

MODELING & SIMULATION OF PYROLYSIS: INFLUENCE OF PARTICLE SIZE AND TEMPERATURE

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ABSTRACT: In the present study, a mathematical model to describe the pyrolysis of a single solid particle of biomass is used to study the influence of particle size and temperature in the pyrolysis of biomass. The pyrolysis rate has been simulated by a kinetic scheme involving three reactions (primary and secondary): two parallel reactions and a third 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 0.00025 m to 0.013 m, and temperature ranging from 303 K to 2700 K. Some very interesting trends are found, especially with respect to the effect of temperature on final pyrolysis time. The final pyrolysis time first decreases at lower values of temperature and then increases as temperature is further increased, providing an optimum value of temperature at which final pyrolysis time is minimum. This interesting phenomenon, which was not reported by investigators earlier, is well explained by means of the pyrolysis kinetics.

Key Words: *Pyrolysis, Modeling, Heat transfer, Simulation, Particle size*

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 |

INTRODUCTION

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 (H₂, CO₂, CO). The study of pyrolysis is gaining increasing importance, as it is not only an independent process, but it is also a first step in the gasification or combustion process. The overall process of pyrolysis can be classified into primary and secondary stages. The heat changes due to the chemical reactions and phase changes contribute to a temperature gradient as a function of time, which is nonlinear. 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. Hence, the influence of particle size and temperature in pyrolysis and the corresponding optimum parameters are important in the design of these reactors. Though the temperature effect has been studied earlier, studies on high temperatures covering the entire range of pyrolysis reactions are not available in literature.

BRIEF REVIEW OF THE LITERATURE

According to Srivastava and Jalan (1994), the pyrolysis process has a great future in the world. The various modeling studies appearing in the literature present different versions or enrich the model suggested by Bamford *et al.* (1946). According to this model, the equation for heat conduction in a pyrolyzing solid is combined with those for heat generation, assuming first order kinetics. However, the heat transfer equation does not consider the effect of change of density as a function of time. Fan *et al.* (1977) developed a model for pyrolysis process, which includes heat and mass transfer in the particle. The reaction is considered to be first order with respect to initial particle concentration, and also product concentrations cannot be analyzed from the above model as the secondary reactions were not considered. Miyanami *et al.* (1977) incorporated the effect of heat of reaction in the above model. The model developed by Bamford *et al.* (1946), was used by Tinney (1965), Roberts and Clough (1963), Tang and Neil (1964), Shafizadeh (1978) and was modified by Kung (1972) in order to incorporate the effects of internal convection and variable transport properties. However, no specific kinetic mechanism was suggested to predict the concentration of the various components produced during pyrolysis. Kansa *et al.* (1977) included the momentum equation for the motion of pyrolysis gases within the solid. A suitable kinetic mechanism has not been utilized and the solution to the heat and momentum balance equation is based on arbitrary boundary conditions.

Studies have been carried out on pyrolysis of biomass and other substances by Srivastava *et al.* (1996), Di Blasi (1998), Demirbaş (2002), Boutin *et al.* (2002), Mastral *et al.* (2002), Bryden *et al.* (2002), and others. Many of the above studies have not included

the secondary reactions in pyrolysis kinetics. Kansa *et al.* (1977) pointed out that secondary reactions are essential to match fully the experimental observations. Keeping the above drawbacks of the existing models in view, Babu and Chaurasia (2002a) presented the kinetic model, which considered the secondary reactions in pyrolysis kinetics. This kinetic model was utilized by Babu and Chaurasia (2002b) and the model was developed for pyrolysis of a single biomass particle, which includes kinetics and heat transfer effects in the particle.

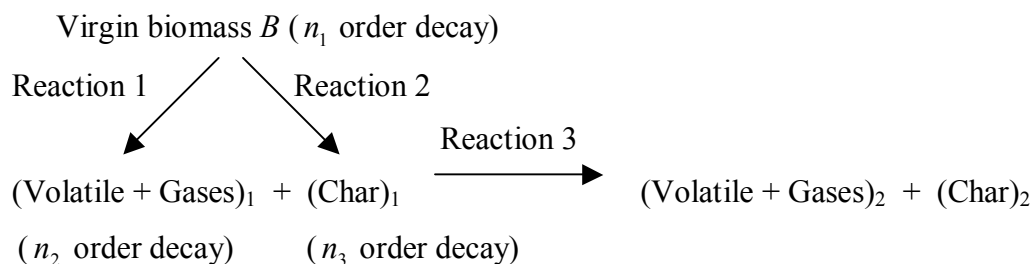
The temperature profiles obtained by Babu and Chaurasia's model (2002b) were compared with (1) those predicted by Pyle and Zaror (1984) in which they utilized Bamford's model, (2) their experimental data, and (3) the temperature profile predicted by Jalan and Srivastava (1999), for different operating conditions. The simulated results obtained by Babu and Chaurasia's model (2002b) was in excellent agreement with the experimental data much better than the agreement with the models proposed by Jalan and Srivastava (1999) and Bamford (1946).

