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HEAT AND MASS TRANSFER IN DISPERSE AND POROUS MEDIA

MODELING OF FAST PYROLYSIS OF A SINGLE BIOMASS PARTICLE IN AN INERT BOILING BED

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We have developed a model of fast pyrolysis of a biomass (wood) particle including the heating of the particle in a boiling bed under regular conditions, the pyrolysis kinetics of the three basic components of the biomass (cellulose, hemicellulose, and lignin), and the destruction kinetics of the intermediate pyrolysis products, as well as a submodel of the particle motion in the free space of the reactor. The numerical optimization of the fast pyrolysis performed by us has shown that the main control parameter of the process determining the yield of liquid biofuel is the temperature of the boiling bed.

Keywords: *fast pyrolysis, biomass, biofuel pyrolysis kinetics, optimization, boiling bed.*

Introduction. Direct burning of the biomass is not always an optimal way of using its energy because of the high moisture content in it, its low compactness, and the dispersal of fuel sources, increasing the cost of its transportation to the place of processing. Quite promising is the thermochemical treatment of biomass with the aim of obtaining synthetic gaseous or liquid fuels that can be used in both power plants with gas-and-oil-fired furnaces, which constitute the overwhelming majority of the boiler stock of the Republic of Belarus, and stationary and transport engines.

One of the main methods permitting such processing of biomass is pyrolysis. As is known [1], depending on the conditions of carrying out the process of pyrolysis, one can obtain a different yield of condensable and gaseous volatile products: at temperatures of 450–600^{o}C and under fast cooling of products, up to 75% of their mass is accounted for by heavy condensable hydrocarbon fractions (tar) forming the basis of the liquid biofuel. Higher temperatures and prolonged pyrolysis lead to a secondary destruction of the heavy fractions, and the product of the process is mainly a mixture of noncondensable gases (pyrogas). The subject of the present paper is fast pyrolysis of the biomass with the aim of obtaining liquid fuel.

Fast pyrolysis in a boiling bed (BB) has many important advantages: extremely high heat transfer coefficients between biomass particles and the inert material of the bed, a high isothermality of the BB, and the possibility of fine control of its temperature and of carrying out a continuous process. Creating industrial plants for fast pyrolysis and obtaining products call for optimizing the process parameters, which can be done most effectively by means of computational modeling on the basis of a theoretical model of the process. We have developed a mathematical model of the fast pyrolysis of a wood particle in a BB of an inert material and carried out a numerical investigation of the given process.

Model of the Fast Pyrolysis of a Wood Particle in a Boiling Bed. The proposed model consists of three submodels: a kinetic model of pyrolysis of various components of the biomass, a thermal model of heating a biomass particle in the reactor, and a model of the particle motion in its free space.

In those cases where the pyrolysis is carried out with the aim of obtaining liquid biofuel (precisely such a process is the object of the analysis in the present paper), the process time should be short enough compared to the time of destruction of the gaseous products of pyrolysis. To this end, the characteristic size of the biomass particle should not exceed 1 mm, since the heating of larger particles proceeds too slowly. Therefore, because of the small sizes of the biomass particles under consideration, as well as due to the formation of macrocracks of the wood in the

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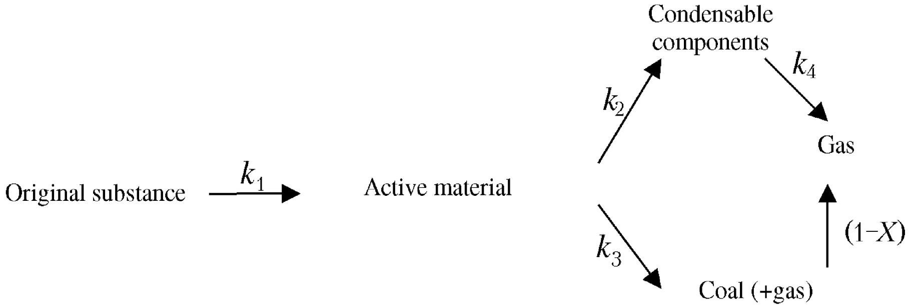

Fig. 1. Kinetic scheme of the decomposition of the biomass components.

TABLE 1. Kinetic Parameters of Pyrolysis of the Wood Components

Parameter	Cellulose				Hemicellulose				Lignin			
	k_1	k_2	k_3	k_4	k_1	k_2	k_3	k_4	k_1	k_2	k_3	k_4
E, kJ/mole	242.4	196.5	150.5	108	186.7	202.4	145.7	108	107.6	143.8	111.4	108
log(A), log(1/sec)	19.447	14.516	10.114	6.631	16.332	15.942	11.415	6.631	8.982	9.176	6.886	6.631

process of pyrolysis, the transport of the gaseous products of pyrolysis from the particle to the gas phase is not the limiting stage of the process and is not considered in the given formulation of the problem.

Composition of the wood and pyrolysis kinetics of its components. The main components of the organic (combustible) part of the wood, which accounts for about 99% of its dry mass, are cellulose (linear polysaccharide with a degree of polymerization of ~1000), hemicellulose (linear noncellulose polysaccharides, derivatives of xylose with a low degree of polymerization of ~100), and lignin (amorphous aromatic polymers with a complex three-dimensional structure). In different kinds of wood the ratio between these components varies, but on average cellulose makes up around 50%, and the other two components account for 20–30% of the dry mass each. The contribution of each of these components in obtaining the desired product of pyrolysis — heavy volatile products forming, by condensing, liquid biofuel (biopetroleum) — varies individually. The main component of the liquid biofuel obtained in the pyrolysis of cellulose (the temperature range from 240 to 450^{o}C) is levoglucosan, which may decompose and volatilize with increasing temperature.

