Exothermic effect during torrefaction

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Abstract. There are presented the results of investigation of exothermal effect taking place during torrefaction process. Experiments were carried out with the help of thermoanalyzer SDT Q600, that gives opportunity to use methods of differential thermogravimetric analysis and differential scanning calorimetry, and at the lab-scale installation modelling the column-type torrefaction reactor with indirect (through the wall) heating of processable raw material. It was ascertained the correspondence between the processes of thermal decomposition of basic organic components of wood (hemicellulose, cellulose and lignin) and the characteristic endo- and exothermic peaks on the curve of effective heat capacity. It was shown that the exothermal effect accompanying thermal decomposition of hemicellulose, taking place during torrefaction, may lead to spontaneous heating of wood biomass to temperatures significantly exceeding the wall temperature.

1. Introduction
Biofuel usage is one of the trends of power complex modernization in order to reduce its negative impact on the environment. However, the biomass usage in the unprepared form in power plants is inexpedient and inefficient, due to the low calorific value and bulk density, but also because of the stringent requirements to storage and the transportation conditions of biofuel. To improve consumer properties of solid biofuel the preliminary heat treatment is used, so-called torrefaction [1]. Torrefaction is a low-temperature pyrolysis of the feedstock in the temperature range 200–300 °C. During torrefaction the drying process and partial decomposition of the main organic components of plant biomass (hemicellulose, cellulose and lignin) occur. As a result of such heat treatment, the thermotechnical characteristics of biomass, as solid fuel, are improving. In particular, combustion heat is increasing and hydrophobic properties are appearing that leads to decreasing the hygroscopicity limit [2–4].

Biomass pyrolysis is accompanied by endothermic and exothermic effects [5]. Since these effects can have a significant impact on the heat balance of the process, definitely, when the development of thermal biomass processing methods it is necessary to have both a qualitative understanding of them and the corresponding quantitative data. The published data on the thermal effects [6–9], which are observed during biomass pyrolysis, for the most part have a qualitative and sometimes contradictory nature. Comparison of these data is difficult due to the difference of the experimental conditions in which they were carried out. A considerable amount of experimental works is devoted to the study of pyrolysis of high molecular weight polymers (hemicellulose, cellulose and lignin), which are the main organic components of the plant biomass [6, 8].
According to the literature data [10, 11] thermal decomposition of hemicellulose occurs in the temperature range of 180–320 °C, cellulose—in the temperature range of 270–370 °C. Thermal decomposition of lignin runs more uniformly in comparison with two other organic components, and is characterized by the temperature interval of 200–540 °C. Thus pyrolysis of hemicellulose and lignin is accompanied by heat evolution, while cellulose pyrolysis at temperatures below 450 °C is an endothermic process and becomes exothermic at higher temperatures [5]. Comparison of these data shows that during torrefaction of plant biomass it is possible appearance of modes, in which spontaneous heating will take place. This paper presents the results of an experimental study of thermal effects accompanying the process of low-temperature pyrolysis of wood biomass. Experiments were carried out at thermoanalyzer SDT Q600 and at a lab-scale installation modelling the column-type torrefaction reactor with indirect (through the wall) feedstock heating.

2. Experiments at thermoanalyzer
Thermoanalyzer SDT Q600 allowed to use the methods of thermogravimetric (TGA) and differential thermogravimetric (DTG) analysis and also differential scanning calorimetry (DSC) for experimental investigations of the process of biomass thermal decomposition. Experiments were performed in the temperature range 50–500 °C in an inert atmosphere (nitrogen). In the experiments the wood samples with characteristic size of 5 mm with a moisture content less than 2% were used. The heating rate was equal to 10 °C/min. Temperature scale was calibrated by the melting points of different metals: tin (231.93 °C), lead (327.5 °C), zinc (419.5 °C), aluminum (660.33 °C). To calibrate the temperature dependence of the instrument relative sensitivity to heat flow, data on the temperature dependence of the heat capacity of sapphire were used. Binding to absolute scale for heat flow was realized by measuring the melting heat of zinc, which was taken as 108.7 J/g. To determine the accuracy of the measurements by DSC method a test experiment was carried out, in which the temperature dependence of the absolute heat capacity of sapphire were measured. From a comparison of results of measurements with data of NBS it follows that the error of measurements did not exceed 2.5%.

