



Kinetic Modeling of the Pyrolysis of Biomass

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ABSTRACT

Pyrolysis is essentially the thermal decomposition of organic matter under inert atmospheric conditions or in a limited supply of air, leading to the release of volatiles and formation of char. Pyrolysis in wood is typically initiated at 200°C and lasts till 450-500°C depending on the species of wood. Modeling of pyrolysis implies the representation of the chemical and physical phenomena in a mathematical form. The basic equations are those of chemical kinetics, heat transfer and mass transfer. The actual reaction scheme of pyrolysis of wood is extremely complex because of the formation of over a hundred intermediate products. Models reported in the literature are based on the single particle model and the kinetic parameters proposed by various models cannot be used directly for the modeling of the of pyrolysis zone of the biomass gasifier. The effect of the size and shape of the particle and the effect of neighboring particles has to be accounted while modeling the pyrolysis zone of the biomass gasifier. A two-step mechanism for the pyrolysis of single particle wood and the corresponding kinetic parameters has been reported in literature.

In this study, a generalized kinetic model is presented which can be applied to any size and shape of the particle. The proposed model is simulated and the best values of the kinetic constants are found by minimizing the least square of the error between the experimental data reported and the results of simulated model. This procedure is applied for different values of pyrolysis temperature (573, 623, 673, 773 and 873 K). By using the proposed model of this study, it is possible to predict the pyrolysis rate over a wide range of particle dimensions using only one set of kinetic parameters.

Keywords: Pyrolysis; Kinetic Modeling; Simulation; Biomass Gasification.

1. INTRODUCTION

Wood, woody, and other forms of biomass are some of the main renewable solid energy resources available and provide the only source of liquid, gaseous, and solid fuels. Biomass potential includes wood, animal and plant wastes. Biomass is the only organic petroleum substitute that is renewable. The term “biomass” refers to forestry, purpose-grown agricultural crops, trees and plants, and organic, agricultural, agro-industrial, and domestic wastes (municipal and solid waste). Biomass is the name given to the plant matter that is created by photosynthesis, in which the sun’s energy converts water and CO₂ into organic matter. Thus biomass materials are directly or indirectly a result of plant growth. These include rewood plantations, agricultural residues, forestry residues, animal wastes, etc. (Demirbas and Arin, 2002).

The thermochemical conversion of biomass (pyrolysis, gasification, combustion) is one of the most promising non-nuclear forms of future energy. It is renewable form with many ecological advantages (Koufopoulos *et al.*, 1989). Decomposition of a compound in the absence of oxygen by the action of heat alone is known as pyrolysis. It is a promising route for the production of charcoal, tar and other organics and gaseous products (H₂, CO₂, CO).

These products are of interest as they are possible alternate sources of energy. Pyrolysis is a process by which a biomass feedstock is thermally degraded in the absence of oxygen/air. The study of pyrolysis is gaining increasing importance, as it is not only an independent process, but also a first step in the gasification or the combustion process (Babu and Chaurasia, 2003). In order to design the necessary equipments for pyrolysis, it is important to provide models describing the kinetics and the governing mechanisms (Koufopoulos *et. al.*, 1991).

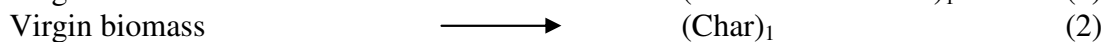
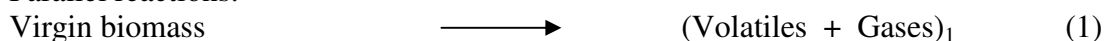
Experimental and modeling studies have been conducted on pyrolysis by many researchers (Babu and Chaurasia, 2003a; Babu and Chaurasia, 2003b; Babu and Chaurasia, 2004a; Babu and Chaurasia, 2004b; Babu and Chaurasia, 2004c). In spite of the numerous experimental studies existing on biomass pyrolysis and on kinetic modeling, there is no generally accepted model that can predict the pyrolysis rate and provide a priori information about final conversion over a wide range of particle size for a particular species of biomass.

In the present work a kinetic model proposed by Koufopoulos *et. al.* (1991) is modified to include the effect of the size and shape of the particle. Rate of pyrolysis reaction is defined based on unit surface area of solid biomass in the kinetic model. The proposed kinetic model is simulated and the best values of the kinetic constants are found by minimizing the least square of the error between the experimental data reported by Koufopoulos *et. al.* (1991) and the results of the simulated model. Kinetic constants found in the present study can be applied to any size and shapes of the particle size as the form of rate equations include the surface area of the biomass. Babu and Sheth (2006) developed a steady state model of the reduction zone of the biomass gasifier. The kinetic parameters proposed by present model can be used directly for the modeling of the of pyrolysis zone of the biomass gasifier.