Hemicellulose begins to decompose at a temperature of 200–260^{o}C. Compared to cellulose, it gives a higher yield of condensable volatile components. Components of the liquid biofuel obtained as a result of the decomposition of hemicellulose are acids such as vinegar and formic acids and furfural derivatives.

Lignin is a binder of the wood structure and decomposes, according to Soltes and Edler [2], at a temperature of 280–500^{o}C. The most massive pyrolysis product of lignin is coal (coke residue), whose yield may reach 55%. The liquid products known as pyroligninic acid consist of an aqueous solution (20% of the weight of dry lignin) and a tar residue (15% of the weight of dry lignin). The aqueous part consists of methanol, vinegar acid, acetone, and water. The tar residue consists mainly of homological phenol compounds. The gaseous products account for 10% of the mass of the original substance and consist of methane, ethane, and CO.

To optimize the process of fast pyrolysis with the aim of obtaining a particular kind of fuel, it is necessary to use kinetic schemes describing the pyrolysis of all basic components of the biomass, since decomposition of each of them occurs in its own temperature range. In developing the model, we used in the present work the kinetics proposed by Miller and Bellan [3]. According to this kinetics, pyrolysis of all components occurs by one and the same scheme given in Fig. 1 but each its own kinetic parameters.

Let is consider this scheme in more detail. The original substance is one of the wood components (cellulose, hemicellulose, or lignin) representing a polymer consisting of monomeric links. The initial reaction (its rate is equal to k_1) is the depolymerization stage and does not lead to a change in the mass. Then, in the course of time, the competing reactions of the formation of tar (products condensing at a temperature lower than 80–120^{o}C), on the one hand, and of noncondensable gases and a solid coke residue on the other hand, take place. The probability of tar or coke and gas formation depends on the activation energy values of the corresponding reactions. All rate constants k_i obey the Arrhenius law $k_i = A_i \exp(-E_i/RT)$, where E_i is the activation energy and A_i is the pre-exponential factor. A characteristic feature of this scheme is the fact that gas and coke are formed simultaneously; however; for each wood component the mass fraction of the gas $(1 - X^i)$ resulting from this transformation is given. In the pyrolysis process, with increasing temperature a secondary reaction of thermal decomposition of tar with the formation of noncondensable gases proceeds. The rate constant k_4 of this reaction is the same for all components, which presupposes the same composition of the tars formed from them.

The kinetic parameters for each component of the kinetic Miller–Bellan scheme are presented in Table 1.

Thermal conditions for the biomass particle. The main factor determining the rate of pyrolytic processes is the local temperature in the particle. In formulating the model, it is important to estimate the inhomogeneity of the temperature field in the particle, since the degree of spatial detail of the pyrolysis depends on this estimate.

In the present paper, we use a simplified isotropic model of the heat transfer in a wood biomass particle. It is known [4] that the mechanisms of heat transfer in a particle along the wood fibers and across them differ considerably. While the main filtration flows of pyrolysis products are directed along the fibers from the center of the particle to its boundary and impede the heating of the particle, the transverse heat transfer is conductive and directed from the boundary of the particle to its center. Therefore the heating time of the particle in the direction perpendicular to the fibers is determining in the case under consideration, and the effective anisotropic heat conductivity coefficient should be chosen close to the heat conductivity in the direction perpendicular to the fibers. Such simplification makes it possible to consider the particle as a spherical one with a certain effective isotropic heat conductivity, which makes the problem one-dimensional and considerably facilitates optimization of the process of fast pyrolysis.

Note first that for dry wood particles with sizes of the order of 500 μm the pyrolysis time (of the order of a few seconds) turns out to be much larger than the time needed for the heating to become regular. Indeed, the onset of the regular regime is characterized by the Fourier number $\mathrm{Fo} = at/d_\mathrm{p}^2 \approx 0.1$ (a is the heat conductivity of the particle material) [5] determined by the transverse heat conductivity of the particle. A heating time of the particle of the particle of about 0.1 sec corresponds to this Fo value. Thus, practically throughout the pyrolytic process the particle heating regime can be considered to be regular and, to characterize it, one can use the coefficient of internal heat exchange of the particle based on the first eigenvalue of κ_1 of the following boundary-value problem [6]:

$$\Delta_\xi \theta = -\kappa_1^2 \theta \, ; \quad \left. \frac{\partial \theta}{\partial \xi} \right|_{\xi=0} = 0 \, , \quad \theta \big|_{\xi=1} = 0 \, , \tag{1}$$

where θ and ξ are an arbitrary function and an argument. With the use of κ_1 the coefficient of internal heat exchange α_int is found as

$$\alpha_\mathrm{int} = \frac{V}{S} \kappa_1^2 \frac{\lambda_\mathrm{p}}{d_\mathrm{p}^2} \, . \tag{2}$$

It determines the specific (per unit area of the outer surface of the particle) heat flow from the outer surface of the particle S to its central part by the average temperature of the particle T_p and the surface temperature of the particle T_s in accordance with the expression

$$q_\mathrm{int} = \alpha_\mathrm{int} (T_\mathrm{s} - T_\mathrm{p}) \, . \tag{3}$$

The external heat exchange is characterized by the coefficient α_ext determined in accordance with the Newton law $q_\mathrm{ext} = \alpha_\mathrm{ext}(T_\mathrm{b} - T_\mathrm{s})$ and calculated by the empirical correlations given below with account for the radiative component. Apparently, the above flows q_ext and q_int should be equal to each other. From this it follows that the effective coefficient of heat exchange of the particle with the boiling bed is determined from the relation (the reciprocal internal and external thermal resistances are added)

$$\frac{1}{\alpha_\mathrm{eff}} = \frac{1}{\alpha_\mathrm{int}} + \frac{1}{\alpha_\mathrm{ext}} \, . \tag{4}$$

Thus, from the viewpoint of heat exchange the heating of the biomass particle in a boiling bed can be described in the case under consideration with the help of the effective heat exchange coefficient α_{eff}.

