Studies on pyrolysis of a single biomass cylindrical pellet—kinetic and heat transfer effects

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Abstract

The present work involves the development of a mathematical model to describe the pyrolysis of a single solid biomass particle. Generally, the phenomena governing the pyrolysis of a single biomass particle is based on both physical and chemical changes. The chemical changes include primary and secondary pyrolysis reactions, and both chemical and physical changes are controlled by the heat transfer phenomena. The proposed energy balance model equation takes into account the non-isothermal reaction of the biomass particle. The equation for the model is solved for a cylindrical pellet under a wide range of operating conditions. The numerical scheme employed is a finite difference, backward implicit scheme for the heat transfer equation and the Runge-Kutta 4th Order Predictor-Corrector method for the equations involving chemical kinetics. Results for various size particles have been obtained to predict the temperature profile as a function of the radial distance at varying time intervals. The results obtained from the model are compared with experimental data from the literature.

Keywords: Pyrolysis; Biomass; Kinetics; Heat transfer

Nomenclature

\[ CB = \text{concentration of initial biomass kg/m}^3 \]
\[ Cc_1 = \text{concentration of Char 1, kg/m}^3 \]
\[ Cc_2 = \text{concentration of Char 2, kg/m}^3 \]
\[ CQ_1 = \text{concentration of (gases and volatiles)i, kg/m}^3 \]
\[ CG_2 = \text{concentration of (gases and volatiles)_2, kg/m}^3 \]
\[ C_p = \text{specific heat, J/kg K} \]
1. Introduction

Biomass consists of organic substances which are thermally unstable, and consequently, when heated in an inert atmosphere, they may be split through a combination of thermal cracking and condensation reactions into gaseous liquid and solid fractions. Generally, the above process is called pyrolysis. In contrast to the process of incineration, the pyrolysis process at high temperatures is endothermic, as discussed by Koufopanos et al. [1].

According to Tchobanoglous et al. [2], depending upon the type of reactors used, the physical form of the solid waste undergoing the process of pyrolysis could vary from unshredded raw wastes to finely ground portions of the wastes.

Before proceeding further, it is essential to understand the characteristics of the three major components discussed above which result during the pyrolysis process.

1. A gaseous stream that contains primarily hydrogen, methane, carbon monoxide, carbon dioxide and various other gases, depending upon the organic nature of the waste being pyrolysed.
2. A liquid stream that consists of a tar and/or oil which remains in the liquid form at room temperature. This contains many chemicals, such as methanol, acetone, acetic acid etc.
A solid fraction which is mainly char and consists of almost pure carbon plus any other inert material that may have entered the process. According to Srivastava and Jalan [3], the pyrolysis process has a great future in the world, however, even today, the process is not fully understood, keeping in view its complexity and the number of reactions involved.

Kung [4] developed a mathematical model for the pyrolysis of a wood slab, one side of which is heated and the other side impervious and insulated. The model of Kung [4] considered heat transfer due to conduction, internal heat convection of volatiles and first order kinetics for the formation of volatiles and char. However, no specific kinetic mechanism was suggested to predict the concentration of the various components produced during pyrolysis. Kansa et al. [5] also developed a mathematical model of the pyrolysis of wood after incorporation of internal forced convection effects, including porous and permeable structural effects. A suitable kinetic mechanism has not been utilized, and the solution to the heat and momentum balance equation is based on arbitrary boundary conditions. Kansa et al. [5] pointed out that secondary reactions are essential to match fully the experimental observations. Miyamani et al. [6] incorporated the heat of reaction in the pyrolysis of a solid particle based on the volume reaction model. The reaction is considered to be first order with respect to the initial particle concentration, and consequently, product concentrations can not be analysed from the above model. In a related work, using a similar set of equations to Miyamani et al. [6], Fan et al. [7] incorporated the effect of the Lewis Number in the above model and the effect of it on the fluid and solid concentration changes and the temperature profile of the particle. A detailed description of various pyrolysis models for coal particles is provided by Anthony and Howard [8], highlighting the importance of secondary pyrolysis reactions. The latest model of pyrolysis of coal discussed by them is the multi-step series competition model developed by Reidelbach and Summerfield [9]. It has been pointed out by Anthony and Howard [8] that rapid heating is a necessary feature of short residence time, however, there is little effect of the heating rate on the volatiles yield in the process of pyrolysis of coal.

