

Mathematical modeling of the dynamics of heat and mass transfer, phase transformations and thermal decomposition at high temperature drying of biomass

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A mathematical model and method for calculating heat and mass transfer, phase transformations and shrinkage during drying of colloidal porous bodies in the form of a final cylinder are presented. A mathematical simulation of high-temperature drying of willow accompanied by the destruction of hemicellulose was carried out using the data obtained on the values of the activation energy of various types of biomass.

Keywords – biomass, drying, thermal destruction, mathematical modeling, dynamics of heat and mass transfer, phase transformations, cylindrical particle, drum dryer, activation energy.

The use of biomass for the production of solid fuels has a high potential for the transition to renewable energy sources in Ukraine and in Europe. Emissions from combustion of biomass are recognized as CO₂-neutral. Quality fuel pellets are obtained from raw materials with humidity of 8 – 12%. In Ukraine, drying of crushed biomass is carried out mainly in drum driers at coolant temperatures $T_c = 120 - 170$ °C. The organization of high-temperature ($T_c = 300 - 500$ °C) drying of biomass intensifies the process and is accompanied by thermal decomposition of biomass. At the initial stage of thermal decomposition, hemicellulose decomposes with the release of oxygen-containing gases and pyrogenic moisture. This contributes to increasing the caloric content of biofuels. At temperatures above 270 °C, cellulose and lignin begin to decompose, and these processes in the presence of air are exothermic for all types of biomass. Their passage contributes to the loss of the combustible component of biofuels. Consequently, the development of technologies for high-temperature drying of biomass is important for compliance with the condition of passing only the first stage of thermal decomposition. The possibilities of experimental methods for investigating high-temperature dehydration and thermal destruction in the particles of small size are substantially limited. More promising is the use of the method of mathematical modeling.

Biomass particles are colloidal capillary-porous bodies of cylindrical shape. Drying in high-temperature coolant involves the passage of heat and mass transfer through diffusion, filtration and phase transformations. Pyrogenetic water is removed along with residues of free and bound biomass moisture. The mathematical model [1] of dynamics of dehydration of biomass was based on the equation of transport of substance (energy, mass) [2]

$$c_{ef} \left(\frac{\partial T}{\partial t} + w_{ef,r} \frac{\partial T}{\partial r} + w_{ef,y} \frac{\partial T}{\partial y} \right) = \frac{1}{r} \frac{\partial}{\partial r} \left(\lambda_{ef} r \frac{\partial T}{\partial r} \right) + \frac{\partial}{\partial y} \left(\lambda_{ef} \frac{\partial T}{\partial y} \right) - LI_V, \quad (1)$$

$$\frac{\partial U_{fl}}{\partial t} + \frac{\partial (w_{fl,r} U_{fl})}{\partial r} + \frac{\partial (w_{fl,y} U_{fl})}{\partial y} = \frac{1}{r} \frac{\partial}{\partial r} \left(D_{fl} r \frac{\partial U_{fl}}{\partial r} \right) + \frac{\partial}{\partial y} \left(D_{fl} \frac{\partial U_{fl}}{\partial y} \right) - I_V - \frac{U_{fl}}{1 - \varepsilon_V} \frac{\partial \varepsilon_V}{\partial t}, \quad (2)$$

$$\frac{\partial U_v}{\partial t} + \frac{\partial (w_{g,r} U_v)}{\partial r} + \frac{\partial (w_{g,y} U_v)}{\partial y} = \frac{1}{r} \frac{\partial}{\partial r} \left(D_v r \frac{\partial U_v}{\partial r} \right) + \frac{\partial}{\partial y} \left(D_v \frac{\partial U_v}{\partial y} \right) + I_V - \frac{U_v}{1 - \varepsilon_V} \frac{\partial \varepsilon_V}{\partial t}, \quad (3)$$

$$\frac{\partial U_{ai}}{\partial t} + \frac{\partial (w_{gas,r} U_{ai})}{\partial r} + \frac{\partial (w_{gas,y} U_{ai})}{\partial y} = \frac{1}{r} \frac{\partial}{\partial r} \left(D_{ai} r \frac{\partial U_{ai}}{\partial r} \right) + \frac{\partial}{\partial y} \left(D_{ai} \frac{\partial U_{ai}}{\partial y} \right) - \frac{U_{ai}}{1 - \varepsilon_V} \frac{\partial \varepsilon_V}{\partial t}. \quad (4)$$

