

# INFLUENCE OF $\text{NaNO}_3$ AND $\text{CuSO}_4$ CATALYTIC ADDITIVES ON COAL OXIDATION PROCESS KINETIC DEPENDENCIES

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**Abstract.** Experimental studies of bituminous coal and lignite oxidation were conducted with the addition of different nature catalytic additives:  $\text{NaNO}_3$  and  $\text{CuSO}_4$ . The results showed that added mineral salts led to a noticeable decrease in the coals initial oxidation temperature and reaction acceleration at an early stage of the process.

## 1 Introduction

According to statistics [1], coal production occupies a leading position in the modern fuel and energy structure along with such conventional fuels as oil and gas. In turn, direct coal combustion in domestic and power-plant boilers is accompanied by a large amount of harmful substances release [2]. Today, the most eco-efficient technology of coal application is its gasification, as a result of which the generator gas is produced [3]. Active work on the development of various methods is conducted in the world as part of this technological process, aimed at improving the reliability and efficiency of gas plants. One possible solution is to use catalytic agents that improve kinetic characteristics of the process and increase the fuel application efficiency [4].

Most of the existing studies on catalytic gasification are directed to the use of alkali, transition and rare-earth metals oxides [5]. The main effect of using such catalytic additives is reduction of temperature at which fuel oxidation process starts. It is known [6], that the inclusion of catalytic additives based on various kinds of metal oxides in the gasification process is manifested most efficiently only at high temperatures (over 500 °C).

It is known [7] that the precursors of metal oxides, such as nitrates and sulfates, have strong oxidizing properties, low melting point (decomposition) and good solubility in water. It simplifies the process of their mixing with coal and improves communication of the “coal-catalyst” system by filling available pores of solid fuel [8].

The results of coal oxidation experimental studies with introduction of catalytic additives of different nature ( $\text{NaNO}_3$  and  $\text{CuSO}_4$ ) are presented in this paper. Also, an assessment of kinetic parameters changes is provided.

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## 2 Experimental setup and study technique

Bituminous coal from Osinnikovskiy coal deposit and lignite from Borodinskiy deposit were considered as initial solid fuel samples in this study. These coals are characterized by their morphology and the degree of metamorphism [9].

Coarse samples were milled in a ball-mill drum under identical conditions, and then sieved through a sieve with cells size of less than 80 microns.

Sieved coal powders were dried in an LF 25/350-VS1 drying oven (Loip, Russia) at 105 °C. Technical characteristics of these samples (Table 1) were determined by means of the existing techniques [10-13].

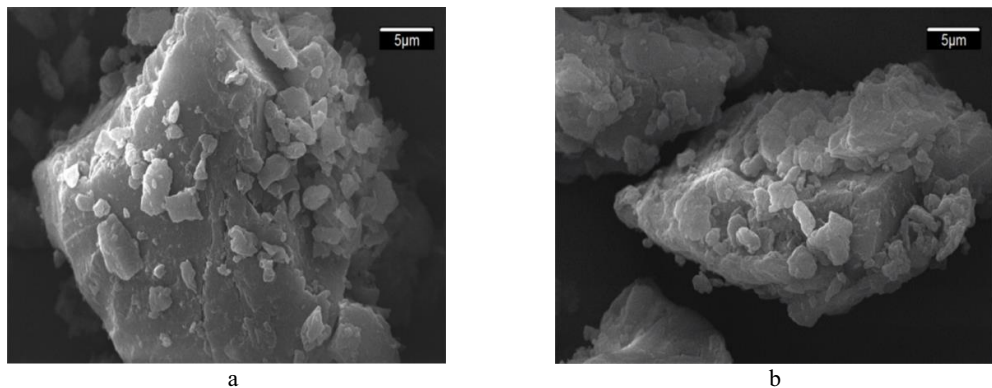
**Table 1.** Initial coal characteristics\*.

Characteristic	Coal	
	Bituminous	Lignite
Ash content, mass %	7	5
Humidity, mass %	0,3	1,1
Volatiles, mass %	29	39
Fixed carbon, mass %	63,7	54,9

\*Samples characteristics are given after their drying at 105°C.

