

Modeling for pyrolysis of solid biomass

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Biomass, especially wood, is one of the first sources of energy used by humans. In developing countries, it is still the major source of energy, while in developed countries a renewed interest in biomass started in the nineteen-seventies.

The thermo-chemical conversion (pyrolysis, gasification, combustion) represents the most common commercial utilization of biomass. It is a renewable source of energy and has many advantages from an ecological point of view.

Pyrolysis is the first stage of both combustion and gasification. So, pyrolysis is not only an independent conversion technology, but also part of the gasification and combustion processes. Pyrolysis consists of a thermal degradation of the initial solid fuel (in the absence of oxygen/air) into: solid (charcoal), liquids (tar and other organics) and gaseous products. Depending on the type of pyrolysis, different species can be obtained.

Pyrolytic degradation is recognized as an effective method for the production of high yields of char or liquid/gaseous fuels.

For the purposes of the current study, biomass pyrolysis models may be divided into two primary categories, micro- and macro-particle models. Micro-particle pyrolysis involves the thermal decomposition of virgin matter with sample sizes sufficiently small such that diffusion effects become negligible and the intensity of pyrolysis is controlled with kinetics. Critical particle size estimates for kinetic control are generally $\sim 0.1\sim 1$ mm and are observed to decrease with increasing pyrolysis temperatures [1]. Particles larger than the critical limit are characterized by relatively large diffusion effects which can strongly affect the pyrolysis evolution due to internal and external temperature gradients, thermal inertia due to heat capacity effects and also temperature variations resulting from endothermic (or exothermic) reactions. In this article, a micro-particle mathematical model of pyrolysis is developed i.e. a kinetic mathematical model.

Understanding the physical phenomena of pyrolysis and representing them with a mathematical model is essential in design of pyrolysis reactors. The products yield varies depending upon the final pyrolysis temperature, type of reactor, operating conditions etc.

When a solid particle of biomass is heated in an inert atmosphere the following phenomena occur. Heat is first transferred to the particle surface by radiation and/or convection and then to the inside of the particle. The temperature inside the particle increases, causing removal of moisture that is present in the biomass particle, the pre-pyrolysis and main pyrolysis reaction takes place as discussed.

During the pyrolysis process, the pores of the solid are enlarged and the solid particle merely becomes more porous, the biomass converts into gases, volatiles and char.

Inside the pyrolysis particle, heat is transmitted by the following mechanisms:

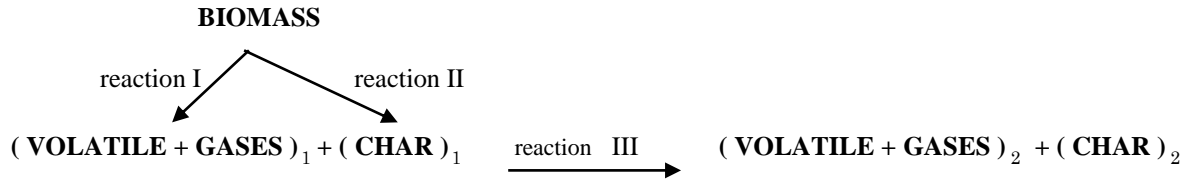
- conduction inside the solid particle,
- convection inside the particle pores and
- convection and radiation from the surface of the particle/pellet.

For simplicity, it is assumed that heat is transmitted inside the solid by conduction only. The heat transfer coefficient represents the overall effect of the above mechanisms.

The aims of this research were to investigate the pyrolysis behavior of wood, to check the influence of experimental conditions on the kinetic parameters and to provide kinetic information for evaluation of the processing of these materials.

Modeling

The pyrolysis reaction can be described by means of the following scheme [2]:



When biomass is heated, it decomposes to volatiles, gases and char. The volatiles and gases may further react with char to produce different types of volatiles, gases and char where the compositions are different.

