MODELING & SIMULATION OF PYROLYSIS OF BIOMASS: EFFECT OF THERMAL CONDUCTIVITY, REACTOR TEMPERATURE AND PARTICLE SIZE ON PRODUCT CONCENTRATIONS

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Abstract
The simultaneous chemical kinetics and heat transfer model is used to predict the effects of the most important physical and thermal properties (thermal conductivity, reactor temperature and particle size) of the feedstock on the convective-radiant pyrolysis of biomass fuels. The effects of these parameters have been analyzed for different geometries such as slab, cylinder and sphere. Finite difference method is employed for solving heat transfer model equation while Runge-Kutta 4th order method is used for solving chemical kinetics model equations. Simulations are carried out for equivalent radius ranging from 0.0000125 m to 0.02 m, and temperature ranging from 303 K to 2100 K.

Keywords: Biomass; Pyrolysis; Physical property; Thermal property; Modeling; Kinetics; Heat transfer; Simulation

1. INTRODUCTION

Biomass has either been processed to increase its energy content or burned directly in furnaces. The processes such as pyrolysis, gasification, anaerobic digestion and alcohol production, have been widely applied to biomass in order to increase its energy content. Energy produced from biomass or its conversion products represents an important part among today's energy sources. As biomass is renewable, abundant and has domestic usage, the sources of biomass can help the world reduce its dependence on petroleum products and natural gas. Biomass can be converted into liquid, solid and gaseous fuels with the help of some physical, chemical and biological conversion processes [Demirbaş., 2000, 2001]. The conversion of biomass materials has a precise objective to transform a carbonaceous solid material, which is originally difficult to handle, bulky and of low energy concentration, into fuels having physico-chemical characteristics that permit economic storage and transferability through pumping systems.

The use of biomass products provides substantial benefits as far as the environment is concerned. Biomass absorbs carbon dioxide during growth and emits it during combustion. Therefore, biomass helps the atmospheric carbon dioxide recycling and does not contribute a net greenhouse effect.

2. BACKGROUND

Several researchers have developed models for pyrolysis of biomass [Bamford *et al.*, 1946; Fan *et al.*, 1977; Miyanami *et al.*, 1977; Liliedahl & Sjöström., 1998; Jalan & Srivastava., 1999]. Many of these models do not include secondary reactions, change of density as a function of time, thermal and specific heat capacity of biomass as a function of temperature and value of convective heat transfer coefficient as a function of Reynolds number and Prandtl number. The above anomaly has been rectified in the model developed by Babu & Chaurasia [2003a], which is used in the present study. The effect of particle size, orders of reaction, heat of reaction, density, shrinkage, thermal and thermodynamic properties have already been discussed by the present authors in their earlier studies [Babu & Chaurasia., 2002a, 2002b, 2003c, 2003d, 2003e, 2003f, 2003g; Chaurasia & Babu., 2003]. In the present study, the effect of thermal conductivity, reactor temperature and particle size on product concentrations of biomass is examined for different geometries (slab, cylinder and sphere). And, the sensitivity analysis [2003c, 2003d] is carried to find out the dominant design variable.

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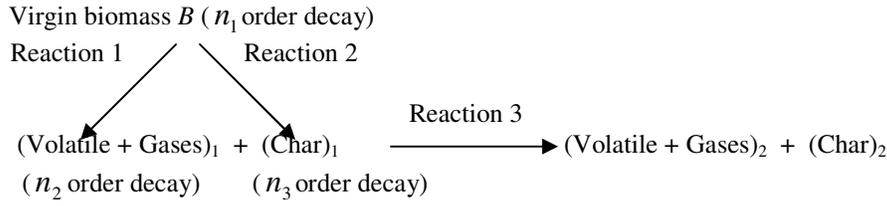Email: bvbabu@bits-pilani.ac.in;   Home Page: http://bvbabu.50megs.com;
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3. MATHEMATICAL MODEL

The pyrolysis reactions can be described by means of following scheme as used by Babu and Chaurasia [2003b].