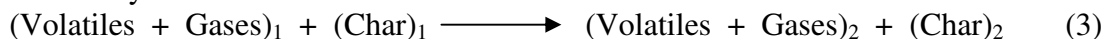
2. KINETIC MODELING & SIMULATION

Different classes of mechanisms were proposed for the pyrolysis of wood and other cellulosic materials. The models are classified into three categories: one-step global models; one-stage multi-reaction models; and two-stage semi-global models. The first category of models considers pyrolysis as a single-step first order reaction.

Parallel reactions:



Secondary Interactions:



The second category of models discuss those mechanisms, which consider simultaneous and competing first order reactions in which virgin wood decomposes into different constitutes of pyrolysis products, namely, tar, char, and gases (Reactions (1) & (2)). The third class of models considers pyrolysis to be a two-stage reaction, in which the products of the first reaction (volatiles and gases) further reacts with the char produced by second reaction to produce volatile and gases of different composition. Thus the primary pyrolysis products participate in secondary interactions (reaction 3) causing a modified final product distribution



(Koufopoulos *et. al.*, 1991). Based on unit surface area of solid in gas solid system, the kinetic equations for the mechanism shown above are as follows

$$r_1 = k_1 B^{n_1} \left(\frac{SA}{V} \right) \tag{4}$$

$$r_2 = k_2 B^{n_2} \left(\frac{SA}{V} \right) \tag{5}$$

$$r_3 = k_3 G_1^{n_3} C_1^{n_3} \left(\frac{SA}{V} \right) \tag{6}$$

Where,

- r_i Rate of Reaction i ; V Volume of the Particle
- k_1 Kinetic constant of reaction 1 ; B Concentration of Biomass
- k_2 Kinetic constant of reaction 2 ; C_1 Concentration of Charcoal I
- k_3 Kinetic constant of reaction 3 ; G_1 Concentration of Volatile Component I
- SA Surface Area of the Particle

Table 1 shows the net rate of production of the different species by chemical reactions in terms of the rate of reactions.

Table-1. Net rate of production of the different species by chemical reactions in terms of the rates of reactions 1 to 3

Species	R_x (kg/sec)
Biomass B	$-r_1 - r_2$
(Volatiles + Gases) ₁ G_1	$r_1 - r_3$
(Char) ₁ C_1	$r_2 - r_3$
(Volatiles + Gases) ₂ G_2	r_3
(Char) ₂ C_2	r_3

To find the kinetic constants for three reactions experimental data for the isothermal mass change of beech wood saw dust reported by koufopoulos *et. al.* (1991) is used.

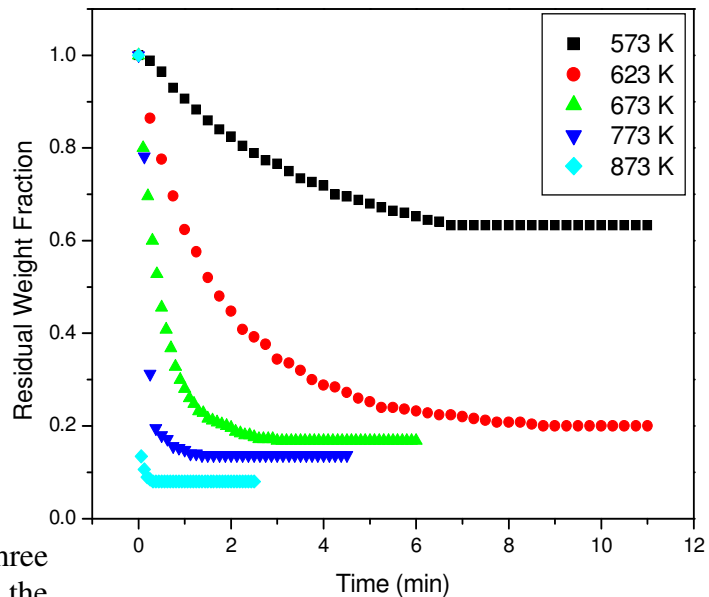


Fig. 1 Isothermal mass change of beech wood saw dust (0.30-0.85 mm)

Fig. 1 shows the mass change for the isothermal pyrolysis of the dry wood saw dust. The saw dust sample of size 0.3 to 0.85 mm is used and experimental run is performed for the temperature of 573, 623, 673, 773 and 873 K. Fig. 1 shows that for the lower temperature of the 573 K takes more time to pyrolyse than for 873 K for the same size of biomass sample. It clearly shows that low temperature pyrolysis produces more charcoal and high temperature pyrolysis produces more amounts of volatiles and gases and less amount of charcoal.

