Mathematical modelling of the steam explosion treatment process for pre-impregnated lignocellulosic material

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Abstract. The article analyses the physical picture of the process of steam explosion treatment of pre-impregnated lignocellulosic material, on the basis of which a mathematical modelling of the process is done. The mathematical modelling is represented in the form of differential equations with boundary conditions. The obtained mathematical description allows identifying the degree of influence of various factors on the kinetics of the process and producing a rational selection of operating parameters for the considered processes in terms of the set of application tasks.

1. Introduction
The lignocellulosic material, particularly wood, has unique thermal properties, as well as the structure and component composition. One of the ways of solving the applied tasks in the field of complex processing of raw materials to chemical components (cellulose, lignin, hemicellulose) or fibrous semi-finished products is the steam explosion treatment at a high-temperature [1-3], which can also be used as a stage of activation of raw wood prior to chemical processing, for example, sulphate pulping.

For regulation and optimization of process parameters of the steam explosion treatment of the pre-impregnated material in the industrial conditions the physical picture of the process was studied and the mathematical description of the ongoing stages was made.

2. Formalization of the process and the mathematical description
The steam explosion treatment of the pre-impregnated lignocellulosic material includes the following stages: 1) impregnation of the material with water or acid solution; 2) heat treatment of the material with high pressured steam and physical and chemical transformations; 3) decompression of the system and material defibering into separate fibers; 4) product unloading from the reactor. Let us consider these steps in more detail.

2.1. Impregnation stage of the material with water or an acid solution
A lignocellulosic material in the form of crushed particles is pre-treated with water or an acid solution up to complete saturation with moisture. The saturation occurs due to capillary and forced impregnation with symptoms of swelling of the polymer matrix.
Taking into account the assumptions about the absence of hydrodynamic flows and heat generation during impregnation, the pre-impregnation stage is described by the equation of moisture transfer [4]:

$$\frac{\partial U}{\partial \tau} = k_m \cdot \frac{\partial^2 U}{\partial x^2}$$

(1)

with initial conditions:

$$U(0, x) = U_0$$

(2)

and boundary conditions:

$$\left. \frac{\partial U}{\partial x} \right|_{x=0} = -\frac{j}{k_m \cdot \rho}$$

(3)

The index of mass conductivity $$k_m$$ (sm²/sec) of wood in tangential direction may be calculated in the first approximation by the equation:

$$k_m = 0.235 \cdot 10^{-31} T^{10} \cdot \gamma^{3.3}$$

(4)

In the radial direction:

$$k_{mr} = k_m (1 + \frac{2P}{100})$$

(5)

where $$P$$ – is the percentage of the medullary rays.

For pine ratio $$\frac{k_{mr}}{k_m}$$ is 1.15, for oak - 1.50, for beech - 1.70.

Thus, the lignocellulosic material, pre-impregnated with water or aqueous acid solution with specified initial mass, is subjected to steam explosion treatment by moisture.

2.2. Heat treatment stage of the material with high pressure steam and physical-chemical transformations

Since the treated lignocellulosic material has high humidity after pretreatment, it is necessary to maintain the conditions of thermodynamic equilibrium between the steam and the liquid in the reactor throughout the whole treatment time, which means it is necessary to treat the material with water saturated steam. Let us make the following assumptions for modelling of the heating stage:

- Due to special training of the reactor, we assume that water steam will obey the laws of ideal gases and will not condense on the inner surface of the reactor, we will neglect the pressure and temperature drop at the initial inlet of steam to the reactor.
- During heat treatment of raw materials water steam has constant thermodynamic parameters and is in equilibrium with the liquid on the surface and inside of the material.
- We ignore the location of individual particles of raw materials and believe that all of the particles are evenly and thoroughly washed by the steam flow, the particle having the form of an unlimited plate [5].