The kinetic equations for the mechanisms shown above:

$$\frac{dC_B}{dt} = -k_1 (C_B)^{n_1} - k_2 (C_B)^{n_1} \quad (1)$$

$$\frac{dC_{G1}}{dt} = k_1 (C_B)^{n_1} - k_3 (C_{G1})^{n_2} (C_{C1})^{n_3} \quad (2)$$

$$\frac{dC_{C1}}{dt} = k_2 (C_B)^{n_1} - k_3 (C_{G1})^{n_2} (C_{C1})^{n_3} \quad (3)$$

$$\frac{dC_{G2}}{dt} = k_3 (C_{G1})^{n_2} (C_{C1})^{n_3} \quad (4)$$

$$\frac{dC_{C2}}{dt} = k_3 (C_{G1})^{n_2} (C_{C1})^{n_3} \quad (5)$$

where,

$$k_1 = A_1 \exp\left[\left(D_1/T\right) + \left(L_1/T^2\right)\right]$$

$$k_2 = A_2 \exp\left[\left(D_2/T\right) + \left(L_2/T^2\right)\right]$$

$$k_3 = A_3 \exp\left[-E_3/(R_c T)\right].$$

Adding eqs. (1), (3) and (5) gives,

$$\frac{dC_B}{dt} + \frac{dC_{C1}}{dt} + \frac{dC_{C2}}{dt} = -k_1 C_B^{n_1} = \frac{d\rho}{dt} \quad (6)$$

Heat transfer model

Consider a slab of thickness 2L. Assume the length of the two other dimensions of the slab to be so large that heat transfer takes place in the one direction only.

$$k \left[\frac{d^2 T}{dx^2} \right] + (-\Delta H) \times \frac{d(-\rho)}{dt} = \frac{d(c_p \rho T)}{dt} \quad (7)$$

As ρ and T are function of t , eq. can be simplified as:

$$k \left[\frac{d^2 T}{dx^2} \right] + (-\Delta H + c_p T) \times \frac{d(-\rho)}{dt} = \rho c_p \frac{d(T)}{dt} \quad (8)$$

Where:

$$c_p = 1112 + 4.85(T - 273) \quad (8a)$$

$$k = 0.13 + 0.0003(T - 273) \quad (8b)$$

The initial and boundary conditions for eq.(8) are:

Initial conditions:

$$t = 0 \quad T(x, 0) = T_0 \quad (9)$$

Boundary conditions:

$$t > 0 \quad x = 0, \quad \left(\frac{dT}{dx} \right)_{x=0} = 0 \quad (10)$$

$$t > 0 \quad x = L, \quad -k \left(\frac{dT}{dx} \right)_{x=L} = h(T_f - T) + \sigma \varepsilon (T_f^4 - T^4) \quad (11)$$

In eq. (11), the external heat transfer is considered to occur by a combination of the convective and radiative mechanisms.

Model results

The set of equations is solved numerically subjected to the initial and boundary conditions and the results are presented. The main results of the mathematical investigation are the mass loss curve for the wood sample as a function of reaction time and heating rate.

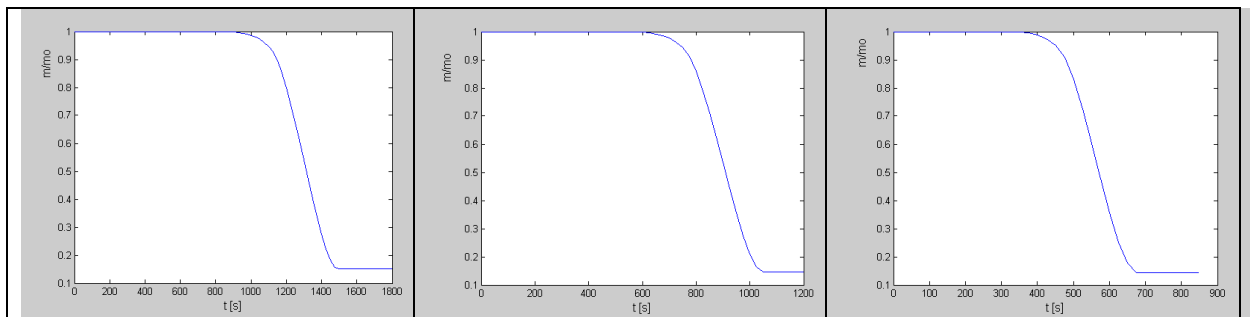


Figure 1. Mass loss of wood sample as a function of reaction time and heating rate
I case: 21⁰C/min, II case: 32⁰C/min, II case: 55⁰C/min

Experimental analysis

To compare mathematical and experimental results, woody biomass was used as experimental sample. The sample was a mixture of six different kinds of woody biomass.