Here U_{fl} , U_v , U_{ai} – volumetric concentrations of liquid, vapor and air phases; T – temperature; t – time; c_{ef} – effective heat capacity, $c_{ef} = c_s \rho_s (1 - \Pi) + c_{fl} U_{fl} + c_v U_v + c_{ai} U_{ai}$; λ_{ef} – effective thermal

conductivity, $\lambda_{ef} = \lambda_s(1-\Pi) + \lambda_{fl}U_{fl}/\rho_{fl} + \lambda_vU_v/\rho_v + \lambda_{ai}U_{ai}/\rho_{ai}$; w_{ef} – effective filtration rate, $w_{ef} = [w_{fl}c_{fl}U_{fl} + w_g(c_vU_v + c_{ai}U_{ai})]/c_{ef}$; w_{fl} , w_g – are the velocity vectors of the filtration motion of the liquid and gas phases, which, according to the Darcy law $w_\chi = -K_0K_\chi/\eta_\chi \nabla P_\chi$ ($\chi = fl, g$), are proportional to gradient the phases ∇P_{fl} and ∇P_g ; L is the heat of phase transformation.

The effective diffusion coefficient of the liquid D_{fl} was determined by the formula obtained by Nikitenko N.I. [3], and a pair of D_v - from the kinetic theory of gas:

$$D_{fl} = \gamma_D [\exp(A_D/RT) - 1]^{-1}, \quad D_v = D_{ai} = \gamma_v T^{3/2}/P_g, \quad \gamma_D, \gamma_v = \text{const.} \quad (5)$$

Here A_D is the activation energy of the liquid molecules for the diffusion process.

The pressures of fluid P_{fl} and gas P_g are expressed in terms of the functions U_{fl} , U_v , U_{ai} and T . Volume fractions of the solid component Ψ_s , liquid Ψ_{fl} and gas Ψ_g in porous body are defined: $\Psi_s = 1 - \Pi$, $\Psi_{fl} = U_{fl}/\rho_{fl}$, $\Psi_g = 1 - \Psi_s - \Psi_{fl}$, partial densities of vapor and air: $\rho_v = U_v/\Psi_g$ and $\rho_{ai} = U_{ai}/\Psi_g$, partial pressures of vapor P_v and air P_B : $P_v = \rho_v R_y T / \mu_v$ and $P_B = \rho_B R_y T / \mu_B$. The pressures of gas and liquid phases: $P_g = P_v + P_{fl}$ and $P_{fl} = P_g + P_c$, where capillary pressure P_c [2]

$$P_c = 2\sigma(T) \int_{r_{min}}^{r_{max}} \frac{\theta(r)}{r} f(r) dr / \int_{r_{min}}^{r_{max}} \theta(r) f(r) dr = \frac{2\sigma(T)}{r^*}, \quad r_{min} < r^* < r_{max}. \quad (6)$$

Here, $\theta(r)$ is the volume fraction of the capillary occupied by the liquid; $f(r)$ is the differential function of pore size distribution; $\sigma(T)$ is the coefficient of surface tension; r^* is the characteristic parameter of the dispersion of pore sizes; r_{min} and r_{max} are the minimum and maximum pore radii of a unit volume.

Intensity of phase transition on the outer surfaces of the biomass particles [4] is as the difference between the evaporating liquid streams and the condensed vapor

$$I = \gamma_c \left\{ \varphi_b|_{v=0} [\exp(A/RT|_{v=0}) - 1]^{-1} - \varphi_{e.m.} [\exp(A/RT_{e.m.}) - 1]^{-1} \right\}, \quad \gamma_c = \varepsilon \rho_{fl} \delta^* / 4 \quad (7)$$

where ε is the radiation coefficient; ρ_{fl} is the density of the liquid; δ^* is the thickness of the condensate layer in which the evaporation process takes place; φ_b is the body moisture, which is determined from the sorption isotherm equation, depending on U_{fl} ; A is the activation energy; R is the universal gas constant; φ_{en} is the relative humidity of the medium, $\varphi_{e.m.} = P_v / P_{eq}$, P_v is the water vapor partial pressure, P_{eq} is the saturation pressure.