The temperature change of an arbitrary point of the particle in the non-stationary heat conduction is determined by the differential Fourier equation:

$$\frac{dt(x, \tau)}{d\tau} = a_s \frac{\partial^2 t(x, \tau)}{\partial x^2}$$

(6)

with initial conditions:

$$t(0, x) = t_0$$

(7)

and boundary conditions:

$$r \cdot j_e = -\lambda \left. \frac{\partial t}{\partial x} \right|_{x=0}$$

(8)

where the flow of condensed moisture is determined from the expression:
\[ j_c = \frac{dm}{\pi dH d\tau} \]  

Thermal diffusivity \( a_x \) in (6) is determined by the formula:

\[ a_x = \frac{\lambda}{c \rho} \]

where \( \lambda, c, \rho \) – indexes of heat conduction, heat capacity and density of the material accordingly, determined by empiric formula [4]:

\[ \lambda = \sqrt{0.0108 + 0.000773 \cdot t^{0.349} + 1.083 \cdot 10^{-4} \exp\left[\frac{173.1}{111.61} \cdot U \cdot \ln(U)\right]} \]

\[ c = 1.173 U \cdot (1 + \frac{t}{100})^{-0.222-\cdot U^{-10^{-4}}} \]

\[ \rho = \frac{m}{V} \]

In equations (11) and (12) \( U \) is assumed to be equal to the initial humidity of the material.

Under the influence of the saturated steam temperature and due to the heat exchange processes in the wet material the reactions of autohydrolysis of hemicelluloses [6] as well as changes in the structure of lignin with its partial transition into a low molecular weight state [7] take place.

For modelling of the stages of hemicelluloses decomposition and lignin mass loss during steam hydrolysis of raw materials we will make the following assumptions:

- As during hydrolysis water is in excess, the change of its concentration during the reaction is neglected, and the hydrolysis reaction is considered to be as a monomolecular one or the reaction of the first order [8].
- Thermophysical properties of steam, material and liquid contained in it, are believed to be unchanged, despite time-varying treatment of the chemical composition of all three environments.

During treatment the hydrolysis speed of hemicelluloses can be written as [8]:

\[ \frac{dC_{0hmc}}{d\tau_{treat}} = k \cdot C_{0hmc} \cdot e^{-k \cdot \tau_{treat}} \]  

In the equation (14) \( k \) is calculated as

\[ k = \alpha N \delta Q_{10} \]

where \( \alpha \) – relative catalytic activity of the catalyzer (acid); \( N \) – normality of the catalyzer, expressed by the number of its gram-equivalents in 1 liter of solution; \( \delta \) – relative factor of polysaccharide stability relatively hydrolysis that characterizes the strength of glycosidic linkages in polysaccharides; \( Q_{10} \) – temperature coefficient.

Changes in the concentration of low molecular lignin will be written in the form of the equation of mass conservation:

\[ \frac{dC_{0lgl}}{d\tau_{treat}} = -k_2 \cdot C_{0lgl} \cdot m_w \]

where \( k_2 \) is an experimentally assignable value.

Since hemicellulose and lignin are binders in the wood substance, they strengthen the bonds. As a result of the destruction of the binder components the intermicellar cohesive forces (and hence the
tensile strength of wood), which are directly dependent on the initial composition of the material (wood species), weaken.

The liquid contained in the material from the moment of supply of saturated water steam tends to thermodynamic equilibrium with steam and turns to the overheated (metastable) condition with temperature increase. This is due to the fact that the nascent bubbles in evaporation sites, which are located on the surface of the micelles and fibers, cease to grow, as the pressure above the liquid surface is higher than the steam pressure in the bubbles. Upon reaching the superheated liquid state, it accumulates in itself the same energy in the form of superheating heat.

2.3. Stage of system decompression and material destruction

After soaking the raw material in the reactor at preset parameters the system decompression is performed by opening a decompression valve that leads to external disturbing factor – the difference between the pressure above the liquid and that in the nascent bubbles, resulting in the transition of the liquid, contained in the material, from a metastable state to a stable one [9].

Since the pressure above the liquid and, consequently, above the bubble with steam decreases, the growth of steam bubbles, the overcoming the surface tension of the overheated liquid, the steam release take place. The speed of change of the bubble radius with time equals:

$$\frac{dr}{d\tau} = \left\{ \frac{2}{\rho^2 \tau} \int_0^\tau \frac{dr}{d\tau}\left[p^m - p\right]dt \right\}^{1/2}$$  \hspace{1cm} (17)

The pressure on the surface of the bubble equals:

$$p = p_0 + \rho_0 R_0^2 \left( \frac{\rho_0}{\rho} \right)^{2/3} \left[ \frac{11}{6} \left( \frac{d\rho}{d\tau} \right)^2 - \frac{d^2\rho}{d\tau^2} \right]$$  \hspace{1cm} (18)

where $p_0$, $R_0$, $\rho_0$ – pressure, radius and density at initial time $\tau = 0$.