METHODOLOGY & SCOPE OF STUDY

1. MODELING

(a) Chemical Kinetics Model

The pyrolysis reactions can be described by means of following scheme as proposed by Babu and Chaurasia (2002a). Though for brevity the details could be avoided, for clarity and continuity, the pyrolysis reactions and the heat transfer model are presented below:



This model 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 are as follows:

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

$$\frac{dC_{G_1}}{dt} = k_1 C_B^{n_1} - k_3 C_{G_1}^{n_2} C_{C_1}^{n_3} \quad (2)$$

$$\frac{dC_{C_1}}{dt} = k_2 C_B^{n_1} - k_3 C_{G_1}^{n_2} C_{C_1}^{n_3} \quad (3)$$

$$\frac{dC_{G_2}}{dt} = k_3 C_{G_1}^{n_2} C_{C_1}^{n_3} \quad (4)$$

$$\frac{dC_{C_2}}{dt} = k_3 C_{G_1}^{n_2} C_{C_1}^{n_3} \quad (5)$$

Adding equations (1), (3) and (5) gives,

$$\frac{dC_B}{dt} + \frac{dC_{C_1}}{dt} + \frac{dC_{C_2}}{dt} = -k_1 C_B^{n_1} \quad (6)$$

which is equal to $d\rho/dt$.

Hence,

$$\frac{d\rho}{dt} = -k_1 C_B^{n_1} \quad (7)$$

The values of rate constants k_1 , k_2 and k_3 are taken from Koufopoulos *et al.* (1991).

(b) Heat Transfer Model

Consider a cylinder of radius R , length l and radial thickness dr . Assume length of cylinder to be so large that heat transfer takes place in radial direction only. It is assumed that heat flows in one dimension and that heat transfer inside the particle occurs by conduction only. Based on the above assumptions, the equation representing the energy balance is given by

$$\frac{d}{dt}(C_p \rho T) = k \left(\frac{b-1}{r} \frac{dT}{dr} + \frac{d^2 T}{dr^2} \right) + (-\Delta H) \left(-\frac{d\rho}{dt} \right) \quad (8)$$

The final form of equation (8) in dimensionless form is given by,

$$\frac{d\theta}{d\tau} = \frac{b-1}{x} \frac{d\theta}{dx} + \frac{d^2 \theta}{dx^2} + \frac{QR^2 k_1 (C_B)^{n_1}}{\alpha} \quad (9)$$

The initial and boundary conditions in dimensionless forms are:

Initial condition:

$$\tau = 0; \quad \theta(x,0) = 1 \quad (10)$$

Boundary conditions:

$$\tau > 0; \quad x = 0, \quad \frac{d\theta}{dx} = 0 \quad (11)$$

$$\tau > 0; \quad x = 1, \quad \frac{d\theta}{dx} = -\theta H \quad (12)$$

The following dimensionless groups are introduced to obtain equation (9).

$$\alpha = \frac{k}{\rho C_p} \quad (13)$$

$$x = \frac{r}{R} \quad (14)$$

$$\tau = \frac{\alpha t}{R^2} \quad (15)$$

$$\theta = \frac{T_f - T}{T_f - T_0} \quad (16)$$

$$H = \left(\frac{R}{k} \right) \left[h + \varepsilon \sigma (T^3 + T^2 T_f + T_f^2 T + T_f^3) \right] \quad (17)$$

$$Q = \frac{(-\Delta H) + C_p T}{\rho C_p (T_f - T_0)} \quad (18)$$

2. METHOD OF SOLUTION

The equation (9) along with initial and boundary conditions given by equations (10)-(12) are solved by finite difference method using pure implicit scheme. The temperature profiles obtained from the heat transfer model based on initial conditions serve as an input to the chemical kinetics model. The equations (1)-(5) are solved by Runge-Kutta fourth order method. The values of various parameters employed in the present study are listed in Tables 1 and 2.

3. SCOPE OF STUDY

In the present work, the effect of particle size, orders of reactions and temperature on pyrolysis of biomass particle have been studied and optimum parameters have been found, utilizing the model developed by Babu and Chaurasia (2002b). The wide ranges of temperature (303-2700 K) and pellet diameters (0.0005-0.026 m) are considered. 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.

ANALYSIS & KEY RESULTS

The simultaneous kinetic and heat transfer model developed by Babu and Chaurasia (2002b) was compared with the experimental data reported by Pyle and Zaror (1984), Bamford's model used by Pyle and Zaror (1984) and the model developed by Jalan and Srivastava (1999). Typical temperature profiles are shown in Figs. 1-3.

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 (1999) and the experimental data obtained by Pyle and Zaror (1984) 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 (1999). 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 (1984) when compared to the other two models. The values used in Figs. (1)-(3) are given in Tables 3-5 also for quantitative comparison of Babu and Chaurasia's model (2002b) 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 (2002b) as compared to the other models.

