Change of brown coal oxidation kinetic characteristics by promoting additives appending in the form of copper salts

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Abstract. Process of brown coal oxidation with 5%wt content of copper-salt additives of various nature (Cu(NO₃)₂, CuSO₄ and Cu(CH₃COO)₂) was studied. The experiment has been performed by thermogravimetric analysis at a heating rate of 2.5°C/min to a maximum temperature of 600°C in the air. Analytical evaluation of oxidation process kinetic characteristics has been conducted based on the results of TGA. It has been established that addition of initiating agents leads to significant reduction in the initial ignition temperature of coal ($\Delta T_i = 15\text{÷}40^\circ\text{C}$), shortening of the sample warm-up time to the ignition point ($\Delta t_e = 6\text{÷}12\text{ min}$) and reduction of the sample burning time ($\Delta t_f = 40\text{÷}54\text{ min}$). The following series of additives activity affecting ignition temperature of coals has been established: Cu(CH₃COO)₂ > Cu(NO₃)₂ > CuSO₄. Additionally, the opposite can be said about the effect of additives on residence time of the sample in its combustion area (CuSO₄ > Cu(NO₃)₂ > Cu(CH₃COO)₂). According to mass spectrometric analysis, presence of NOₓ, SO₂, CO₂ (intense peaks at 190÷290°C) was recorded in oxidation products of modified samples, which is explained by partial or complete decomposition of salts.

1. Introduction

Today, direct burning of coal at power plants is one of the simplest and most common technologies for its transformation [1]. One of the serious problems of this method is chemical underburning of coal in boiler furnaces, which may be due to equipment failure or the use of highly reactive fuels when transferring aggregates to a non-projected fuel type. One of the solutions to increase fuel utilization factor is its catalytic combustion [2], which has significant effect on the kinetics of combustion process [3]. Most research in the field of catalytic combustion is focused on the use of rare-earth, transition and alkali metal oxides [4], which contribute to a change in coals reactivity, which in turn leads to an increase in reaction rate and a shift in temperature area of the process to a lesser extent.
Thus, Li [5] studied the effect of transition metal oxides (CuO, Fe₂O₃, ZnO) on kinetic characteristics of coal oxidation process. Results of thermal analysis have shown that above-mentioned additives have significant effect on ignition temperature reduction of released volatiles and residence time reduction of coals in afterburning area of coke residue. In Yin’s studies [6], similar effects are explained by participation of metal oxides as binding substances of oxygen supply to the oxidant, which leads to weakening of oxygen-containing bonds in molecular structure of coals.

Zhao et al. [7] has conducted comparative analysis of oxide additives effect and their precursors in the form of metal nitrates and chlorides on the process of coal oxidation. Obtained results have shown that precursor additives contributed to a greater decrease in initial oxidation temperature of volatile substances and an increase in reaction rate, reducing residence time of the sample in its active oxidation area. Most probably this effect can be explained by formation of oxide gas-phase products during decomposition of salts at the initial stage of sample’s heating. Influence of a number of initiation additives (Cu(NO₃)₂, CuSO₄, Cu(CH₃COO)₂) on the change in kinetic characteristics of brown coal oxidation process is considered in this paper.

2. Experimental part

2.1 Characteristics of researched samples

Brown coal sample from Borodinskoye mine of Kansk-Achinsk coal basin was used in this research. Coarse samples of the initial coal (5-10 mm) were crushed in a drum mill for 9 hours with equal ratio of grinding bodies mass and studied material mass. After grinding, crushed samples were fractionated on sieves with a mesh size of less than 80 μm. Further, the selected coal powder was dried in an oven at 105°C to constant weight, after which its physical characteristics were determined using standard methods [8]. The results are shown in Table 1.

| Table 1. Physical characteristics of coal |
|------------------------------------------|
| Ash content, %wt.                        | 5.2 |
| Moisture content, %wt.                   | 3.0 |
| Volatile substances, %wt.                | 38.8|
| Carbon, %wt.                             | 55.0|
| Humidity ratio, ml/g                     | 3.2 |

As can be seen from Table 1, the studied sample has high content of volatile substances and low value of mineral residue. Micrograph (Fig. 1) made with SEM JSM-6460LV scanning electron microscope (JEOL, Japan) shows that particles in the test sample have spherical shape with an amorphous structure and a large number of surface depressions and cracks.

