible mechanism of initiating additive action during coal pyrolysis and oxidation it is worth mentioning a number of key chemical reaction equations:

$$Cu(NO_3)_2 \xrightarrow{T,°C} CuO + 2NO_2 + O_2 \quad (1)$$

$$C + NO_2 = CO + NO \quad (2)$$

$$2CO + 2NO_2 = 2CO_2 + N_2 \quad (3)$$

$$NO + \frac{1}{2}O_2 \rightleftarrows NO_2 \quad (4)$$

$$C + O_2 \xrightarrow{CuO_x} CO_2 \quad (5)$$

For the first stage (figure 2a), heating of copper nitrate (up to 180 ° C and above) promotes its decomposition according to equation (1). At the same time, according to the MS analysis data, decomposition of the introduced $Cu(NO_3)_2$ salt begins at lower temperature (140 °C). Nitric oxide decomposition produces NO and NO_2 nitrogen oxides. The NO_2 acts as a strong oxidant by promoting the combustion of carbon and volatile compounds (equations 2 and 3). The interaction of coal with nitrogen dioxide is accompanied by the formation of NO, which is easily oxidized by air oxygen according to reversible reaction (4).

Upon completion of the $Cu(NO_3)_2$ decomposition process, a dispersed non-stoichiometric copper oxide CuO_x is formed. The high catalytic activity of copper oxide for organic substrate and fuel complete oxidation of is well known. It makes it possible to consider the further participation of the formed CuO_x particles as a catalyst for brown coal oxidation acceleration (equation 5).

4 Conclusion

The study on the two-stage (pyrolysis and oxidation) thermal decomposition of the brown coal modified by the copper nitrate additive revealed that the main effect of changing

process temperature regime is concentrated in the temperature range of volatile substance sublimation during active decomposition of copper nitrate. The initiation of volatile matter sublimation occurs as a result of the released NO_x oxidizing properties. In turn, it was found that the resulting non-stoichiometric copper oxide also affects the subsequent process of sample carbon residue oxidation.

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