Pyrolysis, also designated as thermal cracking or simply cracking was analysed by Dente and Ranzi [10]. They have analysed the various mathematical models developed for the pyrolysis of hydrocarbons with many reaction mechanisms. It has been pointed out by them that less extensive mechanistic, molecular or semi-kinetic models show reliable predictions only over a limited range of conditions.

Dermer and Crynes [11] studied the pyrolysis of various types of biomass, including wood, municipal solid waste, cattle manure etc. The flash pyrolysis of municipal solid waste or dried sewage sludge at 87°C yields
- 65 to 80% oil and gases
- 20 to 30% char
which is in conformity with data reported by Srivastava and Jalan [3] and Srivastava et al. [12].

Albright and Tsai [13] have studied the effect of the surface of a coal particle on the kinetics of pyrolysis and coke formation on metal surfaces. Such information is helpful in developing improved designs and operating conditions. Come [14] has analysed the versatility of the reactor as a kinetic tool. However, along with it, the range of experimental conditions must also be considered. Srivastava [15] has analysed the performance of a thermal cracker and
predicted the kinetic parameters for hydrocarbon cracking of benzene. Srivastava and Gunn [16] and Srivastava et al. [17] showed the importance of pyrolysis used for the fertilizer industry and for other lighter gaseous hydrocarbons, respectively.

Ross [18] has analysed non-conventional technology for the design of pyrolysis reactors, including the antithermal reactor, cyclic reactor, molten bed reactor, heterogeneous reactor and catalytic reactors. Ferrero [19] is of the view that waste management by pyrolysis of solid urban waste poses certain problems, whereas the pyrolysis of wood is feasible and successful. However, according to Grassi [20], three types of pyrolysis processes are being utilized commercially. These are (i) general pyrolysis which produces gas (used as fuel gas), liquid (used as oil or liquid fuel substitution) and solid char (used as solid fuel or slurry fuel), (ii) flash pyrolysis which produces mostly liquid used for oil or liquid fuel substitution and (iii) slow pyrolysis which produces solid char, mainly used as a slurry fuel or solid fuel. It is pointed out that biomass has a potential energy contribution of around 10% of primary energy needs by conversion of biomass through pyrolysis. In Europe alone, 300 million MT/year of biomass could be pyrolysed for energy requirements.

Beenackers and Bridgwater [21] have discussed the gasification and pyrolysis of biomass in Europe, and according to them, biomass, which is the only renewable source of fixed carbon has attracted considerable attention as a renewable energy resource in Europe. The products of slow and flash pyrolysis are given below.

<table>
<thead>
<tr>
<th></th>
<th>Slow pyrolysis</th>
<th>Flash pyrolysis</th>
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</thead>
<tbody>
<tr>
<td>Gas (% wt on dry feed)</td>
<td>up to 40%</td>
<td>up to 70%</td>
</tr>
<tr>
<td>Liquid (% wt on dry feed)</td>
<td>up to 30%</td>
<td>up to 70%</td>
</tr>
<tr>
<td>Solid (% wt on dry feed)</td>
<td>up to 30%</td>
<td>up to 30%</td>
</tr>
</tbody>
</table>

The above figures are typical and can vary considerably according to the technology and operating conditions.

Diebold and Stevens [22] pointed out that the U.S. Department of Energy is sponsoring research on a regular basis for the production of fuels by pyrolysis and gasification through its Biomass and Municipal Waste Technology Division. The potential impact of this research would be a seven-fold increase in the contributions of biomass to the energy consumed in the U.S., from the current level of 3% to over 20%. Research is presently in progress to utilize Refuse Derived Fuel (RDF) by the process of pyrolysis to produce gasoline. Antonelli [23] has discussed the development of the process of pyrolysis and the utilization of charcoal (the solid product produced from pyrolysis) as an industrial fuel. Helt and Agarwal [24] studied the pyrolysis of municipal solid waste (MSW) to produce liquid fuels and in order to understand the basic thermo-kinetic mechanisms associated with the pyrolytic conversion of MSW. Cheremisinoff and Morresi [25] have discussed, in detail, pyrolysis as a process in energy recovery, and according to them, now it is a viable alternative for resource recovery of solid waste.