Estimates and preliminary calculations show that the use of the average particle temperature for calculating the pyrolysis kinetics is also justified. Indeed, the rate of formation of condensable products (tars forming the basis for liquid biofuel) becomes noticeable at temperatures of the order of 750 K. Such a temperature is attained on the surface of a particle of diameter 500 μm after 0.15–0.20 sec. This time corresponds to a Fourier number of 0.27–0.35. Using the analytical solutions of the problem on the heating of a spherical particle with constant properties [4], we obtain that by the considered instant of time (when the surface temperature of the particle reaches 750 K) the temperature at its center is 670 K, and the average temperature is 730 K. At the same time, the characteristic temperature range in which the rate of the reactions determining the process changes *e* times is 20–30 K. In the example considered, the determination of the pyrolysis rate from the average temperature of the particle gives an error of about 25% compared to the averaging of the rate over the particle volume (by means of the approximate analytical solution for the temperature distribution). Taking into account the model errors connected with the indefiniteness of its thermophysical and kinetic parameters, it may be concluded that the approximation made is satisfactory, especially for small-sized particles.

Convective and radiative heat exchange of the particle with the boiling bed. In developing the model of the external heat exchange of the particle with the bed surrounding it, the convective and radiative energy transfer was taken into account. The thermal balance of the particle is written as follows:

$$m_{\text{p}} c_{\text{p}} \frac{dT_{\text{p}}}{dt} = \pi d_{\text{p}}^2 (T_{\text{b}} - T_{\text{p}})\, \alpha_{\text{eff}} \, . \tag{5}$$

To calculate the coefficient of internal heat exchange, we used the transformed expression (2):

$$\alpha_{\text{int}} = \frac{2}{3} \pi^2 \frac{\lambda_{\text{p}}}{d_{\text{p}}} \, . \tag{6}$$

The external heat exchange is defined by the coefficient

$$\alpha_{\text{ext}} = \frac{\lambda_{\text{g}}}{d_{\text{p}}} \text{Nu} \, ,$$

where the Nusselt criterion consists of two terms: $\text{Nu} = \text{Nu}^{\text{r}} + \text{Nu}^{\text{conv}}$. To calculate the radiative component, we use the Stefan–Boltzmann law:

$$\text{Nu}^{\text{r}} = d_{\text{p}} \sigma \left(T_{\text{b}}^2 + T_{\text{p}}^2\right) \left(T_{\text{b}} + T_{\text{p}}\right) . \tag{7}$$

To calculate Nu^{conv}, it is necessary to take into account the fact that the biomass particle size varies continuously in the pyrolysis process and, consequently, one has to use interpolation of results obtained for various size ratios between the biomass particle and the bed particle. In the present paper, we use the approach proposed in [7] consisting of the interpolation of experimental correlations for the following three cases:

1) equality of sizes of biomass and inert bed particles, $d_{\text{p}} = d_{\text{i}}$;

2) the size of the biomass particle is much larger than the size of the inert bed particle, $d_{\text{p}} >> d_{\text{i}}$;

3) the size of the biomass particle is much smaller than the size of the bed particle, $d_{\text{p}} << d_{\text{i}}$.

The experimental correlations for the Nusselt number for these cases are, respectively, as follows:

$$\text{Nu}_1^{\text{conv}} = 6 + 0.117\text{Ar}^{0.39}\text{Pr}^{0.33} \, , \qquad \text{Nu}_\infty^{\text{conv}} = 0.85\text{Ar}^{0.19} + 0.006\text{Ar}^{0.5}\text{Pr}^{0.33} \, , \qquad \text{Nu}_0^{\text{conv}} = 2 + 1.8\text{Re}^{1/2}\text{Pr}^{1/3} \, .$$

Generalizing (interpolating) the above correlations in accordance with [7], we get

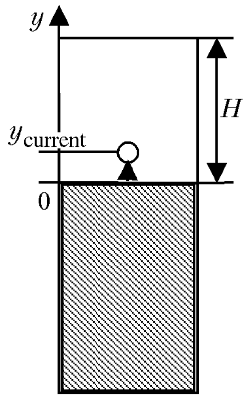

Fig. 2. Scheme of the particle motion in the reactor.

$$\mathrm{Nu}^{\mathrm{conv}} = \begin{cases} \left(\dfrac{d_{\mathrm{i}}}{d_{\mathrm{p}}}\right)^{2/3} \left(\mathrm{Nu}_1^{\mathrm{conv}} - \mathrm{Nu}_\infty^{\mathrm{conv}}\right) + \mathrm{Nu}_\infty^{\mathrm{conv}} , & 0 < d_{\mathrm{i}}/d_{\mathrm{p}} < 1 ; \\ \left(\dfrac{d_{\mathrm{p}}}{d_{\mathrm{i}}}\right)^{2/3} \left(\mathrm{Nu}_1^{\mathrm{conv}} - \mathrm{Nu}_0^{\mathrm{conv}}\right) + \mathrm{Nu}_0^{\mathrm{conv}} , & 0 < d_{\mathrm{p}}/d_{\mathrm{i}} < 1 . \end{cases} \tag{8}$$

