Analysis of Pyrolysis Kinetics of Biomass Particle Under Isothermal and Non-Isothermal Heating Conditions using Differential Transformation Method

By M. G. Sobamowo, S. J. Ojolo & C. A. Osheku

University of Lagos

Abstract- "In this study, differential transformation method is applied to analyze pyrolysis kinetics of biomass particle under isothermal and non-isothermal heating conditions. The developed analytical solutions to the system of pyrolysis kinetic models are used to investigate the effects of heating conditions and heating rates on the pyrolysis residence time and technologies. Also, in order to verify the analytical solutions, the developed analytical solutions of the kinetic models using differential transformation method are compared with the results of the solutions of exact analytical method. Additionally, good agreements are established between the present results and the past works. It is therefore expected that this study will enhance the understanding of the pyrolysis process by giving physical insights into the various factors and the parameters affecting the phenomena."

ANALYSISOFPYROLYSISKINETICSOFBIOMASSPARTICLEUNDERISOTHERMALANDNONISOTHERMALHEATINGCONDITIONSUSINGDIFFERENTIALTRANSFORMATIONMETHOD

Strictly as per the compliance and regulations of:

Analysis of Pyrolysis Kinetics of Biomass Particle Under Isothermal and Non-Isothermal Heating Conditions using Differential Transformation Method

M. G. Sobamowo [α], S. J. Ojolo [σ] & C. A. Osheku [ρ]

Abstract- "In this study, differential transformation method is applied to analyze pyrolysis kinetics of biomass particle under isothermal and non-isothermal heating conditions. The developed analytical solutions to the system of pyrolysis kinetic models are used to investigate the effects of heating conditions and heating rates on the pyrolysis residence time and technologies. Also, in order to verify the analytical solutions, the developed analytical solutions of the kinetic models using differential transformation method are compared with the results of the solutions of exact analytical method. Additionally, good agreements are established between the present results and the past works. It is therefore expected that this study will enhance the understanding of the pyrolysis process by giving physical insights into the various factors and the parameters affecting the phenomena."

Keywords: biomass particle; pyrolysis kinetics; isothermal temperature; non- isothermal heating rates; differential transformation method.

I. Introduction

The important and the centrality of pyrolysis process in the thermochemical biomass conversion processes of biomass have increased the research interests in the studies of the energy conversion processes. In the study of biomass gasification processes, although, overall process of pyrolysis appears simple but the sequence of reactions is complex and involves both endothermic and exothermic processes whose thermodynamics and kinetics are poorly understood [1]. Under such complex phenomena, it is impossible to formulate a complete mathematical model of pyrolysis which will still be mathematically tractable. However, as a compromise between mathematical tractability and accuracy of description, simplified models are employed under certain defined conditions to predict the conversion process of biomass particle. In fact, the need for the simple rationally-based models of pyrolysis as a basis for reactor design has been identified in the survey of low temperature (i.e. less than 600^{0}C) pyrolytic conversion of biomass to usable forms of energy since the complications involved in the numerical solution of a more sophisticated models make them unsuitable for design and prediction purposes [1]. One angle of approach had been adopted to develop simple and economic models which aggregate the more important aspects of the sequence of events as a solid sample is pyrolyzed. The heat conduction equations in a pyrolysizing solid fuel such as wood were first combined with those for heat generation by Bamford [2], assuming a first order single step reaction. The model developed by Bamford has been used by various researchers [3, 4, and 5]. The effects of internal convection and variable transport properties were later incorporated by Matsumoto et al [6], Roberts [7] and Kung [8]. The effect of char formation was considered by Kung [8], and the rate of char removal by oxidation was modelled by Matsumoto et al [6]. Temperature-dependent property variation was also studied by Matsumoto et al [6], Kung [8], Maa and Baille [9], Kansa *et al*. [10], Chan et al, [11]. Multi-step reaction schemes have been presented by Kung [8], Chan *et al*. [11] and Koufopanos *et al*. [12]. The heat of reaction of pyrolysis have been modelled by Lee *et al*. [13], while the effect of anisotropy of the pyrolysing medium has been considered by Kansa *et al*. [10]. Maa and Baille [9] proposed an 'unreacted shrinking core model' for high temperatures. Miyanamie [14] studied the effects of heat of reaction and Lewis number on the pyrolysis of solid particle. For the motion of the gases within the solid, a momentum equation was included [10]. Fan *et al*. [15] developed a 'volume reaction' model taking into account simultaneous heat and mass transfer in the particle. Pyle and Zaror [1] experimentally investigated the pyrolysis of biomass. Simmons [16] analysed a simplified heat transfer model with an assumed first order reaction for the estimation of an upper bound for biomass particle size in conducting experimental pyrolysis kinetic. Villermaux *et al*. [17] presented a Volatilization Thermal Penetration model (VTP) for any kind of solid reaction where volatilization is controlled by heat conduction from the outer surface. On the

Author α: Department of Mechanical Engineering, University of Lagos, Akoka, Lagos, Nigeria. e-mail: mikegbeminiyiprof@yahoo.com
Author σ: Centre for Space Transport and Propulsion, National Space Research and Development Agency, Federal Ministry of Science and Technology, FCT, Abuja, Nigeria.

modeling of pyrolysis of biomass particle, particularly on the studies of the kinetic, thermal and heat transfer effects, Koufopanos et al. [12] assumed the pyrolysis process to be primary and secondary kinetic reactions.