According to Tchobanoglous et al. [2], the product yield of the various streams during pyrolysis is given below
However, according to Sushil [26], the product yields are as follows

<table>
<thead>
<tr>
<th></th>
<th>Weight</th>
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<tbody>
<tr>
<td>Gases</td>
<td>25%</td>
</tr>
<tr>
<td>Liquids</td>
<td>20-80%</td>
</tr>
<tr>
<td>Solids</td>
<td>17-25%</td>
</tr>
</tbody>
</table>

The products yield varies depending upon the final pyrolysis temperature, type of reactor, operating conditions etc. In a recent paper, Srivastava and Jalan [3], predicted the product yields as mentioned below

<table>
<thead>
<tr>
<th></th>
<th>Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gases and Liquids</td>
<td>40-61%</td>
</tr>
<tr>
<td>Solids</td>
<td>13-30%</td>
</tr>
</tbody>
</table>

The above model predicts only the quantity of solids accurately, compared to data of Sushil [26] and Tchobanoglous et al. [2], as the kinetic model of Srivastava and Jalan [3] had in it an intermediate product which remained till the end of the reaction and was difficult to define and measure physically. However, in a subsequent work, Srivastava et al. [12] dispensed with the concept of intermediate, and the product yield is in conformity with the results reported by Sushil [26] and Tchobanoglous [2] as given below

<table>
<thead>
<tr>
<th></th>
<th>Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas and Volatiles</td>
<td>75-85%</td>
</tr>
<tr>
<td>Char</td>
<td>13-20%</td>
</tr>
</tbody>
</table>

Keeping in view the above, the kinetic model utilized by Srivastava et al. [12] is proposed in the modelling of pyrolysis of a single biomass particle.

In the earlier work done by Srivastava and Jalan [3] and Srivastava et al. [12], a linear relationship between temperature and time has been assumed. However, in the present analysis, the temperature profile would be predicted, based on the proposed heat transfer equation and the boundary conditions developed by Koufopanos et al. [1] and Pyle and Zaror [27]. It is observed in the present model that the linear relationship between time and temperature throughout the pellet is not realistic, as temperature varies with time at every point within the particle in a nonlinear fashion. The temperature profile of the above model is compared with
the temperature profile predicted by Pyle and Zaror [27] and their experimental data for a number of operating conditions and parameters.

However, the kinetic model utilized by Pyle and Zaror [27] is a first order kinetics, based on the density of the initial biomass. Therefore, their model does not allow for the prediction of the final char yield. Further, the kinetic model of Koufopanos et al. [1] does not permit the prediction of the concentration and the final yield of gaseous and volatile products. Koufopanos et al. [1] and Pyle and Zaror [27] have solved the heat transfer equation by not considering the effect of the change in density as a function of time of the single biomass particle. In the present analysis, however, the above anomaly has been rectified. The results presented by them in the field have highlighted the effect of particle size, radial distance and time on the temperature profile for lower temperatures only (380-500°C) and cylindrical pellets of diameters from 0.006 to 0.022 M. However, in the present analysis, the temperature range considered is 303-900 K and pellet diameters of 0.002-0.022 M. The effect of particle size, radial distance and time on the temperature profile have not been analysed in the model developed by Koufopanos et al. [1].

The model being developed would enable prediction of both char and gaseous and volatile product yields. The effect of particle size, constant wall temperature and the boundary condition at the wall, equating conduction heat flux to the sum of convective and radiative heat flux, has been analysed.

The effect of particle size on the temperature profile, the variation of temperature with radial distance and various times during the pyrolysis process for a wide range of temperatures is presented. The above analysis would throw more insight into the complex process of pyrolysis.

2. Model development

Whenever a biomass particle is heated in an inert atmosphere, heat is first transferred to the particle surface by means of radiation and/or forced or natural convection, and then, heat is transferred inside the particle by conduction and through the pores (if considered) by convection. Therefore, the temperature inside the particle increases, causing initially the removal of the moisture that is present in the biomass particle, and subsequently, the pre-pyrolysis and main-pyrolysis reactions take place as discussed by Srivastava et al. [12]. The effect of heat transfer results in a phase change inside the particle, which contributes to a temperature gradient as a function of time, which is nonlinear. Gaseous products, including volatiles, pass through the pores of the particle and are involved in the transfer of heat and effects the change of density. The pyrolysis process reactions commence with a rate depending on the local temperature.

During pyrolysis, according to Curtis and Miller [28], the pores of the particle/pellet are enlarged, however, the particle becomes more porous as the biomass is converted to gases, volatiles and char. Consequently, the larger size of the pores results in many additional reaction sites for the volatiles and gaseous products and permit them to interact with the hot particle, as discussed by Ekstrom and Rensfelt [29] and Anthony and Howard [8].