The density of the steam inside the bubble is:

$$\rho(\tau) = \rho_0 \left[ 1 - \beta T - \left( 1 - \frac{\rho''}{\rho'} \right) v'' \right]$$  \hspace{1cm} (19)

where $\beta$ – index of the temperature expansion of the liquid; $v''(\tau)$ – specific volume steam quantity.

The equation of the growth rate of the bubble volume that emerged at time $\tau$ is the following:

$$\frac{dv}{d\tau} = k b \left[ p(\tau) \right] (\tau - \tau_0)^{k-1}$$  \hspace{1cm} (20)

Thus, the greater the vent rate (less than reset time), the greater rate $J$ of boiling centers formation in the superheated liquid inside of the lignocellulosic material.

$$\ln J = 88 - G$$  \hspace{1cm} (21)

where $G = \frac{W_c}{RT}$ – a free Gibbs number, and $W_c$ is a work of critical bubble formation:

$$W_c = \frac{16\pi\sigma^3}{3(p_s - p')^2(1 - \frac{v'}{v''})}$$  \hspace{1cm} (22)

The increase in the pressure drop over the superheated liquid (steam pressure) and in the bubble causes a decrease in the critical work of bubble formation, and therefore Gibbs number reduces and the number of steam formation centers in the superheated liquid increases.

Also, the nucleation intensity increases with a decrease in average waiting time $\bar{\tau}$ of occurrence of the nucleating seed (the time of pressure change) in volume of metastable (superheated) liquid $V_{shl}$:

$$J = \left( \frac{\bar{\tau}}{V_{shl}} \right)^{-1}$$  \hspace{1cm} (23)
That is, from (23) it follows that if the time of pressure drop decreases, the intensity of steam formation, the amount of the steam expanding inside of the material, as well as the energy stored by superheated liquid increase.

All the above-mentioned conclusions give grounds to assert that the greater the pressure drop for the least period of time, the more energy-carrying expanding steam is formed and the larger force of tension arises inside of the material.

Generally, during decompression of the reactor the liquid boils sharply, releasing the accumulated energy. The expanding steam in the pores and cavities provides the mechanical effect (tensile stress) on the weakening as a result of autohydrolysis bonds. The power influence of the expanding steam results in overcoming the tensile strength of these bonds and their rupture. Thus, there is a separation of the material particles (fibers) from each other with the formation of new surfaces as a result of the performed work.

The potential energy accumulated in the system “compressed steam–superheated fluid” prior pressure drop, is spent not only for boiling up the liquid and for the increase in the specific surface of the material (overcoming tensile strength), but also for pushing the material and steam out of the reactor, as well as the overcoming of the hydraulic and pneumatic resistance. The rest unused energy remains in the form of heat.

The emerging force causes tensile stresses along the width of the particle (chip) making efforts to change the width:

\[ \Delta A = F_a \Delta a \]  

(24)

As far as in this case the work is done at the expense of the potential energy store, it equals the loss of potential energy on the segment of axis \( \Delta a \). Then

\[ F_a \Delta a = - \Delta W_p \]  

(25)

This ratio is valid for any direction in space, so the value of resultant force is:

\[ F_p = - \nabla W_p \]  

(26)

Turning to the issue of energy balance, it can be written as:

\[ W_{shl} = W_1 + W_2 + W_3 + W_4 + W_5 + W_6 + W_7 \]  

(27)

where \( W_{shl} \) – the energy of superheated liquid in the form of heat;

\[ W_1 = \frac{16\pi \sigma^3}{3(p_s - p')^2(1 - v'/v'')^2} \] – energy spent for the formation of critical bubbles;

\[ W_2 = m_{shl} \cdot r \] – energy spent for steam formation;

\[ W_3 = pdV \] – energy spent for steam expansion;

\[ W_4 = \frac{\sigma \cdot aP_{mat} \cdot dF}{E} \] – energy spent for mechanical deformation of the body, for overcoming the tensile strength across the grain and formation of a new surface;

\[ W_5 \] – the energy of motion, spent for a filtration flow of steam from inner layers of the material to the outer ones;

\[ W_6 \] – the energy spent during condensation of the steam at a saturation temperature;

\[ W_7 \] – energy in the heat form retained in the vapors of boiling.

