Convective and Radiative Heat Transfer in Pyrolysis of a Biomass Particle

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Pyrolysis is a process by which a biomass feedstock is thermally degraded in the absence of air/oxygen. It is used for the production of solid (charcoal), liquid (tar and other organics) and gaseous products. In the present study, a mathematical model to describe the pyrolysis of a biomass particle is used to study the importance and effect of convective and radiative heat transfer on its surface. Pyrolysis rate has been simulated by a scheme consisting of two parallel primary reactions and a third reaction for secondary interactions between volatile and gaseous products and the char. Finite difference method using pure implicit scheme is used for solving heat transfer equation and Runge-Kutta 4th order method for chemical kinetics equations. The model equation is solved for cylindrical pellets, spheres and slab geometries of equivalent radius ranging from 0.003 m to 0.011 m, and temperature ranging from 303 K to 1000 K. Proposed model is validated with reported experimental data, and further exhaustive simulations are carried out for understanding the pyrolysis phenomena. The work carried out in the present study is important and useful for optimal design of the biomass gasifiers, reactors, etc. It is very useful in the design of industrial pyrolysis units also.

There are many different ways in which the energy around us can be stored, converted and amplified for use. Energy sources play an important role in the world's future. The energy sources have been split into three categories: fossil fuels, nuclear sources and renewable sources. The fossil fuels are coal, petroleum and natural gas.

A point has been reached where with a few exceptions the cost for producing energy from fossil fuels exceeds the cost of biomass fuels. Biomass is the term used to describe all biologically produced matter.

The thermochemical conversion of biomass (pyrolysis, gasification, combustion) is one of the most promising non-nuclear forms of future energy. It is a renewable source of energy and has many advantages from ecological point of view. The pyrolysis process consists of the thermal degradation of biomass feedstock, in the absence of oxygen/air, leading to the formation of solid (charcoal), liquid (tar and other organics) and gaseous products. Pyrolysis can be used as an independent process for the production of useful energy (fuels) and/or chemicals. It also occurs as the first step in gasification or combustion process.

Several researchers have developed models for pyrolysis of biomass [1-6]. 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 [7], which is used in the present study. Extensive studies are carried out by the Babu & Chaurasia in their earlier studies [8-16]. In the present study, the importance of convective and radiative heat transfer on the surface of the particle of biomass is discussed. Simulations are also carried out to examine the temperature profile for different geometries (slab, cylinder and sphere).

Theory

The overall process of pyrolysis can be classified into primary and secondary stages. When a solid particle of biomass is heated in an inert atmosphere the following phenomena occurs. 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, (1) removal of moisture that is present in the biomass particle, (2) the pre-pyrolysis and main pyrolysis reaction takes place as discussed by Babu and Chaurasia [17]. The heat changes due to the chemical reactions and phase changes contribute to a temperature gradient as a function of time, which is nonlinear. Volatiles and gaseous products flow through the pores of particle and participate in the heat transfer process. The pyrolysis reactions proceed with a rate depending upon the local temperature.

Inside the pyrolyzing particle, heat is transmitted by the following mechanisms: (a) conduction inside solid particle, (b) convection inside the particle pore, (c) convection and radiation from the surface of the 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.

Mathematical model

The pyrolysis reactions can be described by means of following scheme as used by Babu and Chaurasia [17]:

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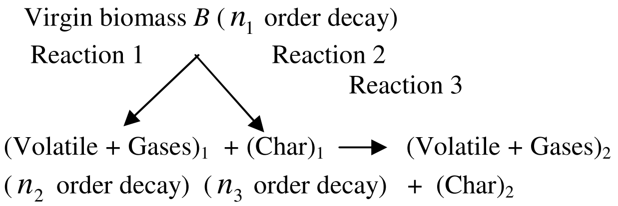

This kinetic scheme indicates that the biomass decomposes to volatiles, gases and char. The volatiles and gases may further react with char to produce different types of volatiles, gases and char where the compositions are different. Therefore, the primary pyrolysis products participate in secondary 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:

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

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

$$\frac{\partial(C_{C1})}{\partial t} = k_2 C_B^{n_1} - k_3 C_{G1}^{n2} C_{C1}^{n_3} \tag{3}$$

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

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

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

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:

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

$$t > 0; \quad r = R,$$

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

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 [18] utilizing Tri-Diagonal Matrix Algorithm [19]. Simulations are carried out for equivalent radius ranging from 0.003 m to 0.011 m, and temperature ranging from 303 K to 1000 K. The values of various parameters employed in the present study are given in Tables 1 and 2. It may be noted that thermal diffusivity is taken to be constant and based on initial temperature of wood, which is a representative value in pyrolysis. When separate values for wood at different temperatures were tried in the simulation, it was found that for the same iteration the pyrolysis time was different for different radial positions. The pyrolysis time cannot be different in a given iteration and hence a representative constant value corresponding to initial condition of biomass is used as shown in the Table-1 taken from Jalan and Srivastava [6].

Table-1. Values of Parameters used in the numerical solution of the model

Property	Value	Source
Convective heat transfer coefficient	$h = 8.4$ W/m^2 K	**[20]**
Wood specific heat	$C_p = 1112.0 + 4.85(T - 273)$, J/kg K	**[4]**
Char specific heat	$C_p = 1003.2 + 2.09(T - 273)$, J/kg K	**[4]**
Wood thermal conductivity	$k = 0.13 + 0.0003(T - 273)$, W/ m K	**[4]**
Char thermal conductivity	$k = 0.08 - 0.0001(T - 273)$, W/ m K	**[4]**
Heat of reaction	$\Delta H = -255000$ J/kg	**[4]**
Initial density of wood	$\rho_0 = 650$ kg/m^3	**[4]**
Initial thermal diffusivity of wood	$\alpha = 1.79 \times 10^{-7}$ m^2/s	**[6]**

Table-2. Nominal values of Parameters employed in the present study

Parameters	Values
Geometry factor	b =2, dimensionless
Initial concentration of B	C_{B_0} =650 kg/m^3
Initial concentration of G_1	$C_{G_{1_0}}$ =0 kg/m^3
Initial concentration of C_1	$C_{C_{1_0}}$ =0 kg/m^3
Initial concentration of G_2	$C_{G_{2_0}}$ =0 kg/m^3
Initial concentration of C_2	$C_{C_{2_0}}$ =0 kg/m^3
Order of reaction 1	n_1=0-1,dimensionless
Order of reaction 2	n_2=1.5, dimensionless
Order of reaction 3	n_3=1.5, dimensionless
Particle radius range	R =(0.003-0.011) m
Initial temperature	T_0=303 K
Final temperature range	T_f =(303-1000) K
Emissivity coefficient	ε =0.95, dimensionless
Stefan Boltzmann constant	$\sigma = 5.67 \times 10^{-8}$ W/m^2 K^4

Results and discussion

Experimental validation and comparison

In the present study, the model developed by Babu and Chaurasia [7] is utilized. The simultaneous kinetics and heat transfer model developed was compared with the experimental data reported by Pyle and Zaror [20], Bamford *et al.* model used by Pyle and Zaror [20], the model developed by Jalan and Srivastava [6] and Liliedahl and Sjöström [5] model. The model is in better agreement with the experimental data of Pyle and Zaror [20]. Typical temperature profiles and conversion profile are shown in Figs. 1-4. The details of experimental validation results are given in the literature [7]. Fig. 1 shows the temperature profile as a function of time at the centre (i.e. x=0) of the cylindrical pellet of radius 0.003 m. This was compared with profiles obtained by Jalan and Srivastava [6] and the experimental data obtained by Pyle and Zaror [20] at the centre of the cylindrical pellet. It was found that the model developed was in excellent agreement with the experimental data better than the agreement with the Jalan and Srivastava's model [6]. Figs. 2 and 3 show the temperature profiles as a function of dimensional radial distance for the final temperature of 643 K and 753 K respectively. The temperature profiles obtained were in much better agreement with the experimental data of Pyle and Zaror [20] when compared to the other two models. Fig. 4 shows the conversion profile as a function of time with cylindrical pellet of radius 0.011 m and final temperature of 753 K. As can be seen from figure, the model developed is in better agreement as compared to Liliedahl and Sjöström [5] model, while the latter underpredicts the conversion at higher values of pyrolysis time. This may be due to fact that while developing the model, Liliedahl and Sjöström [5] did not considered thermal and specific heat capacity of biomass as a function of temperature. The values used in Figs. (1)-(3) are given in Tables 3-5 also for quantitative comparison of Babu and Chaurasia's model [7] with the earlier models and the literature data. In all the cases it was found that the average percentage error and standard deviation from experimental data were significantly less in the model developed by Babu and Chaurasia [7] as compared to the other models.