When using the DSC the heat flux \( Q \) (W/g), required to maintain a given heating rate of the sample under study, is measured. If the heating rate \( \delta T = \Delta T/\Delta t \), where \( T \)—temperature of the sample, \( t \)—time, is known, the value of the so-called effective heat capacity \( C_{\text{eff}} = Q/\delta T \) in J/(g°C) can be easy calculated from experimental data. The term “effective heat capacity” implies the fact that at the measurement the sample is not in an equilibrium state because chemical processes, that lead to thermal decomposition of the material and change in its mass, proceed in it.

Figure 1 shows the temperature dependence of \( C_{\text{eff}} \), which is determined from the results of DSC, and the temperature dependence of the mass loss rate \( dm/dt \) (so called DTG curve) due to thermal decomposition of the wood sample during heating. As follows from figure 1 the effective heat capacity of wood at temperatures below 100 °C is about 1.6 J/(g°C), what is in a good agreement with literature data. Comparison of dependencies \( C_{\text{eff}} = C_{\text{eff}}(T) \) and \( dm/dt = f(T) \) allows to conclude that there is a good correspondence between the characteristic peaks observed on each of them. As one can see from figure 1 at the initial stage of heating (up to temperature of 170 °C) with increasing the temperature the effective heat capacity is reduced practically twice under actually unchanging mass of the sample. In the temperature range 170–250 °C a stabilization of the value \( C_{\text{eff}} \) is observed. Next decrease of the effective heat capacity is related to thermal decomposition of hemicellulose (see characteristic kink on DTG curve), which is accompanied by a noticeable exothermic effect at temperature above 250 °C.

In this case heat generation can be sufficient to change the sign of the effective heat capacity. For the torrefied sample, not having hemicellulose in its composition (as evidenced by the absence of a characteristic kink on the DTG curve), exothermic peak, associated with the decomposition
Figure 1. The temperature dependence of the effective heat capacity (black curves) and the mass loss rate (red curves) of wood sample: solid curves—initial sample, dashed curves—torrefied sample.

of hemicellulose, on dependence $C_{\text{eff}} = C_{\text{eff}}(T)$ is absent, and the effective heat capacity has almost constant (slightly increasing) value (see figure 1).

The thermal decomposition of cellulose (maximum speed at 346 °C) is accompanied by an endothermic effect. The thermal decomposition of lignin, which at temperatures above 370 °C can be observed in the pure state because at this moment hemicellulose and cellulose are practically absent in composition of the sample, is accompanied by considerable heat generation, which leads to a change in sign of the effective heat capacity. At temperatures above 475 °C the effective heat capacity becomes positive and increases with increasing temperature.

The heat capacity of the sample after heat treated at the temperature 270 °C, measured at temperatures below 270 °C, is the true heat capacity of the material at these temperatures. At temperatures above 270 °C the curve of the effective heat capacity for the thermally treated sample repeats qualitatively similar curve for the initial sample: there is a small endothermic effect, associated with the thermal decomposition of cellulose, and exothermic effect that accompanies decomposition of lignin. Quantitative differences and the shift of the maxima to lower temperatures are due to the structural changes that have occurred during the heat treatment of the sample at temperature of 270 °C.

Thus, from the results of experiments at thermoanalyzer it follows that during torrefaction at temperatures above 250 °C, spontaneous heating of woody biomass can occur.
Figure 2. Scheme of lab-scale installation: 1—argon bottle; 2—flexible bridge; 3—reactor; 4—heat exchanger; 5—liquid collecting container; V-1–V-4—valves; M-1–M-3—manometers; T1–T11—thermocouple; H-1–H-5—heaters. Area of reactor occupied by pellets is marked yellow.