The expression for the intensity of evaporation I_V in the unit volume of the body follows from formula (6) under the condition of a local thermodynamic phase equilibrium

$$I_V = \gamma_v \left\{ \exp(A/RT - 1) \right\}^{-1} [\varphi_b - \varphi] S. \quad (8)$$

where φ is the relative humidity of the gas in the pores of the body, $\varphi = U_v / [\Psi_g P_{sat}(T)]$; S is the area of the contact surface of the liquid and gas phases. To determine the function S in pores of the unit volume of a body, which is not completely filled with liquid, the formula [5] was obtained

$$S = \frac{2\sqrt{1-\varphi_b}}{\rho_{fl}\delta^*} \frac{\partial U_{fl}}{\partial \varphi_b}, \quad (S_{min} \leq S \leq S_{max}), \quad (9)$$

where the derivative $\partial U_{fl}/\partial \varphi_b$ is found from the sorption isotherm equation. If the isotherm equation is given in the form $U_{fl} = U_{max} \varphi_b^g$, $g = \text{const}$, then $\partial U_{fl} / \partial \varphi_b = U_{max} g \varphi_b^{g-1}$. The data on the equilibrium moisture content W_{eq} for wood [6] accurately describes the equation $W_{eq}^{-1} = W_{max}^{-1} - 0,12 \ln \varphi$, W_{max} corresponds to $\varphi=1$ and at 100°C equals 16%, $U_{fl} = 0,01 W \rho_b$.

Volumetric deformation ε_V was determined on the basis of the thermoconcentration deformation equation of Nikitenko N.I. [5], that was solved in [7] analytically for the case of an osseo-symmetric stressed cylinder state due to the heterogeneity of the temperature fields and the concentration of the components of the bound substance.

On the surfaces of the particles in contact with the drying agent, the boundary conditions of the heat-mass transfer of the third kind are given.

$$\lambda_{ef} \frac{\partial T}{\partial v} \Big|_{v=0} = \alpha(T_{e.m.} - T \Big|_{v=0}) - LI, \quad D_{fi} \frac{\partial U_{fi}}{\partial v} \Big|_{v=0} = I, \quad (10)$$

$$-D_v \frac{\partial U_v}{\partial v} \Big|_{v=0} = \gamma_{ve.m.} (U_v \Big|_{v=0} - \rho_{ve.m.} \Psi_v), \quad U_{ai} \Big|_{v=0} = \frac{P_{ve.m.} \Psi_g \mu_{ai}}{R T \Big|_{v=0}} - U_v \Big|_{v=0} \frac{\mu_{ai}}{\mu_v}. \quad (11)$$

The solution of differential equations (1) - (4) under the conditions (10) - (11) was carried out by a numerical method developed on the basis of an explicit three-layer recalculated difference scheme of Nikitenko N.I. [5] and procedures for splitting the algorithm into physical factors. Difference approximation of the transfer equations (1) - (4) are presented in [1].

To confirm the adequacy of the mathematical model and the efficiency of the numerical method, a physical modeling of the kinetics of drying of energy willow particles of cylindrical form in the air flow and mathematical modeling of the process at the same initial data was carried out: $T_0 = 303$ K; $W_0 = 1,3$ kg/kg; $A = A_D = 0,4205 \cdot 10^8$ J/kmol; $\Pi = 0,58$. The results of the calculation and the experimental data presented in Figure 1 are well-coordinated.

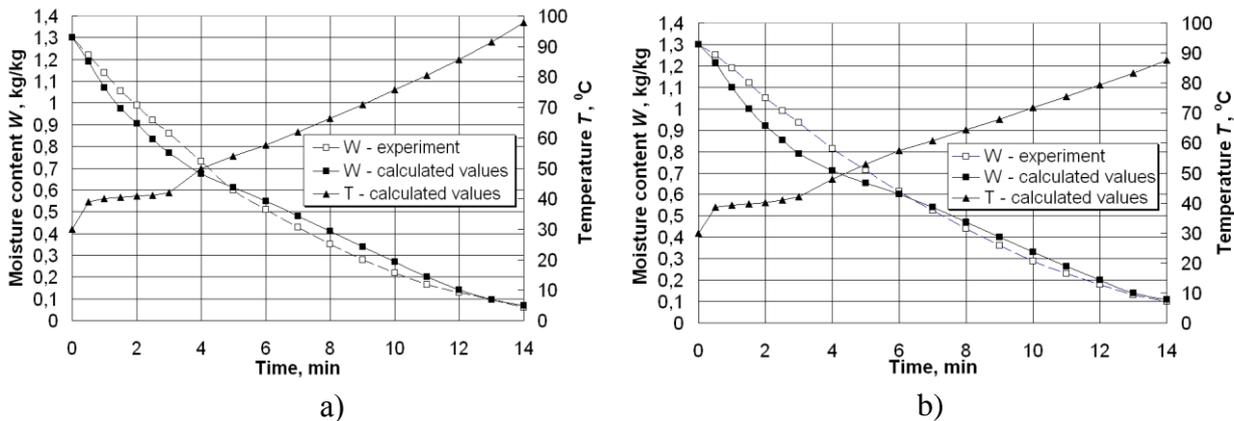


Fig. 1. Change in time of the average moisture content W and temperature T of energy willow of cylindrical particles with dimensions $d/h = 4,2/10$ mm (a) and $d/h = 5,6/10$ mm (b) when drying in the air stream with the parameters: $T_{e.m.} = 120$ °C, $w_{e.m.} = 2$ m/s, $d_{e.m.} = 18$ g/kg s.ai.