Let us introduce the dimensionless temperature

$$\Theta = \frac{T_{\mathrm{p}} - T_0}{T_{\mathrm{b}} - T_0} . \tag{9}$$

Then $T_{\mathrm{p}} = T_0 + \Theta(T_{\mathrm{b}} - T_0)$ and, consequently, $dT_{\mathrm{p}} = d\Theta(T_{\mathrm{b}} - T_0)$. Equation (5) for the dimensionless temperature will take on the form

$$\frac{d\Theta}{dt} = \frac{6\,(1 - \Theta)\,\alpha_{\mathrm{eff}}}{d_{\mathrm{p}}\rho_{\mathrm{p}}c_{\mathrm{p}}} . \tag{10}$$

Equation of particle motion in the bed. As a result of pyrolysis, the mass and size of the wood particle decrease and at a certain instant of time the gas flow begins to expel it from the reactor. Consider the model of the particle motion in the bed. Let the height of the superbed space be equal to *H*. Let us denote the vertical coordinate of the particle in the reactor by *y* and measure it from the upper boundary of the bed (Fig. 2).

In the process of pyrolysis, a large quantity of gaseous products is released from the particle and create around it an original gas cushion. As a result, the particle floats in the near-surface layer until the drag force acting on it from the side of the gas flow becomes greater than gravity. The drag force is determined as [8]

$$F_{\mathrm{a}} = \frac{\rho_{\mathrm{g}}\,(U - U_{\mathrm{p}})^2\,\pi d_{\mathrm{p}}^2 C_d}{8} , \tag{11}$$

where

$$C_d = \begin{cases} 24/\mathrm{Re} , & \mathrm{Re} < 0.4 ; \\ 10/\mathrm{Re}^{1/2} , & 0.4 < \mathrm{Re} < 500 ; \\ 0.43 , & 500 < \mathrm{Re} < 200\,000 . \end{cases} \tag{12}$$

Once the above condition has been fulfilled, the particle begins to escape from the reactor by the law

$$\frac{dU_{\text{p}}}{dt} = \frac{F_{\text{a}}}{m_{\text{p}}} - g\,, \tag{13}$$

$$\frac{dy}{dt} = U_{\text{p}}\,. \tag{14}$$

The escaping process ends when the particle reaches the upper cross-section of the reactor. In modeling, the reactor blow rate U was chosen to be equal to 1.1 of the hovering velocity of the coal particle formed from the initial particle upon its complete pyrolysis.

Decomposition of volatile pyrolysis products. In the pyrolysis process, at each instant of time the biomass particle releases tar (light fraction condensing under the standard conditions), coal, and gas. Recording at each time step the released portion of tar (biofuel) and integrating these portions at the reactor exit, we can analyze the final yield of pyrolytic fuel.

We shall further use the dimensionless masses of the chemical components ($\mu^i_{\text{v,a,c,t,g}}$) representing the ratio of the corresponding dimensional mass to the initial particle mass m_{w0}. Let as a result of the pyrolysis in time dt from the active substance μ^i_{a} a portion of tar of mass $d\mu^i_{\text{t}} = k^i_2\mu^i_{\text{a}}(t)dt$ be liberated. Calculating the subsequent pyrolysis of each such portion upon its motion in the reactor (together with the blown gas), we can determine the part of this portion that has reached the reactor end: $d\mu^i_{\text{t}} \exp(-k_4 t_{\text{vol}}(t))$, where t_{vol} is the residence time of the given portion in the reactor:

$$t_{\text{vol}} = \frac{H - y(t)}{U}\,. \tag{15}$$

Integrating with respect to the whole time of the process (from the beginning of pyrolysis to the particle escape from the reactor) and summing over all components of the wood, we obtain the total yield of liquid biofuel (with respect to the initial mass of the particle m_{w0}):

$$\mu_{\text{t,fin}} = \sum_{i=1}^{3} k^i_2 \int_0^{t_{\text{fin}}} \mu^i_{\text{a}}(t) \exp(-k_4 t_{\text{vol}}(t))\, dt\,. \tag{16}$$

The total relative quantity of the gas obtained as a result of the tar decomposition can be given as

$$\mu_{\text{g,fin}} = \sum_{i=1}^{3} k^i_2 \int_0^{t_{\text{fin}}} \mu^i_{\text{a}}(t)\,(1 - \exp(-k_4 t_{\text{vol}}(t)))\, dt\,. \tag{17}$$

Moreover, gaseous products of pyrolysis are formed at a rate $k_3(1 - X)$ simultaneously with the transformation of the active biomass to coal (see the kinetic scheme in Fig. 1).

General system of equations. From the foregoing it follows that the general model of the wood particle pyrolysis in the boiling bed apparatus is represented by the following system of equations:

$$\begin{gathered}
\frac{d\Theta}{dt} = \frac{6(1-\Theta)\alpha_{\text{eff}}}{d_{\text{p}}\rho_{\text{p}}c_{\text{p}}}\,, \quad \frac{d\mu^i_{\text{v}}}{dt} = -k^i_1\mu^i_{\text{v}}\,, \quad \frac{d\mu^i_{\text{a}}}{dt} = -\left(k^i_2 + k^i_3\right)\mu^i_{\text{a}} + k^i_1\mu^i_{\text{v}}\,, \\
\frac{d\mu^i_{\text{c}}}{dt} = k^i_3\mu^i_{\text{a}}X^i\,, \quad \frac{d\mu^i_{\text{t}}}{dt} = k^i_2\mu^i_{\text{a}}\,, \quad \frac{d\mu^i_{\text{g}}}{dt} = k^i_3\mu^i_{\text{a}}(1 - X^i)\,, \\
\frac{dU_{\text{p}}}{dt} = \begin{cases} 0\,, & \dfrac{F_{\text{a}}}{m_{\text{p}}} - g \le 0\,; \\ \dfrac{F_{\text{a}}}{m_{\text{p}}} - g\,, & \dfrac{F_{\text{a}}}{m_{\text{p}}} - g > 0\,; \end{cases} \quad \frac{dy}{dt} = U_{\text{p}}\,,
\end{gathered} \tag{18}$$