Di Blasi [18] analysed the effects of convection and secondary reactions within porous solid fuels undergoing pyrolysis. Melaaen and Gronli [19] presented models on moist wood drying and pyrolysis. Jalan and Srivastava [20] explored kinetic and heat transfer effects on the pyrolysis of a single biomass cylindrical pellet. Ravi [21] proposed a semi-empirical model for pyrolysis of sawdust in an annular packed bed using pseudo-first order reaction for the chemical reaction of the pyrolysis. In their model, Babu and Chaurasia [22] considered time-dependent density and temperature-dependent specific heat capacity of biomass to investigate the dominant design variables in pyrolysis of biomass particles of different geometries in a thermally thick regime. In the recent time, Sheth and Babu [23], presented Kinetic Model for biomass pyrolysis and concluded that pyrolysis in wood is typically initiated at 200°C and lasts till 450-500°C, depending on the species of wood. Yang et al [24] presented that the major stage of biomass pyrolysis occurs between 250-450°C. Mandl et al. [25], pointed out in their work that the pyrolysis of softwood pellets takes place at around 425K and char particles and volatiles are formed while Weerachanchai et al. [26] submitted that the major decomposition of all biomasses occurred in the range of 250-400°C. Slopiecka et al. [27], in their studies of poplar wood, concluded that the decomposition of hemicelluloses and cellulose take place in active pyrolysis in the temperature from 473-653K and 523-623K, respectively. They then added that Lignin decomposes in both stages: active and passive pyrolysis in the range from 453-1173K without characteristics peaks.

Studies on the analysis of biomass kinetics have been based on numerical approach because of the non-linear nature of the developed models. However, the classical way of finding analytical solution is obviously still very important since it serves as an accurate benchmark for numerical solutions. Therefore, as a mean of investigating and presenting the exact effects of various parameters in the pyrolysis kinetics thereby increasing the predictive power, this study also presents the analytical solutions of pyrolysis kinetics of biomass particle using differential transform method (DTM). Although, this concept was introduced by Zhou [40], its applications to both linear and non-linear differential and system of differential equation have fast gained ground or appeared in many engineering and scientific research. The potentiality of the method is displayed in the provisions of symbolic or analytical solutions to both linear and non-linear integral and differential equations without linearization, discretization or perturbation. DTM is capable of greatly reducing the

size of computational work while still accurately providing the series solution with fast convergence rate.

As good and accurate the method presents itself, to the best of the authors' knowledge, it has not been applied for the study and the analysis of biomass pyrolysis kinetic and thermal decomposition. Therefore, in this study, differential transformation method is applied to study the pyrolysis kinetics of biomass particle under isothermal and non-isothermal heating conditions. Also, through the solutions of the method for the problems under investigation, simulations are carried out to study the effects of pertinent models parameters, isothermal and non-isothermal heating conditions on the pyrolysis kinetics of biomass particles.

II. Pyrolysis Kinetics and Heat Transfer

Heat is transferred to the biomass particle surface from gaseous surrounding by conduction, radiation and/ or convection and then to the interior of the particle mainly by conduction. The temperature inside the particles increases as the heat penetrates more into the interiors of the solid causing moisture evaporation i.e. drying off the moisture. The rate of drying depends upon the temperature, velocity, and moisture content of the drying gas, as well as the external surface area of the feed material, the internal diffusivity of moisture and the nature of bonding of moisture to that material, and the radiative heat transfer. As the temperature increases, biomass particle decomposes into charcoal, tar and gaseous products. The amounts of each of these products vary depending on the zone temperature, rate of heating, structure, and composition and size of catalysts.

The kinetic scheme as shown in fig.1 describes the process of pyrolysis (primary and secondary) which involves thermal decomposition of biomass into gases, tar (liquid product of biomass pyrolysis, known as bio-oil or pyrolysis oil) and char, and the tar further decompose into char and gases
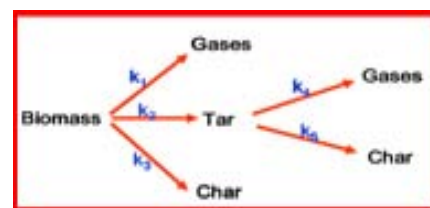

Fig. 1: Two-stage parallel reaction model of biomass pyrolysis

This two-stage parallel reaction model of biomass pyrolysis has previously been used by other researchers [10,13, 17, 18, 19, 21, 35]. According to the two-stage parallel reaction model, the biomass undergoes thermal degradation according to primary reactions $(k_1; k_2; k_3)$ giving gas, tar and char as

products. Tar may undergo secondary reactions (k_4, k_5). This model shows to be the most classical models for wood pyrolysis (Prakash and Karunanithi [39]).