Where, residual weight fraction is defined as below.

$$\text{Residual Weight Fraction } (W) = \frac{(\text{Residual} - \text{Ash Weight})}{(\text{Initial weight} - \text{Ash Weight})} \quad (7)$$

Residual weight fraction can be found out theoretically as follows:

$$W = B_1 + C_1 \quad (8)$$

$$\frac{dB}{dt} = -(k_1 + k_2)B(\text{Surface Area}) \quad (9)$$

$$\frac{dC}{dt} = k_1 B(\text{Surface Area}) \quad (10)$$

Biomass weight fraction (B) and charcoal weight fraction (C) after every time interval is found out by applying explicit finite difference technique. Using the experimental data of W (Fig. 1), the analytical expression of the residual weight fraction at every time interval in terms of k_1 and k_2 is formulated. The values of the k_1 and k_2 are found out by using the nonlinear regression technique of the minimization of the following equation.

$$F(k_1, k_2) = \sum_{j=1}^n (W_{\theta, j} - W_{\pi, j}) \quad (14)$$

To solve the above mentioned minimization problem “*fminsearch*” function of the MATLAB software is used. The values of kinetic constants were found for the temperature of 573, 623, 673, 773 and 873 K.

3. RESULTS AND DISCUSSION

Fig. 2 and 3 shows the variation of kinetic constants k_1 and k_2 with isothermal temperature of the pyrolysis respectively.

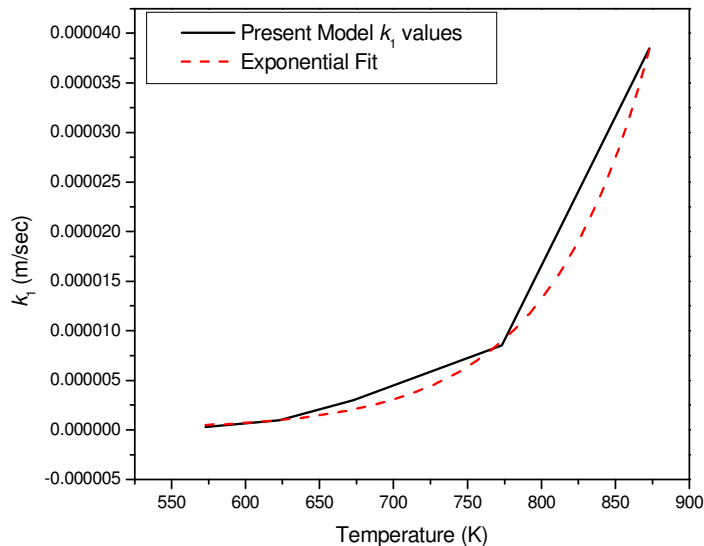


Fig. 2. Variation of kinetic constant k_1 with Temperature

$$k_1 = 1.1183E - 10 \exp\left(\frac{T}{68.48684}\right) \text{ m sec}^{-1} \quad (15)$$

The kinetic constant values are increasing exponentially with the temperature in both cases. Eq. (15) and Eq. (16) shows the exponential fit function to the simulated model values in the temperature range of 550 K to 900 K. The predicted values of the kinetic constants by Eq. (15) and Eq. (16) can be applied to any size and shape of beech wood biomass.



$$k_2 = 8.10156E - 10 \exp\left(\frac{T}{104.5661}\right) \text{ m sec}^{-1} \quad (16)$$

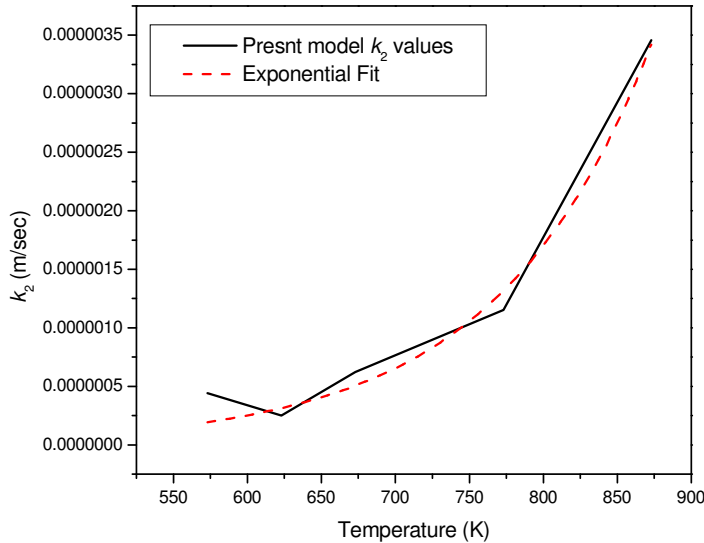


Fig. 3. Variation of kinetic constant k_1 with Temperature

Koufopoulos *et al.* (1991) proposed the relation of kinetic parameters with temperature based on the modified arhenius equation, which is represented by Eq. (17). and Eq. (18).