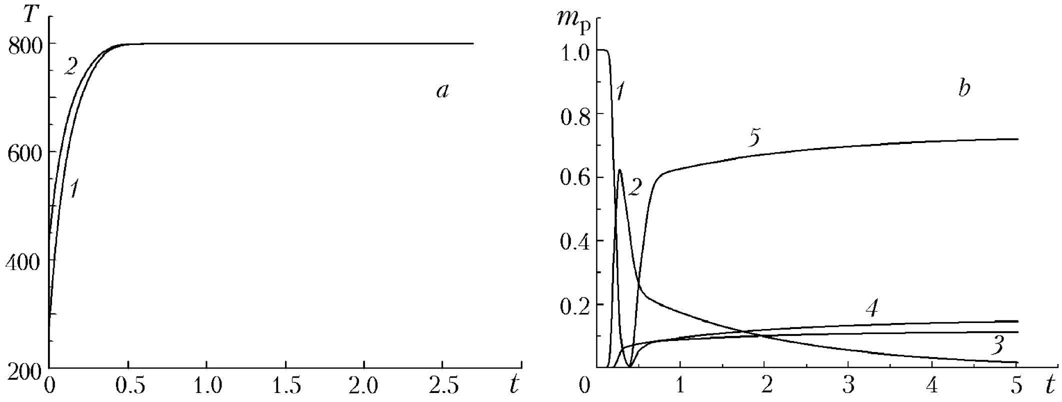

Fig. 3. Results of modeling fast pyrolysis of the biomass in a boiling bed under the optimal conditions of the process: T_b = 776 K, d_p = 440 μm, d_i = 940 μm: a) temperature profiles [1) particle average, 2) on the particle surface]; b) integral biomass decomposition curves (sum over the three components) [1) original substance, 2) active substance, 3) coal (coke), 4) condensable products (biofuel), 5) noncondensable products (gas). T, K; t, sec.

where i = 1 is cellulose, 2 is hemicellulose, and 3 is lignin.

Note that the equations for the formation of tar from the three wood components (the fifth equation of system (18)) contain no term characterizing its decomposition upon leaving the particle. The "history" of the transformations of each portion of tar upon its formation from the initial wood is followed individually up to its leaving the reactor by formula (17). The initial conditions for the unknowns in the system of equations (18) are

$$\mu_c^i = 0\,,\ \ \mu_g^i = 0\,,\ \ \mu_i^i = 0\,,\ \ \mu_a^i = 0\ \ (i = 1, 2, 3)\,,\ \ \mu_v^1 = 0.40\,,\ \ \mu_v^2 = 0.35\,,\ \ \mu_v^3 = 0.25\,. \tag{19}$$

The physical properties of the system are calculated by the relations given in the Appendix.

Results of the Modeling and Optimization of the Fast Pyrolysis of Biomass Particles. ***Dynamics of the fast pyrolysis of a biomass particle in a boiling bed and factors influencing it.*** Computational modeling permits following the dynamics of the fast pyrolysis of the biomass in a boiling bed.

A wood particle of diameter 500 μm is heated to the boiling bed temperature (≈800 K) in about 0.5 sec (Fig. 3a). The typical integral pyrolysis curves of a wood particle (total yield of products) are given in Fig. 3b. If we consider the decomposition of the wood components (Fig. 4), we can see that decomposition of each of them begins at approximately one and the same time (at approximately one and the same temperature), but there are great differences in the pyrolysis rates. Cellulose and hemicellulose decompose in approximately the same manner, and by the moment of complete heating of the particle the pyrolysis of these components ends. Lignin pyrolysis is slower. For example, cellulose begins to decompose at a temperature of about 570 K and by the moment a temperature of 800 K is reached its decomposition is completed. Lignin begins to decompose at a temperature of 550 K, but as 800 K is reached only half of it turns out to be decomposed.

As is seen from Fig. 3, decomposition of the wood begins at a temperature of about 550 K. The initial biomass goes into the active state and at a temperature of about 750 K this process is completed. At this point a maximum of the active fraction is observed. Along with the transition to the active state, decomposition of the active component into tar, coal, and gas is observed. The thus formed tar, being heated in turn, decomposes transforming into gas. Both these pyrolysis products are carried out of the reactor by the liquefying gas flow into a cooled condenser where the tar condenses. The slowest process is the pyrolysis of lignin.

Criteria and parameters of the optimization of the low-temperature pyrolysis of biomass. The main condition for optimizing the process of low-temperature fast pyrolysis is the attainment of the maximum yield of liquid fuel.

Among the main parameters influencing the yield of the desired product are the blow rate of the reactor, its temperature, the particle size of the biomass and of the inert boiling bed, as well as the height of the superbed space. Not all of the above parameters are independent therewith. Let us consider the role of each of the parameters listed above.