Fig. 4 shows the temperature profile as a function of radial distance for cylindrical pellet of various radii at 900 K at the time of completion of pyrolysis for orders of reactions of $n_1=1, n_2=n_3=1.5$. It is found that as the particle radius increases, the time for completion of pyrolysis also increases. Time required for completion of pyrolysis of particle of radius 0.00025 m is least (53 s), while it is maximum for particle radius of 0.013 m (717 s). For smaller particle of radii 0.00025 m and 0.001 m, there is no change in temperature along the radial position, while for the other particle radii it is minimum at the centre and maximum at wall. Fig. 5 shows the temperature profile as function of radial distance for final temperature of 1200 K. It is seen that as the temperature increases, the pyrolysis completes faster. The trends obtained are same as that of Fig. 4 and can be explained similarly. Fig. 6 shows the temperature profile as a function of radial distance at 900 K at the time of completion of pyrolysis for orders of reactions of $n_1=0, n_2=n_3=1.5$. The trends obtained are same as discussed earlier. When comparison is made between Figs. 4 and 6, it is found that the time of completion of pyrolysis is less for orders of reactions of $n_1=0, n_2=n_3=1.5$ as compared to $n_1=1, n_2=n_3=1.5$ for all particle radii. This is due to the fact that for orders of reactions of $n_1=0, n_2=n_3=1.5$, the model equations (1)-(3) become independent of the initial biomass concentration as discussed by Babu and Chaurasia (2002a).

Based on the observation made in Figs. 4 and 5 above that as the temperature increases the pyrolysis completes faster, the model is simulated for wide range of temperatures ranging from 300 K to 2700 K and particle radii ranging from 0.00025 m to 0.013 m and the results are presented in Figs. 7, 8 and 9 for particle radii of 0.005m and 0.00025 m for cylinder and for particle radius of 0.005 m for sphere. Interestingly, it is found that as the temperature increases, time of completion of pyrolysis decreases up to certain extent giving the optimum pyrolysis time and then goes on increasing with further increase in

temperature. For the particle radius of 0.005m, the optimum time of completion of pyrolysis is found to be 88 s for final furnace temperature of 1645 K as shown in Fig. 7. This can be well explained by the pyrolysis kinetics with the help of data presented in Tables 6 and 7 for optimum final furnace temperature of 1645 K and 2100 K respectively. As the final furnace temperature is increased from 1645 to 2100 K, the decrease in concentration of biomass is more for 2100 K up to certain time (74 s). The maximum concentration of char 1 is obtained in 38 s for final furnace temperature of 2100 K as compared to 46 s for 1645 K. So after 38 s the concentration of char 1 decreases, and hence the consumption of biomass also decreases for final furnace temperature of 2100 K. It is also observed that after 74 s, the decrease in concentration of biomass is less for 2100 K as compared to 1645 K, because the char 1 left is less for 2100 K as compared to 1645 K. So the time of completion of pyrolysis to reach the desired final concentration of biomass (i.e. zero) increases though the final furnace temperature is more. Similar explanation could be given for the results shown in Figs. 8 and 9 also. The optimum values of the parameters are given in Table-8. From the Table-8, it is observed that the final pyrolysis time and final pyrolysis temperature are less for sphere as compared to cylinder for the same radius of 0.005 m.

Fig. 10 shows the temperature profiles for different geometries (slab, cylinder and sphere) as the function of radial distance at the time of completion of pyrolysis. 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 (pyrolysis time=153 s) and slowest for slab (pyrolysis time=296 s), 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 (9) and hence the observed trends in temperature profile.

CONTRIBUTION TO THEORY, PRACTICE, POLICY & TECHNOLOGY

As discussed above, it is seen from Figs. 1-3 that the temperature profiles obtained by Babu and Chaurasia's model (2002b) are in much better agreement with the experimental

data of Pyle and Zaror (1984) when compared to Jalan and Srivastava's model (1999) and Bamford's model (1946). Thus, the experimental results of Pyle and Zaror (1984) were in accordance with the predictions of the theory based on the data presented here. The knowledge of temperature profiles is very important and essential in the design of pyrolysis reactor and biomass gasifiers. Because, due to the exothermic and endothermic nature of the pyrolysis reactions, as a designer one should know, *in priori*, the extent of amount of supply and/or removal of heat. Due to high operating temperatures, there is a danger of hot spot formation and subsequently resulting in reactor runaway in the exothermic catalytic reactions. The modeling and simulation results of the present study and their close agreement with the reported experimental data substantiates the importance and contribution to theory, practice and technology, keeping the dangers mentioned above in view. Biomass gasification and pyrolysis are the most important areas in renewable energy on which the government in general, and MNES (Ministry of Non-Conventional Energy Sources) in particular are very much focused and lot of policy decisions have been made to encourage the use of these energies. From this perspective, the results of present study would be definitely useful in policy decision-making.

SUMMARY

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 study is carried out for wide range of temperature from 303-2700 K and of particle diameter from 0.0005-0.026 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. It is observed that, for particle sizes below 1mm, the process is controlled by the primary pyrolysis reactions and, possibly, by the external heat transfer. For particles greater than 1mm, heat transfer, primary pyrolysis and secondary pyrolysis control the pyrolysis process. The pyrolysis is fast for zeroth order as compared to first order of reaction 1, as the rates are independent of initial biomass concentration for zeroth order.

