Experimental study of thermal decomposition of mechanochemical formations of solid fuel

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Abstract. To establish an unobvious relationship between the structure and properties of solid fuels, obtained under various conditions of preliminary machining of individual fuel components and the joint mechanochemical treatment of fuel components before burning, with the observed physicochemical processes in the combustion chamber, the physicochemical and thermophysical properties of pine sawdust were studied using various methods. The combustion of the samples was carried out in two stages, the times of the maximum burning rate and the heat flux during combustion of the samples at both stages varied depending on the crystallinity index of the samples.

1. Introduction

Co-burning of coal and biomass in the last decade has been recognized as a prospective direction of the development of highly efficient and cleaner green energy. In modern devices, combustion in an air stream disperses particles of fuel with sizes of the order of 100 microns. Particles of coal and biomass have different chemical compositions and burn differently, at different distances from the injection site of the fuel particles. However, they have to burn simultaneously and at one place, otherwise the equipment becomes extremely complicated. In currently operating plants, mixtures with 5% biomass can be burnt. The main idea of the work is to make fuel not a mechanical mixture of particles, but the so-called mechanocomposite particles, each consisting of small particles of coal and biomass. In a conventional mixture, the phase contact surface is about 1% of the total area, and in the mechanocomposite it is about 90%. The combustion reaction, starting at a more active phase, can quickly spread to the neighboring particle of a different phase, coal and biomass can burn simultaneously, and the percentage of biomass can be increased. To establish an unobvious relationship between the structure and properties of solid fuels, obtained under various conditions of preliminary machining of individual fuel components and joint mechanochemical processing of fuel components before burning, with the observed physicochemical processes in the combustion chamber, two methods are used: ignition in a vertical tube furnace and synchronous thermal analysis.

2. Experimental methods and results

The vertical tubular reactor used in the study (Fig. 1) is a vertical heat-insulated steel pipe of 1 m long with an internal diameter of 0.4 m. The pipe is electrically heated using a system of low-voltage transformers. Photodiodes and thermocouples are located along the length of the combustion chamber in special holes with a step of 0.1 m, designed to record the flash and temperature, respectively. In order to stabilize the temperature at the inlet to the reactor, as well as to remove stray convective flows and combustion products, an air stream is fed into the chamber at a speed of 0-1 m / s.
The trigger mechanism consists of a magnetic valve and a chamber with a volume of $12 \times 10^{-5}$ m$^3$. Above the valve there is a powder fuel (dust) feeder, where samples weighing from 0.1 to 1 g are filled into. Then air is pumped into the chamber and dust is injected into the reactor. The maximum temperature that can be obtained using existing transformers is 1000 °C. The intake of dust into the combustion chamber is recorded by a microphone connected to the Lcard Analog-to-Digital Converter (ADC).

The ignition control system consists of photosensors, an excitation circuit, a signal processing circuit, a data acquisition unit, and signal processing software (Fig. 2). The flame detector has a photodiode with a lens focusing the flame light on the spectral band between 400 and 1100 nm on a special window. This technique allows determining the minimum dust ignition temperature, as well as the ignition time, depending on the temperature of the reactor.

During the experiment, the minimum ignition temperature - the boundary temperature of the reactor at which ignition is possible - is studied. This parameter shows the necessary energy to start the ignition process and further combustion of the fuel. To measure the minimum ignition temperature, the temperature in the reactor is successively reduced by 10 °C until finding the boundary temperature below which ignition of the fuel sample does not occur [1–3].
Previously, a series of experiments was performed to assess the effect of the amount of dust loaded into the chamber (0.1, 0.3, and 0.5 g) with a constant amount of air. When the sample was increased to 0.3 - 0.5 g, the scatter of the results became insignificant (up to 5%). Therefore, in further studies, the mass of the sample was taken equal to 0.5 g.

![Temperature distribution](image)

**Figure 3.** Temperature distribution in a tubular reactor.

The ignition delay time was measured at various temperature distributions in the tubular reactor. Three different modes were selected, with a maximum temperature of 520°C, 580°C, 690°C (Fig. 3).

Table 1 presents the studied biomass samples.

| Sample No. | Mechanical Activation Conditions | Residual moisture, % | Crystallinity index (CI), % |
|------------|---------------------------------|----------------------|-----------------------------|
| 1          | Centrifugal-roller activator RM-20, rotation frequency 40Hz, initial humidity 5%, fraction with particle sizes 100-200 microns | 7.83 | 62 |
| 2          | Disintegrator Desi-11, disk rotation speed of 14,000 rpm, three-time processing, fraction with dimensions of 200-300 microns | 8.36 | 62 |
| 3          | Attritor, processing time 5 minutes, initial humidity 19%, fraction with sizes 40-100 microns | 9.31 | 61 |
| 4          | Centrifugal-roller activator RM-20, rotation frequency 40 Hz, initial humidity 16%, fraction with particle sizes 100-200 microns | 9.36 | 68 |
| 5          | Attritor, processing time 5 minutes, processing temperature 95 °C, initial humidity 1%, fraction with particle sizes 40-100 microns | 7.85 | 54 |
| 6          | Centrifugal-roller activator RM-20, rotation frequency 40 Hz, initial humidity 10%, fraction with particle sizes 40-100 microns | 8.55 | 54 |
| 7          | Centrifugal-roller activator RM-20, rotation frequency 40 Hz, initial humidity 16%, fraction with particle sizes 200-300 microns | 8.82 | 64 |

With increasing average particle size, the ignition delay time increases. For samples with CI 54 in all three modes, the time increases approximately twofold upon transition from a sample with a size of...
40–100 μm to 100–200 μm. When changing the particle size from 100-200 μm to 200-300 μm, we observe an increase in the ignition delay time, but with slight differences.