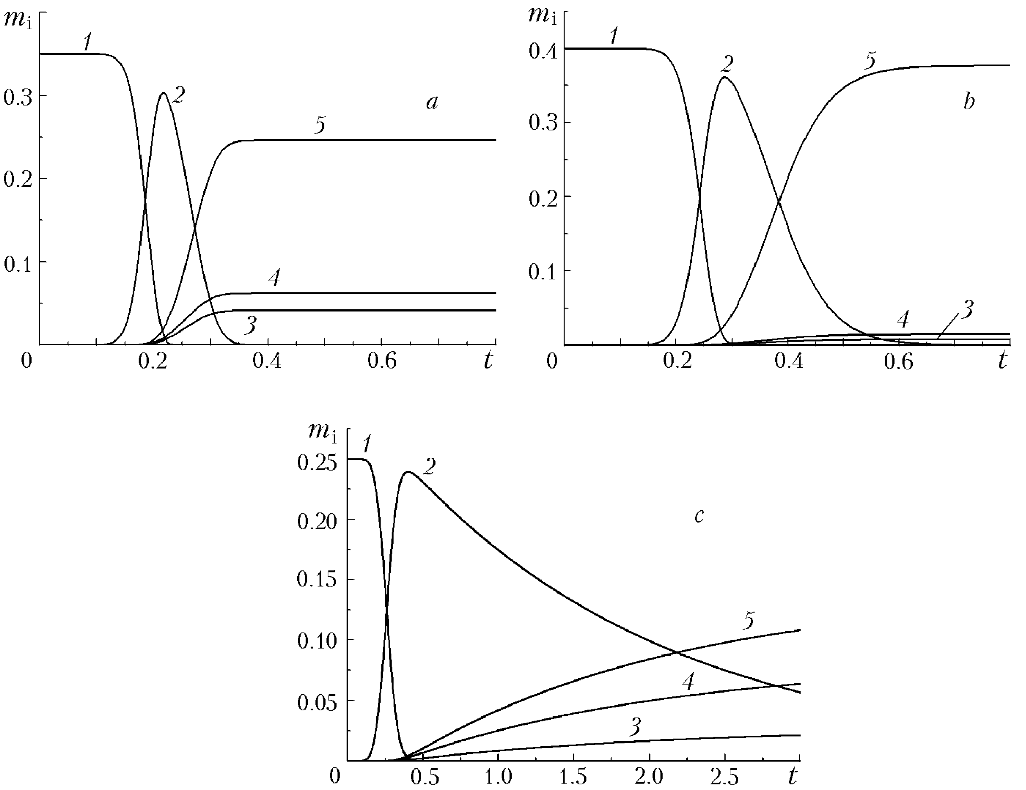

Fig. 4. Decomposition curves of hemicellulose (a), cellulose (b), and lignin (c). Notation 1–5 same as in Fig 3b. *t*, sec.

The choice of the liquefying gas velocity is based on several criteria: first, the blow rate should be higher than the rate of minimum pseudoliquefaction of the bed (quartz) particles; secondly, the blow rate should be such that the coal particles formed upon completion of pyrolysis are carried out of the reactor. Proceeding from this, the blow rate of the reactor should be higher than the minimum pseudoliquefaction rate of the bed and somewhat exceed the rate of carry-over of coke particles upon completion of pyrolysis. As mentioned above, the blow rate in the calculations was chosen to be equal to 1.1 of the hovering velocity of end coal particles.

Another parameter is the size of bed particles, since the ratio of their size to the biomass particle size plays the determining role for the process of heat exchange of a particle with the inert bed and the reactor on the whole.

An important role in carrying out the process is also played by the height of the superbed space, since it determines the residence time of the biofuel in the reactor. In fact, at a given temperature of the process the parameter under consideration determines what part of the tar will decompose into noncondensable components. Consequently, the height of the superbed space should have the least possible value determined by the technical parameters of the reactor design. For theoretical calculations, we chose the value of $H = 0.1$ m as a minimum feasible, in terms of the design, limit of this parameter.

Proceeding from the foregoing, for basic optimization parameters we chose the following quantities: particle size, diameter of bed particles, and reactor temperature. The following restrictions were imposed on the parameters: $d_i \le 1 \cdot 10^{-3}$ mm, 0.1 mm $\le d_p \le 1$ mm. To optimize the parameters of the fast pyrolysis of biomass, we used the simplex optimization method of [9].

Optimization results. The numerical optimization of the process led to the following values for the previously chosen variable parameters: $T_b = 776$ K, $d_p = 440$ μm, $d_i = 940$ μm. The yield of biofuel thereby was 72%. In Fig. 3, the integral decomposition curves of the wood (also integral with respect to the components) are given precisely for the above optimal parameters.

Sensitivity of the optimization results to variations of the optimal parameters. *Size of biomass particles and of inert particles of the bed.* The investigation of the dependence of the biofuel yield on the size of biomass particles

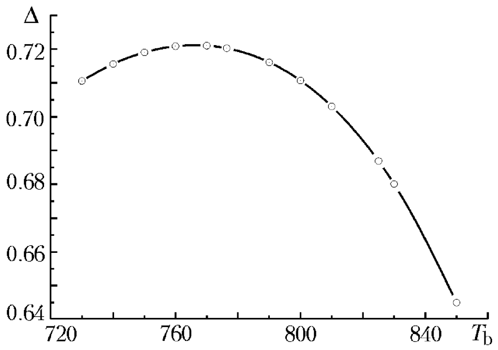

Fig. 5. Influence of the reactor temperature on the integral yield of biofuel (Δ) at the initial size of the biomass particle d_p = 440 μm and d_i = 940 μm. T_b, K.