To compare the present model with koufopoulos model (1991), both the equations are simulated to produce the isothermal change of residual weight fraction with time for the temperature of 573, 623, 673, 773 and 873 K.

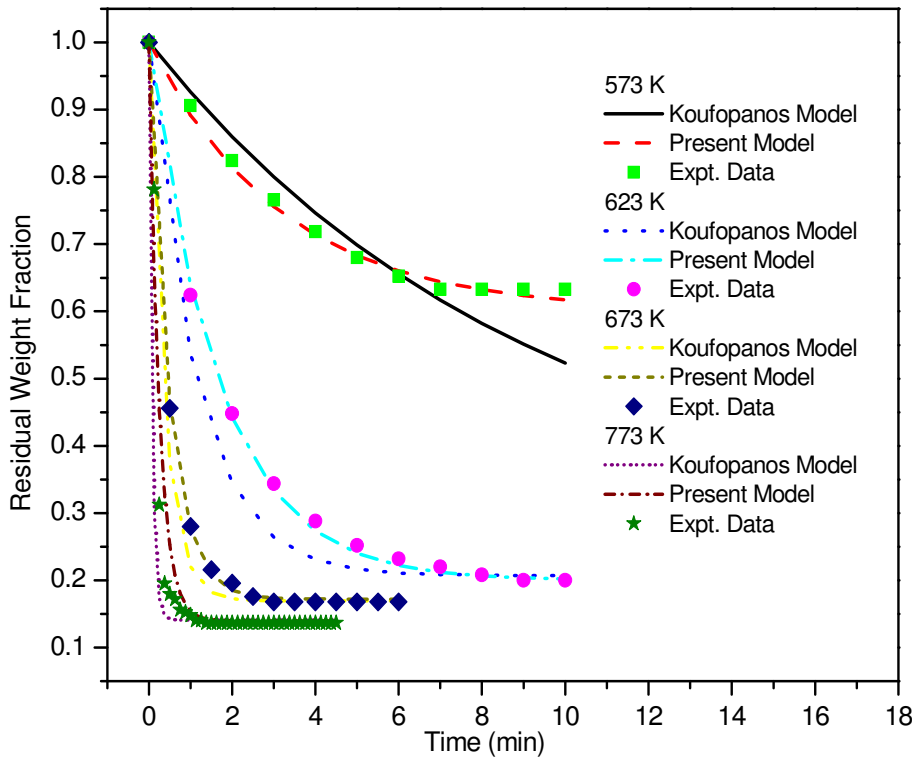


Fig. 4. Comparison of Residual Weight Fraction Simulated using Koufopoulos Model (1991) and Present Model with Experimental Data

Fig. 4 shows the residual weight fraction comparison found using koufopoulos model (1991) and the present proposed Model with experimental data of the isothermal pyrolysis of the beech wood saw dust.

It clearly shows that the for all the isothermal temperature change experimental data present model fits better than the model proposed by koufopoulos *et al.* (1991).

$$k_1 = 9.973 e - 05 \exp\left[\left(\frac{17254.4}{T}\right) + \left(\frac{-9061227}{T^2}\right)\right] \quad (17)$$

$$k_2 = 1.068 \text{ e } - 03 \exp \left[\left(\frac{10224.4}{T} \right) + \left(\frac{-6123081}{T^2} \right) \right] \quad (18)$$

4. CONCLUSIONS

The present model predicts the rate of pyrolysis of beech wood biomass of any size and shape. Using the experimental data of isothermal pyrolysis reported by Koufopoulos et al. (1991), kinetic parameters are found for different temperature values varying from 523 K to 873 K. The proposed kinetic model is simulated and the best values of the kinetic constants are found by minimizing the least square of the error between the experimental data reported by Koufopoulos et al. (1991) and the results of the simulated model. Based on the results obtained and discussions in the earlier sections, the following conclusions are drawn.

- Present proposed model considers the reaction scheme based on unit surface area of solid in gas-solid system of pyrolysis.
- Eq. (15) and Eq. (16) predicts kinetic parameters of the pyrolysis of beech wood biomass of any size and shape for the temperature range of 550 K to 900 K.
- Present model fits better to the experimental data than the kinetic model reported by the koufopoulos et al. (1991).

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