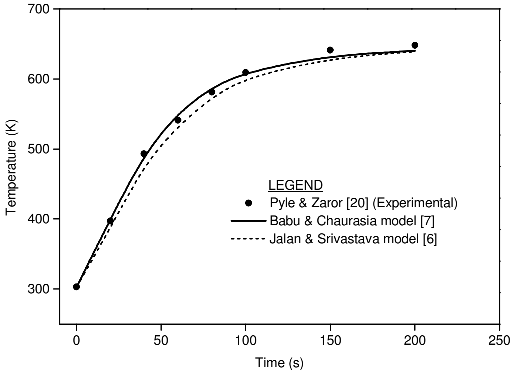

Fig. 1. Temperature profile as a function of time at the centre of the cylindrical pellet (R=0.003 m, T_0=303 K, T_f=643 K, x=0).

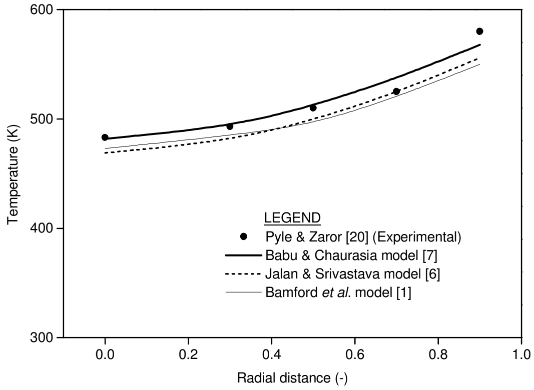

Fig. 2. Temperature profile as a function of radial distance with cylindrical pellet (R=0.011 m, T_0=303 K, T_f=643 K, t=4 min).

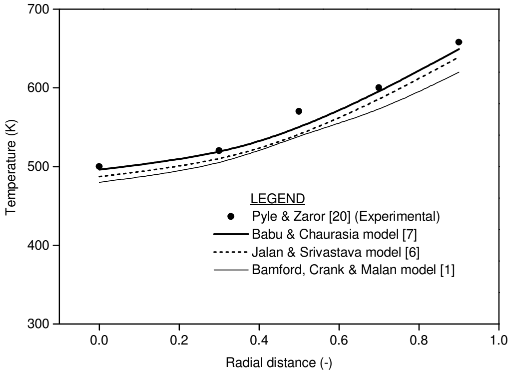

Fig. 3. Temperature profile as a function of radial distance with cylindrical pellet (R=0.011 m, T_0=303 K, T_f=753 K, t=3 min).

Table-3. Comparison of present model results with those of earlier models for various stages of pyrolysis (time) at the centre of cylindrical pellet
(R = 0.003 m, T_0 = 303 K, T_f = 643 K)

Time (s)	Temperature		
	Pyle and Zaror [20] (Experimental)	Babu and Chaurasia's Model [7]	Jalan and Srivastava's Model [6]
0	303	303	303
20	397	400	387
40	493	493	478
60	541	552	533
80	581	588	574
100	609	610	602
150	641	634	630
200	648	640	639
Average Percentage Error		0.75	1.56
Standard deviation		0.0106	0.0189

