Research of the chemical activity of microgrinding coals of various metamorphism degree

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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, aged for some time, were compared. The experiments showed a decrease in the ignition temperature of mechanically activated coals - deactivation of fuel, as well as the effect of mechanical activation on the further process of thermal-oxidative degradation.

Introduction
Coal is one of the most important energy sources in the world. According to forecasts, by 2020, the share of coal in the global energy sector will reach 50%, primarily due to the very likely reduction in oil and gas consumption, as well as the revision of the policy on the development of nuclear energy [1].

At present, most coal-fired power plants operate using petroleum products to start and color the boiler during operation. The cost of these petroleum products significantly exceeds the cost of the coal itself, and therefore the introduction of new technologies that allow to exclude petroleum products from the energy processes that take place at the CHPP (Central Heating and Power Plant) is topical [2, 3]. One of such technologies is the technology of mechanical activation of microgrinding coal obtained at mills-disintegrators. In this paper, coal studies are conducted using two different methods: determination of the self-ignition temperature of coals in a vertical tubular furnace and thermogravimetric analysis because the first method allows you to observe the processes of ignition of coal, and the results of the second one can conclude about the further process of thermal decomposition of coal.

Vertical furnace tube
An experimental setup was created for investigating the process of ignition of pulverized-coal fuel with its preliminary grinding in mills different in energy intensity and impact on coal matter. The layout of the stand is shown in Figure 1a, the general view in Figure 1b. The main elements of the structure are: furnace, coal feeder, starting mechanism, supply air heater [4].

The furnace is a vertical heat-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 with a pitch of 100
mm are located in special holes for recording the flash and temperature, respectively. To stabilize the temperature at the entrance to the furnace, as well as to remove stray convective currents and combustion products, a stream of air pre-heated to the temperature in the chamber with a velocity of 0-100 mm/sec is fed into the chamber.

The trigger 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 0.1-1g are poured. Then air is pumped into the chamber (1atm) and coal dust is injected into the furnace. The maximum temperature that can be obtained when using existing transformers is 1000 °C. The arrival of dust into the combustion chamber is recorded by a microphone. The flash is recorded with thermocouples and photodiodes.

In order to remove the external moisture, which can greatly affect the experimental results, the coal was pre-dried in a drying oven at 105 °C for 4 hours before grinding.

Figure 2a show average times of ignition of coal dust of Kuznetsk coal for different temperatures and methods of grinding. It can be seen that the ignition time decreases with increasing temperature and a decrease in the size of the carbon particles. But it is important to note that the ignition time after grinding in the vibrating centrifugal mill is less than the ignition time after grinding in the disintegrator for all the cases under consideration. A similar result is observed for coal of a different degree of metamorphism - brown (Figure 2b). With increasing temperature, the differences in ignition timing become less. The results of the conducted experiments show that, after grinding in the disintegrator and some time holding, deactivation is possible a decrease in the reactivity of coal dust. It is known that the preliminary oxidation reduces the reactivity of coal [5]. The lower activity of aged coal is explained by the disappearance of active oxidation centers.
Figure 2a. Time of ignition of coal dust of Kuznetskiy coal in relation to temperature. o - after grinding the coal in the disintegrator, Δ - after grinding the coal in the vibrating centrifugal mill.

Figure 2b. Time of ignition of coal dust of brown coal in relation to temperature. o - after grinding the coal in the disintegrator, Δ - after grinding the coal in the vibrating centrifugal mill.

Crushing in the disintegrator allows to achieve a more complete disclosure of organomineral splices in comparison with the vibrational centrifugal mill and makes coal more active. But at the same time, the rate of oxidation in air increases at room temperature. Sifting of coal dust also intensifies the process of coal oxidation when interacting with air oxygen and causes the decrease of coal activity with time.

At the same time, the observed decrease in the reactivity of coal dust after grinding in the disintegrator - decontamination of coal, indirectly confirms the initial more complete disclosure of organomineral intergrowths compared to a vibrating centrifugal mill.

**Thermogravimetric analysis**

Synchronous thermal analysis (STA), which included simultaneous thermogravimetric determinations (TG), differential scanning calorimetry (DSC), and mass-spectrometric analysis of the recovered gas was performed on a STA 449F1 Jupiter® instrument combined with a quadrupole mass-spectrometer QMS 403D Aëolos® (Figure 3). The experiments were carried out in a temperature range of 30-700 °C in an atmosphere of synthetic air (80% vol. Ar, 20% v / v O₂), gas flow rate 20 ml/min argon, 5 ml/min oxygen. Open crucibles of Al₂O₃ were used, the heating rate was 10 degree/min.

Figure 3. Photo of the experimental stand.
The processing of the experimental data was carried out using the Proteus analysis software package.

The experiments also used brown and hard coal, which were processed by a vibrating centrifugal mill and a disintegrator, aged for some time. Figures 4-5 show the results of thermogravimetric analysis.

**Figure 4a.** Results of the derivatographic analysis of brown coal treated with a disintegrator. Black – TG, green – DTG, red – DSC.

**Figure 4b.** Results of the derivatographic analysis of brown coal treated with a vibrating centrifugal mill. Black – TG, green – DTG, red – DSC.

The ignition temperature is determined by the method of tangents and is marked "Onset" [6], it is worth noting that for brown coals, the ignition temperature of coals treated with a disintegrator is also higher than the ignition temperature of coals treated with a vibrating centrifugal mill, which correlates with the results obtained in experiments on a tubular furnace. However, the main process of thermal decomposition takes place more efficiently in coals processed on a disintegrator, which is characterized by a more complete burning out of the samples (Residual Mass) and a more abrupt energy release (DSC curve).

**Figure 5a.** Results of the derivatographic analysis of Kuznetskiy coal treated with a disintegrator. Black – TG, green – DTG, red – DSC.

**Figure 5b.** Results of the derivatographic analysis of Kuznetskiy coal treated with a vibrating centrifugal mill. Black – TG, green – DTG, red – DSC.

For coal, the temperature determined by the method of tangents turned out to be slightly lower for coal treated on a disintegrator, but, as in the case of brown coal, positive changes in the dynamics of the thermal decomposition process are seen.
Conclusion

1. It should be noted the increase in the ignition time of mechanically activated coals in comparison with coals treated with a vibrating centrifugal mill.
2. The results of the experiments showed the effect of exposure after grinding on the ignition temperature of coals.
3. Derivatographic analysis data show positive changes in the behavior of the thermal decomposition process for mechanically activated microgrinding coals and a more complete burnout of coal dust samples.

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