Let us turn to the problem of modeling of material failure (overcoming the tensile strength of bonds). Boiling liquid, turning into vapor, spends the stored energy for steam formation and the breaking of bonds in the material. And a part of the energy of vapor expansion at constant temperature transforms into work, which is performed at stretching and rupture of the weakened as a result of hydrolysis bonds in the lignocellulosic material, that is, this part of energy is converted into mechanical.
\[ dA = -pdV = Vdp \]  

where \( dA \) is a change of work of steam expansion.

The work that should be applied to the wood particle for its internal deformation and fracture (that is, the formation of new specific surface area) is equal to [10]:

\[ A = \frac{\sigma V_p P_{mat}}{2E} \]  

where \( \sigma \) is a tensile strength of the material under tension; \( V_p \) is the volume of the particle; \( E \) is the Young's modulus. Converting (29) and differentiating it with regard to

\[ tF = \sigma \]  

\[ \frac{dA}{dt} = \frac{\sigma aP_{mat} dF}{E} \]  

where \( a \) is the width of the particle, \( P_{mat} \) is the porosity of the material.

As at material destruction of the forces of the expanding inner steam affects the individual bonds [11], and the particle has a capillary-porous structure, we can write:

\[ dV_1 dp = \frac{\sigma aP_{mat} dF}{E} \]  

where \( V_1 \) is volume of steam after expansion.

Thus, the change of the tensile force in the particle will appear as:

\[ dF_1 = \frac{EV_1 dp}{\sigma aP_{mat}} \]  

And a single tear condition is:

\[ \Delta P \geq \frac{\sigma^2 V_p P_{mat}}{EV_1} \]  

A specific surface of obtained product \( \overline{A} \) is characteristic of the grinding degree of the fibrous material, obtained as a result of steam explosion. At a first approximation one can imagine, that

\[ \overline{A} = f(\Delta P, \tau_{dec}) \]  

However, in reality this value depends not only on the conditions of decompression pressure drop \( \Delta P \) and decompression time \( \tau_{dec} \), but also on the conditions of the heat treatment of the lignocellulosic material itself, because the change of physico-chemical and mechanical properties of the material contributes to the formation of a new surface. Therefore, this value is not amenable to rigorous mathematical description, and can only be determined on the basis of experimental data.

2.4. Stage of product unloading

For modeling of the process of unloading as a result of decompression, we agree that:

- At the time of pressure relief the possible effects of drying and reduction of the moisture content of the material are not taken into account, since the duration time of these effects is not large, and the processes of condensation begin to dominate right after the reduction of the pressure till the saturation pressure.
- Due to the complex pattern of simultaneously occurring phenomena of liquid boiling, steam expanding, shredding and material unloading for a short time of decompression, we believe that these phenomena occur successively.
During decompression the expanding steam increases in volume. At the exit of the reactor, it creates a rarefaction wave, its energy is partly spent for pushing of the material, the rest of the energy remains in the steam itself in the form of heat.

The amount of kinetic energy obtained when expanding 1 kg of steam can be defined by the equation:

\[ W_k = \frac{c^2}{2g} \]

(36)

where \( c \) – the steam velocity.

On the other hand, when expanding 1 kg of steam from \( p_0 \) to \( p_1 \) a heat drop will be equal to \( i_0 - i_1 \). Using the concept of mechanical equivalent of heat [11], we can write that work of 1 kg of steam at its extension will be equal to:

\[ W = 427 \cdot (i_0 - i_1) \]

(37)

where 427 – is a mechanical equivalent of heat.

Since \( W = W_k \), we can determine the average exit velocity of steam:

\[ v_{av} = 91.5 \sqrt{i_0 - i_1} = 91.5 \sqrt{p_0 V_0 - p_1 V_1} \]

(38)

where for steam it is:

\[ V_1 = \frac{mRt}{M_p} \]

(39)

The steam flow passing through the pore channels of the layer, exerts pressure on the individual particles, which is totally expressed in a pressure loss. The increase in the speed of steam flow increases the pressure drop in a fixed layer of the material. The layer retains a fixed state until the weight of the layer per unit of its area becomes equal to a pressure drop. With further increase of speed the layer turns into a movable state. With the increase of velocity the layer expands, that is, the concentration of a solid phase in a unit volume of the layer decreases.

3. Conclusion

The physical picture of the steam explosion treatment of the pre-impregnated lignocellulosic material has allowed developing the mathematical model and the algorithm of process calculation. The results of the calculations can be modeled on a computer and compared with the experimental data that will allow identifying the degree of influence of various factors on the kinetics of the process and to produce a rational selection of operating parameters for the considered processes in terms of the assigned applied problems.

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