Model Simulation

Fig. 5 shows the temperature profiles as a function of radial distance at various times of progression of pyrolysis of 3 s, 15 s, 30 s, 45 s and 60 s for the particle radius of 0.009 m, considering both convection and radiation on the wall (surface of the particle). It is observed that as pyrolysis time increases, temperature increases at a given radial position. The rate of increase is high at the radial position close to the wall compared to that at the centre of the particle. In the initial stages of pyrolysis, the temperature profile is very steep near the wall (refer the temperature profile corresponding to 3 s in Fig. 5), and as the time progresses the steepness in the temperature profile near the wall decreases. This can be explained with the fact that when the heat transfer takes place by both the mechanisms of convection and radiation from the wall surface, the resistance offered for heat transfer near the wall at initial stages of pyrolysis is very high

Table-4. Comparison of present model results with those of earlier models for pyrolysis time = 4 min
(R = 0.011 m, T_0 = 303 K, T_f = 643 K)

x	**Temperature**			
	Pyle and Zaror [20] (Experimental)	**Babu and Chaurasia's Model [7]**	**Jalan and Srivastava's Model [6]**	**Bamford *et al.* Model [1]**
0	**483**	**482**	**469**	**473**
0.3	**493**	**493**	**480**	**485**
0.5	**510**	**512**	**499**	**495**
0.7	**525**	**537**	**524**	**520**
0.9	**580**	**568**	**556**	**550**
Average Percentage Error		**0.94**	**2.40**	**2.55**
Standard deviation		**0.0156**	**0.0305**	**0.0329**

Table-5. Comparison of present model results with those of earlier models for pyrolysis time = 3min
(R = 0.011 m, T_0 = 303 K, T_f =753 K)

x	**Temperature**			
	Pyle and Zaror [20] (Experimental)	**Babu and Chaurasia's Model [7]**	**Jalan and Srivastava's Model [6]**	**Bamford *et al.* Model [1]**
0	**500**	**496**	**487**	**480**
0.3	**520**	**515**	**506**	**500**
0.5	**570**	**548**	**539**	**540**
0.7	**600**	**594**	**584**	**570**
0.9	**658**	**649**	**639**	**620**
Average Percentage Error		**1.60**	**3.26**	**4.78**
Standard deviation		**0.0220**	**0.0384**	**0.0540**

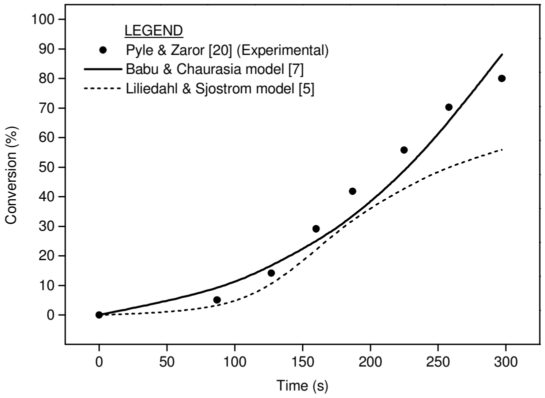

Fig. 4. Conversion profile as a function of time with cylindrical pellet (R=0.011 m, T_0=303 K, T_f=753 K).

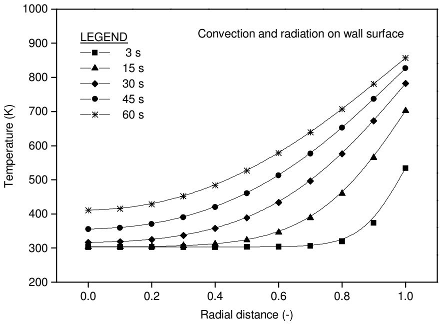

Fig. 5. Temperature profile as a function of radial distance considering both convection and radiation on the wall (R=0.009 m, T_0=303 K, T_f=1000 K).