Virgin biomass B (n_1 order decay)

Reaction 1 / \ Reaction 2

Reaction 3

(Volatile + Gases)$_1$ + (Char)$_1$ $\longrightarrow$ (Volatile + Gases)$_2$ + (Char)$_2$

(n_2 order decay)   (n_3 order decay)

This kinetic scheme indicates that the biomass 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. Therefore, the primary pyrolysis products participate in secondary interactions (Reaction 3), resulting in modified final product distribution. The kinetic equations for the mechanism shown above along with heat transfer model equation and initial and boundary conditions are as follows:

$$\frac{\partial(C_B)}{\partial t} = -(k_1 + k_2)C_B^{n_1} \tag{1}$$

$$\frac{\partial(C_{G1})}{\partial t} = k_1 C_B^{n_1} - k_3 C_{G1}^{n_2} C_{C1}^{n_3} \tag{2}$$

$$\frac{\partial(C_{C1})}{\partial t} = k_2 C_B^{n_1} - k_3 C_{G1}^{n_2} C_{C1}^{n_3} \tag{3}$$

$$\frac{\partial(C_{G2})}{\partial t} = k_3 C_{G1}^{n_2} C_{C1}^{n_3} \tag{4}$$

$$\frac{\partial(C_{C2})}{\partial t} = k_3 C_{G1}^{n_2} C_{C1}^{n_3} \tag{5}$$

$$\frac{\partial}{\partial t}(C_p \rho T) = k\left(\frac{b-1}{r}\frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial r^2}\right) + (-\Delta H)\left(-\frac{\partial \rho}{\partial t}\right) \tag{6}$$

Initial conditions:

$$t = 0; \quad C_B = C_{B0}, \ C_{G1} = C_{C1} = C_{G2} = C_{C2} = 0, T(r,0) = T_0 \tag{7}$$

Particle boundary conditions:

$$t > 0; \quad r = 0, \quad \left(\frac{\partial T}{\partial r}\right)_{r=0} = 0 \tag{8}$$

$$t > 0; \quad r = R, \quad k\left(\frac{\partial T}{\partial r}\right)_{r=R} = h(T_f - T) + \sigma\varepsilon(T_f^4 - T^4) \tag{9}$$

4. NUMERICAL SOLUTION AND SIMULATION

The equations (1)-(6) are solved simultaneously. Equations (1)-(5) are solved by Runge-Kutta fourth order method with fixed step size. The equation (6) along with initial and boundary conditions given by equations (7)-(9) are solved numerically by finite difference method using pure implicit scheme as discussed by Ghoshdastidar [1998] utilizing Tri-Diagonal Matrix Algorithm [Carnahan *et al.*, 1969]. Simulations are carried out for equivalent radius ranging from 0.0000125 m to 0.02 m, and temperature ranging from 303 K to 2100 K. The values of various parameters employed and the notations used in the present study are the same as given by Babu and Chaurasia [2003a]. The model is valid for wide range of temperatures and particle radius. The details of model validation results are given in the literature [2003a]. Extensive simulations are carried for different geometries (slab, cylinder and sphere) for the ranges of particle radius and temperatures as mentioned above. The trends for all the three geometries are found to be similar. Some of the typical results for cylindrical geometry are presented below.

