The Theoretical Research of Torrefaction Process in a Flow Reactor

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Abstract — The processes of heat and mass transfer, such as drying, pyrolysis and heating of biomass particles during torrefaction in a flow reactor are considered. It is shown that for small particle size ($\sim 1 \text{ cm}$) heat transfer between the heating flow and the particles does not depend on mass transfer and the characteristic time torrefaction determined by the pyrolysis of biomass particles. Analytical dependences of concentration of the waste component of pellets under the condition of small time of heating and evaporation in comparison to the time of pyrolysis are made.

Keywords—pellets; torrefaction; pyrolysis

I. INTRODUCTION

The processes of heat and mass transfer in porous medium are determining in many devices of chemical and energy industries. But despite the wide industrial application of porous materials, their uniform description is extremely difficult [1]. Most often some guesses based on experimental data for a specific process are used. Mass transfer and heat transfer are usually considered separately. Especially difficult to describe the processes in materials in which heat transfer is not only correlated with the mass transfer, but also changes the structure of the material. This also applies to torrefaction of organic substances which decompose when heated, and its different have different speeds of pyrolysis.

Torrefaction is the process of thermal processing of chopped or granulated biomass at temperatures up to 300 °C. Torrefaction is not only removing of moisture, i.e. drying of raw materials, but also thermal degradation of hemicellulose, which is part of the biomass. Typically, the process of torrefaction is described for a single sample biomass whether wood chips or pellets [2,3]. Description of this process most often based on a macroscopic energy considerations [4].

In this paper the mutual influence of heat and mass transfer (drying, pyrolysis, heating pellets) between pellets and hot gas stream during torrefaction of biomass in a flow reactor is considered. The existing experimental data for the coefficients of heat and mass transfer is involved.

II. INFLUENCE OF PYROLISYS ON HEATING OF PELLETS

The heat equation for a single pellet is:

$$\left[(1-\varepsilon)\rho_{s}c_{ps}+\varepsilon\rho_{\nu}c_{p\nu}\right]\frac{\partial T_{s}}{\partial t}=\Delta T_{s}-L\rho_{i}k_{i}e^{-\frac{E_{i}}{RT_{s}}}$$
(1)

Indexes *s* and *v* refer to the solid skeleton and the pore space respectively, ρ - density, c_p - specific heat at constant pressure, *T* - temperature, ε - porosity, Δ - Laplacian. The last member corresponds to the pyrolysis of the core and the yield to the gas phase the exhaust components (we denote their accessories by index *i*) with the specific heat of phase transformation *L* and the activation energy $E \gg RT_s$.

If we represent the last member in (1) in the form of the time derivative of the weight loss, it is easy to estimate:

$$(1-\varepsilon)\rho_s c_{ps} \gg L\rho_i k_i \frac{E_i}{RT_s^2} e^{-\frac{E_i}{RT_s}}$$
(2)

Specific numerical data were taken from [5].

Thus, to determine the temperature in the pellet it can be neglected the heat losses for outgoing components in comparison with the heat to heating of the pellet.

A similar estimate can be made regarding the impact of the gaseous products of pyrolysis of pellets on the density and velocity of the heating gas flow. Indeed, in a unit volume of pellet bed per unit time weight released

$$\sim 6(1-\varepsilon)/dke^{-\frac{L_l}{RT_s}}$$

where d is the diameter of the pellet. This value is several orders of magnitude less than the density of the gas stream which means that changing the velocity and density of the heating flow can be neglected.

If there is water in the pores it is necessary to consider its evaporation. We assume that water evaporation takes place at temperature of 100°C. Then the motion of the evaporation surface of radius r_0 deep into the particle radius *R* is given by:

$$\varepsilon \rho_l L \xi \, \frac{dr_0}{dt} = \frac{\lambda \Delta T}{r_0 (1 - r_0/R)} \tag{3}$$

where λ - thermal conductivity of the dry core, ρ_l - water density, *L* - its boiling heat, ξ - its mass concentration in the pores which in normal conditions is not more than 10%, ΔT - temperature difference between the surface of the pellet and the evaporation temperature.

In equation (3), it was taken into account that the rate of evaporation is small in comparison to the speed of vapor movement through the pores, as density of bound water is much higher than vapor density.

Solving (2), we find that at temperature of $150 \div 180$ °C for $3.3 \div 2.8$ min. the pellets will be completely dried up from the pore water. As shown below, the temperature difference correspons to the temperature of the gas flow

and is set in a time much shorter than the time of pyrolysis. Thus, drying pellets is much faster pyrolysis processes.

III. HEATING OF PELLETS

Let us consider the temperature field in the pellet having size of about a centimeter. Its Fourier number has the following order [5]:

$$Fo = \frac{at}{R^2} \cong 0.13t \quad , \tag{4}$$

where a - thermal diffusivity, R - radius of the pellet, ttime in seconds.

Solution of the problem of thermal conduction in the sphere for a given surface temperature T_R and different numbers of Fourier is shown in Figure 1 [6]. It is easy to see that after 3 - 4 seconds the temperature field in the particle will actually homogeneous. For processes that are tens minutes last to neglect four seconds is acceptable. Note that this applies to the vapor diffusion in the pores.

The estimates give reason to believe that the heat exchange between the heating flow and pellets is independent of the mass transfer and the temperature distribution in the pellets is uniform.