Some interesting trends have been obtained, especially with respect to effect of final furnace temperature on completion of pyrolysis time. The results obtained using a wide range of operating conditions in the present study show that the final pyrolysis time initially decreases and then increases as the final temperature is increased, giving an optimum final pyrolysis time corresponding to final temperature. The above interesting trends are observed for different orders of reactions and for different geometries. These interesting trends that were not reported earlier could be well explained from the kinetics by systematically generating huge data upon simulating the model equations. 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.

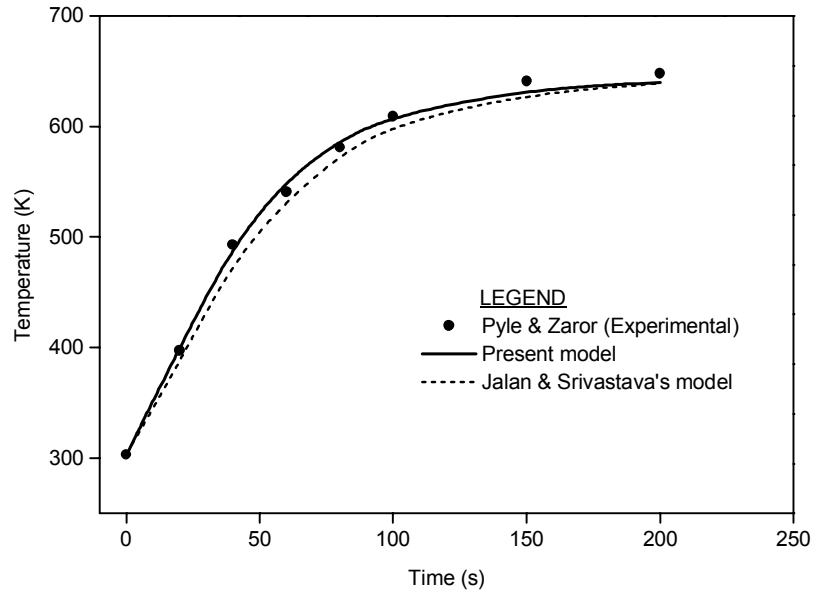


Fig. 1. Temperature profile as a function of time at the centre of the cylindrical pellet. ($R=0.003$ m, $T_0=303$ K, $T_f=643$ K, $x=0$)

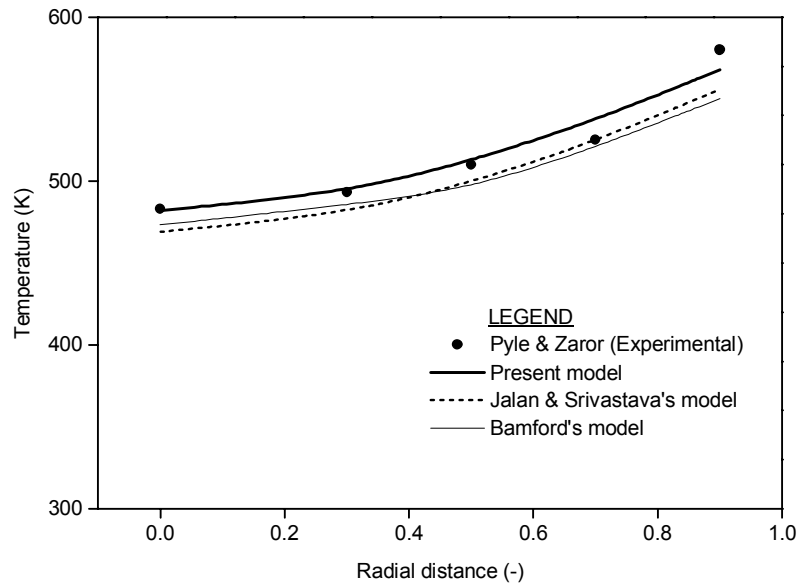


Fig. 2. Temperature profile as function of radial distance ($R=0.011$ m, $T_0=303$ K, $T_f=643$ K, $t=4$ min).