5. RESULTS AND DISCUSSION

5.1. Effect of Thermal Conductivity of Biomass (k)

Biomass thermal conductivities are reported [Kanury & Blackshear., 1970] to vary in the range of 0.03 – 0.4 W/mK. This range is considered to reveal the functional dependence of the variables of interest better on this parameter and so considered in the present study. The effects of this parameter on average product concentrations and conversion time with cylindrical pellet are shown in Fig. 1 for R=0.009 m. It is found that, the average product concentration of (char)$_1$
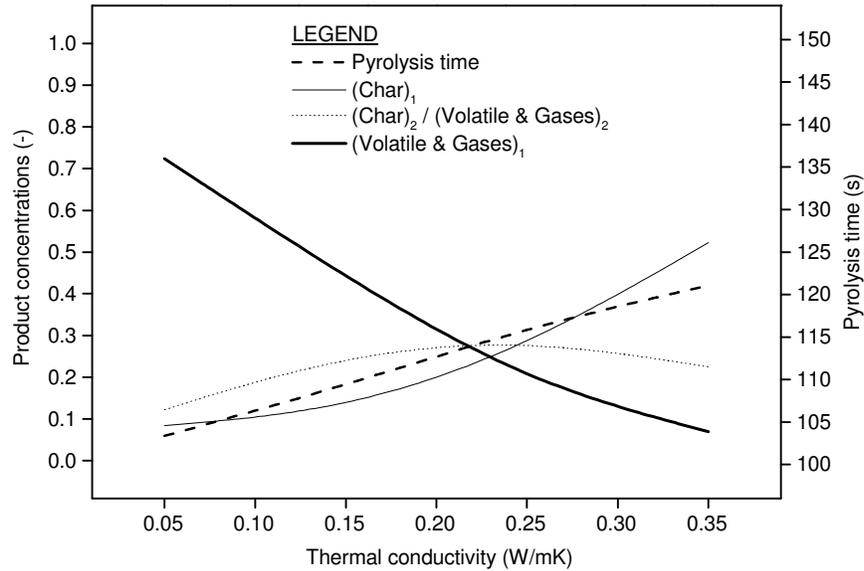

Fig. 1: Average product concentrations and pyrolysis time as functions of thermal conductivity with cylindrical pellet (R=0.009 m, T_0=303 K, T_f=1100 K)

increases while the concentration of (volatile & gases)$_1$ decreases as thermal conductivity increases. The concentration of (volatile & gases)$_2$ increases up to k=0.25 W/mK and then decreases as k is further increased. This is due to the fact that for the value of k=0.25 W/mK, the concentrations of primary products are equal and thereafter the concentration of (char)$_1$ increases at the expense of decrease in (volatile & gases)$_1$ showing the trade-off between these two concentrations. A significant increase in pyrolysis time is observed as k increases. A comparison of the product concentrations of primary pyrolysis and secondary pyrolysis indicates that the activity of the primary reactions is significant as compared to the activity of secondary reactions.

Fig. 2 shows the temperature profile as a function of radial distance for different values of k, which can be used to explain the simulated variations in the product distribution shown in Fig. 1. In Fig. 1, we have seen that concentration of (char)$_1$ increases while the concentration of (volatile & gases)$_1$ decreases as k is increased. This is a consequence of decrease in temperature at any radial position with respect to increase in k value. Therefore the charring reactions (favoring the char formation) are successively more favored. The pyrolysis time increases linearly with k, given successively slower particle heating rate. The results shown in Fig. 1 are in accordance with those reported by Shafizadeh [1979]. He also reported increase in char concentration and decrease in the concentration of volatile & gases as temperature is decreased (i.e. heating rate is slow).

