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Influence of CuSO₄ initiation additive on kinetic characteristics of coal oxidation and pyrolysis processes

K.B. Larioinov¹, I.V. Mishakov¹,², A.A. Gromov¹,³, A.S. Matveev¹ and A.V. Zenkov¹
¹Tomsk Polytechnic University, Tomsk, Russian Federation
²Boreskov Institute of Catalysis SB RAS, Russian Federation
³Nurnberg Technical University Georg-Simon-Ohm, Nurnberg, Germany

e-mail: laryk070@gmail.com

Abstract. Coals oxidation and pyrolysis processes of different metamorphic grades containing 5%wt of initiation additive were studied. The experiment was performed by thermogravimetric analysis method at a heating rate of 2.5°C/min to a maximum temperature of 600°C in an atmosphere of air and nitrogen. Based on the results of TGA, an analytical evaluation of kinetic characteristics of pyrolysis and oxidation processes was conducted. It has been established that addition of CuSO₄ initiating agent leads to significant decrease in the initial temperature of oxidation and pyrolysis processes, which promotes the shift of the reaction to a low-temperature region. Change of the initial reaction temperature \( \Delta T_i \) for oxidation process was 30°C, \( \Delta T_d \) for pyrolysis was 45°C. Effect of initiation additive was also expressed in significant reduction of sample residence time with volatile substances sublimation zone: for oxidation \( \Delta t_i \) was 14 minutes, for pyrolysis \( \Delta t_d \) was 18 min. For modified sample characterized by lower stage of metamorphism, the decrease in oxidation time \( \Delta t_f \) was the greatest (22 min), which is explained by the high content of volatile substances. According to mass-spectrometric analysis, presence of SO₂ (intense peaks at 290°C and 440°C) was recorded in modified samples oxidation products, which is explained by partial hydrolysis of copper sulfate.

1. Introduction
The modern vector of coal-fired power industry development is aimed at technological improvement of equipment and processes taking place in it, with the purpose of improving ecological, technical and economic performance of fuel-burning plants [1]. One of the promising technologies is catalytic combustion of coal in boiler furnaces [2]. Catalytic additives application for oxidation processes intensification of solid fuels has a significant effect on the kinetics of the process. The shift of oxidation reaction to the low-temperature region helps to reduce emissions of nitrogen and sulfur oxides, while the average combustion rate increases [3]. Most of the research in the field of fuel catalytic conversion [1-4] is aimed at the use of rare earth and transition metal oxides, which promote a decrease in activation energy of volatile substances sublimation, which leads to a shift in the initial ignition temperature of coal. In particular, Gong [4] considered the effect of CeO₂ and Fe₂O₃ additives on oxidation kinetic characteristics of coals at different metamorphism stages. Thus, Liu et al. [5] mention that activation of metal oxides with carbon during layer decomposition appears in the high-temperature region beginning at 550°C. In studies by Zhao et al. [6], the effect of additives-precursors of metal oxide forms based on salts and bases was considered, which had a significant effect on the nature of the process in the low-temperature oxidation region. In previous paper [7] we carried out a study of the effect of additives with different nature (NaNO₃ and CuSO₄) on the kinetics of lignite and bituminous coal oxidation. It was shown that addition of nitrate additives promotes acceleration of
volatile substances release and subsequent ignition in the region of lower temperatures comparing to the reference samples. In this paper, the effect of CuSO$_4$ initiation additive on the change in kinetic characteristics of bituminous coal oxidation and pyrolysis processes is considered.

2. Experimental section

2.1. Characteristic of researched samples

Samples of bituminous coal from "Osinnikovskaya" (sample 1) and "Listvyazhnaya" (sample 2) mines, located in Kemerovo region, were used within this work. Coarse samples of the initial coals (5-10 mm) were pulverized in a drum mill for 9 hours with equal mass ratio of grinding bodies and mill feed material. After grinding, the samples were fractionated on sieves with a mesh size of less than 80 μm. The particle size distribution was determined using Analysette 22 laser particle diffraction analyzer (Fritsch, Germany). The measurement results are shown in Table 1.

| Sample | X$_{10}$ | X$_{50}$ | X$_{90}$ |
|--------|---------|---------|---------|
| 1      | 4.6     | 20.4    | 57.6    |
| 2      | 3.6     | 21.1    | 53.2    |

The selected coal powders were dried in a drying oven at 105°C to a constant weight. Then, their physical characteristics were determined using standard methods [8]. The results are shown in Table 2.

| Characteristic | Samples |
|---------------|---------|
| #1            | #2      |
| Ash content, %wt | 16  | 12  |
| Moisture content, %wt | 4   | 3   |
| Volatile substances, %wt | 15  | 29  |
| Carbon, %wt     | 65     | 56  |
| Humidity ratio, ml/g | 2.7  | 2.9  |

As can be seen from Table 2, samples of coal #1 and #2 have comparable values of carbon amount and humidity ratio, while their content of volatile substances and ash differ significantly. Differences in characteristics are explained by different stage of metamorphism. It should be noted that morphology of the examined coal particles also differs significantly, which can be seen from the micrographs in Fig. 1, obtained with the SEM JSM-6460LV (JEOL, Japan) scanning electron microscope with an ion focused beam.