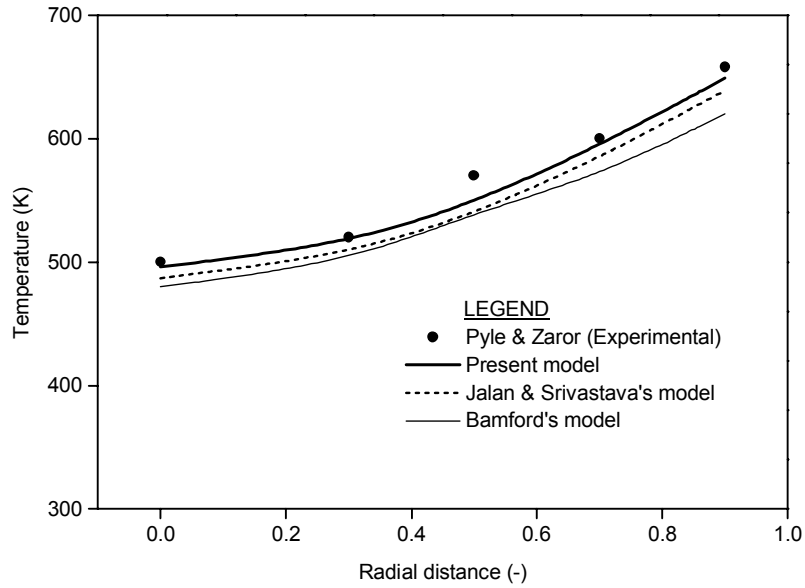


Fig. 3. Temperature profile as function of radial distance ($R=0.011$ m, $T_0=303$ K, $T_f=753$ K, $t=3$ min).

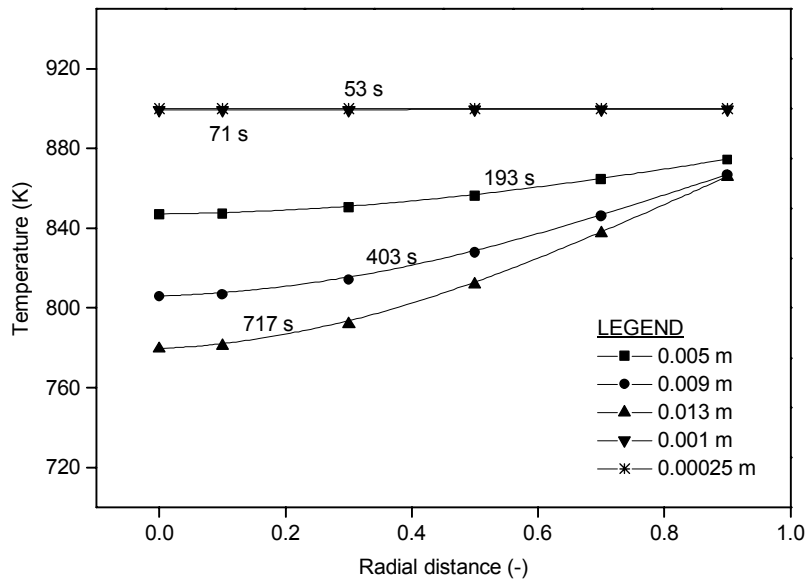


Fig. 4. Temperature profile as a function of radial distance for various particle radii at 900 K at the time of completion of pyrolysis ($n_1=1, n_2=n_3=1.5, T_0=303$ K, $T_f=900$ K).

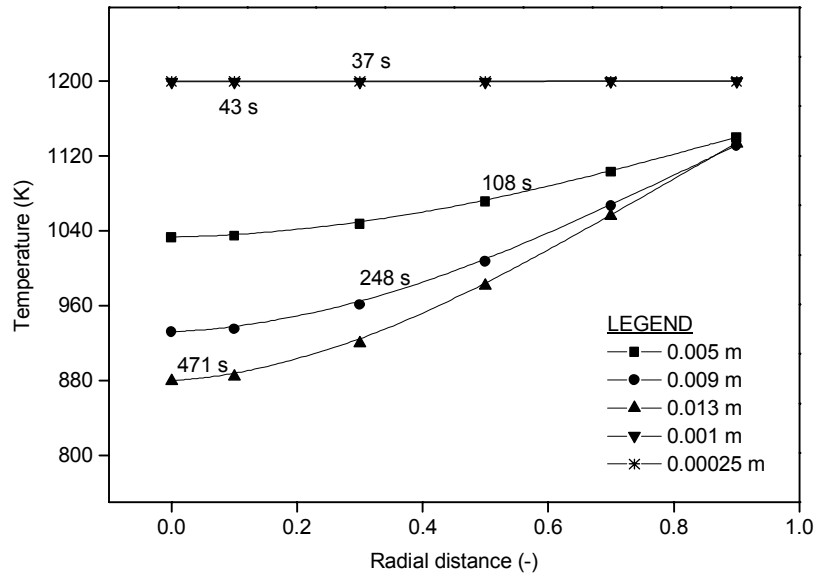


Fig. 5. Temperature profile as a function of radial distance for various particle radii at 1200 K at the time of completion of pyrolysis ($n_1=1, n_2=n_3=1.5, T_0=303 \text{ K}, T_f=1200 \text{ K}$).