![Figure 1. SEM micrograph of brown coal sample (x3000)](image-url)
2.2 Application of initiation additives
Copper salts of different nature (Cu(NO$_3$)$_2$·3H$_2$O, CuSO$_4$·5H$_2$O и Cu(CH$_3$COO)$_2$·H$_2$O) were chosen as initiating additives, which were introduced into the coal powders by impregnation with respect to humidity ratio [9]. The content of additives in modified samples was 5% by weight. Water-alcohol solution was used for impregnation in the ratio H$_2$O/C$_2$H$_5$OH = 50:50. When the salt was completely dissolved, the solution was evenly applied to the coal sample using mechanical dispenser. After the additive was applied, the moistened samples were kept in a drying oven at a temperature of 105°C for 20 hours. Further, the resulting agglomerates were milled in a mortar until powdery appearance was achieved.

2.3 Analysis by DTA and MS
Study of coal samples oxidation process has been conducted using STA 449 C Jupiter synchronous thermal analyzer (Netzsch, Germany). Experiments have been performed under the same conditions, at a heating rate of 2.5°C/min in a corundum crucible with perforated cover (sample mass ~ 25 mg) in temperature range 45-600°C. Mixture of air (60 ml/min) and nitrogen (10 ml/min) was used as oxidizing medium. Nitrogen was used as protective gas to ensure reliable operation of analyzer and correct registration of obtained data. In addition, qualitative determination of oxidation products composition has been performed for all considered samples using STA attachment in the form of QMS 403 D Aeolos quadrupole mass spectrometer (Netzsch, Germany). All experiments have been conducted at atmospheric pressure.

2.4. Kinetic analysis
Kinetic parameters of coal oxidation process have been determined graphically (Fig. 2) using obtained TG and DTG curves.

![Figure 2. TG- and DTG-curves for non-modified coal sample](image)

Points A and B on TG curve characterize ignition temperature of exiting volatiles (T$_i$) and the end of combustible mass loss of the sample (T$_f$). Characteristic point C on DTG curve shows maximal value of reaction rate (w$_{max}$) and temperature at a given moment (T$_1$).

3. Results and discussion

3.1 Influence of copper-salt additives on brown coal oxidation process
Based on the obtained results of thermal analysis presented in the form of TG and DTG-curves (Fig. 3), it can be concluded that process of coal oxidation conditionally consists of four stages. The first stage (up to 100°C) is associated with evaporation of external moisture. The next stage (100-295°C) is...
characterized by sublimation of volatile substances from the surface and from within the particles as a result of thermal destruction. The third and fourth stages (295-505°C) are associated with ignition and combustion of combustible mass of sample consisting of pyrolysis products and coke residue.

Considering high content of volatile components (Table 1) in researched coal sample, their combustion proceeds along with coke residue, as evidenced by obtained peaks at DTG curves, which have monomodal distribution in this region of the process. Also, it can be seen from Fig. 3 that samples modified with copper-salt additives have different character of TG and DTG-curves inclination in contrast to the reference samples. This change in the curves is explained by shift of volatile substances release into the low-temperature area of oxidation process, which contributed to a decrease in initial ignition temperature and an increase of coal combustion intensity. It should also be noted that for samples with appending of Cu(NO₃)₂·3H₂O and CuSO₄·5H₂O, an additional peak is observed in the temperature region of 120°C, which is associated with dehydration of salt with monohydrate formation.

Large mass loss is observed in the temperature range of volatile substances sublimation for modified samples, in contrast to the reference samples, which is explained by complete or partial decomposition of salts. Decomposition of salts deposited in structure of coal particles promotes significant shift of ignition temperature to the low-temperature area. Maximal decrease in Tᵢ parameter is observed for the sample with addition of Cu(NO₃)₂, whereas minimal effect is defined for the sample modified by CuSO₄, which can be explained by the highest value of this salt decomposition temperature within investigated series of promoters.

Figure 3 shows MS-curves of NOₓ (m/z=30), COₓ (m/z=44) and SOₓ (m/z=48) emissions in composition of the gas-phase oxidation products of modified samples during decomposition of researched additives. It can be seen that oxidation products featured for these promoters yield in the temperature range 130-250°C for all samples with initiation additives. For the sample with addition of Cu(NO₃)₂, formation of NOₓ precipitation peak (Fig. 4a) in the low-temperature area of the process (190°C) is explained by destruction of applied nitrates, which corresponds to its decomposition temperature [10]. In turn, appearance of additional SOₓ emission peak (Figure 4b) for the sample modified by CuSO₄ promoter in the low-temperature region (290°C) can be explained by partial hydrolysis of this additive.