The kinetic equations of pyrolysis, the heat transfer model and the corresponding initial and boundary conditions are given as

$$\frac{\partial C_B}{\partial t} = -(k_1 + k_2 + k_3)C_B \qquad (1a)$$

$$\frac{\partial C_T}{\partial t} = k_2 C_B - \varepsilon(k_4 + k_5)C_T \qquad (1b)$$

$$\frac{\partial C_C}{\partial t} = k_3 C_B + \varepsilon k_5 C_T \qquad (1c)$$

$$\frac{\partial C_G}{\partial t} = k_1 C_B + \varepsilon k_4 C_T \qquad (1d)$$

where

$$k_i = A_i \exp\left[\left(\frac{-E_i}{RT}\right)\right] \qquad i = 1-5$$

The initial conditions for the kinetic equations are;

$$t = 0, C_B = C_{B0}, \quad C_C = C_G = C_T = 0 \qquad (2)$$

For the Isothermal condition, $T=T_o$

$$k_i = A_i \exp\left[\left(\frac{-E_i}{RT_o}\right)\right] \qquad i = 1-5 \qquad (3)$$

Srivastava [23] assumed that in the thermo-gravimetric analysis, the temperature and time have a linear relationship (non-isothermal heating condition).

This therefore led to the appropriate representation to describe the Srivastava's assumption as;

$$T = T_o + \beta t \qquad (4)$$

where T_o is the initial temperature in K, β is the heating rate in K/s and t is the time in s.

Which makes

$$k_i = A_i \exp\left[\left(\frac{-E_i}{R(T_o + \beta t)}\right)\right] \qquad i = 1-5 \qquad (5)$$

The above kinetic models were non-dimensionalized as using the following dimensionless parameters;

$$\overline{C}_B = \frac{C_B}{C_{Bo}} \qquad \overline{C}_{G1} = \frac{C_{G1}}{C_{Bo}} \qquad \overline{C}_{C1} = \frac{C_{C1}}{C_{Bo}} \qquad \overline{C}_{G2} = \frac{C_{G2}}{C_{Bo}} \qquad \overline{C}_{C2} = \frac{C_{C2}}{C_{Bo}} \qquad C_{C2} = \frac{\overline{C}_{C2}}{C_{Bo}} \qquad (6)$$

However, for the sake of cleanliness, the bars are removed in the solutions and the non-dimensionless form of Eqs. (1a-1d) still look like the same equation. In order to avoid seemingly similar equations, the non-dimensionless forms of Eqs. (1a-1e) were not written out in this work.

III. METHOD OF SOLUTION: DIFFERENTIAL TRANSFORM METHOD

The simultaneous kinetic models in Eqs. (1a)-(1d) are solved using differential transformation method as introduced by Zhou [50]. The basic definitions and the operational properties of the method are as follows: If $u(t)$ is analytic in the domain T, then the function $u(t)$ will be differentiated continuously with respect to time t.

$$\frac{d^p u(t)}{dt^p} = \varphi(t, p) \text{ for} \qquad \text{all } t \in T \qquad (7)$$

for $t = t_i$, then $\varphi(t, p) = \varphi(t_i, p)$, where p belongs to the set of non-negative integers, denoted as the p-domain. We can therefore write Eq. (7) as

$$U(p) = \varphi(t_i, p) = \left[\frac{d^p u(t)}{dt^p}\right]_{t=t_i} \qquad (8)$$

where U_p is called the spectrum of $u(t)$ at $t = t_i$

Expressing $u(t)$ in Taylor's series as

$$u(t) = \sum_{p}^{\infty}\left[\frac{(t - t_i)^p}{p!}\right] U(p) \qquad (9)$$

where Equ. (9) is the inverse of $U(k)$ us symbol 'D' denoting the differential transformation process and combining (8) and (9), we have

$$u(t) = \sum_{p=0}^{\infty}\left[\frac{(t - t_i)^p}{p!}\right] U(p) = D^{-1}U(p) \qquad (10)$$

Table 3: Operational properties of differential transformation method

S/N	Function	Differential Transform
1	$u(t) \pm v(t)$	$U(p) \pm V(p)$
2	$\alpha u(t)$	$\alpha U(p)$
3	$\dfrac{du(t)}{dt}$	$(p+1)U(p+1)$
4	$u(t)v(t)$	$\displaystyle\sum_{r=0}^{p} V(r)U(p-r)$
5	$u^m(t)$	$\displaystyle\sum_{r=0}^{p} U^{m-1}(r)U(p-r)$
6	$\dfrac{d^n u(t)}{dx^n}$	$(p+1)(p+2)\cdots(p+n)U(p+n)$
7	$\sin(\omega t + \alpha)$	$\dfrac{\omega^p}{p!}\sin\left(\dfrac{\pi p}{2!}+\alpha\right)$
8	$\cos(\omega t + \alpha)$	$Z(p) = \dfrac{\omega^p}{p!}\cos\left(\dfrac{\pi p}{2!}+\alpha\right)$