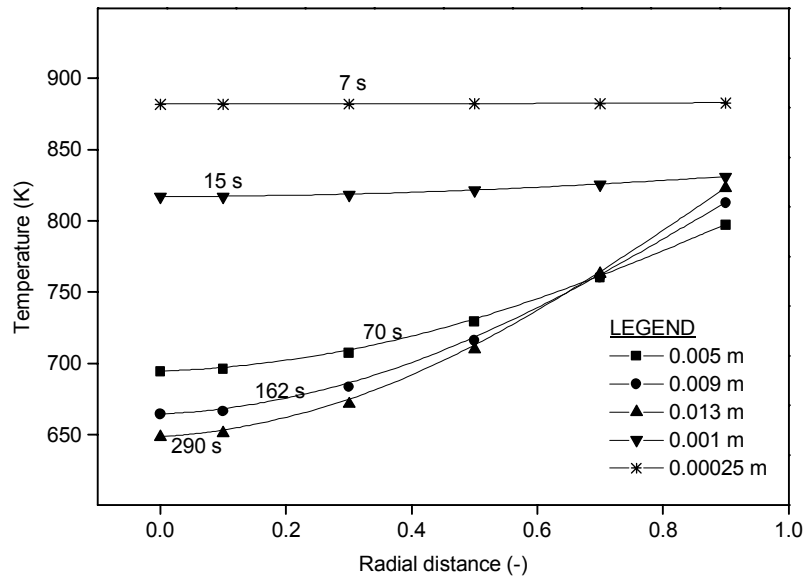


Fig. 6. Temperature profile as a function of radial distance for various particle radii at 900 K at the time of completion of pyrolysis ($n_1=0, n_2=n_3=1.5, T_0=303 \text{ K}, T_f=900 \text{ K}$).

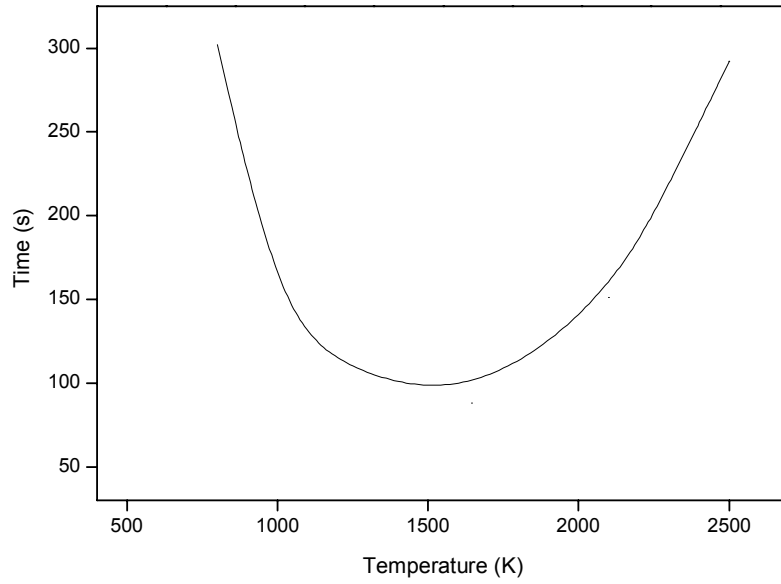


Fig. 7. Time of completion of pyrolysis as a function of temperature for particle radius of 0.005 m.
 $(n_1=1, n_2=n_3=1.5, T_0=303)$

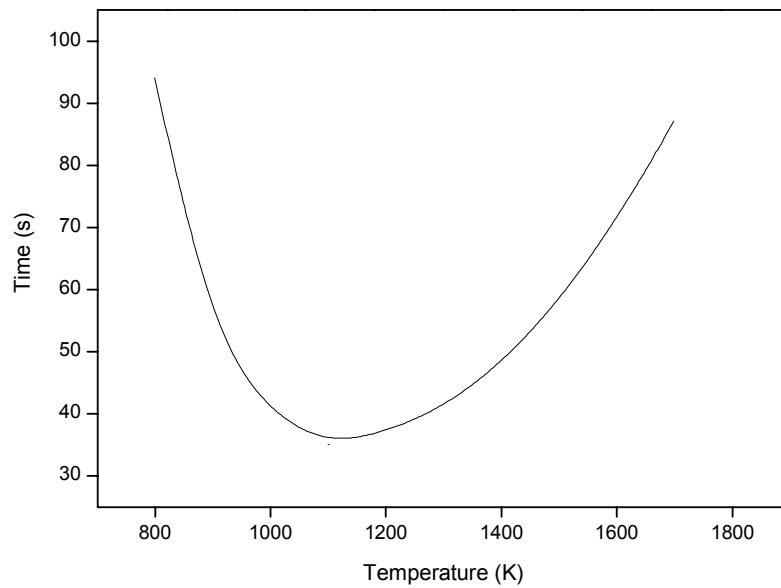


Fig. 8. Time of completion of pyrolysis as a function of temperature for particle radius of 0.00025 m.
 $(n_1=1, n_2=n_3=1.5, T_0=303)$