The results in Table 1 show that bituminous coal, unlike lignite, has a higher content of connected carbon and mineral residue. In turn, the opposite can be said about the value of volatile substances output, due to different metamorphism degree of presented in the research coal types [10].

Microscopy of the researched samples (Figure 1) was performed via SEM JSM-6460LV device (JEOL, Japan) with focused ion beam to assess their morphological characteristics.



**Fig. 1.** Coal samples microphotograph with x3000 zoom (a – bituminous coal, b – lignite).

According to Figure 1, the bituminous coal particles have a dense oblong appearance. In turn, lignite particles have multi-faceted spherical shape and amorphous surface.

Next, obtained samples were mixed by capillary impregnation with catalytic additives  $\text{NaNO}_3$  and  $\text{CuSO}_4$ , previously saluted in a water-alcoholic medium at a volumetric ratio of 1:1. The catalytic additive weight content was 5 % of the studied sample total weight (5 mass % of the catalytic additive and 95 mass % of coal).

The obtained slurry was dried in drying oven at 105 °C for 20 hours. After that, agglomerated samples were mixed in a stamp for 7 minutes to obtain a powder-shaped

state. It is necessary to add that reference samples were prepared for comparative analysis of catalytic additives influence. These samples were exposed to identical preparation procedures, but mentioned above additives were not added.

A serial number was assigned to each sample, in order to facilitate conduction of subsequent experimental work and results analysis. List of the prepared samples is presented in Table 2.

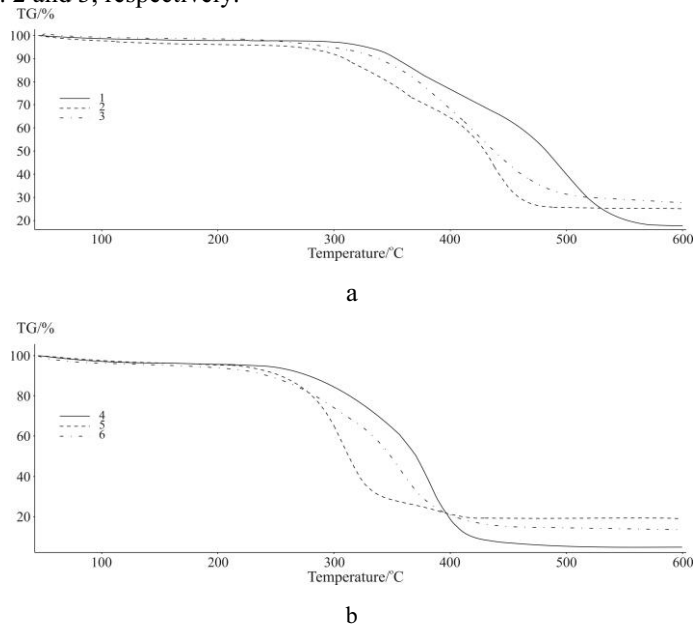
**Table 2.** List of synthesized samples.

Sample name	Serial number of the sample
<i>Bituminous coal</i>	
Bituminous coal reference sample	1
Bituminous coal + 5% NaNO <sub>3</sub>	2
Bituminous coal + 5% CuSO <sub>4</sub>	3
<i>Lignite</i>	
Lignite reference sample	4
Lignite + 5% NaNO <sub>3</sub>	5
Lignite + 5% CuSO <sub>4</sub>	6