Inside the single particle undergoing pyrolysis, heat is transmitted by the methods given below:
— conduction inside solid particle
— convection inside the particle pore
— convection and radiation from surface of pellet
— constant temperature at the surface of pellet.

For simplicity of solution, it is assumed that heat transfer inside the solid is by conduction only, and the effect of the porosity of the solid pellet has not been considered, which would be valid for dense particles and various kinds of hard wood being considered in the above studies.

As the radial temperature inside the particle increases along with the increase in time, it is natural that greater quantities of volatiles and gases are formed. Changes in heating conditions could alter the rate of reaction and affect the overall pyrolysis rates.

3. Derivation of modelling equations

Considering a cylindrical shell of radius \( r \), length \( z \) and radial thickness, \( dr \), heat transfer occurs only in the radial direction, as the aspect ratio is large enough so the heat transfer in the axial direction is negligible. It is assumed that heat transfer takes place within the solid by conduction only.

The generalized form of the heat balance equation is developed, which in the present case results in the following equation

\[
\frac{k}{r} \left( \frac{1}{r} \frac{d}{dr} \left[ \frac{dT}{dr} \right] + \frac{d^2T}{dr^2} \right) \frac{d(-\rho)}{dt} = \frac{d(C_p\rho T)}{dt},
\]

Consider \( C_p \) to be independent of time, however, actually \( C_p \) is a function of temperature and temperature is a function of time. Therefore, indirectly \( C_p \) is also a function of time. However, the above consideration that \( C_p \) is independent of time is considered for facilitating solution of the equation. Subsequently, \( C_p \) values are taken as a function of temperature.

\[
\frac{d(C_p T)}{dt} = C_p \frac{d(p)}{dt},
\]

\[
\frac{d(\rho T)}{dt} = \rho \frac{dT}{dt} + T \frac{d\rho}{dt}.
\]

Combining Eqs. (1)-(3) yields:

\[
k \left( \frac{1}{r} \frac{d}{dr} \left( \frac{d}{dr} \right) \right) \frac{v}{dt} = \frac{\rho}{\gamma} \frac{d(\rho T)}{dt}.
\]

The variation of \( C_p \) and \( k \) as a function of temperature is calculated based on the equations of Koufopanos et al. [1], as given below:
\[ C_p = 1112 + 4.85 \ (T - 273) \]  
\[ k = 0.13 + 0.0003 \ (T - 273) \]

where \( T \) is in Kelvin.

The above equation is based on the following boundary and initial conditions:

**Initial condition**

\[ \text{At } t = 0 \quad T(r, 0) - T_o \]

**Boundary conditions**

\[ t > 0 \quad r = 0, \quad \frac{\partial T}{\partial r} = 0 \]

\[ i = \hat{u}, \quad r = R, \quad \left\{ l-k \frac{dT}{dr} \right\}_{r=R} = h(T_r - T) + ae(T_r^4 - T^4). \]

Eq. (7) considers that external heat transfer occurs by a mechanism of convective and radiative heat transfer.

The following parameters are introduced in Eq. (4)a), (5), (6) and (7) in order to facilitate the solution of the heat transfer equation:

\[ \xi = \frac{f r}{\rho C_p} \]

\[ x = \frac{r}{R} \]

\[ t = \frac{\xi^2}{F} \]

\[ \zeta = \frac{\gamma}{\zeta^2} \]

which gives

\[ \frac{d9}{dx} \frac{d9}{dx} \frac{d^2 B}{dx^2} \frac{d(-p)}{dx} \]

The initial and boundary conditions of Eq. (13), based on the above parameters are given below.
Initial condition

\[ x = 0, \ G(x, 0) = 1 \]  \hspace{1cm} (14)

Boundary conditions

\[ T > 0, \ x = 0; \ \frac{\partial T}{\partial x} = 0 \] \hspace{1cm} (15)

\[ T > 0, \ x = l; \ \frac{\partial T}{\partial x} = -6H \] \hspace{1cm} (16)

where

\[ H = \frac{R}{k} \left( h + \epsilon \sigma \left( R_1^2 + T^2 T_1^2 + (T_1 T_2 + T_2 T_1) \right) \right) \]  \hspace{1cm} (17)

Now it is possible to solve the set of Eqs. (13)–(17). However, in order to solve Eq. (13), it is essential to obtain the value of \( \frac{d(\rho - \rho_0)}{dt} \) from the kinetic mechanism discussed by Srivastava et al. [12].