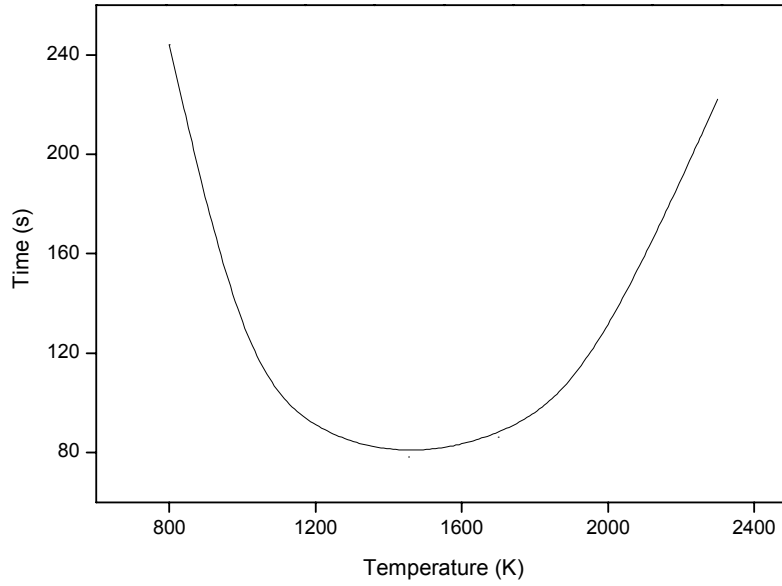


Fig. 9. Time of completion of pyrolysis as a function of temperature for spherical particle of radius 0.005 m ($n_1=1, n_2=n_3=1.5, T_0=303$).

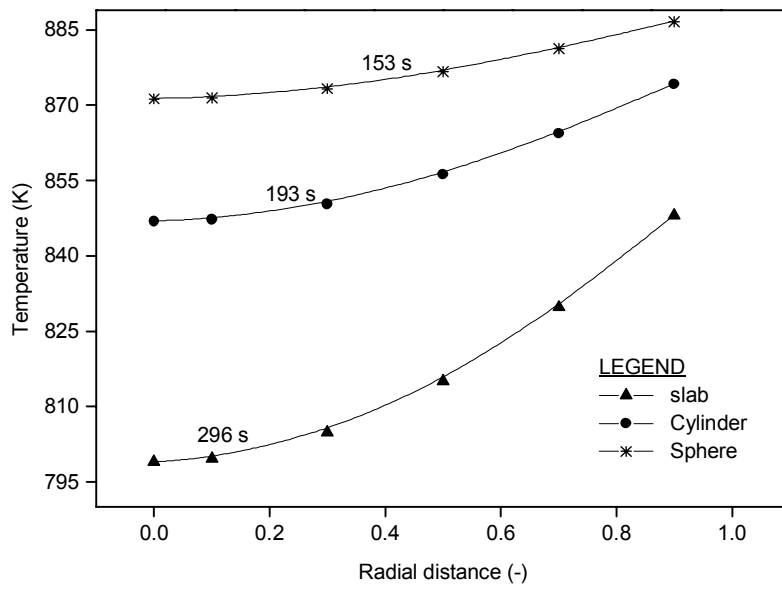


Fig. 10. Temperature profile as a function of radial distance for different geometries at the time of completion of pyrolysis ($n_1=1, n_2=n_3=1.5, R=0.005$ m, $T_0=303$ K, $T_f=900$ K).

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

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

P&Z: Pyle & Zaror (1984); *K*: Koufopoulos *et al.* (1991); *J&S*: Jalan & Srivastava (1999)

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

| Parameters | Values |
|--------------------------------|--|
| Geometry factor | $b = 2$, dimensionless |
| Initial concentration of B | $C_{B_0} = 650 \text{ kg/m}^3$ |
| Initial concentration of G_1 | $C_{G_1_0} = 0 \text{ kg/m}^3$ |
| Initial concentration of C_1 | $C_{C_1_0} = 0 \text{ kg/m}^3$ |
| Initial concentration of G_2 | $C_{G_2_0} = 0 \text{ kg/m}^3$ |
| Initial concentration of C_2 | $C_{C_2_0} = 0 \text{ kg/m}^3$ |
| Order of reaction 1 | $n_1 = 0$, dimensionless |
| Order of reaction 2 | $n_2 = 1.5$, dimensionless |
| Order of reaction 3 | $n_3 = 1.5$, dimensionless |
| Particle radius range | $R = (0.00025-0.011) \text{ m}$ |
| Initial temperature | $T_0 = 303 \text{ K}$ |
| Final temperature range | $T_f = (303-1000) \text{ K}$ |
| Emissivity coefficient | $\varepsilon = 0.95$, dimensionless |
| Stefan Boltzmann constant | $\sigma = 5.67 \times 10^{-8} \text{ W/m}^2 \text{ K}^4$ |

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 (1984) (Experimental) | Babu and Chaurasia's Model (2002b) | Jalan and Srivastava's Model (1999) |
| 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 |

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 (1984) (Experimental) | Babu and Chaurasia's Model (2002b) | Jalan and Srivastava's Model (1999) | Bamford's Model (1946) |
| 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 (1984) (Experimental) | Babu and Chaurasia's Model (2002b) | Jalan and Srivastava's Model (1999) | Bamford's Model (1946) |
| 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 |