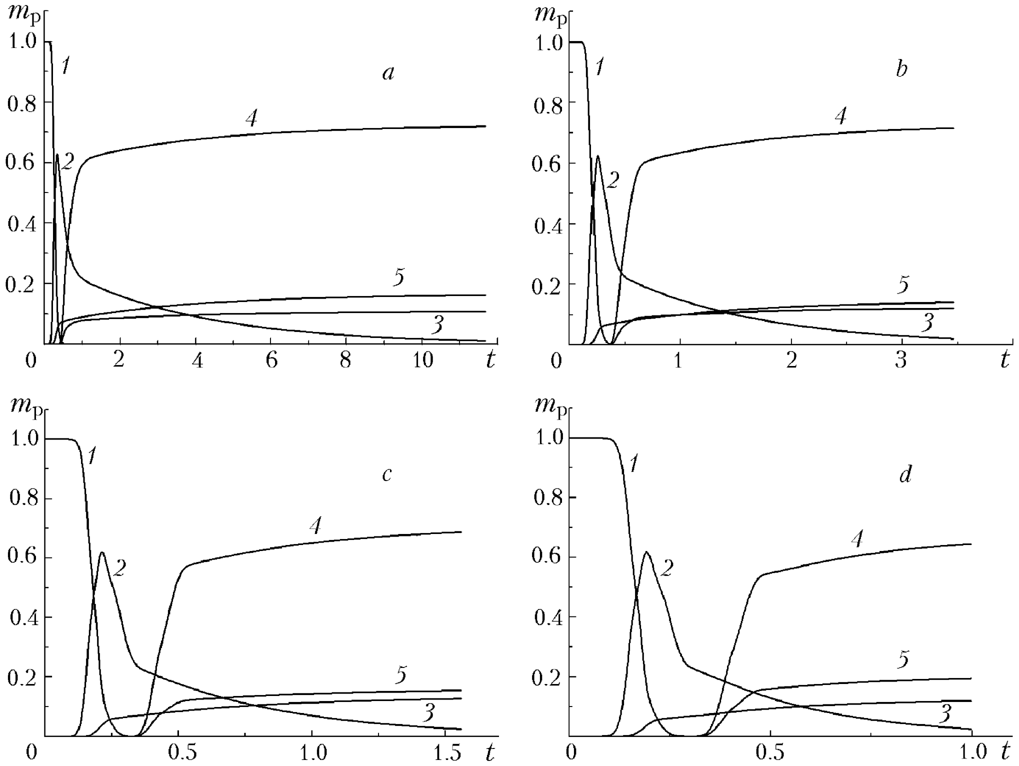

Fig. 6. Dynamics of the integral yield of biomass pyrolysis products at d_p = 440 μm, d_i = 940 μm at various temperatures: a) T_b = 750 K; b) 790; c) 825; d) 850. Notation 1–5 same as in Fig 3b. t, sec; m_p, kg.

at fixed other parameters corresponding to the obtained optimum has shown that the influence of the given parameter on the process is not strong and its variation in the above range leads to an insignificant decrease in the biofuel yield — by 1–2%. Despite the fact that the time of completion of the process changes with varying particle sizes rather strongly (from 4 to 8 sec as d_p is varied from 400 to 1000 μm), its influence on the results is weak, since in any event the pyrolysis time at the optimal temperature turns out to be much longer than the heating time of the particle. Thus, it may be concluded that, being restricted to the introduced range of biomass particle sizes, the biofuel yield is largely determined by the pyrolysis kinetics.

Because of the short heating time of the biomass particle compared to the pyrolysis time, the diameter of inert particles of the bed (on which the conditions of external heat exchange of the biomass particle depend) also has a weak effect on the biofuel yield.

Boiling bed temperature (*reactor temperature*). No doubt, the reactor temperature is the most important optimization parameter of the fast pyrolysis. It should be noted that the optimum of liquid biofuel production turns out to be less sensitive to a decrease in the process temperature than to its increase (Fig. 5). This is primarily due to the fast decomposition of the heavy fractions of pyrolysis with increasing temperature. At pyrolysis temperatures below the optimal one the coke yield begins to increase, as a result of which the portion of the biofuel obtained in the process decreases. This is seen from Fig. 6 illustrating the change in the composition of pyrolysis products for each component of the wood with varying temperature of the reactor.

In general, it may be stated that in the given formulation of the problem the optimum yield of liquid biofuel is reached primarily due to the competition between the pyrolysis process of lignin as the most slowly decomposing component and the destruction of tarry (condensable) products of pyrolysis. As is seen from the results presented, the contribution of lignin to the total yield of liquid biofuel is 10–15%. Therefore, if we consider, as the condition for the optimal process, not the attainment of the maximum yield of the liquid product but the attainment of the maximum efficiency, then the latter can be increased markedly (2–3 times) by dropping the slow decomposition of lignin (with a loss of the corresponding part of the products) and reducing the process time.

Conclusions. The developed model of fast pyrolysis of biomass (wood) particles in a boiling bed has made it possible to optimize the process in terms of the yield of liquid biofuel. Analysis of the modeling results has shown that the most important parameters for obtaining the maximum yield of biofuel in the process of fast pyrolysis are the reactor temperature and the height of the superbed space. The particle sizes of the biomass and of the inert boiling bed influence the biofuel yield insignificantly. This means that the fast pyrolysis in the considered case proceeds in a regime close to the kinetic one. As a result of the optimization, a maximum yield of biofuel constituting 72% of the initial mass of the particle at a reactor temperature of 776 K, a mean diameter of biomass particles of 440 μm, and a mean diameter of inert bed particles of 940 μm have been attained. However, the efficiency of the process under the above optimal conditions as to the yield of the desired product turns out to be relatively low — the time of complete conversion of lignin is large (5–7 sec). Dropping the complete conversion of lignin (with a loss of 10–15% of the mass of the obtained liquid biofuel) makes it possible to reduce the time of the process to 1–2 sec and thus increase considerably its efficiency.