According to the kinetic mechanism of Srivastava et al. [12], it is observed that (Appendix I)

\[ \frac{dp}{dt} = \frac{dC_B}{dt} + \frac{dC_{ci}}{dt} + \frac{dC_{C2}}{dt}, \]  \hspace{1cm} (18)

As CQ1 and CQ2 are liberated in the gaseous form, they do not contribute to the change in density as a function of time.

Introducing \( T = \alpha t/R^2 \) in Eq. (18) gives

\[ \frac{dp}{dx} - \frac{dC_B}{dx} + \frac{dC_{ci}}{dx} + \frac{dC_{C2}}{dx} \]  \hspace{1cm} (19)

Based on the kinetic scheme discussed in Appendix I

\[ \frac{dC_{B}}{dt} + \frac{dC_{Cl}}{dt} + \frac{dC_{C2}}{dt} = -k_1(C_B)^{n_1} \]  \hspace{1cm} (20)

and

\[ t = \frac{\tau}{\alpha} \]

\[ dt = \frac{R^2 d\tau}{\alpha} \]

and therefore

\[ \frac{\alpha}{R^2} \frac{dC_B}{d\tau} + \frac{dC_{Cl}}{d\tau} + \frac{dC_{C2}}{d\tau} = -k_1(C_B)^{n_1}. \]  \hspace{1cm} (21)

Introducing Eq. (21) in Eq. (19) gives
Introducing Eq. (22) in Eq. (13) results in the following heat transfer equation

\[
\frac{d(e)}{dx} = \frac{1}{a} \int \frac{d^2 e}{dx^2} \cdot \frac{Q^2 \cdot J \cdot C \cdot B \cdot T}{a}.
\]  

Now, it is essential to solve the above equation based on the initial and boundary conditions given by Eqs. (14)–(16).

4. Numerical scheme

The equations derived earlier as Eq. (23), with the initial and boundary conditions specified in Eqs. (14)–(16) were converted to finite difference equations utilizing a backward implicit scheme, as given below (Fig. 1)

\[
\left(1 - \frac{1}{2H^2} \right) \left( \theta_{J,I+1} - \theta_{J,I-1} \right) + \left( \frac{1}{H^2} \right) \hat{\theta}_{J,I+1} + \left( \frac{Q^2 k_1 a}{a} \right) - \left( \frac{\theta_{J,I} - \theta_{J-1,I}}{H^2} \right) = \left( \frac{1}{2H^2} \right) \theta_{J,I+1} + \left( \frac{1}{H^2} \right) \theta_{J,I-1} + \left( \frac{Q^2 k_1 a}{a} \right) \left( \frac{1}{2H^2} H_{J+1} K \right).
\]  

Combining similar terms having the same subscripts in Eq. (24) leads to the following equation which, in the form given below, would facilitate numerical solution

\[
\left( \frac{1}{2H^2 X} + \frac{1}{H^2} \right) \theta_{J,I+1} + \left( -\frac{2}{H^2} \right) \theta_{J,I} + \left( -\frac{1}{H^2} \right) \theta_{J,I-1} + \left( \frac{Q^2 k_1 a}{a} \right) \left( \frac{1}{H^2} \right) \theta_{J+1,I} = \left( \frac{1}{H^2} \right) \theta_{J-1,I} - \left( \frac{Q^2 k_1 a}{a} \right) \left( \frac{1}{H^2} \right) \theta_{J,I}.
\]  

The above equation, along with the boundary conditions, results in a tridiagonal banded matrix for points 7 = 1 (Centre of pellet), 7 = 2, to 7 = M and I = M (wall of pellet). The above tridiagonal matrix is utilized for computation of the unknown temperatures from 7 = 1 to 7 = Max at the unknown level J = 2 from the known temperature at level I = 1. Once the temperatures at I = 2 are computed, it is possible to compute the temperatures at I = 3 and the process could be continued iteratively further, depending upon the conditions of the problem, and in this case, till the time when no further reactions take place (say I = N).

The above representation results in a tridiagonal matrix of the solution, and in order to conserve storage space in the computer, the Mx M matrix is converted to Mx 3. The above
The equation in matrix notation is of the form
\[ AX = B. \]

\( X \) is the solution vector at \( I = 1 \) to \( M \), denoting the change in temperature at a particular \( I \), when the values at \( J-1 \) are known a priori. The value of \( X \) is obtained based on a method developed by Srivastava [15].