Table-6. Simulated results with the optimum temperature (1645 K) for pyrolysis of cylindrical pellet of radius 0.005 m ($n_1=1$; $n_2=n_3=1.5$)

| t | T | C_B | C_{G_1} | C_{C_1} | C_{G_2} | C_{C_2} |
|------|-------------|------------|-----------|------------|------------|------------|
| 1.0 | 303.041416 | 650.000000 | 0.000000 | 0.000000 | 0.000000 | 0.000000 |
| 15.0 | 421.921449 | 649.965228 | 0.000003 | 0.034769 | 0.000000 | 0.000000 |
| 30.0 | 620.145975 | 535.048255 | 14.281696 | 99.831749 | 0.419150 | 0.419150 |
| 38.0 | 657.662178 | 385.407963 | 44.324157 | 179.732538 | 20.267671 | 20.267671 |
| 39.0 | 662.221267 | 366.467356 | 46.767841 | 184.470246 | 26.147278 | 26.147278 |
| 46.0 | 703.340007 | 230.944809 | 57.246921 | 184.793708 | 88.507281 | 88.507281 |
| 47.0 | 711.305786 | 210.836541 | 58.023858 | 180.265779 | 100.436911 | 100.436911 |
| 48.0 | 720.086499 | 190.575671 | 58.567103 | 174.558063 | 113.149581 | 113.149581 |
| 73.0 | 1220.206339 | 0.038576 | 2.747890 | 21.643747 | 312.784893 | 312.784893 |
| 74.0 | 1234.605217 | 0.026305 | 2.364912 | 21.253188 | 313.177797 | 313.177797 |
| 75.0 | 1248.412790 | 0.018079 | 2.043245 | 20.926480 | 313.506098 | 313.506098 |
| 76.0 | 1261.670650 | 0.012521 | 1.771999 | 20.651856 | 313.781812 | 313.781812 |
| 88.0 | 1387.710904 | 0.000253 | 0.414538 | 19.287125 | 315.149042 | 315.149042 |

Table-7. Simulated results with temperature = 2100 K for pyrolysis of cylindrical pellet of radius 0.005 m ($n_1=1$; $n_2=n_3=1.5$)

| t | T | C_B | C_{G_1} | C_{C_1} | C_{G_2} | C_{C_2} |
|-------|-------------|------------|------------|-----------|------------|------------|
| 1.0 | 303.073899 | 650.000000 | 0.000000 | 0.000000 | 0.000000 | 0.000000 |
| 15.0 | 462.544327 | 649.857429 | 0.000469 | 0.142102 | 0.000000 | 0.000000 |
| 30.0 | 650.049746 | 504.244613 | 45.436203 | 96.004217 | 2.157483 | 2.157483 |
| 38.0 | 695.304910 | 36.019862 | 104.855115 | 131.66940 | 38.727808 | 38.727808 |
| 39.0 | 703.247479 | 311.758513 | 111.097880 | 129.60329 | 48.770158 | 48.770158 |
| 46.0 | 800.150481 | 120.676965 | 141.162004 | 65.012529 | 161.574251 | 161.574251 |
| 47.0 | 825.229412 | 93.974519 | 142.913731 | 50.361562 | 181.375094 | 181.375094 |
| 48.0 | 855.242754 | 69.844726 | 144.101093 | 36.229038 | 199.912571 | 199.912571 |
| 73.0 | 1636.091153 | 0.030624 | 153.513662 | 0.003811 | 248.225952 | 248.225952 |
| 74.0 | 1652.552961 | 0.025688 | 153.515172 | 0.003240 | 248.227950 | 248.227950 |
| 75.0 | 1668.394619 | 0.021661 | 153.516367 | 0.002772 | 248.229600 | 248.229600 |
| 76.0 | 1683.645462 | 0.018355 | 153.517318 | 0.002386 | 248.230971 | 248.230971 |
| 88.0 | 1828.787031 | 0.003332 | 153.521042 | 0.000549 | 248.237539 | 248.237539 |
| 89.0 | 1838.269943 | 0.002941 | 153.521113 | 0.000496 | 248.237725 | 248.237725 |
| 152.0 | 2072.129027 | 0.000007 | 153.521442 | 0.000009 | 248.239271 | 248.239271 |

Table-8. Optimum Parametric values for different particle radii and geometries at the centre ($n_1=1$; $n_2=n_3=1.5$)

| Optimum Parameters | Cylinder | | Sphere |
|--|--------------------|----------|---------|
| | Particle radii (m) | 0.00025 | 0.005 |
| Final pyrolysis time (s) | 35.0 | 88.0 | 78 |
| Final temperature of furnace (K) | 1100 | 1645 | 1455 |
| Final pyrolysis temperature (K) | 1099.99 | 1387.751 | 1350.09 |
| Final concentration of initial biomass (kg/m^3) | 0 | 0 | 0 |
| Final concentration of Char 1 (kg/m^3) | 0.00715 | 19.3174 | 64.3383 |
| Final concentration of Volatile 1 (kg/m^3) | 366.985 | 0.41275 | 0.0299 |
| Final concentration of Char 2 (kg/m^3) | 141.504 | 315.135 | 292.816 |
| Final concentration of Volatile 2 (kg/m^3) | 141.504 | 315.135 | 292.816 |

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