The scheme of laboratory facility used for woody biomass pyrolysis and the list of measurement points are demonstrated in figure 2. The laboratory facility is designed and constructed in the Institute for Energetics, Process Technique and Protection of Environment at the Faculty of Technical Sciences in Novi Sad [4].

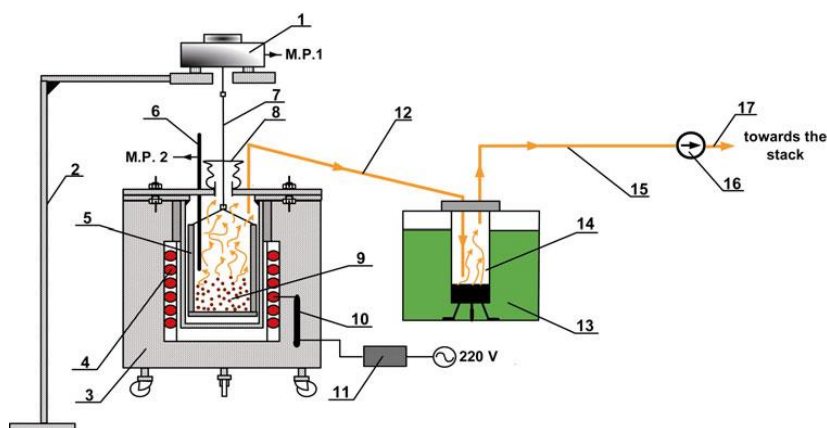


Figure. 2 The scheme of experimental facility (and metering points) for woody biomass pyrolysis [4]

(1) digital scale, (2) scale stand, (3) furnace, (4) electrical heaters, (5) container for woody biomass sample, (6) thermocouple (device for measuring temperature in the biomass container), (7) flexible connection between the scale and biomass container, (8) flexible teflon wrap, (9) woody biomass sample, (10) temperature control sensor, (11) temperature controller, (12) flow of gaseous pyrolysis products, (13) cooler, (14) bottle for liquid phase separation, (15) dry gaseous pyrolysis products, (16) pump, (17) gas emission into the atmosphere

During the experimental investigation of pyrolysis process, initial sample mass was 10g. The mixture samples were placed into the biomass sample container and then into the reactor. The heating process was performed by using electrical heaters and after achieving the temperature of 650°C, that temperature was maintained within a narrow range around 650°C until the sample mass in the reactor was stabilized. Gaseous pyrolysis products were emitted to the atmosphere through the cooler. After the experiment, liquid phase and char mass were measured.

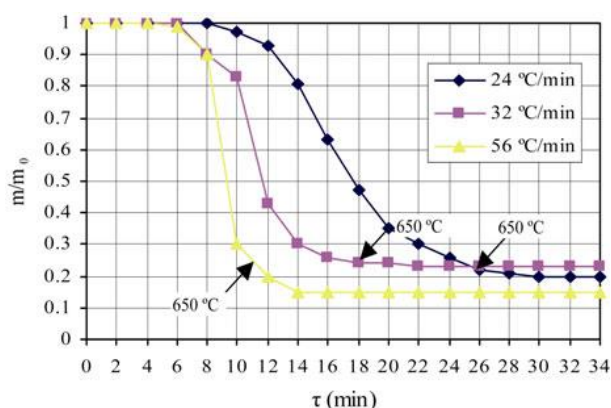


Fig. 3 Mass loss curve for the sample of woody biomass mixture as a function of reaction time and heating rate [4]

The process of biomass mixture pyrolysis was carried out with controlling the temperature and mass of the sample. The sample were subjected to the temperature range of 25-650°C, and the average heating rates were 24, 32 and 56°C/min. All the experiments were conducted at atmospheric pressure.

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