It was essential to ascertain the most appropriate grid sizes, i.e. the values of \( H_1 \) and \( H_2 \). Commencing with a value of \( H_1 = 0.1 \), results were obtained and compared with \( M = 21 \), \( M = 51 \), \( M = 81 \), \( M = 101 \) and \( M = 126 \). It was observed that there was no difference in the results obtained for \( M = 101 \) and \( M = 126 \), and in order to save computer time, \( M = 101 \) was considered as the grid size, so that stability of the solution is assured. Further, in the axial
direction, values of $Hi$ were varied from 0.05, 0.1 and 0.2, and no difference was observed in the results obtained. Therefore, $Hi = 0.1$ has been considered in the present study.

The physical parameters for the solution of the above model are given below, and the biomass considered is wood:

\[ AH = -255 \times 10^3 \text{ J/kg} \]

\[ C_p = 1112 \pm 4.85 \times (T-273) \text{ J/kg K} \]

\[ \text{Pin} = 650 \text{ kg/m}^3 \]

\[ T_F = 873.0 \text{ K} \]

\[ T_o = 473.0 \text{ K} \]

\[ RR = 0.005 \text{ m} \]

\[ a = 1.79 \times 10^{-7} \text{ m}^2/\text{s} \]

\[ k = 1.13 \times 0.003(T-273) \text{ W/m K} \]

\[ s = 0.95 \]

\[ a = 5.67 \times 10^{-8} \text{ W/m}^2\text{K}^4 \]

\[ h = 0.322 \text{ W/m}^2 \text{ K.} \]

5. Results and discussion

In an earlier work done by Srivastava et al. [12], concentration profiles of the products were obtained based on the kinetic mechanism shown in Appendix I. Typical concentration profiles for the isothermal condition of 773 K are shown in Fig. 2. However, in the non-isothermal case, the concentration profiles change significantly as shown in Figs. 3 and 4 based on a heating rate of 25 and 80 K/min.

The above concentration profiles were obtained keeping in view the linear relationship between time and temperature. However, when the heat transfer Eq. (23) is solved, the temperature profile as a function of radial distance at various time intervals is shown in Fig. 5 for a particle size of 0.005 m. Similar profiles are obtained for other sizes of particles ranging from 0.002 to 0.022 m.

Figs. 6, 7 and 8 show the temperature profiles at various time intervals when constant temperatures are applied to the surface of the pellet of 600, 750 and 900 K, respectively. It is observed that, as the constant wall temperature is increased, the pyrolysis is completed faster. In the case of 900 K, the pyrolysis is completed within 1.4 s.

Figs. 9 and 10 depict and compare the results obtained without considering, first, the effect of convective heat transfer and, subsequently, of radiative heat transfer at the wall, separately. It is observed that, in the absence of convective heat transfer at the wall (Fig. 9), no appreciable difference is seen in the temperature profile when compared to the original (Fig. 5). In the absence of radiative heat transfer effects at the wall, the reaction takes place very slowly, and the increase in temperature is insignificant, as shown in Fig. 10. Further, in the absence of radiative heat transfer at the wall and an increase by 10 times of the convective heat transfer coefficient, as shown in Fig. 11, the effect of convection on the temperature profile is observed,
Fig. 2. Concentration vs time.

Temperature K

Fig. 3. Concentration vs time/temperature.
Fig. 4. Concentration vs time/temperature.

Fig. 5. Radial distance vs temperature.
Fig. 6. Radial distance vs temperature.

Fig. 7. Radial distance vs temperature.
Fig. 8. Radial distance vs temperature.

Fig. 9. Radial distance vs temperature.
Fig. 10. Radial distance vs temperature.

Fig. 11. Radial distance vs temperature.
and a temperature increase of 20 K is achieved, when compared to the very marginal increase in Fig. 10.

6. Experimental validation and comparison

The model developed in the present study is compared with the model developed by Pyle and Zaror [27] and also with the experimental results obtained by them. The experimental procedure used by Pyle and Zaror [27] for the pyrolysis of wood is discussed below, keeping in mind that the main components of the pyrolysis of wood are virtually carbonised at temperatures about 430°C. Pyle and Zaror [27] performed carefully controlled studies on the course of pyrolysis of cylindrical samples of wood. The experiments were performed in an inert constant temperature environment. Independent measurements of the instantaneous sample weight and the radial temperature profile were made. It is noteworthy that all the parameters required to test the model were either independently and directly measured or estimated from the literature.

