Research of lignite oxidation kinetic parameters modified by $CuSO_4$ and $NaNO_3$ initiation additives

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Abstract. An experimental study and subsequent analytical assessment of activation energy change in lignite oxidation process with addition of $NaNO_3$ and $CuSO_4$ mineral salts were conducted. The results showed that injection of catalytic additives leads to reduction of coal activation energy and reaction initial temperature.

1 Introduction

Nowadays, coal is one of the most popular traditional fuel types [1]. Current trends in the development of coal-based energetics are concentrated on new technologies aimed at improving environmental, technical and economic performance of the fuel combustion installations [2]. One of the most promising coal application technologies for heat and electricity production is its promoting combustion [3]. The use of initiation additives to intensify the solid fuel combustion processes has a significant effect on the kinetics of the process. Drop of the reaction temperature range leads to reduction of sulfur and nitrogen oxides high-temperature emissions and the average burn rate increase [4]. All of these effects happen due to activation energy reduction. Activation energy is the amount of energy that needs to be provided to the system to ensure that the reaction occurs. Thus, the effectiveness of a particular catalytic additive can be assessed by the amount of activation energy.

In this paper the effect of $NaNO_3$ and $CuSO_4$ initiation additives on the change in kinetic characteristics of brown coal oxidation process is considered.

2 Experimental setup and study technique

Samples of Borodinskoe deposit lignite were used in this research. Initial fuel was grinded in a ball-mill pulverizer and sifted through a sieve with a mesh size of 80 microns. Composition of the researched fuel was determined according to standard methods [5] and is shown in Table 1.

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Table 1. Composition of the initial coal.

Index	Unit of measure	Value
Analytical moisture	wt./%	11.6
Volatile content		40.8
Ash content		4.0
Carbon content		43.6

The studies were conducted with the use of Netzsch STA 449 F3 Jupiter (Germany) simultaneous thermal analyzer. All experiments were performed under identical conditions with the sample heating rate of 2.5℃/min in a corundum crucible (sample weight approximately 7mg) at the temperature range 50-600℃. A mixture of air and nitrogen was used as an oxidizing medium with a flow rate of 60 ml/min and 10 ml/min respectively.

Synthesis of coal samples with initiation additive was performed by incipient wetness impregnation method by their dissolving in alcohol-water medium in the bulk concentration of 1:1. The additives weight content is 5% of the sample total mass. Coals were dried after impregnation in a drying oven at 105°C for 20 hours.

Equation, which links the reaction rate to kinetic parameters, was used to determine activation energy of oxidation reaction of pure brown coal and samples modified by promoting additives.

The reaction rate is expressed as a first time derivative of the conversion degree dα/dt. In turn, conversion degree is equal to the proportion of reacted product and is converted into equation [6]:

$$\alpha = \frac{m_i - m}{m_i - m_f}, \tag{1}$$

here m_i is initial mass; m_f is final mass; m is current mass.

The reaction rate represents multiplication of two functions [6]:

$$\frac{d\alpha}{dt} = f(T)g(\alpha), \tag{2}$$

here $f(T)$ is function depending only on temperature; $g(\alpha)$ is function depending only on conversion degree.

Function of temperature is expressed as the Arrhenius equation [6]:

$$f(T) = Aexp\left(-\frac{E}{RT}\right), \tag{3}$$

here A is pre-exponential factor; E is activation energy; R is absolute gas constant; T is absolute temperature.

In turn, a function of the conversion degree can be considered as a first order model [6]:

$$g(\alpha) = (1 - \alpha). \tag{4}$$

Thus, the activation energy can be found with the use of the experimental data and these equations. But differentiation of dα/dt is associated with a significant loss in accuracy, so different approximate solutions of this differential equation are often used in practice. Following approximate solution was used in this paper [6]:

$$ln\left[-\frac{\ln(1-\alpha)}{T^2}\right] = ln\left[\frac{AR}{\beta E}\right] - \frac{E}{RT}, \tag{5}$$

here β is sample heating rate.

It is sufficient to plot a dependence of $ln\left[-\frac{\ln(1-\alpha)}{T^2}\right]$ from 1/T using experimental data in order to use this equation to determine the activation energy. Then, it is necessary to approximate, while the angular coefficient is equal to the value of E/R, where it is easy to determine the activation energy E from.

3 Experimental results

The results of researched samples thermal analysis are presented in Figure 1 as a TG curve.

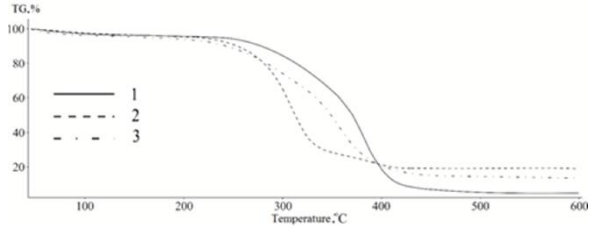

Fig 1. Thermogravimetric curves (TG) of coal samples oxidation (1 – lignite comparison sample, 2 - lignite + $NaNO_3$, 3 - lignite + $CuSO_4$).

According to figure 1, reaction start temperature of the initial sample 1 was 278°C. This temperature is 244°C for a sample with the addition of $NaNO_3$ and 255°C with the addition of $CuSO_4$. Thus, the largest shift in the direction of oxidation beginning temperature decrease is observed in the sample 2, for which the change was 34°C.

Certain activation energy numerical values of the samples are presented in Table 2.

Table 2. Activation energy of coal samples.

Sample	**1**	**2**	**3**
E, kJ/mol	72.0	67.4	69.6
A, 1/min	24332	19244	16314

It is seen from obtained results that the use of initiation additives reduces kinetic parameters values. The smallest value of activation energy is achieved in the case of $NaNO_3$ application and differs from the initial sample by 6.4%.

4 Conclusion

Conducted experimental and numerical studies have shown that the injection of promoting additives in the form of $NaNO_3$ and $CuSO_4$ mineral salts greatly influences the nature of the reaction. It turns out, that $NaNO_3$ is more active than $CuSO_4$, which is proved by lower value of activation energy.

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