Particles in sample #1 have an elongated shape, close to cylindrical, with relatively uniform surface, while sample #2 consists of polyhedral spherical particles with amorphous structure and many surface cavities and cracks.

![Figure 1. REM images of bituminous coal samples: a - sample #1, b - sample #2. REM data (x10000)](image-url)
2.2. Application of initiation additive
CuSO₄ promoting additive was added into composition of coal samples by penetration method considering humidity ratio [9]. The content of copper sulfate in the prepared sample was 5%wt. Water-alcohol solution was used for penetration in the ratio H₂O/C₂H₅OH = 50:50. When the salt was completely dissolved, the solution was capillary applied to the prepared coal powders using mechanical dispenser. Further, the resulting slurries were placed in drying oven at 105°C for 20 hours. After drying, the agglomerated samples were pulverized until powdery state was achieved.

2.3. DTA and MS analyses
Research of coal samples thermal decomposition (oxidation) process 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 corundum crucible with perforated cover (sample weight ~ 25 mg) in the temperature range 45-600°C. An inert gas, nitrogen, was used to organize the process in pyrolysis mode. A mixture of air (60 ml/min) and nitrogen (10 ml/min) was used as oxidizing medium. In the latter case, nitrogen was used as a shielding gas to ensure reliable operation of the analyzer and correct registration of the obtained data. For series of samples #1, calorimetric measurements (DSC) were performed to define thermal effects, as well as qualitative determination of oxidation products composition using STA attachment in the form of QMS 403 D Aeolos quadrupole mass spectrometer (Netzsch, Germany). All experiments were conducted at atmospheric pressure.

2.4. Kinetic analysis
Kinetic parameters of coal oxidation and pyrolysis were determined graphically (Fig. 2) using the obtained TG and DTG curves. In the oxidation mode (Fig. 2a), the points A and B on the TG curves characterize ignition temperature of exiting volatiles (Tᵢ) and the end of combustible sample mass loss (Tᵢ). Considering incomplete removal of volatile components during coal pyrolysis process (Fig. 2b) for given heating mode and selected maximum temperature, analysis of initiation additive effect was conducted taking into account temperature of sublimation beginning Td (point A). In both cases, the characteristic point C on DTG curves reflects maximal value of reaction rate (wₘₐₓ) and temperature at a given moment (T₁).

![Figure 2. TG and DTG profiles for unmodified coal sample #1 during oxidation (a) and pyrolysis (b)](image)

3. Results and discussion

3.1. Influence of initiation additive on coal oxidation and pyrolysis processes
Figure 3 shows experimental TG and DTG curves for oxidation and pyrolysis of coal samples, from which it follows that samples modified by CuSO₄ promoting additive have different character of the process in contrast to the reference samples.
Fig. 3. TG and DTG curves for oxidation (a) and pyrolysis (b) of the researched coal samples

Obtained in oxidation mode of unmodified coal samples DTG curves (Fig. 3a) have four distinct peaks. The first peak is due to evaporation of external moisture (up to 100°C), while the second and the third peaks (320–410°C) refer to combustion of volatile substances released from the surface and from the volume of particles as a result of their thermal destruction. The origin of the fourth peak (450–500°C) can be explained by intense burning of coke residue. In turn, two clearly pronounced maxima for test samples pyrolysis process associated with the removal of moisture (up to 100°C) and release of volatile substances (about 430°C) can be identified on DTG curves. It can be seen that series #2 samples pyrolysis occurs in a lower temperature range compared to samples of series #1, which is apparently explained by high content of volatile substances and presence of amorphous component in samples #2. Data analysis of samples containing 5%wt of copper sulfate shows that the presence of initiation additive leads to appearance of additional peak on DTG curve at T = 120°C, which is associated with dehydration of CuSO₄·5H₂O salt to form CuSO₄·H₂O monohydrate. The process is accompanied by marked decrease in the initial volatile substances release temperature and characteristic displacement of the curves corresponding to the process of coal oxidation and pyrolysis to the low-temperature region. Decrease in temperature values at reference points, where the rate of reactions has maximal value, also should be noted. It can be seen from Fig. 3a that DTG curves of modified samples oxidation process have monomodal form, which is explained by joint burning of volatile substances and coke residue formed on the surface of the particles. For the record, modified coal samples pyrolysis (Fig. 3b) is characterized by appearance of one more peak on DTG curves (220–240°C), which can be explained by partial destruction of copper sulfate as a result of hydrolysis.

