Thermoanalytical study of drying kinetics of lignocellulosic fuels

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Abstract. Lignocellulosic matter is usually hydrophilic, so its drying, in addition to the heat of the phase transition for water, also requires compensation of adsorption energy. In the present work experimental studies have been carried out to quantify the moisture adsorption energy, for wood sawdust, cellulose and lignin with varying moisture content. The experiments were performed on the basis of a thermal analysis complex STA449F1. The data were obtained for isothermal drying conditions at different temperatures. A mathematical model is proposed for the evaporation rate of various water energy forms in lignocellulosic fuel. A method is proposed for the experimental determination of the binding energy of water molecules with organic matter and its dependence on moisture content.

1. Introduction
The process of drying fuel biomass is an inherent initial stage of any thermal processing method. It is to be considered that water in the organic mass is in different energy states, which affects the kinetics of dehydration of fuel particles. Usually, three main types of moisture state in the organic mass are distinguished [1]: 1 – monomolecular sorption layer directly contacting macromolecules of the organic phase (up to 5% moisture content); 2 – polymolecular adsorption, which forms a continuous film of water in the micropores of fuel particles (up to 13% moisture); 3 – condensation moisture in micropores (up to 40-50% moisture). At humidity above ~50%, the moisture properties do not differ from the properties of free water. It is obvious that the drying of fuel particles occurs in a continuous mode with a gradual transition between states of evaporating moisture [2]. Moreover, under the conditions of energy processing of lignocellulosic fuels (gasification, incineration), the drying process takes place simultaneously with pyrolysis and combustion processes due to the thermal inhomogeneity of the reaction space (both individual particles and their aggregates) [3]. This must be taken into account in kinetic models of the multiphase reactive flow, since the evolved moisture affects both the composition of the gas phase and the internal structure of the fuel particle and its interaction with external flows [4, 5].

2. Thermodynamic relations
Evaporation of moisture could be considered as a two-stage process: first, the liquid molecules pass from the volume of the condensed phase to the surface layer, which, from the point of view of chemical kinetics, corresponds to a reversible process, and then the diffusion of molecules to the gas phase occurs from the surface layer. Since diffusion processes are often slower than chemical ones, generally, the diffusion stage limits kinetics of evaporation process. Therefore, the molecules of the surface layer and the liquid phase are in equilibrium, so their chemical potentials are equal: \( \mu_l = \mu_g \).
Hence: \( \mu_0 = \mu_g^0 + RT \ln \left( \frac{p_{sw}}{p_0} \right) \), where \( p_{sw} \) is the saturated vapor pressure at a given temperature, \( p_0 \) is the total pressure in the system. Hence the well-known relation can be stated:

\[
p_{sw} = p_0 \exp \left( \frac{\mu_0 - \mu_g^0}{RT} \right), \quad (1)
\]

The limiting diffusion flux, which determines the evaporation rate under these conditions, can be found from the standard diffusion equation considering experimental conditions. For the one-dimensional case following equation is valid:

\[
J_{ev} = \frac{D_{ev}S}{\delta RT} (p_{sw} - p_0) = \frac{p_0D_{ev}S}{\delta RT} \left[ \exp \left( \frac{\mu_0 - \mu_g^0}{RT} \right) - P_W \right] , \quad (2)
\]

where \( S \) is the area of the evaporation surface; \( D_{ev} \) is the diffusion coefficient; \( \delta \) - thickness of the diffusion layer; \( P_W \) - partial pressure of moisture in the external gas phase. If there are external forces in the liquid phase, such as adsorption forces, its Gibbs energy will decrease, i.e. \( \mu^{eff}_l = \mu^0_l - g^ad_l \), and relationship (2) should be written as:

\[
J_{ev} = \frac{p_0D_{ev}S}{\delta RT} \left[ \exp \left( \frac{\mu^0_l - g^ad_l - \mu_g^0}{RT} \right) - P_W \right] . \quad (2a)
\]

Thus, if the drying rate of various lignocellulosic samples is measured at a constant temperature, the value of the adsorption energy can be determined. It is adsorption energy at different distances from the sorption surface, as the sorption layer becomes thin as the sample dries. The fact that lignocellulosic substances have a porous structure is not an obstacle, since interphase equilibrium is established already inside the pores irrespective of the degree of their filling, and evaporation occurs through their stomas, whose diameter changes slightly during the drying process so the evaporation surface can be considered constant. It should be noted that all these assumptions are valid only for thermally homogeneous particles of small sizes.