As shown in [8], the onset of the thermal decomposition of hemicellulose in the drying process of different types of biomass is characterized by a sharp change in the effective energy of activation of the microparticles of the bound substance. Some results obtained in [8] are given in Table 1.

Table 1

Effective activation energy at different stages of biomass dehydration

№	A sample of biofuels	Change of temperature of material, °C	Activation energy, J/mol	Change of temperature of material, °C	Activation energy, J/mol
1	Wheat straw	28-168/(87)	59300	168-318/(268)	93100
2	Trench of oak	23-190/(95)	51600	190-315/(300)	91300
3	Tern of poplar	28-183/(109)	59400	183-351/(311)	75250
4	Trench is pine	28-168/(85)	54900	178-335/(315)	10400
5	Miskanthus	28-180/(91)	57400	180-335/(284)	90500

Since the process of thermal decomposition, like diffusion and evaporation [5], is an activating, in mathematical modeling of joint processes of drying and thermal destruction in the calculation program developed on the basis of (1) – (4), in expressions (6), (7) and for D_{fl} after material temperature has reached the beginning of thermal decomposition, the value of the activation energy of water is changed to a value corresponding to the temperature interval of decomposition of hemicellulose [8] (Tab.1). For hardwood species of trees $A_{ef} = A_{Def} = 0,7525 \cdot 10^8 \text{ J / kmol}$. Figure 2 shows the results of numerical experiments.

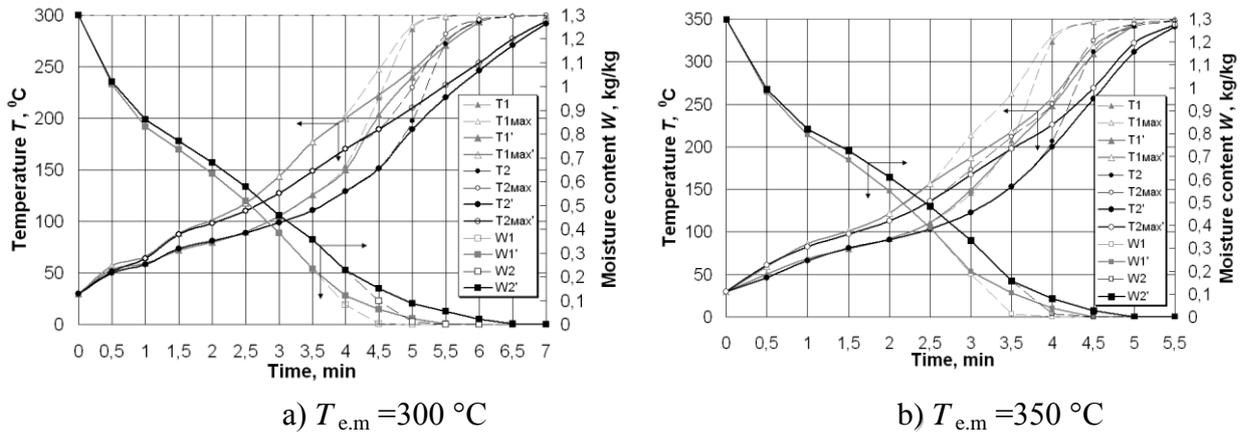


Fig. 2. Change in time of the average moisture content W , temperature T , and maximum temperature T_{max} on the surface of energy willow particles in the sizes $d/h = 5,6/10 \text{ mm}$ (curve 1) and $d/h = 5,6/10 \text{ mm}$ (curve 2) at drying without and with taking into account thermal decomposition (W' , T' , T_{max}') in flue gases with parameters: $w_{e,m} = 2 \text{ m/s}$, $d_{e,m} = 18 \text{ g/kg}$

Conclusion

The process of thermal decomposition, as well as the processes of diffusion and evaporation, is activating. Taking into account the mathematical model of this phenomenon will allow to organize the process of biomass drying effectively and improve the quality of biofuels.

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