Studying kinetics of thermal decomposition of coals and combustion of mechanoactivated microgrinding coals

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Abstract. In this paper, we investigate the effect of mechanically activated coal grinding by two different methods - determination of the flash time in a vertical tubular furnace and thermogravimetric analysis. In the experiments, the coals processed in a disintegrator and initial coal were compared. The experiments have shown a decrease in the ignition temperature of mechanically activated coals, as well as the effect of mechanical activation on further thermal-oxidative degradation.

1. Introduction

At present, most coal-fired power plants operate using petroleum products to start and colour the boiler during operation. The cost of these petroleum products is much higher than that of coal itself, which indicates the relevance of the introduction of new technologies to exclude petroleum products from the energy processes taking place at the CHP.

The technology of mechanoactivation grinding, studied at IT SB RAS, allows excluding gas or fuel oil from the operation cycle of an industrial boiler; this technology was tested on a large fire stand with a capacity of 5 MW. As a result of the experiments, it has been found that mechanically activated carbon increases its chemical activity, ignites, burns and then reaches the auto-thermal regime similar to gas-oil fuels. [1]

The reaction characteristics of coals obtained during mechanoactivation grinding and the effect of mechanoactivation on ignition and subsequent combustion of coal remains a topical issue. In this paper, coal is studied using two different methods: determining the self-ignition temperature of coals in a vertical tubular furnace, Figure 1, and thermogravimetric analysis, Figure 2.

When macromolecules deform, the structure of molecular chains changes, the interatomic and intermolecular distances change, which is accompanied by a weakening of intra- and intermolecular bonds and a corresponding increase in the free energy of matter. When the electronic shells deform, the energy barrier of reactions decreases. When coal is dispersed, structural changes take place with a decrease in the packing density and a decrease in the fraction of carbon atoms ordered into layers, etc. These processes approximate the burning of pulverized coal fines to the combustion of gas-oil fuels. In this paper, we investigate coals of varying degrees of metamorphism and grinding type using two different techniques, namely, thermogravimetric analysis and determination of the ignition temperature in the "Vertical tube furnace" setup. Studies of the kinetics of thermal decomposition of coal using thermogravimetric analysis (TGA) allow determining the main effects of slow thermal decomposition of fuel samples (10 ÷ 30 °C/min), which does not correspond to the actual processes of

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ignition and combustion of coal dust in the combustion chambers of boiler plants. Therefore, it is of great interest to study the processes of ignition and the initial stage of combustion of coal dust particles in thermal conditions close to real combustion devices. In addition, the characteristic time for mechanically activated grinding of fuels is a fraction of a second with possible short-term retention of highly reactive properties of coal particles after grinding, which requires studying the chemical activity of fuels also under rapid thermal decomposition. These conditions maximally correspond to the methodology of studying the ignition and combustion of dust particles in a batch feed to a vertical tubular furnace.

![Figure 1. Vertical furnace tube](image1.jpg)

![Figure 2. STA 449F1 Jupiter.](image2.jpg)

2. Experimental part

Synchronous thermal analysis (STA), which includes simultaneous thermogravimetric determination (TG) of differential scanning calorimetry (DSC) and mass spectrometric analysis of the recovered gas (ABG-MS), was performed on a STA 449F1 Jupiter® instrument combined with a quadrupole mass spectrometer QMS 403D Aëolos® (NETZSCH, Germany). The experiments were carried out using a high-temperature furnace with a graphite heater and water cooling. We used a measuring sensor DSC/TG Cp S TC: type S (0 ... 1650 °C). The experiments were carried out in a temperature range of 50-800 °C in the atmosphere of synthetic air (80% by volume of Ar, 20% by volume of O₂), gas flow rates of 20 ml / min of argon, and 5 ml / min of oxygen. Open crucibles from Al₂O₃ were used. The heating rate was 10 °C/min. The processing of the experimental data was carried out using the Proteus analysis software package.