Fig. 12 shows the temperature profile as a function of time at the centre of the cylindrical pellet, \( r/R = 0.0 \). This is compared with the experimental data of Pyle and Zaror [27] obtained.
Fig. 13. Time vs temperature.

Fig. 14. Time vs temperature.
for the centre of the pellet. The experimental data shows excellent agreement with the present model predictions.

However, when the final temperature is increased from 643 to 780 K keeping the particle size constant, the variation between the experimental data and the temperature profile obtained in the present model at the centre of the pellet is greater, as shown in Fig. 13. The marginally higher variation from the experimental data and the present model at higher temperatures is due to the fact that, at higher temperatures, the cellulose polymers begin to decompose rapidly, suggesting that secondary pyrolysis reactions and convective effects are important.

Figs. 14, 15 show the temperature profiles when the particle size is increased from 0.003 to 0.0075 m, and the final temperature is increased from 660 to 773 K, respectively. Similar observations to those drawn for Figs. 12 and 13 are clear from Figs. 14 and 15 also.

However, Figs. 16, 17, 18 and 19 show the temperature profiles for a cylindrical pellet as a function of radial distance for 2, 4, 6 and 11 min, respectively, for a final temperature of 643 K. The model developed by Pyle and Zaror [27] shows excellent agreement in both cases. Further, it is also showing negligible variation when compared to the experimental data shown in Figs. 16-19, as shown in Table 1.

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![Diagram](image-url)

**Legend**
- Present model
- Experimental (Pyle & Zaror)

**Fig. 15. Time vs temperature.**
Fig. 16. Radial distance vs temperature.

Fig. 17. Radial distance vs temperature.
Fig. 18. Radial distance vs temperature.

Fig. 19. Radial distance vs temperature.
Fig. 20. Radial distance vs temperature.

RR = 0.011 m (radius), To = 303.0 K, Tf = 753.0 K, Time = 2 min.

Fig. 21. Radial distance vs temperature.

RR = 0.011 m (radius), To = 303.0 K, Tf = 753.0 K, Time = 3 min.
Table 1
$T_o = 303, T_F = 643, RR = 0.011 \text{ m}$

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Figs. 20 and 21 show the above temperature profiles at an elevated final temperature of 753 K as a function of radial distance for 2 and 3 min, respectively, showing excellent correlation, as shown in Table 2.

Therefore, the experimental results [27], based on the data presented here are in accordance with the predictions of the theory.

7. Summary and conclusion

The major conclusion resulting from the present study is the possibility of modelling the process of pyrolysis of a single biomass particle by coupling together the heat transfer equation with the pyrolysis rate kinetic equations, which are based on the fundamental mechanism of pyrolysis, where a number of differential equations describe the mass change of the biomass and the secondary reactions of the products during the pyrolysis process. However, the model of Pyle and Zaror [27] assumes first order kinetics for the rate equation while developing the mathematical model for pyrolysis. Consequently, the model developed by the authors is closer to the experimental data obtained by Pyle and Zaror, when compared to the mathematical model of Pyle and Zaror [27], as is clear from Tables 1 and 2.

The pyrolysis rate has been simulated by a kinetic scheme involving three chemical reactions, i.e. two parallel reactions for the primary conversion and a third secondary reaction between the volatiles and gaseous products and char. The secondary reactions enable the carbon

Table 2
$T_o = 303, T_F = 753, RR = 0.011 \text{ m}$

<table>
<thead>
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<th>$r/r_0$</th>
<th>Temp. exp.</th>
<th>Model present (2 min)</th>
<th>Pyle-Zaror</th>
<th>Temp. exp.</th>
<th>Model present (3 min)</th>
<th>Pyle-Zaror</th>
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</table>
enrichment of the final residue. By using the above suggested model, it is possible to predict
the rate of pyrolysis and the concentrations of the various substances involved over a wide
range of temperature and particle dimensions. However, the model of Pyle and Zaror [27] is
able to predict the temperature profile accurately at low temperatures. However, the present
model provides more accurate temperature prediction at both low and high temperatures. The
effects are more pronounced at higher temperatures, as the present model is based on less
restrictive assumptions with respect to the accumulation term and the reaction rate term, when
compared to the model of Pyle and Zaror [27]. It is observed that, for particle sizes below
1 mm, the process of pyrolysis is controlled by the primary pyrolysis reactions and possibly, by
the external heat transfer. For particles greater than 1 mm, heat transfer, primary pyrolysis and
secondary pyrolysis control the pyrolysis process. As the pyrolysis temperature and particle size
increases, the relative importance of heat transfer and secondary reactions increases, and in
such cases, the model of the authors provides more accurate predictions.