5.2. Effect of temperature (T_f)

The effect of final temperature on product concentrations and pyrolysis time is shown in Fig. 3 with cylindrical pellet for R=0.009 m. It is observed that at low temperature (below 800 K) the yield of (char)$_1$ is favored while high temperature (above 1300 K) is characterized by high gas production i.e. (volatile & gases)$_1$ at the expense of decrease in (char)$_1$. At 1250 K, the concentration of (char)$_1$ and (volatile & gases)$_1$ are equal at which the concentration of (char)$_2$ / (volatile & gases)$_2$ is maximum. Above this temperature, the concentration of (char)$_1$ decreases while the concentration of (volatile & gases)$_1$ increases i.e. there is a trade-off between these concentrations. The results shown are in agreement with Buekens & Schoeters [1980]. They also found that pyrolysis at lower temperatures favors the production of char; whereas at higher temperatures results in the fission, dehydration, disproportionation, decarboxylation, and decarbonylation reactions, which favors gas production.
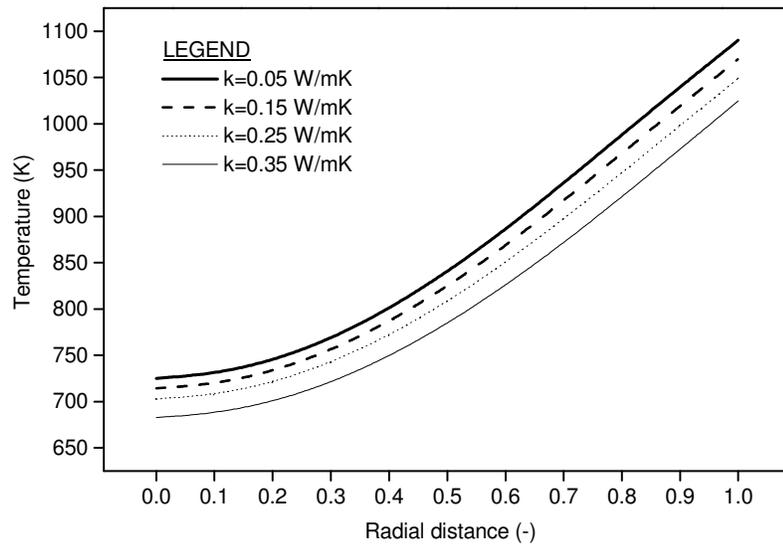
Fig. 2: Temperature profile as a function of radial distance for different values of thermal conductivity with cylindrical pellet (R=0.009 m, T_0=303 K, T_f=1100 K)
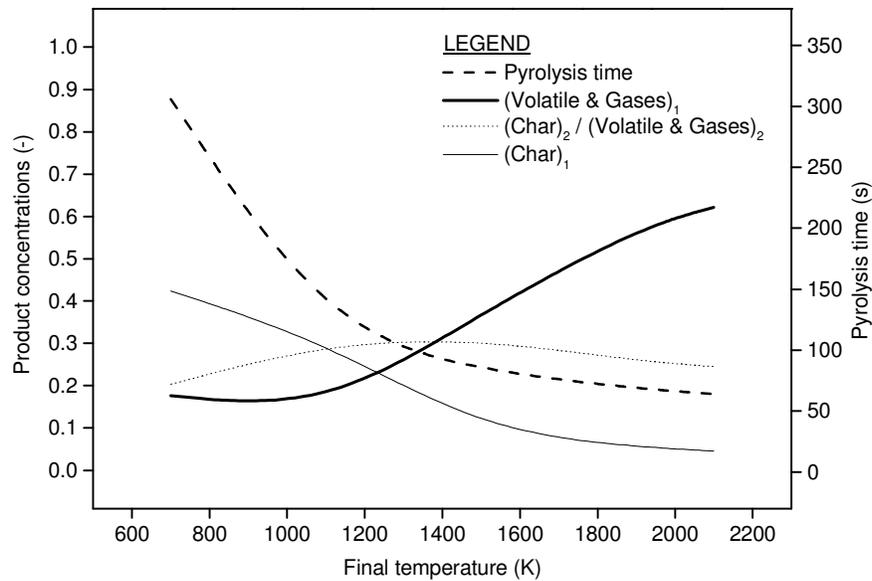

Fig. 3: Average product concentrations and pyrolysis time as functions of final temperature with cylindrical pellet (R=0.009 m, T_0=303 K)

