Study of kinetic characteristics of mechanical activated micro grinding coals in the process of thermal decomposition and ignition

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Abstract. In this paper, we investigate the effect of mechanically activating grinding of coals of various degrees of metamorphism by two different methods - determination of the flash time in a vertical tubular furnace and thermogravimetric analysis. In the experiments, the coals that had been processed on a vibrating centrifugal mill and a disintegrator were compared. The experiments showed a decrease in the ignition temperature of mechanically activated coals, as well as the effect of mechanical activation on the further process of thermal-oxidative degradation.

1. Introduction

Coal is one of the most important energy carriers in the world. At present, most coal-fired power plants operate using petroleum products to start and maintain energy boilers. The cost of these petroleum products significantly exceeds the cost of the coal itself, and therefore the introduction of new technologies that allow excluding petroleum products from energy processes is very important [1].

Approximation of the reaction properties of mechanically activated micropole coals to the properties of gas and fuel oil opens up wide possibilities for replacing fuels in gas-oil boilers with mechanically activated coals. Under mechanical effects on coal, certain chemical bonds disintegrate with the formation of free radicals, which accelerate the subsequent course of chemical reactions [2,3]. This also causes deformation of the organic component of the fuel, which represents a high molecular weight formation. While the 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. While 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, as well as a decrease in the fraction of carbon atoms ordered into the layers, etc. These processes approximate the burning of pulverized coal 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" installation. Studies of the kinetics of thermal decomposition of coal using thermogravimetric analysis (TGA) make it possible to determine 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 processes of ignition and the initial stage of combustion of coal dust particles in thermal conditions close to those taking place in real combustion devices. In addition, the characteristic time for mechanically activating grinding of fuels is a fraction of a second with the possible short-term preservation of the highly reactive properties of coal particles after grinding, which requires studies of the chemical activity of fuels also under conditions of rapid thermal decomposition. These conditions correspond to the maximum extent to the methodology for studying the ignition and combustion of dust particles in a batch feed to a vertical tubular furnace.

2. Experimental part
Synchronous thermal analysis (STA), which includes simultaneous thermogravimetric determinations (TG) of differential scanning calorimetry (DSC) and mass spectrometric analysis of the recovered gas (ABG-MS), was performed using 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 within a temperature range of 50-800°C in an 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 measurement error was about 0.2%.

The calibration procedure was carried out using a standard calibration kit that included the following high purity substances: In, Sn, Bi, Zn, Al, Ag, and 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 1.

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 within 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 within the interval of 220-520°C is accompanied by a significant exothermic effect and leads to a loss of ~ 64% of the mass. The main gaseous products released at this stage are 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 the combustion of coal but depending on the type of coal at this stage, coking processes can occur, leading to the formation of appreciable

![Figure 1](image-url)
amounts of coke. Further combustion of coke takes place within the range of 520-660 °C. The main gaseous product is CO\(_2\) (m/z 44). The fireproof residue is 13%.

Studies of the kinetics of thermal decomposition of coal using thermogravimetric analysis (TGA) make it possible to determine 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 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 times for mechanically activated grinding of fuels are fractions of a second with the possible short-term preservation of highly reactive properties of the coal particles after grinding, which requires studies of the chemical activity of fuels also under conditions of rapid thermal decomposition. These conditions correspond to the maximum extent of the methodology for 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 3. The "Vertical tube furnace" setup is a vertical insulated steel pipe 1 m long, with an internal diameter of 40 mm, suspended vertically. Using the system of low-voltage transformers, electrical heating is carried out. Over the entire length of the combustion chamber, photodiodes and thermocouples (TCA) are disposed in special holes at a distance 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 mm\(^3\). Above the valve there is a dust collector, where samples weighing 0.1 to 1 g are filled. Then air is

![Figure 2](image)

**Figure 2.** 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
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 dust ignition, depending on the temperature of the furnace.

3. Results

The processing of the experimental data was carried out using the Proteus analysis software package. The ignition temperature is determined by the method of tangents. A number of other temperatures were also determined to calculate the kinetic parameters, and the residual value of the mass.

Figure 3. Vertical furnace tube.

Figure 4. Results of thermogravimetric analysis of coal, black – initial dust, green - dust grinding by VCM, red - grinding by disintegrator.
Maximum burning rate \( DTG_{\text{max}} = \left( \frac{dw}{dt} \right)_{\text{max}} \).

Ignition index \( D_i = \frac{DTG_{\text{max}}}{t_p t_i} \), where \( t_p \) is the maximum burning time, \( t_i \) is the ignition time.

Burnout index \( D_f = \frac{DTG_{\text{max}}}{\Delta t_{1/2} t_p t_f} \), where \( \Delta t_{1/2} \) is the time range \( \frac{dt}{dw} \) or \( \frac{dw}{dt} \).