Using the operational properties of the differential transformation method, the differential transformations of Eqs. (1a)-(1d) under isothermal condition are

$$C_B(p+1) = -\frac{k_1 + k_2 + k_3}{(p+1)}C_B(p) \qquad (11a)$$

$$C_T(p+1) = \frac{k_2}{(p+1)}C_B(p) - \frac{\varepsilon(k_4 + k_5)}{(p+1)}C_T(p) \quad (11b)$$

$$C_C(p+1) = \frac{k_3}{(p+1)}C_B(p) + \frac{\varepsilon k_5}{(p+1)}C_T(p) \qquad (11c)$$

$$C_G(p+1) = \frac{k_1}{(p+1)}C_B(p) + \frac{\varepsilon k_4}{(p+1)}C_T(p) \qquad (11d)$$

The solutions of the of the kinetic equations for the isothermal condition are given as follows:

The analysis of $C_B(p+1)$:

From Equ. (11a), we have

$$C_B(p+1) = \frac{-(k_1 + k_2 + k_3)}{p+1}C_B(p)$$

Analyzing the differential transform in Eq. (11a), we have

$$C_B(1) = -(k_1 + k_2 + k_3)C_{Bo}, \quad C_B(2) = \frac{(k_1 + k_2 + k_3)^2}{2}C_{Bo}, \quad C_B(3) = \frac{-(k_1 + k_2 + k_3)^3}{6}C_{Bo}$$

$$C_B(4) = \frac{(k_1 + k_2 + k_3)^4}{24}C_{Bo}, \quad C_B(5) = \frac{-(k_1 + k_2 + k_3)^5}{120}C_{Bo}, \quad C_B(6) = \frac{(k_1 + k_2 + k_3)^6}{720}C_{Bo}$$

$$C_B(7) = \frac{-(k_1 + k_2 + k_3)^7}{5040}C_{Bo}, \quad C_B(8) = \frac{(k_1 + k_2 + k_3)^8}{40,320}C_{Bo}, \ldots \; C(n) = (-1)^n\frac{(k_1 + k_2 + k_3)^n}{n!}C_{Bo}$$

Applying the inverse differential transform,

$$C_B(t) = C_B(0) + C_B(1)t + C_B(2)t^2 + C_B(3)t^3$$

$$+ C_B(4)t^4 + C_B(5)t^5 + C_B(6)t^6 + C_B(7)t^7 + C_B(8)t^8 + \ldots + C_B(n)t^n \qquad (12)$$

After substituting the results in the above analysis into Eq. (12), we have

$$C_B(t) = C_{Bo} - [(k_1 + k_2 + k_3)]C_{Bo}t + \left[\frac{(k_1 + k_2 + k_3)}{2}\right]C_{Bo}t^2 - \left[\frac{(k_1 + k_2 + k_3)^3}{6}\right]C_{Bo}t^3 + \left[\frac{(k_1 + k_2 + k)^4}{24}\right]C_{Bo}t^4$$

$$- \left[\frac{(k_1 + k_2 + k_3)^5}{120}\right]C_{Bo}t^5 + \frac{(k_1 + k_2 + k_3)6}{720}C_{Bo}t^6 - \left[\frac{(k_1 + k_2 + k_3)^7}{5040}\right]C_{Bo}t^7 + \left[\frac{(k_1 + k_2 + k_3)^8}{40,320}\right]C_{Bo}t^8$$

$$-\left[\frac{(k_1+k_2+k_3)^9}{362880}\right]C_{Bo}t^9+\left[\frac{(k_1+k_2+k_3)^{10}}{3628800}\right]C_{Bo}t^{10}-\left[\frac{(k_1+k_2+k_3)^{11}}{39916800}\right]C_{Bo}t^{11}+\left[\frac{(k_1+k_2+k_3)^{12}}{479001600}\right]C_{Bo}t^{12}$$

$$-\left[\frac{(k_1+k_2+k_3)}{6227020800}\right]C_{Bo}t^{13}+\left[\frac{(k_1+k_2+k_3)}{87178291200}\right]C_{Bo}t^{14}-\left[\frac{(k_1+k_2+k_3)}{1307674368000}\right]C_{Bo}t^{15}+... \tag{13}$$