On the contrary when heat transfer from wall surface takes place only by convection and with no radiation, the resistance offered for heat transfer near the wall is not as higher as in the above case which is clearly demonstrated by plotting the simulation results as shown in Fig. 6. It is also observed that the increase in temperature at various radial positions at different times of progression of pyrolysis is not significant which is obvious due to the reasons mentioned above. Interestingly, to see the extent of effect of convection on temperature profile, simulations are carried out for a case where there is no radiation at the wall surface, but having ten times of convective heat transfer. The results are plotted in Fig. 7 for various times of pyrolysis progression. As expected, the results obtained are almost similar to those corresponding to combined convection and radiation case of Fig. 5. This consolidates the explanation given above in terms of resistances offered by various heat transfer mechanisms. It means that more the resistance offered for heat transfer near the wall of the particle (either by combined convection and radiation, or by convection alone but at higher convective rate) the more will be the difference (increase) in temperature profiles. In the present case the total net resistance offered by convection and radiation is approximately equal to ten times of convective resistance with no radiation at the wall of the particle. The above results shown in Figs. 5-7 and the justifiable and logical explanation given therein have a lot of practical importance and physical significance in industrial pyrolysis applications. The results obtained consolidate the fact that it is possible to get the same extent of conversion of biomass and with lesser pyrolysis time under controlled conditions by increasing convective heat transfer at much lower operating temperatures which are much safer than at higher operating temperatures leading to combined convective and radiative heat transfer mechanisms which are not safe. In pyrolysis process, the reactions that take place at low conversions, which practically means the temperature below 573 K, are endothermic in nature and the reactions that take place at high conversions are exothermic as discussed by Koufopanos *et al.* [4]. As the reactions are exothermic at higher conversions, it becomes important to remove the excess heat liberated due to exothermicity of the pyrolysis reactions, which can be considered as waste heat recovery that can be utilized to cater the needs of utility requirements such as steam etc. This situation corresponds to isothermal operating conditions.

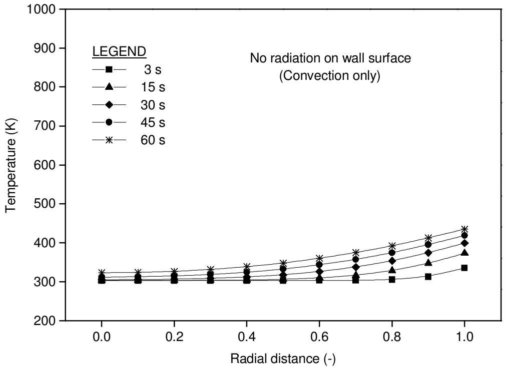

Fig. 6. Temperature profile as a function of radial distance considering convection only with no radiation on the wall (R=0.009 m, T_0=303 K, T_f=1000 K).

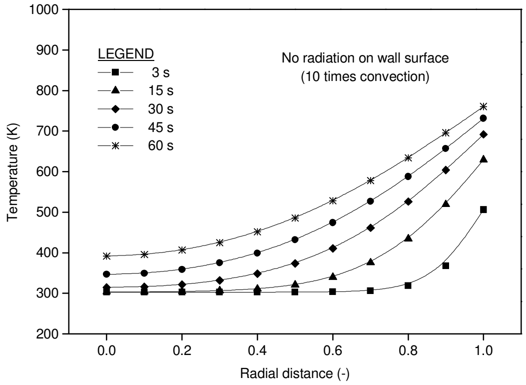

Fig. 7. Temperature profile as a function of radial distance considering ten times convection with no radiation on the wall (R=0.009 m, T_0=303 K, T_f=1000 K).

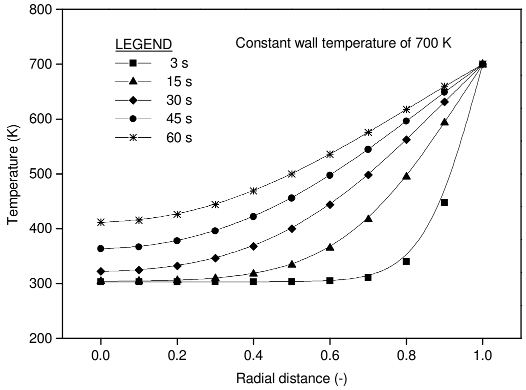

Fig. 8. Temperature profile as a function of radial distance considering constant wall temperature of 700 K (R=0.009 m, T_0=303 K).