3. Experimental study

In the present work, experiments on the drying rate were performed on the basis of the thermal analysis complex STA449F1 combined with the mass spectrometer QMS403C. The experiment was carried out as follows. The shredded unsorted (\( \delta < 1.5 \) mm) fragments of lignocellulosic substance were moistened excessively (up to 70-80% by weight) with water and placed in a cylindrical corundum crucible (\( d = 5 \) mm, \( h = 4 \) mm), which was installed in a thermal analysis unit and aged at different preset temperatures with the registration of the weight until a constant value is established. The adsorption energy of the outer layers of evaporating moisture varied from zero energy at a moisture content above ~ 50% (free water) to a maximum energy at a given temperature, when the transition of water molecules from the condensed phase to the surface layer becomes limiting stage. The experiments were carried out with pine sawdust, laboratory treated lignin (extracted by treatment with sulfuric acid [6]) and cellulose (filter paper). The process of evaporation occurred in an atmosphere of an absolutely dry argon (up to 0.0003% by weight vapor) at temperatures of 50, 70 and 90 °C.

In experimental conditions, the value \( P_W \) in equation (2a) can be neglected. Then:

\[
J_{ev} = \frac{p_0D_{ev}S}{\delta RT} \exp \left( \frac{\mu^0_l - \mu_g^0}{RT} \right) \exp \left( -\frac{g^ad_l}{RT} \right) = J_{ev}^W \exp \left( -\frac{g^ad_l}{RT} \right)
\]

where \( J_{ev}^W \) is the evaporation rate at the initial portion of the curve, when it can be assumed equal to zero. Under isothermal conditions, it can be regarded as a constant, since the binary diffusion coefficient is proportional to the \( T^{1.5} \) [7]. In this case, the surface area of evaporation and the thickness of the diffusion layer in the evaporation range of the non-adsorbed moisture change slightly, and, apparently, the change in their ratio during desorption evaporation is not significant compared with the
exponential factor. Thus, the initial section of moisture evaporation curves from the moist lignocellulosic substance should be linear (excepting start of sample heating, when temperature regime could be irregular). Fig. 1 shows the drying curves of cellulose, pine sawdust and lignin at various temperatures. As can be seen from the figure, the initial sections of all evaporation curves are linear. The value is found as the slope of the linear section. So equation for adsorption energy can be written as follows:

$$g_{ad} = -RT \ln \left( \frac{J_{ad}}{J_{w}} \right)$$

For all samples, the thermogravimetric curves were processed, resulting in the dependence of sorption energy on humidity and temperature. These dependences are shown in Fig. 2. The same qualitative picture is observed for all samples: at a moisture content of 40%, the sorption energy is negligible (fiber saturation point is reached). In the drying process, sorption layers with higher sorption energy begin to evaporate, and up to a moisture content of 5-10%, the curves for different temperatures slightly differ for each material. At a certain critical moisture content, which value depends on the temperature and nature of wet material, a sharp increase in sorption energy begins (at 2 kJ/mol). It can be supposed that this is not a “physical” evaporation, but rather a chemisorption decay and breaking of the weak chemical bonds between water molecules and lignocellulosic material. Critical humidity decreases with temperature increase. Integrating the curves in Fig. 2, it is possible to estimate the wetting heat for all studied materials. These values are given in Table 1. As can be seen, the values obtained from the thermogravimetric curves are in good agreement with the published data [8], where the value for the cellulose is about 10 cal/g. Our study allows to obtain not only integral value of sorption heat but also differential adsorption curves using a simple experimental technique. Moisture strongly associated with lignocellulosic material can evaporate at temperatures higher than the boiling point of water, and therefore can interact with pyrolysis products during combustion processes. Therefore, the estimated adsorption heat values (both differential and integral) are necessary for modeling the processes of thermochemical conversion of plant biomass and lignocellulosic waste.

**Figure 1.** Thermogravimetric drying curves: whole sample mass loss (a) and moisture mass loss in the steady isothermal regime (b).
Figure 2. Dependence of the heat of moisture sorption from humidity for different materials and drying temperatures.
Table 1. Wetting heat for lignocellulosic materials, J/g.

|         | 50°C | 70°C | 90°C |
|---------|------|------|------|
| Lignin  | 24.0 | 28.1 | 34.4 |
| Cellulose| 22.4 | 26.9 | 37.2 |
| Sawdust | 28.6 | 34.6 | 51.2 |

Conclusions
Thermoanalytical studies of the drying kinetics of lignocellulosic materials (pine sawdust, cellulose and lignin) were carried out. The difference between evaporation of free moisture and adsorbed moisture makes it possible to estimate the heat of adsorption. The measurements are made for different temperatures (50, 70 and 90 °C). Results show that at a moisture content of 40 to 10%, the moisture adsorption energy depends slightly on the temperature. With a decrease in the moisture content to a threshold value, which depends both on the sample material and on the temperature, the moisture adsorption energy increases sharply, that indicates a stronger bonds between the lower layers of adsorbed moisture and the material, which may have a chemical nature. The obtained data can be used for modeling of drying processes of lignocellulosic materials.

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