Which can be written as

$$C_B(t)=C_{Bo}\left[\begin{array}{l}1-(k_1+k_2+k_2)t+\dfrac{\left(k_1+k_2+k_2\right)^2}{2}t^2-\dfrac{\left(k_1+k_2+k_3\right)^3}{6}t^3+\dfrac{\left(k_1+k_2+k_3\right)^4}{24}t^4\\[2mm]-\dfrac{\left(k_1+k_2+k_3\right)^5}{120}t^5+\dfrac{\left(k_1+k_2+k_3\right)^6}{720}t^6-\dfrac{\left(k_1+k_2+k_3\right)^7}{5040}t^7+\dfrac{\left(k_1+k_2+k_3\right)^8}{40320}t^8\\[2mm]-\dfrac{\left(k_1+k_2+k_3\right)^9}{362880}t^9+.\dfrac{\left(k_1+k_2+k_3\right)^{10}}{3628800}t^{10}-\dfrac{\left(k_1+k_2+k_3\right)^{11}}{39916800}t^{11}+\dfrac{\left(k_1+k_2+k_3\right)^{12}}{479001600}t^{12}\\[2mm]-\dfrac{\left(k_1+k_2+k_3\right)^{13}}{6227020800}t^{13}+\dfrac{\left(k_1+k_2+k_3\right)^{14}}{87178291200}t^{14}-\dfrac{\left(k_1+k_2+k_3\right)}{1307674368000}t^{15}+...\end{array}\right] \tag{14}$$

Equ. (14) can be written as

$$C_{B0}(t)=C_{Bo}\sum_{p=0}^{N}\frac{(-1)^p}{p!}(k_1+k_2+k_3)^p t^p = C_{Bo}\,e^{-((k_1+k_2+k_3)t)} \tag{15}$$

The analysis of $C_T(p+1)$ *:*

From Equ. (11b)

$$C_T(p+1)=\frac{k_2}{(p+1)}C_B(p)-\frac{\varepsilon(k_4+k_5)}{(p+1)}C_T(p)$$

On analyzing the differential transform in Eq. (11b), we have

$$C_T(1)=k_2C_{Bo}$$

$$C_T(2)=-\left\{\frac{k_2(k_1+k_2+k_3)}{2}+\frac{\varepsilon k_2(k_4+k_5)}{2}\right\}C_{Bo}$$

$$C_T(3)=\left\{\frac{k_2(k_1+k_2+k_3)^2}{3}+\left\{\varepsilon k_2(k_4+k_5)\left[\frac{(k_1+k_2+k_3)}{6}+\frac{[\varepsilon(k_4+k_5)]^2}{6}\right]\right\}\right\}C_{Bo}$$

$$C_T(4) = -\left\{ \frac{k_2(k_1+k_2+k_3)^3}{24} + \frac{\varepsilon(k_4+k_5)}{4}\left\{ \frac{k_2(k_1+k_2+k_3)^2}{3} + \left\{ \varepsilon k_2(k_4+k_5)\left[\frac{(k_1+k_2+k_3)}{6} + \frac{[\varepsilon(k_4+k_5)]^2}{6} \right] \right\} \right\} \right\} C_{Bo}$$

$$C_T(5) = \left\{ \frac{k_2(k_1+k_2+k_3)^4}{120} + \frac{\varepsilon(k_4+k_5)}{5}\left\{ \frac{k_2(k_1+k_2+k_3)^3}{24} + \frac{\varepsilon(k_4+k_5)}{4}\left\{ \frac{k_2(k_1+k_2+k_3)^2}{3} + \left\{ \varepsilon k_2(k_4+k_5)\left[\frac{(k_1+k_2+k_3)}{6} + \frac{[\varepsilon(k_4+k_5)]^2}{6} \right] \right\} \right\} \right\} \right\} C_{Bo}$$

$$C_T(6) = -\left\{ \frac{k_2(k_1+k_2+k_3)^5}{720} + \frac{\varepsilon(k_4+k_5)}{6}\left\{ \frac{k_2(k_1+k_2+k_3)^4}{120} + \frac{\varepsilon(k_4+k_5)}{5}\left\{ \frac{k_2(k_1+k_2+k_3)^3}{24} + \frac{\varepsilon(k_4+k_5)}{4}\left\{ \frac{k_2(k_1+k_2+k_3)^2}{3} + \left\{ \varepsilon k_2(k_4+k_5)\left[\frac{(k_1+k_2+k_3)}{6} + \frac{[\varepsilon(k_4+k_5)]^2}{6} \right] \right\} \right\} \right\} \right\} \right\} C_{Bo}$$

and so on

Therefore, the differential transformation solution of C_T is given as

$$C_T(t) = C_T(0) + C_T(1)t + C_T(2)t^2 + C_T(3)t^3 + C_T(4)t^4 + C_T(5)t^5 + C_T(6)t^6 + ... + C_T(n)t^n \quad (16)$$

The analysis of $C_C(p+1)$:

From Equ. (11c)

$$C_C(p+1) = \frac{k_3}{(p+1)} C_B(p) + \frac{\varepsilon k_5}{(p+1)} C_T(p)$$

Analyzing Eq. (11c) as before, we have

$$C_C(1) = k_3 C_{Bo},$$

$$C_C(2) = -\left\{ \frac{k_3(k_1+k_2+k_3)}{2} - \frac{\varepsilon k_3 k_5}{2} \right\} C_{Bo}$$

$$C_C(3) = \left\{ \frac{k_3(k_1+k_2+k_3)^2}{3} - \left\{ \varepsilon k_3 k_5 \left[\frac{(k_1+k_2+k_3)}{6} + \frac{[\varepsilon k_3 k_5]^2}{6} \right] \right\} \right\} C_{Bo}$$

$$C_C(4) = -\left\{ \frac{k_3(k_1+k_2+k_3)^3}{24} - \frac{\varepsilon k_3 k_5}{4} \left\{ \frac{k_3(k_1+k_2+k_3)^2}{3} + \left\{ \varepsilon k_3 k_5 \left[\frac{(k_1+k_2+k_3)}{6} + \frac{(\varepsilon k_3 k_5)^2}{6} \right] \right\} \right\} \right\} C_{Bo}$$

$$C_C(5) = \left\{ \frac{k_3(k_1+k_2+k_3)^4}{120} - \frac{\varepsilon k_3 k_5}{5} \left\{ \frac{k_3(k_1+k_2+k_3)^3}{24} - \frac{\varepsilon k_3 k_5}{4} \left\{ \frac{k_3(k_1+k_2+k_3)^2}{3} - \left\{ \varepsilon k_3 k_5 \left[\frac{(k_1+k_2+k_3)}{6} - \frac{(\varepsilon k_3 k_5)^2}{6} \right] \right\} \right\} \right\} \right\} C_{Bo}$$

$$C_C(6) = -\left\{\frac{k_3(k_1+k_2+k_3)^5}{720} - \frac{\varepsilon k_3 k_5}{6}\left\{\frac{k_3(k_1+k_2+k_3)^4}{120} - \frac{\varepsilon k_3 k_5}{5}\left[\frac{k_3(k_1+k_2+k_3)^3}{24} - \frac{\varepsilon k_3 k_5}{4}\left[\frac{k_3(k_1+k_2+k_3)^2}{3} - \left\{\varepsilon k_3 k_5\left[\frac{(k_1+k_2+k_3)}{6} - \frac{(\varepsilon k_3 k_5)^2}{6}\right]\right\}\right]\right]\right\}\right\}C_{Bo}$$

and so on

The differential transformation solution of C_C is given as

$$C_C(t) = C_C(0) + C_C(1)t + C_C(2)t^2 + C_C(3)t^3 + C_C(4)t^4 + C_C(5)t^5 + C_C(6)t^6 + \ldots + C_C(n)t^n \quad (17)$$

The analysis of $C_C(p+1)$:

 From Equ. (11d)

$$C_G(p+1) = \frac{k_1}{(p+1)}C_B(p) + \frac{\varepsilon k_4}{(p+1)}C_T(p)$$

On analyzing Eq. (26d) as before, we have

$$C_G(1) = k_1 C_{Bo}$$

$$C_G(2) = -\left\{\frac{k_1(k_1+k_2+k_3)}{2} - \frac{\varepsilon k_1 k_4}{2}\right\}C_{Bo}$$

$$C_G(3) = \left\{\frac{k_1(k_1+k_2+k_3)^2}{3} - \left\{\varepsilon k_1 k_4\left[\frac{(k_1+k_2+k_3)}{6} + \frac{(\varepsilon k_1 k_4)^2}{6}\right]\right\}\right\}C_{Bo}$$

$$C_G(4) = -\left\{\frac{k_1(k_1+k_2+k_3)^3}{24} - \frac{\varepsilon k_1 k_4}{4}\left\{\frac{k_1(k_1+k_2+k_3)^2}{3} + \left\{\varepsilon k_1 k_4\left[\frac{(k_1+k_2+k_3)}{6} + \frac{(\varepsilon k_1 k_4)^2}{6}\right]\right\}\right\}\right\}C_{Bo}$$

$$C_G(5) = \left\{ \frac{k_1(k_1+k_2+k_3)^4}{120} - \frac{\varepsilon k_1 k_4}{5} \left\{ \begin{array}{c} \dfrac{k_1(k_1+k_2+k_3)^3}{24} \\ -\dfrac{\varepsilon k_1 k_4}{4} \left[\begin{array}{c} \dfrac{k_1(k_1+k_2+k_3)^2}{3} \\ -\varepsilon k_1 k_4 \left[\begin{array}{c} \dfrac{(k_1+k_2+k_3)}{6} \\ -\dfrac{(\varepsilon k_1 k_4)^2}{6} \end{array} \right] \end{array} \right] \end{array} \right\} \right\} C_{Bo}$$

$$C_G(6) = -\left\{ \begin{array}{c} \dfrac{k_1(k_1+k_2+k_3)^5}{720} \\ -\dfrac{\varepsilon k_1 k_4}{6} \left\{ \dfrac{k_1(k_1+k_2+k_3)^4}{120} - \dfrac{\varepsilon k_1 k_4}{5} \left\{ \begin{array}{c} \dfrac{k_1(k_1+k_2+k_3)^3}{24} \\ -\dfrac{\varepsilon k_1 k_4}{4} \left[\begin{array}{c} \dfrac{k_1(k_1+k_2+k_3)^2}{3} \\ -\varepsilon k_1 k_4 \left[\begin{array}{c} \dfrac{(k_1+k_2+k_3)}{6} \\ -\dfrac{(\varepsilon k_1 k_4)^2}{6} \end{array} \right] \end{array} \right] \end{array} \right\} \right\} \end{array} \right\} C_{Bo}$$

and so on

The differential transformation solution of C_C is given as

$$C_G(t) = C_G(0) + C_G(1)t + C_G(2)t^2 + C_G(3)t^3 + C_G(4)t^4 + C_G(5)t^5 + C_G(6)t^6 + ... + C_G(n)t^n \quad (18)$$