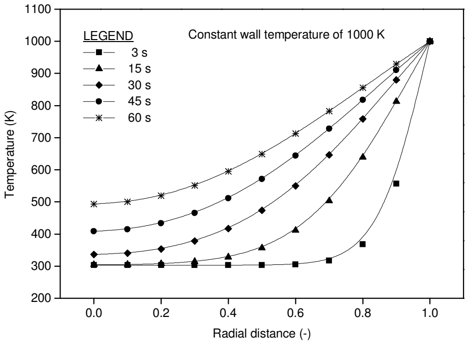

Fig. 9. Temperature profile as a function of radial distance considering constant wall temperature of 1000 K (R=0.009 m, T_0=303 K).

Keeping this in view, the simulations are carried out for the pyrolysis under isothermal condition corresponding to constant wall temperature and the results are presented in Figs. 8 and 9 for constant wall temperature of 700 K and 1000 K. Here again in both cases, the trends in the results obtained are almost similar to the earlier cases, the only difference being the wall temperature is constant. It is seen that, pyrolysis is much faster for 1000 K as compared to 700 K, because higher the temperature faster will be the pyrolysis rate.

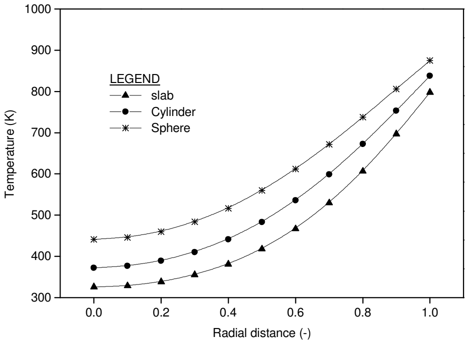

Fig. 10. Temperature profile as a function of radial distance for different geometries (R=0.009 m, T_0=303 K, T_f=1000 K, t=50 s).

Fig. 10 shows the temperature profiles for different geometries (slab, cylinder and sphere). The radii of cylinder and sphere are taken as half the thickness of slab. It is found that pyrolysis is faster in case of sphere and slowest for slab, while the trend in temperature profiles obtained for all the three geometries being same. Geometrically the sphere has got a more heat absorbing capacity as compared to cylinder and slab and it is the least for slab. Mathematically it is reflected in the value of parameter b (b=1, 2 and 3 for slab, cylinder and sphere respectively) in the model equation (6) and hence the observed trends in temperature profile. Similar profiles were obtained for particle radius of 0.003 m to

0.011 m and for the temperatures ranging from 303 K to 1000 K.

Conclusions

- The model used in the present study are in excellent agreement with the experimental data of Pyle and Zaror [20], in comparison with the mathematical model of Jalan and Srivastava [6], Bamford *et al.* model used by Pyle and Zaror [20] and Liliedahl and Sjöström [5] model as is clear from Figs. (1)-(4) and Tables (3)-(5).
- 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 model used in the present study is valid for wide range of temperature from 303-1000 K and of particle radius from 0.003-0.011 m.
- As the particle size increases, the time required for completion of pyrolysis at a certain pyrolysis temperature and the effect of secondary reactions increase.
- As the constant wall temperature is increased, the pyrolysis is completed faster.
- A simple model as used in the present study with very few realistic and restrictive assumptions combined with the thermal properties variation with temperature, can describe the overall progress of a set of processes of great complexity such as pyrolysis.
- The model used can be utilized to predict the temperature and concentration profiles for different types of biomass for a wide range of particle dimensions and temperatures.
- As the model is simple and accurate, it is very useful in the design of industrial pyrolysis units.