3.2. Kinetic characteristics analysis

Kinetic characteristics of the process in oxidation and pyrolysis modes are presented in Tables 3 and 4, respectively.
Table 3. Kinetic characteristics of oxidation process

| Sample | $T_i$, ºC | $T_f$, ºC | $w_{max}$, %/min | $t_i$, min | $t_f$, min | $\Delta T_i$, ºC | $\Delta T_f$, ºC | $\Delta t_i$, min | $\Delta t_f$, min |
|--------|-----------|-----------|------------------|------------|------------|----------------|----------------|----------------|----------------|
| #1     | 330       | 590       | 1.17             | 114        | 104        | 35             | 85             | 14             | 20             |
| #1+CuSO₄ | 295      | 505       | 1.13             | 100        | 84         | 45             | 18             |                |                |
| #2     | 300       | 570       | 1.15             | 102        | 108        | 25             | 80             | 10             | 22             |
| #2+CuSO₄ | 275      | 490       | 1.11             | 92         | 86         |                |                |                |                |

Table 4. Kinetic characteristics of pyrolysis process

| Sample | $T_d$, ºC | $w_{max}$, %/min | $t_d$, min | $\Delta T_d$, ºC | $\Delta t_d$, min |
|--------|-----------|------------------|------------|------------------|------------------|
| #1     | 395       | 0.11             | 140        | 45               | 18               |
| #1+CuSO₄ | 350      | 0.13             | 122        |                  |                  |
| #2     | 370       | 0.23             | 130        | 30               | 12               |
| #2+CuSO₄ | 340      | 0.18             | 118        |                  |                  |

Analyzing the obtained results (Tables 3 and 4), it can be concluded that addition of CuSO₄ initiation additive leads to a significant decrease of ignition temperature and sublimation of volatile substances. Maximal temperature decrease is observed for the samples, decomposition process of which took place in an inert medium (45°C for the sample {#1 + CuSO₄} and 30°C for the sample {#2 + CuSO₄}). In case of additionally modified samples #1 and #2 oxidation, the decrease in ignition temperature was 35°C and 25°C, respectively. The greatest temperature shift is observed for modified samples of series #1, characterized by a lower content of volatile substances (Table 1) and the nature of metamorphism. In [4] this effect is explained by relatively smaller number of longitudinal and transverse oxygen-containing bonds in molecular structure of high-carbon coals. It is important to note that the greatest intensity of change in the rate of mass loss coincides with the stages of oxidation and volatile substances release. A decrease in ignition temperature leads to a corresponding decrease in residence time of sample in the region of volatile substances sublimation $t_i$ and $t_d$. It should also be noted that doping of the additive reduces total residence time of the sample, from the start of volatiles ignition to the mineral residue production $t_f$, which leads to an increase in average flow rate of the process. The observed temperature effects are most likely due to the weakening of oxygen-containing molecular bonds in the coal structure, which leads to a more active release of volatile substances. Figure 4 shows thermal effects and results of mass spectrometric analysis (m/z = 48, SO₂) recorded in oxidation mode of series #1 samples.

Figure 4. DSC curves (a) and MS profile of SO₂ evolution (b) for series #1 samples oxidation process
It can be seen that characteristic shape of DSC heat absorption and heat dissipation curves (Figure 4a) is largely similar to corresponding DTG profiles presented in Figure 3a. Endothermic and exothermic effects are associated with removal of coal external moisture, dehydration of salt and further oxidation of pyrolysis gas and coke residue. SO\(_4\) (m/z = 48) was detected in the gas-phase of modified sample oxidation products, and its isolation has bimodal nature (Fig. 4b). Two distinct peaks at temperatures of 290°C and 440°C are most likely due to the partial hydrolysis of CuSO\(_4\) additive, thereby initiating more intensive process of coal oxidation.

4. Conclusion
The study shows that addition of CuSO\(_4\) initiation additive (5% by weight) to composition of coal samples helps to reduce the temperature corresponding to the beginning of release and ignition of volatile substances, irrespective of the process mode (pyrolysis or oxidation). The greatest change in the initial temperature refers to the modified samples, thermal decomposition of which was conducted in inert medium. Most importantly, this effect appeared in series #1 modified samples, which have low content of volatile substances. In general, as a result of the modification, there is a decrease in samples' residence time at the stage of volatile substances sublimation. As a result of oxidation time reduction of the samples combustible mass in the air, an increase in average reaction rate occurs, which facilitates shift of the process to lower temperatures. The result is associated with dehydration and partial hydrolysis of copper sulfate, as evidenced by appearance of SO\(_2\) in reaction products. Destruction of initiation additive in carbon matrix pores contributes to intensification of mass and heat transfer processes, thereby accelerating the overall process of oxidation (pyrolysis).

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