APPENDIX

Dependences for the physical characteristics of the investigated system:
degree of conversion of a particle

$$\eta = 1 - \sum_{i=1}^{3} \left(\mu_{\mathrm{v}}^{i} - \mu_{\mathrm{a}}^{i}\right) ,$$

particle density depending on the degree of conversion

$$\rho_{\mathrm{p}} = \rho_{\mathrm{w0}} - \eta\,(\rho_{\mathrm{w0}} - \rho_{\mathrm{c}}) ,$$

particle mass

$$m_{\mathrm{p}} = m_{\mathrm{w}}^{0} \sum_{i=1}^{3} \left(\mu_{\mathrm{v}}^{i} + \mu_{\mathrm{a}}^{i} + \mu_{\mathrm{c}}^{i}\right) ,$$

particle diameter

$$d_{\mathrm{p}} = \sqrt[3]{\frac{6m_{\mathrm{p}}}{\rho_{\mathrm{p}}\pi}} ,$$

heat capacity of a biomass particle according to the empirical relation of [8]

$$c_{\mathrm{p}} = (3.867T_{\mathrm{p}} + 103)\,(1 - \eta) + \eta\,\left(-\,334 + 4.41T_{\mathrm{p}} - 3.16\cdot10^{-3}T_{\mathrm{p}}^2 + 1.01\cdot10^{-6}T_{\mathrm{p}}^3 - 119\cdot10^{-12}T_{\mathrm{p}}^4\right) ,$$

liquefying gas viscosity

$$\ln\mu = \ln 0.1 - 1.75\cdot10^1 \ln (T_{\mathrm{b}})^0 + 2.83 \ln (T_{\mathrm{b}})^1 - 3.00\cdot10^{-1} \ln (T_{\mathrm{b}})^2 + 1.38\cdot10^{-2} \ln (T_{\mathrm{b}})^3 ,$$

gas density

$$\rho_{\mathrm{g}} = \frac{0.028P}{RT_{\mathrm{b}}} ,$$

heat capacity of the gas

$$c_{\mathrm{g}} = \frac{R}{0.028}\left(3.30 + 1.41\cdot10^{-3}T_{\mathrm{b}} - 3.96\cdot10^{-6}T_{\mathrm{b}}^2 + 5.64\cdot10^{-9}T_{\mathrm{b}}^3 - 2.44\cdot10^{-12}T_{\mathrm{b}}^4\right) ,$$

heat conductivity of the gas

$$\ln\lambda = 5 \ln 0.1 + 1.49\cdot10^1 - 4.42 \ln (T_{\mathrm{b}})^1 + 7.79\cdot10^{-1} \ln (T_{\mathrm{b}})^2 - 3.85\cdot10^{-2} \ln (T_{\mathrm{b}})^3 .$$

NOTATION

c_{p}, heat capacity of the wood particle, J/(kg·K); d_{p}, diameter of the wood particle, m; d_{i}, diameter of the inert bed particle residing in the reactor, m; g, gravitational acceleration; H, height of the superbed space; k_1^i, decomposition constant of the initial ith component into the active one; k_2^i, decomposition constant of the active ith component into coal; k_3^i, decomposition constant of the active ith component into condensable products of pyrolysis; k_4^i, decomposition constant of condensable products of pyrolysis from the ith component into noncondensable products; m_{p}, current particle mass, kg; m_{w0}, initial mass of the wood particle, kg; Nu, Nusselt number; Nu^{r}, radiative component of the Nusselt number; $\mathrm{Nu}^{\mathrm{conv}}$, convective component of the Nusselt number; P, pressure, Pa; q, heat flow, W/m^2; R, universal gas constant; Re, Reynolds number; S, surface area of the particle, m^2; T_0, initial temperature of the boiling bed, K; T_{b}, temperature of the boiling bed; K; T_{p}, temperature of the wood particle, K; T_{s}, surface temperature of the particle; t, pyrolysis time, sec; U, blow rate of the reactor, m/sec; U_{p}, rate of motion of the particle in the reactor, m/sec; V, particle volume, m^3; X^i, portion of the coal formed from the ith component; α_{eff}, effective coefficient of heat exchange, W/(m^2·K); α_{int}, coefficient of internal heat exchange, W/(m^2·K); α_{ext}, coefficient of external heat exchange, W/(m^2·K); η, degree of conversion; Θ, dimensionless temperature; λ, heat conductivity, W/(m^2·K); μ, gas viscosity, Pa·sec; μ_{v}^i, relative mass of the initial ith component of the wood; μ_{a}^i, relative mass of the active ith component of the wood; μ_{c}^i, relative mass of coal obtained from the ith component of the wood; μ_{t}^i, relative mass of obtained volatile products of pyrolysis; μ_{g}^i, relative mass of obtained noncondensable volatile products of pyrolysis; ρ_{c}, density of obtained coal, kg/m^3; ρ_{p}, density of the wood particle in the reactor, kg/m^3; ρ_{w0}, density of the initial wood, kg/m^3; σ, Stefan–Boltzmann constant. Subscripts: p, particle; i, inert; w, wood; r, radiative; conv, convective; b, bed; s, surface; eff, effective; int, internal; ext, external; c, coal; a, active; g, gas; t, tar; v, initial; vol, volatiles; fin, final.

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