References

1. Bamford, C. H., Crank, J., and Malan, D. H., *Proceedings of the Cambridge Philosophical Society*, **42**, pp.166 (1946).
2. Fan, L. T., Fan, L. S., Miyanami, K., Chen, T. Y., and Walawender, W. P., *Can. J. Chem. Eng*., **55**, 47 (1977).
3. Miyanami, K., Fan, L. S., Fan, L. T., and Walawender, W. P., *Can. J. Chem. Eng*., **55**, 317 (1977).
4. Koufopanos CA, Papayannakos N, Maschio G, and Lucchesi A, *Can. J. Chem. Eng*., **69**, 907 (1991).
5. Liliedahl, T., and Sjöström, K., *Biomass Bioenergy*., **15**, 503 (1998).
6. Jalan, R. K., and Srivastava, V. K., *Energy Convers. Mgmt*., **40**, 467 (1999).
7. Babu, B. V., and Chaurasia, A. S., *Energy Convers. Mgmt*., **44**, 2251 (2003).
8. Babu, B. V., and Chaurasia, A. S., *Proceedings of International Conference on Multimedia and Design*., Mumbai, India, September 23-25, **4**, pp.103 (2002).
9. Babu, B. V., and Chaurasia, A. S., *Proceedings of International Symposium & 55th Annual Session of IIChE (CHEMCON-2002)*, OU, Hyderabad, India, December 19-22, 105 (2002).
10. Babu, B. V., and Chaurasia, A. S., *Energy Convers. Mgmt*., **45**, 53, (2004).
11. Babu, B. V., and Chaurasia, A. S., *Chem. Eng. Sci*., **59**, 611, (2004).
12. Babu, B. V., and Chaurasia, A. S., *Chem. Eng. Sci*., **59**, 1999, (2004).
13. Babu, B. V., and Chaurasia, A. S., *Energy Convers. Mgmt*., **45**, 1297, (2004).
14. Babu, B. V., and Chaurasia, A. S., *Proceedings of International Symposium on Process Systems Engineering and Control (ISPSEC '03) - For Productivity Enhancement Through Design and Optimization*., IIT-Bombay, Mumbai, India, January 3-4, pp.181 (2003).
15. Chaurasia, A. S., and Babu, B. V., Presented at *International Conference on Energy and Environmental Technologies for Sustainable Development (ICEET-2003)*, Jaipur, India, October 8-10, 2003.
16. Chaurasia, A. S., and Babu, B. V., Presented at *International Conference on Desert Technology-7 (DT-7)*, Jodhpur, India, November 9-14 (2003).
17. Babu, B. V., and Chaurasia, A. S., *Energy Convers. Mgmt*., **44**, 2135 (2003).
18. Ghoshdastidar, P. S., *Computer Simulation of Flow and Heat Transfer*, New Delhi: Tata McGraw-Hill Publishing Company Limited (1998).
19. Carnahan, B., Luther, H.A., and James, O.W., *Applied Numerical Methods*, New York: John Wiley & Sons (1969).
20. Pyle, D. L., and Zaror, C. A., *Chem. Eng. Sci*., **39**, 147 (1984).

Note: Soft copies in PDF format of references 8,9 and 14 are available at http://discovery.bits-pilani.ac.in/discipline/chemical/BVb/index.html

Nomenclature

b = geometry factor (slab=1, cylinder=2, sphere=3)
B = virgin biomass
G_1 = gases and volatiles 1
C_1 = char 1
G_2 = gases and volatiles 2
C_2 = char 2
C_B = concentration of B, kg/m^3
C_{G_1} = concentration of G_1, kg/m^3
C_{C_1} = concentration of C_1, kg/m^3
C_{G_2} = concentration of G_2, kg/m^3
C_{C_2} = concentration of C_2, kg/m^3
C_p = specific heat, J/kg K
h = convective heat transfer coefficient, W/m^2 K
H = modified Biot number
k = thermal conductivity, W/m K
k_g = thermal conductivity of gas, W/m K
k_1, k_2, k_3 = rate constants, s^{-1}
l = axial length of cylinder, m
n_1, n_2, n_3 = orders of reactions, dimensionless
$\Pr$ = Prandtl number
Q = heat of reaction number, m^3/kg
r = radial distance, m
R = radius for cylinder and sphere; half thickness for slab, m
Re_l = Reynolds number
t = time, s
T = temperature, K
T_0 = initial temperature, K
T_f = final temperature, K

x = dimensionless radial distance
ΔH = heat of reaction, J/kg
$\Delta \tau$ = axial grid length, dimensionless
Δx = radial grid distance, dimensionless
ρ = density, kg/m^3
α = thermal diffusivity, m^2/s
τ = dimensionless time
θ = normalized temperature
ε = emissivity coefficient
σ = Stefan Boltzmann constant