It follows from Fig. 4c that MS-curve for the sample with addition of Cu(CH₃COO)₂ has similar rate with DTG-curve for this sample. Released during decomposition of copper acetate CO, which can be related to the first maximum of MS-curve at a temperature of 220°C, interacts with the blown
oxidizing medium and is converted to CO$_2$, thereby initiating ignition of coal. Thus, yield of oxide gas-phase products during complete or partial decomposition of copper-salt additives contribute to a more intensive process of coal oxidation.

![Figure 4. MS-curve of NO$_x$ (a), CO$_2$ (b) and SO$_2$ (c) yield.](image)

3.2 Analysis of kinetic characteristics

Kinetic characteristics of oxidation process of researched coal samples are presented in table 2.

| Sample                          | $T_i$, °C | $T_f$, °C | $W_{\text{max}}$, %/min | $t_i$, min | $t_f$, min | $\Delta T_i$, °C | $\Delta T_f$, °C | $\Delta t_i$, min | $\Delta t_f$, min |
|---------------------------------|-----------|-----------|--------------------------|------------|------------|------------------|------------------|------------------|------------------|
| Reference sample                | 280       | 590       | 1.50                     | 94         | 124        | -                | -                | -                | -                |
| Sample with Cu(NO$_3$)$_2$ additive | 250       | 460       | 1.10                     | 82         | 84         | 30               | 130              | 12               | 40               |
| Sample with Cu(CH$_3$COO)$_2$ additive | 240       | 420       | 1.45                     | 78         | 72         | 40               | 170              | 16               | 52               |
| Sample with CuSO$_4$ additive    | 265       | 440       | 1.55                     | 88         | 70         | 15               | 150              | 6                | 54               |

It can be concluded after analysis of the obtained results (Table 2) that appending of initiating additives (Cu(NO$_3$)$_2$, CuSO$_4$ and Cu(CH$_3$COO)$_2$) significantly reduces ignition temperature and sublimation of volatile substances. Maximal decrease in temperature is observed for samples with addition of Cu(CH$_3$COO)$_2$ (40 °C). In case of oxidation of samples modified by Cu(NO$_3$)$_2$ and CuSO$_4$, decrease in ignition temperature was 30°C and 15°C, respectively. It is important to note that the greatest intensity of change in the rate of mass loss coincides with stages of oxidation and volatile
substances release. Decrease in ignition temperature leads to corresponding decrease in residence time of the sample in sublimation area of volatiles $t_r$, maximal decrease of which is observed for the sample with addition of Cu(CH$_3$COO)$_2$ (16 min). It should also be noted that appending of an additive reduces total residence time of the sample, from the beginning of volatiles ignition until production of mineral residue $t_r$, which leads to increase in average flow rate of the process. Maximal decrease in residence time of the sample in combustion area is observed for coal with addition of CuSO$_4$ (54 min). Minimal reduction is defined for the sample with addition of Cu(NO$_3$)$_2$ (40 min).

4 Conclusion

It was shown, as a result of the study, that appending of copper-salt additives by impregnation method with respect to humidity ratio (Cu(NO$_3$)$_2$, Cu(CH$_3$COO)$_2$, CuSO$_4$) (5% by weight) in the brown coal sample helps to lower the temperature corresponding to the beginning of release and ignition of volatile substances. Research of samples oxidation by TGA method allowed determining following order of initiation additives influence on initial ignition temperature of coals: Cu(CH$_3$COO)$_2$ > Cu(NO$_3$)$_2$ > CuSO$_4$. Thus, decrease in residence time of the samples at the stage of volatile substances sublimation is noted as a result of modification. When residence time of the sample in oxidation zone of combustible mass is shortened, the average reaction rate increases, which facilitates shift of the process to a lower temperatures area. The obtained effect is explained by partial or complete decomposition of salts, as evidenced by appearance of oxide gas-phase reaction products, which interact with coal particles during their oxidation. Destruction of initiation additive in pores of carbon matrix contributes to intensification of mass and heat transfer processes, thereby accelerating the overall oxidation process.

5 References

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