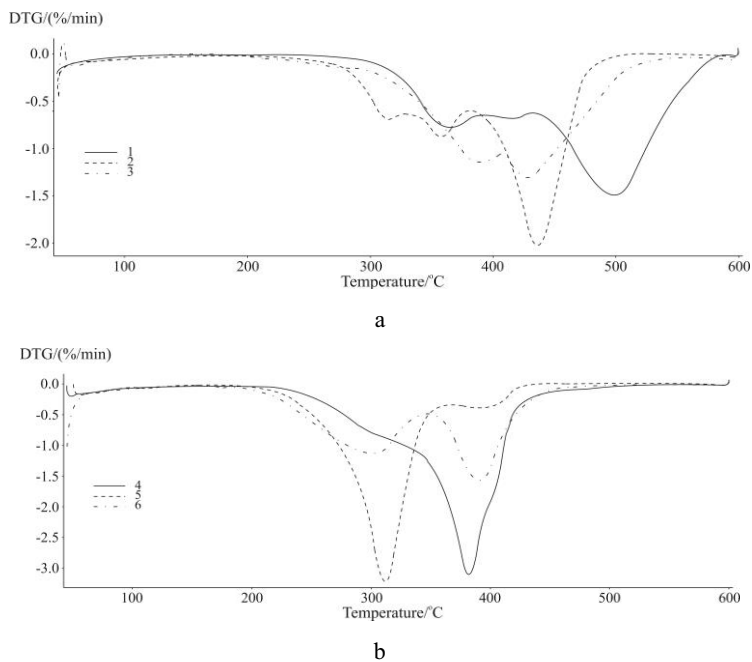
Determination of the kinetics of prepared coal samples oxidation was conducted with the use of Netzsch STA 449 °C Jupiter thermogravimetric analyzer (Germany). All experiments were carried out in similar conditions at a heating rate of 2.5 °C/min in a corundum crucible (sample weight of about 7 mg) in the temperature range of 50-600 °C. Mixture of air (60 ml/min) and nitrogen (10 ml/min) was used as an oxidizing medium.

### 3 Experimental results

Results of researched samples thermal analysis are presented in the form of TG and DTG curves in Fig. 2 and 3, respectively.



**Fig. 2.** Thermogravimetric curves (TG) of coal samples oxidation (a - bituminous coal samples, b - lignite samples).



**Fig. 3.** Differential curves (DTG) of coal samples oxidation (a – bituminous coal samples, b – lignite samples).

According to Fig. 2, the temperature corresponding to 10 % in mass loss for initial samples 1 and 4 was 356 °C and 278 °C, respectively. For coals with addition of  $\text{NaNO}_3$  (samples 2 and 5), this temperature is 338 °C and 244 °C (sample 5), and with the addition of  $\text{CuSO}_4$  (samples 3 and 6) – 310 °C and 255 °C. Thus, the largest shift towards reduction of initial stage oxidation temperature is observed in samples 3 and 5, for which the change was 44 °C and 34 °C, respectively. Despite the fact that the addition of  $\text{NaNO}_3$  has considerable catalytic effect at the initial stage of lignite oxidation process, the total reaction time in comparison with the original sample increased by 15 % because of residual carbon oxidation for both samples ends in the same temperature range (about 480 °C).

In turn, the greatest value of reaction maximum speed, determined from DTG data (Figure 3), corresponds to the samples with addition of  $\text{CuSO}_4$ . This figure rises by 37 % for bituminous coal and by 7 % for lignite. It should also be noted, that addition of catalytic additive is accompanied by increased reaction rate at an early stage of the oxidation. This is most clearly expressed for bituminous coal samples, which have lower content of longitudinal and transverse molecular bonds.

The effect of coal oxidation reaction rate increase (reduction of process start temperature) for samples with different catalytic additives is directly related to the decomposition of salts, which is observed at low temperatures area, with respect to the process of volatiles release. Oxide gas compounds, which act as transporters of oxygen from the oxidant to the oxidized substrate, are released as a result of salts decomposition. This process is accompanied by decrease of molecular bonding strength during intensified chain reaction, especially oxygen-containing groups, which leads to an earlier volatilization of volatile compounds and their subsequent ignition. In addition, synergy of this effect is reduction of diffusion resistance, because of coal structure thermal degradation, consisting of a large number of micro- and macropores.

## 4 Conclusion

The experimental studies have shown that the introduction of  $\text{NaNO}_3$  and  $\text{CuSO}_4$  mineral salts catalytic additives leads to a noticeable acceleration of the coal oxidation process as a result of oxide gas release at the decomposition stage. Released at an earlier stage of the process volatiles are split into light gases and enriched with carbon fine particles, making it easier to burn.

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