Figure 1. The temperature distribution in the sphere at different times. The numbers on the curves indicate the number of Fourier.

Heat exchange between the gas flow and the pellets that have the same effective diameter d and porosity ε_m is described by the following equations:

$$\frac{\partial \theta_f}{\partial \tau} + \frac{\partial \theta_f}{\partial z} = a(\theta_s - \theta_f)$$
(5)

$$\frac{\partial \theta_s}{\partial \tau} = \theta_f - \theta_s \tag{6}$$

where $\theta_f = (T_f - T_{s0})/(T_{f0} - T_{s0})$ and $\theta_s = (T_s - T_{s0})/(T_{f0} - T_{s0})$ are dimensionless temperatures of

flow and pellets respectively (the index 0 refers to the initial values),

$$a = \left((1 - \varepsilon_m) \left[(1 - \varepsilon) \rho_s c_{ps} + \varepsilon \rho_v c_{pv} \right] \right) / (\varepsilon_m \rho_f c_{pf}),$$

 $\tau = \alpha_T t / (1 - \varepsilon_m) \left[(1 - \varepsilon) \rho_s c_{ps} + \varepsilon \rho_v c_{pv} \right]$ is dimensionless time, $z = \tau x/u$ – dimensionless spatial coordinate; indexes f, s and v refer to the flow, hard core of pellets and its porous volume respectively, u – average velocity of the flow, α_T – heat transfer coefficient between the flow and the pellets [7]:

$$\alpha_T = 2.74\lambda (1 - \varepsilon_m)^{1.36} \varepsilon_m^{-1} R e^{0.64} P r^{1/3} / d^2 \quad (7)$$

where the Re – Reynolds number: $30 < Re < 8 \cdot 10^4$; Pr– Prandtl number.

The initial and boundary values for the system (5), (6): $\theta_{s0} = 0, \, \theta_{f0}(z=0,\tau) = 1, \, \theta_{f0}(z,\tau=0) = 1.$

At fixed flow temperature pellets will have a temperature:

$$\theta_s = \theta_f (1 - \exp(-\tau)) \tag{8}$$

When substituting the characteristic parameters in (7) (mean flow velocity u = 0.5 m / s) after 5 second the pellets temperature will be different from the flow temperature by $\sim 2\%$.

But at the entry to the pellet layer the flow temperature is fixed, so the initial temperature difference at the entrance will be quickly leveled and the flow will not lost temperature on heating already heated pellets, i.e. heat wave will run by layer. The velocity, with which it will be distributed, can be obtained as follows. For the temperature difference we have solution [8]:

$$\theta_f - \theta_s = \exp(-\xi - \eta) I_0(\sqrt{2\xi\eta})$$
 (9)

where I_0 is modified Bessel function, $\xi = za$, $\eta = \tau - z$.

Function $I_0(\sqrt{2\xi\eta})$ has maximum at $\xi = \eta$, i.e. at $za = \tau - z$. But a is a big value, so $\approx \tau$. Considering what is z and τ , we obtain the maximum propagation velocity of the temperature difference: U =

$$= u/a$$
 (10)

For the conditions under consideration, it is ~ 0.33 cm/s, i.e. by meter-thick layer of heating wave will run for about 5 minutes. We emphasize that this is exactly a wave, as if there was a zero right-hand side of (5), the left-hand side is exactly the wave equation. But, as we have shown previously, in our case the initial temperature difference quickly vanishes.

Thus, it can be argued that under these conditions the pellet heating is much faster than its pyrolysis, and thus, pyrolysis can be viewed at a specific temperature.

IV. CONCENTRATION OF EXHAUST COMPONENTS IN THE PELLETS.

Experimental data on the change in the total mass of pellets summarizes the various dependencies:

$$\frac{1}{m_0} \frac{\partial m_i}{\partial t} = -\left(\frac{m_i}{m_0}\right)^n k_i(T_s) \tag{11}$$

where $k_i(T_s) = A_i exp(-E_i/RT_s)$ is the pyrolysis constant, A_i is the preexponential factor, E_i is the activation energy, m_0 and m_i are initial and current mass of the pellet, n is the reaction order, which is usually equal to 1, but for example in [9] it is equal to 1.8. If the current mass of the exhaust components in the solid skeleton is m_i , then its concentration $(x_i = m_i/m)$ satisfies the following equation:

$$\frac{\partial x_i}{\partial t} = -\left(\frac{m_i}{m_0}\right)^{n-1} k_i(T_s) x_i(1-x_i) \tag{12}$$

The solution of (11), (12) at a fixed temperature is trivial. Figure 2 shows the mass concentration of the volatiles of the flow at different temperatures (initial concentration $0.3, E_i = 220$ kJ/mol, $A_i = 2 \cdot 10^{17}$ 1/c, n = 1.8 [9]).

The figure illustrates the strong dependence of the evolution of pellets composition on the temperature of the flow.



Figure 2. The time dependence of the mass concentration of the exhaust components at different gas temperatures.

V. CONCLUSION

It is shown that pellets are heated to the temperature of the gas flow is much faster than its pyrolysis proceeds. This applies to the initial pellets pore water evaporation. It can be assumed that the pyrolysis process most of the time takes place at a constant temperature equal to the temperature of the gas flow. The characteristic time of torrefaction is determined by the pyrolysis of biomass. We emphasize that this result relates to the small size of pellets (~ 1 cm).

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