5.3. Effect of Particle Size

The effect of particle radius on pyrolysis products is shown in Fig. 4. Extensive simulations are carried out for particle radius ranging from 0.0001 to 0.02 m for final temperature of 900 K. The formation of $(char)_1$ and $(volatiles \& gases)_2$ or $(char)_2$ are favored at the expense of decrease in $(volatiles \& gases)_1$ formation as the particle radius is increased. This is due to the high residence time of volatiles & gases within the particle, thicker char layer and slow rates of

formation of pyrolysis products. The yield of (volatiles & gases)$_1$ decreases up to a particle radius of 0.015 m and then again increases at the expense of decrease in (char)$_1$ formation. This is a consequence of successively higher temperatures at the surface due to increase in the pyrolysis time as particle size is increased. On the whole, the increase in particle radius favors the attainment of larger yields of (char)$_1$ at the expense of decrease in the formation of other two products.
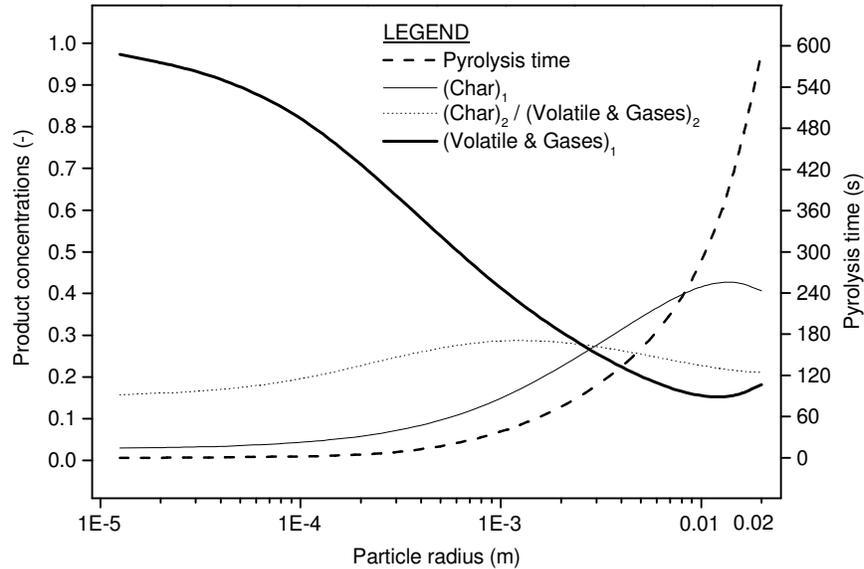

Fig. 4: Average product concentrations and pyrolysis time as functions of particle radius with cylindrical pellet (T_0=303 K, T_f=900 K)

6. SENSIVITY ANALYSIS
To establish the extent to which each property is important in terms of average product concentrations and pyrolysis time (conversion time), a further set of simulations were carried out for sensitivity analysis [2003c, 2003d] in this study. It was found that in relation to increase in the concentration of (char)$_1$, reactor temperature is the most important variable.

7. CONCLUSIONS
- Simulations are carried out using the models developed by Babu and Chaurasia [2003a] for a temperature ranging from 303-1900 K and the particle radius ranging from 0.0001-0.009 m.
- The pyrolysis rate has been simulated by two parallel primary reactions and a third secondary reaction between the volatile and gaseous products and char. The secondary reactions are responsible for carbon enrichment of the final residual.
- The effects of the parameters such as thermal conductivity, reactor temperature and particle size on product concentrations have been analyzed based on the validated model [2003a].
- The conversion time becomes successively longer as the thermal conductivity and particle size of the biomass increases and/or reactor temperature decreases, thus affecting the reactor throughput.
- It should be noted that in many cases the desired product is char. High char concentration is associated with high thermal conductivity and particle size.
- In relation to increase in the concentration of (char)$_1$, reactor temperature is the most important variable.
- It has been observed that the activity of primary reactions is greatly affected by all the three parameters as compared to secondary reactions.
- The results of the parametric study to predict the dependence of average product concentrations and conversion time on thermal and physical properties during convective/radiant pyrolysis are applicable to both gasification (devolatilization stage) and pyrolysis units.
- The results discussed above have a lot of practical importance and physical significance in industrial pyrolysis applications. The results are also important and useful for design of biomass gasifiers, reactors, etc.

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