For the purpose of verifying the solution of the differential transformation method, exact analytical solutions using Laplace transform have been developed for Eqs. (1a)-(1d) subject to isothermal condition as

$$C_T = \frac{k_2 C_{Bo} \left[e^{-((k_1+k_2+k_3)t)} - e^{-\varepsilon((k_4+k_5)t)} \right]}{\varepsilon(k_4+k_5) - (k_1+k_2+k_3)} \quad (19b)$$

$$C_B = C_{Bo} \, e^{-((k_1+k_2+k_3)t)} \quad (19a)$$

$$C_C = \left\{ \frac{k_3 \left(1 - e^{-((k_1+k_2+k_3)t)}\right)}{(k_1+k_2+k_3)} - \frac{\varepsilon k_2 k_5 \left[\dfrac{\left(1 - e^{-((k_1+k_2+k_3)t)}\right)}{(k_1+k_2+k_3)} + \dfrac{\left(1 - e^{-(\varepsilon(k_4+k_5)t)}\right)}{\varepsilon(k_4+k_5)} \right]}{\varepsilon(k_4+k_5) - (k_1+k_2+k_3)} \right\} C_{Bo} \quad (19c)$$

$$C_G = \left\{ \frac{k_1\left(1-e^{-((k_1+k_2+k_3)t)}\right)}{(k_1+k_2+k_3)} - \frac{\varepsilon k_2 k_4 \left[\frac{\left(1-e^{-((k_1+k_2+k_3)t)}\right)}{(k_1+k_2+k_3)} + \frac{\left(1-e^{-(\varepsilon(k_4+k_5)t)}\right)}{\varepsilon(k_4+k_5)} \right]}{\varepsilon(k_4+k_5)-(k_1+k_2+k_3)} \right\} C_{Bo} \tag{19d}$$

Table 2: Kinetic constants used in the simulations

i	Reaction	$A_i(s^{-1})$	E_i (kJ/mol)	Source
1	Biomass→Gas	1.3×10^8	140	[11]
2	Biomass→Tar	2.0×10^8	133	[11]
3	Biomass→Char	1.08×10^7	121	[11]
4	Tar→Gas	4.28×10^6	107	[34]
5	Tar→Char	1.0×10^6	107	[34]

Table 3: Change in enthalpy values used in the simulations

i	Reaction	Δh_i (kJ/kg)	Source
1	Biomass→Gas	-418.0	[11]
2	Biomass→Tar	-418.0	[11]
3	Biomass→Char	-418.0	[11]
4	Tar→Gas	42.0	[12]
5	Tar→Char	42.0	[12]

IV. RESULTS AND DISCUSSION

a) Effects of isothermal heating temperature on pyrolysis yields

According to the two-stage parallel reaction model used in this work, as the pyrolysis zone temperature increases, the biomass undergoes thermal degradation according to primary reactions giving gas, tar and char as products. Tar also undergoes secondary reactions to give gas and tar. Since the amounts of each of these products vary depending mainly on the zone temperature, the influences of heating conditions on the particle residence time and pyrolysis yield are studied using the differential transformation method. Figs. 2-21 show the effects of isothermal heating temperatures on the particle resident time. Also, the figures demonstrate the agreement between the exact analytical solutions and the approximate analytical solutions developed by using differential transformation method. Figs. 22-25 show the effects of isothermal heating temperature (where the pyrolysis temperature is maintains a selected constant temperature in a pyrolyzing chamber) on the pyrolysis yield. From the results, thermal decomposition takes more time at temperature of 473 K and 573 K than

that of higher isothermal heating temperature for the biomass particle of the same size. The figures clearly depict that low temperature pyrolysis produces more char and high temperature pyrolysis enhances the production of gas and tar, i.e. an increase in the isothermal heating temperature increases the yield of gaseous products and the decreases char production.