Comprehensive index \( S_{\text{mean}} = \frac{DTG_{\text{max}} DTG_{\text{mean}}}{t_i^2 t_f} \).

Tables 1 to 5 show the values of the kinetic parameters under different conditions: for coals of different stages of metamorphism and grinding type, at different temperatures [6]. For anthracites and brown coals, the results are divided into two temperature intervals. This is due to the coking of the sample in the TGA process. For coal, this effect was observed only for the sample obtained on the disintegrator, which can be seen in figure 4.

It should be noted that the parameter of the maximum burning rate (\( DTG_{\text{max}} \)) for samples of coals ground by the activator mills is higher, which indicates a more intensive process of their ignition. The parameter \( D_i \) - the index of ignition, indicates that the ignition of samples of mechanically activated

### Table 1. Kinetic parameters of the process of coal oxidation (condition 1).

| 200-500 °C | Kinetic parameters |
|------------|-------------------|
| Type of coal | Type of grinding | DTG max, %/min | \( D_n \), 1/min³ | \( D_p \), 1/min⁴ | \( S \), 1/min²°C³ |
| Initial | | 0.28 | 0.0012 | 0.0002 | 9.5E-10 |
| Anthracites | VCM | 1.04 | 0.0055 | 0.00036 | 1.8E-08 |
| | Disintegrator | 1.11 | 0.00574 | 0.0012 | 1.5E-08 |

### Table 2. Kinetic parameters of the process of coal oxidation (condition 2).

| 500-800 °C | Kinetic parameters |
|------------|-------------------|
| Type of coal | Type of grinding | DTG max, %/min | \( D_n \), 1/min³ | \( D_p \), 1/min⁴ | \( S \), 1/min²°C³ |
| Initial | | 3.1 | 0.0022 | 0.00023 | 3.78E-08 |
| Anthracites | VCM | 3.11 | 0.0029 | 0.0018 | 4.77E-08 |
| | Disintegrator | 2.65 | 0.0024 | 0.001 | 3.68E-08 |

### Table 3. Kinetic parameters of the process of coal oxidation (condition 3).

| 200-500 °C | Kinetic parameters |
|------------|-------------------|
| Type of coal | Type of grinding | DTG max, %/min | \( D_n \), 1/min³ | \( D_p \), 1/min⁴ | \( S \), 1/min²°C³ |
| Initial | | 3.1 | 0.045 | 0.0032 | 2.25E-07 |
| Brown coal | VCM | 2.16 | 0.1 | 0.0088 | 1.97E-07 |
| | Disintegrator | 3.17 | 0.03 | 0.0036 | 1.78E-07 |

### Table 4. Kinetic parameters of the process of coal oxidation (condition 4).

| 500-700 °C | Kinetic parameters |
|------------|-------------------|
| Type of coal | Type of grinding | DTG max, %/min | \( D_n \), 1/min³ | \( D_p \), 1/min⁴ | \( S \), 1/min²°C³ |
| Initial | | 0.84 | 0.0006 | 0.00014 | 3.08E-09 |
| Brown coal | VCM | 1.08 | 0.0007 | 0.00027 | 4.56E-09 |
| | Disintegrator | 1.4 | 0.0009 | 0.00024 | 7.68E-09 |
Table 5. Kinetic parameters of the process of coal oxidation (condition 5).

| 200-600 °C | Kinetic parameters |
|-------------|--------------------|
| Type of coal | Type of grinding | DTG max, %/min | $D_a$, 1/min$^3$ | $D_f$, 1/min$^4$ | $S$, 1/min$^2$°C$^3$ |
| Initial     | VCM                | 2.65            | 0.01             | 0.00035         | 1.07E-07        |
| Coal        | Disintegrator      | 3.03            | 0.01             | 0.0003         | 1.63E-07        |
| Disintegrator|                    | 4.23            | 0.03             | 0.001          | 1.25E-07        |

coals passes not only more intensively, but also occurs at a lower temperature, as the activated samples are ignited earlier, which correlates with studies of the ignition temperature, table 6.

Also, worth noting is the more complete burning out of the dust samples obtained on the disintegrator, figure 4, which is also confirmed by the parameter - burnout index, $D_f$.

Experiments to determine the ignition temperature were carried out for the same types of coals. Table 6 lists the temperature values, as well as the temperature determined by the tangential method from the results of TGA.

Table 6. The ignition temperature of coal.

| Type of grinding | Type of coal | Brown coal | Coal | Anthracites |
|------------------|--------------|------------|------|-------------|
|                  | Ver. Tube | TGA | Ver. Tube | TGA | Ver. Tube | TGA |
| Initial          | 537       | 300 | 386       | 417 | 714       | 602 |
| VCM              | 375       | 352 | 352       | 360 | 600       | 534 |
| Disintegrator    | 348       | 375 | 375       | 323 | 600       | 538 |

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 indeterminate 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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