The most surprising result of this study is that a simple model with very few restrictive
assumptions, when compared to models developed earlier by Pyle and Zaror [27],
Koufopanous et al. [1] etc., can describe the overall progress of a set of processes of great
complexity like pyrolysis.

The findings of this study are also relevant for reactor design, since it has been observed that
simple models, like the one developed in this paper, are generally adequate for this purpose.
The implications of this work for reactor modelling need to be analysed in detail.

This model could be utilized to predict the concentration profiles for all types of biomass for
a wide range of isothermal and non-isothermal conditions and temperature. Therefore, the
model could be universally applied to obtain concentration and temperature profiles for all
types of biomass. also, the concentration of char, volatiles and gases could be predicted by the
model and could also be measured experimentally in order to verify the model equations and
assumptions, which has been done to a limited extent by Pyle and Zaror [27]. Although, it has
not been possible to test the theory over the complete range of relevant parameters, the
theoretical predictions are consistent with experimental results and more accurate than other
models developed for pyrolysis in the past, including that of Pyle and Zaror [27].

Appendix I

Srivastava et al. [12] proposed the following mechanism for description of the kinetics of the
pyrolysis of biomass
Virgin Biomass ($n_2$ order decay) \[ \rightarrow \]

1 reaction \[ \rightarrow \]

2 reaction \[ \rightarrow \]

3 reaction \[ \rightarrow \]

(Volatile + Gases) \[ \rightarrow \]

(Char) \[ \rightarrow \]

(Volatile+Gases) + (Char)

This model indicates that the biomass decomposes to volatile, gases and char. 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 a modified final product distribution.

1.0.1. Modelling equations

The ordinary differential equations describing the mass change of the biomass and secondary reactions of products based on the above kinetic mechanism are given below for the process of pyrolysis:

\[
\frac{dC_B}{dt} = -k_1(C_B)^{n_1} - k_2(C_B)^{n_2} = -(k_1 + k_2)(C_B)^{n_1} \quad (A1)
\]

\[
\frac{dC_{Gl}}{dt} = k_1(C_B)^{n_1} - k_3(C_{Gl})^{n_3}(C_{Cl})^{p_3} \quad (A2)
\]

\[
\frac{dC_{Cl}}{dt} = k_2(C_B)^{n_2} - k_3(C_{Gl})^{n_3}(C_{Cl})^{p_3} \quad (A3)
\]

\[
\frac{dC_{G2}}{dt} = k_3(C_{Gl})^{n_3}(C_{Cl})^{p_3} \quad (A4)
\]

\[
\frac{dC_{G1}}{dt} = MC_{Gl}^{n_3}XClP \quad (A5)
\]

where (Koufopanos et al. [1])

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

\[
k_2 = A_2 Q_{x_1} \sqrt{D_2/T} + \left( \frac{L_2}{t} \right)
\]
\[ k_3 = A_3 \exp \left( -\frac{E_3}{RT} \right) \]

and

\[ A_1 = -9.973 \times 10^{-5} \text{V}^{-1} \]
\[ A_2 = 1.068 \times 10^{-3} \text{V}^{-1} \]
\[ A_3 = 8.3 \times 10^2 \text{V}^{-1} \]
\[ D_1 = 17254.4 \text{K} \]
\[ D_2 = 10224.4 \text{K} \]
\[ L_1 = -9061227 \text{K}^2 \]
\[ L_2 = -6123081 \text{K}^2 \]
\[ \xi_3 = 81 \text{kJ/mol} \]

Adding eqns (A1), (A3) and (A5) gives

\[
\frac{dC_B}{dt} + \frac{dC_{C1}}{dt} + \frac{dC_{C2}}{dt} = -k_1 (C_B)^n
\]

which is equal to \(\frac{dp}{dt}\).

Hence

\[
\frac{dp}{dt} = -k_1 (C_B)^n.
\]

References