Figure 4 shows the ignition delay time for all 7 samples at various temperatures in a tubular reactor.

![Figure 4](image.png)

**Figure 4.** Ignition delay time for the studied samples of pine sawdust at temperature conditions 1–3.

Obviously, the minimum value of the ignition delay time is observed for samples numbered 3 and 6 (Table 1) obtained on devices with a constrained impact (RM-20 mill and attritor) and characterized by medium (62%) or lowered (54%) crystallinity index. Samples obtained by free blow processing in the DESI-11 disintegrator are minimally active. Samples with a high crystallinity index (68%) do not exhibit minimum ignition delay times. Thus, it has been previously shown that sample processing under the conditions of product formation with a minimum crystallinity index (the highest degree of cellulose amorphization) is more active at the ignition stage.

The physico-chemical structure during dispersion of the studied samples of plant materials is studied by synchronous thermal analysis depending on the particle size and the presence of paramagnetic centers on the surface.

3. **Synchronous thermal analysis of plant samples**

Studies of the kinetic characteristics of the combustion of selected experimental samples in air are carried out using a STA 449F1 Jupiter® synchronous thermal analyzer.

The weight of the sample is 9.7–0.3 mg. The experiments are carried out in a temperature range of 30-600 °C in an atmosphere of synthetic air (80% vol. Argon, 20% vol. Oxygen) and at the gas flow rate of 10 ml / min. Open crucibles from corundum are used. The heating rate is 5, 10, and 30 °C / min.

The experimental data are processed using the Proteus analysis and NETZSH Thermokinetics 3.1 software packages [4-5].

The results of experimental data processing are represented by a set of thermal analysis curves. The TG curve describes the temperature dependence of the change in the sample mass. The DTG curve being a derivative of the TG curve (the rate of mass change) allows separating the overlapping steps in the process of thermal decomposition and set the temperature at which weight changes most quickly. The DSC curve represents the temperature dependence of the heat flux and allows evaluating the thermal effects that occur in the sample when it is heated or cooled.
Figure 5. TG, DTG-curves of thermal analysis of experimental samples obtained in an atmosphere of synthetic air at a heating rate of 10°C/min.

Curves resulting from thermal analysis of samples in a synthetic air atmosphere at a heating rate of 10 °C / min are presented in Figure 5-6. Samples are stable up to a temperature of about 200°C. Thermogravimetric curves show a sharp increase in weight loss in the range of 250–450°C. In the interval of 320-360, the curve of the mass loss is bent, and the decomposition of the sample slows down; after passing through this interval, the decomposition rate increases. The observed processes correspond to the combustion reactions of hemicelluloses and cellulose. Samples 3 and 6 reach a weight loss value of 94% at a temperature of 385°C, for other samples this value is reached at a temperature of 440–470°C.

Above 470 °C, the main process is the combustion of the carbon residue, which ends at temperatures above 600 °C. The non-combustible residue is ~ 4% of the initial mass of the samples.

Figure 6. DSC-curves of thermal analysis of experimental samples obtained in an atmosphere of synthetic air at a heating rate of 10°C/min.
In Figure 6, two peaks are highlighted for all samples. The first peak in terms of heat dissipation and temperature range lies in the same range for all samples with slight deviations. Significant differences are observed for the second peak of heat release: for samples numbered 3 and 6 it lies in the range from 350 °C to 380 °C with a maximum intensity of 36 mW, under numbers 4 and 7 it is in the range from 370 °C to 450 °C with a maximum intensity of 11 mW, and under numbers 1, 2, 5 it is in the range from 430 °C to 450 °C with a maximum intensity of 30 mW.

Thus, by the method of synchronous thermal analysis of samples of pine sawdust it is shown that the combustion of the samples is carried out in 2 stages. The times of the maximum burning rate and the heat flux during combustion of the samples at both stages varies depending on the crystallinity index of the samples.

Conclusions
The ignition temperatures and times in a vertical tube furnace have been studied depending on the size and degree of disordering of the vegetable raw material particles. The minimum value of the ignition delay time is for samples obtained on devices with a constrained impact and characterized by an average (62%) or low (54%) crystallinity index CI. Samples with increased CI (68%) do not exhibit minimum ignition delay times. Samples with minimal CI (the highest degree of cellulose amorphization) are more active at the ignition stage.

By the method of synchronous thermal analysis, it is shown that the combustion of the samples is carried out in two stages. The times of the maximum burning rate and the heat flux during combustion of the samples at both stages vary depending on the crystallinity index of the samples.

Experiments have shown that the type of mill device and the nature of the grinding also affect the process of ignition and thermal decomposition.

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