The calibration procedure was realized using a standard calibration kit with the following high purity substances: In, Sn, Bi, Zn, Al, Ag, Au. The calibration was carried out under the same conditions that were subsequently used in the experiments (heating rate, atmosphere, sample holder, crucible material, temperature interval, etc.). The melting temperature of the standard substances was taken to be the peak temperature (according to ISO 11357-1, DIN 51007) [4]. The obtained values were used to construct a calibration graph and create a temperature calibration file - Figure. 3.
Figure 3. Temperature calibration of the STA device in an atmosphere of synthetic air.

Measurement of coal samples was carried out according to the following scheme:
- baseline measurement (two empty crucibles) using a temperature calibration file;
- measurement of the coal sample being examined.

Typical curves for thermal analysis with MC curves for a sample of coking coal are shown in Figure 2. The first stage of decomposition for all types of coals occurs in the temperature range of 50-200 °C and is the removal of water. In this case, only the ion current with m/z is recorded in the mass spectrum of gaseous products. The second stage of decomposition in the interval 220-520 °C is accompanied by a significant exoeffect and leads to a loss of ~64% of the mass. The main gaseous product released at this stage is CO₂ and H₂O (m/z 44 and 18). In addition, insignificant ion currents with m/z 15, 29, 30, 41 and 42 are recorded, which indicates the release of gaseous hydrocarbon products. The main process at this stage is coal combustion but depending on the type of coal at this stage, coking processes can occur, leading to the formation of appreciable amounts of coke. Further combustion of coke takes place in the range of 520-660 °C. The main gaseous product is CO₂ (m/z 44). The fireproof residue is 13%.

Studies of the kinetics of thermal decomposition of coal using thermogravimetric analysis (TGA) allow determining the main effects of slow thermal decomposition of fuel samples (10 ÷ 30 °C/min), which does not correspond to the actual processes of ignition and combustion of coal dust in the combustion chambers of boiler plants. Therefore, it is of great interest to study the ignition and the initial stage of combustion of coal dust particles in thermal conditions close to real combustion devices. In addition, the characteristic times for mechanically activated grinding of fuels are fractions of a second with possible short-term retention of highly reactive properties of the coal particles after grinding, which requires studying the chemical activity of fuels also under rapid thermal decomposition. These conditions maximally correspond to the methodology of studying the ignition and combustion of dust particles in a batch feed to a "Vertical tube furnace." [5]

"Vertical tube furnace" stand is shown in Figure 4. The "Vertical tube furnace" setup is a insulated 1 m long steel pipe with an internal diameter of 40 mm, suspended vertically. Electrical heating is carried out using the system of low-voltage transformers. Over the entire length of the combustion chamber, photodiodes and thermocouples (TCA) are disposed in special holes in steps of 100 mm, designed to record the flash and temperature, respectively. To stabilize the temperature at the entrance to the furnace, as well as to remove parasitic convective currents and combustion products, air flow with a velocity of 0-100 mm/sec is fed into the chamber.

The starting mechanism consists of a magnetic valve and a chamber with a volume of 45 mm³. Above the valve there is a dust collector, where samples weighing from 0.1 to 1 g are fed. Then air is pumped into the chamber (1atm) and coal dust is injected into the furnace. The maximum temperature that can be obtained using existing transformers is 1000 °C. The arrival of dust into the combustion chamber is recorded by a microphone connected to the Lcard. The flash is recorded using thermocouples and photodiodes. The thermocouples are connected to the analog input module MVA8,
which in turn is connected to the computer. The photodiodes through the amplifier are connected to the Lcard EP 14-440 ADC, which is connected to the computer to record the acquired time data using the L-graph program. This technique allows determining the minimum ignition temperature of coal dust, as well as the time of ignition of dust, depending on the temperature of the furnace.