3. Experiments at laboratory test-bench
Schematic diagram of the lab-scale installation, that models the torrefaction reactor, is shown in figure 2. The reactor was a cylindrical metal heat-insulated pipe with internal diameter of 66 mm and length of 1100 mm. It was equipped with several independent heating elements and thermocouples, the arrangement of which is shown in figure 2. Before carrying out the experiment, the reactor was filled with feedstock and purged with an inert gas. The volatile pyrolysis products forming during heating of the feedstock escaped from the reactor under the influence of the arising excess pressure, then they entered the heat exchanger and then—container for liquid collecting. During the experiments the excess pressure in the reactor did not exceed 0.02 atm and was maintained at this level by the valve V-2.

The heating of the reactor walls was carried out up to temperature of 250 °C. When approaching to the specified temperature the power of heaters was reduced and then they were switched off. Experiments were conducted with dry wood pellets (moisture content less than 1%) (figure 3) and pre-torrefied pellets (figure 4). In the DTG curves, corresponding to the torrefied wood pellets, the kink caused by thermal decomposition of hemicellulose was completely absent. That was evidence of practically complete absence of hemicellulose in torrefied pellets.

Temperature profiles of the reactor wall in different cross-sections during its heating are shown in figures 3(a) and 4(a). Heaters switching-off time is indicated by vertical dotted lines. Temperature profiles in the bed of pellets at the axis of the reactor in its different cross-sections are shown in figure 3(b) and 4(b).

From the temperature dependences presented in figure 3(a), it is seen that a slight overheating of the wall (20 °C) by the H-3 heater (thermocouple T5) has led to the fact that even after switching off the heater the temperature of the wall continued to grow, and after 21 min reached
the value of 340 °C. Note that the thermal inertia of the empty reactor and the reactor filled with torrefied pellets was resulted in the wall heating (after heater was switched off) not more than 3–5 °C and was observed not more than during 5 min. From the foregoing it follows that the temperature rise, observed in the near-wall region (thermocouple T5 in figure 3(a)), is due to heat release during thermal decomposition of wood biomass. As one can see from figure 3(b) at the same time the heating of the central region in the same cross-section (thermocouple T6 and T7) continues due to the heat input from the near-wall region.

After 13 min of the turn-off the heater H-3 the temperature on the reactor axis (thermocouple T7) leveled off with the temperature at the periphery, and then exceeded it, reaching values of 370 °C. This demonstrates the determining role of the exothermic reactions occurring in the axial region. The maximum temperature value of 425 °C was observed on the axis of the reactor

Figure 3. Temperature changing in various points of the reactor during the heating process of wood pellets: (a) wall; (b) pellet.

Figure 4. Temperature changing in various points of the reactor during the heating process of pre-torrefied wood pellets: (a) wall; (b) pellet.
in the upper layer of pellets (thermocouple T8). Increasing the amplitude of the overheating along the reactor height (that follows from a comparison of readings of thermocouple T4, T7 and T8) can be explained as follows. Part of the volatile products formed as a result of thermal decomposition of the feedstock in the lower layers, does not have time to react and moving up brings the heat, released as a result of exothermic reactions, to the top layers. Proof of this are the temperature peaks observed in the reactor zone, free from biomass (thermocouple T9 and T10) after 11 min after turning off the heater H-4. In similar experiments, carried out with pre-torrefied wood pellets, the overheating was not detected (figure 4).

It is correct to assume that the exothermic effect observed in experiments at the laboratory test-bench with wood pellets is caused by thermal decomposition of hemicellulose, and growth of heat release along height of reactor is evidence of the determining role of the volatile torrefaction products in the process of overheating.

4. Conclusion

From the experiments carried out at the laboratory installation, simulating a torrefaction reactor with indirect (through the wall) heating of processable raw material, follows that when torrefaction of wood biomass at temperatures above 250 °C there is observed the exothermic effect leading to spontaneous heating of biomass to temperatures significantly above the heater temperature. The observed effect is due to the process of thermal decomposition of hemicellulose. The results of experiments at the laboratory installation are in a good qualitative agreement with the results, obtained during studying the thermal effects using the methods of differential thermogravimetric analysis and differential scanning calorimetry. The obtained results can be used under development of methods of biomass thermal processing.

References

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