![Thermal analysis curves with MC curves for a sample of coking coal obtained in a synthetic air atmosphere at a heating rate of 10 °C / min](image)

**Figure 4.** Thermal analysis curves with MC curves for a sample of coking coal obtained in a synthetic air atmosphere at a heating rate of 10 °C / min

### 3. Results

The analytical solution of the problem of self-ignition in a flow with allowance for the reaction of a complex of particles is based on the assumption of adiabatic conditions in the chamber. In a dimensionless form, the equation for ignition can be written in the following form [6]:

$$\frac{d\theta}{d\tau} = \frac{1}{B^2} e^{-1/\theta}, \text{ at } \tau=0, \theta=\theta_0, \theta \text{ is the dimensionless temperature, } \tau \text{ is the dimensionless time.}$$

$$\lg \tau^0_B = \frac{A}{\theta_0} - B,$$

where A is the line slope to the abscissa; and B is the value of $\lg \tau^0_B$ for $1/\theta_0 = 0$. The values of A and B depend on the accuracy of the solution of the equation and the approximation of the obtained solutions. With sufficient accuracy for practical calculations, they can be taken equal to $A = 0.322$ and $B = 2.824$.

$$\tau^0_B = t \frac{Q_H \beta C_0 \mu_0 f^{2.73} R^3}{C_{CM} E^3},$$

$Q_H$ is the heat of fuel combustion, $\beta$ is the stoichiometric coefficient, $C_0$ is the initial concentration of oxygen, $\mu_0$ is the initial concentration of the fuel, $f$ is the specific surface of the dust, $R$ is the universal gas constant, $t$ is the time, $C_B$ is the heat capacity of the air, $C_a$ is the heat capacity of the dust, and $E$ is the activation energy.
This equation is universal for any fuels and regime parameters. A sharp rise in temperature corresponds to self-ignition. The value of the dimensionless time \( \tau \) at a given moment corresponds to the time from the beginning of the process to the onset of self-ignition \( \tau_0 \). In the coordinate system \( \lg \tau \ = f \left( \frac{1}{\theta_0} \right) \), the time dependence during which autoignition takes place at a given value of \( \theta_0 \) is expressed by a straight line:

\[
\tau_0^0 = M_B K_0 \theta_0^{-3}, \quad \text{where} \quad M_B = \left( \frac{\theta_0}{\mu_B + \mu_G + \mu_n} \right)^{\frac{1}{2} \theta_0^2 R^3}.
\]

The \( M_B \) complex includes all the quantities known from the experiment. If the experimental data is processed in the form of the dependence \( \lg M_B = f \left( \frac{1}{\theta_0} \right) \), and if \( K_0 \) and \( E \) are constant values, a straight line is obtained which can be described by equation \( E = \frac{R}{\theta} \). If the experimental data is processed in the form of the dependence \( \lg M_B = f \left( \frac{1}{\theta_0} \right) \), and if \( K_0 \) and \( E \) are constant values, a straight line is obtained which can be described by equation \( E = \frac{R}{\theta} \).

To obtain the activation energy, thermogravimetric analysis was carried out at three different heating rates, Figure 5.

![Figure 5. TGA of brown coal at different heating rates.](image)

To obtain the activation energy based on the results of TGA, the Avrami Erofeev model was used.

**Table 1. Energy of activation**

| Brown coal     | E, kJ/mol |
|----------------|-----------|
|                | Ver. Tube | TGA     |
| Initial        | 115385    | 117154  |
| Disintegrator  | 103126    | 104367  |

The ignition temperatures of coal were also determined depending on the type of grinding.

**Table 2. The ignition temperature of coal determined by various methods**

| Type of grinding | T, °C |
|------------------|-------|
|                  | Ver. Tube | TGA |
| Initial          | 537    | 400 |
| Disintegrator    | 348    | 375 |

**4. Conclusion**

The results obtained by different methods correlate with each other. They show a decrease in the ignition temperature of micropole coal during mechanically activated grinding. For undetermined reasons, the ignition temperature of the original brown coal, determined by the results of TGA, is significantly different, since coal is a non-uniform substance. Perhaps this is due to the accuracy of dust sampling for analysis.
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