The reduced production of tar and gas at low isothermal heating temperature may be due to some resistances to mass or heat transfer inside the particles of the biomass which can be broken by high heating temperature thereby resulting in greater primary decomposition of the sample and higher production of gas and tar at the higher temperature. In each case of the isothermal heating, as the pyrolysis reaches completion, the char production becomes constant.
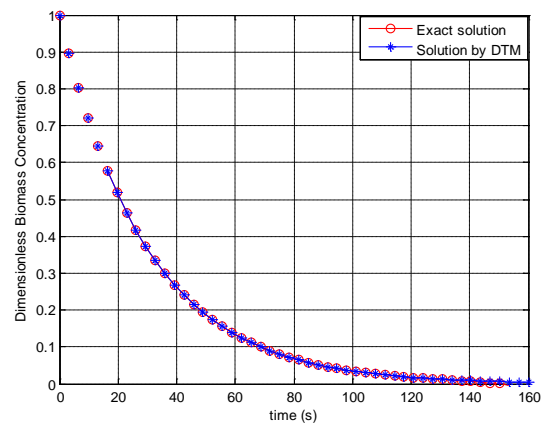
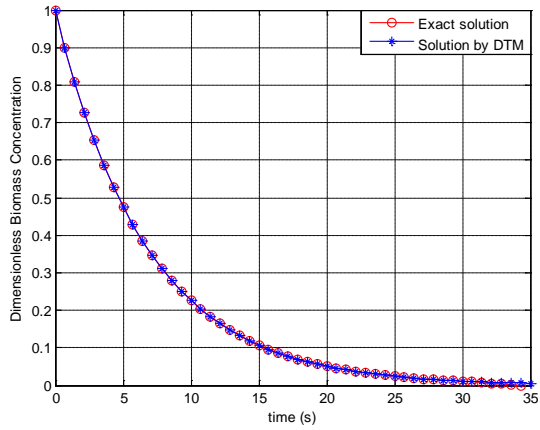Fig. 2: Biomass concentration against time at an isothermal temperature of 673K

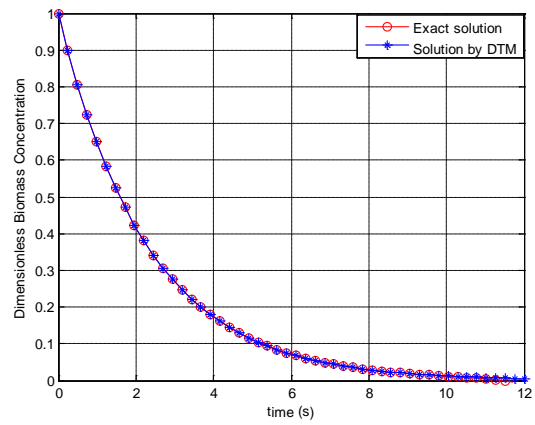*Fig. 3:* Biomass concentration against time at an isothermal temperature of 773K

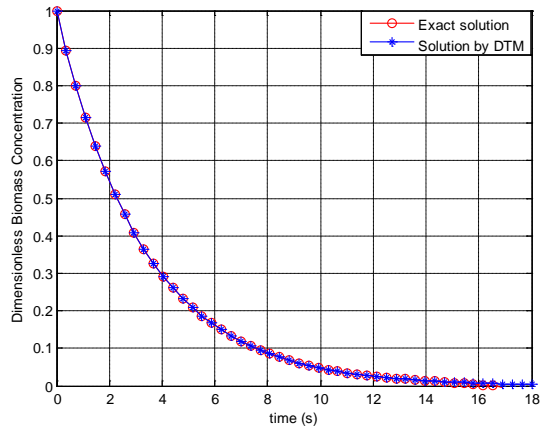*Fig. 6:* Biomass concentration against time at an isothermal temperature of 1073K

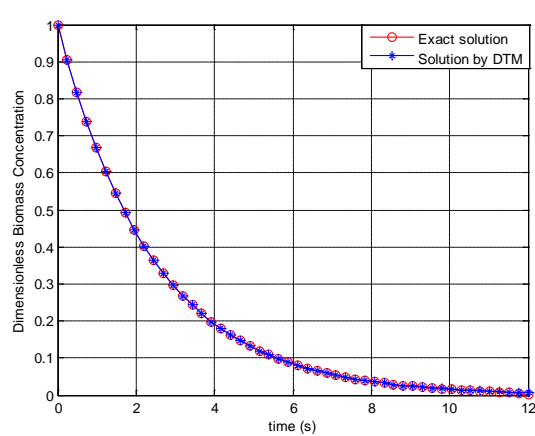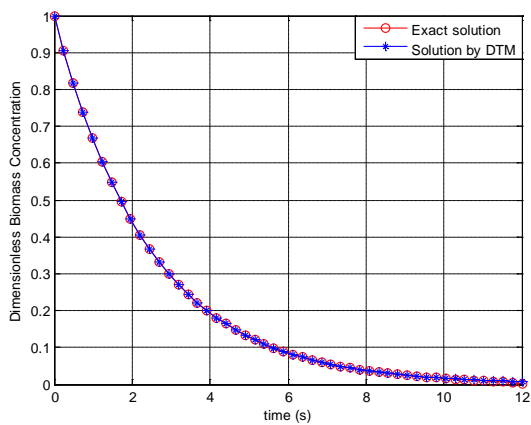*Fig. 4:* Biomass concentration against time at an isothermal temperature of 873K

Fig. 7: Biomass concentration against time at isothermal temperature of 1173K

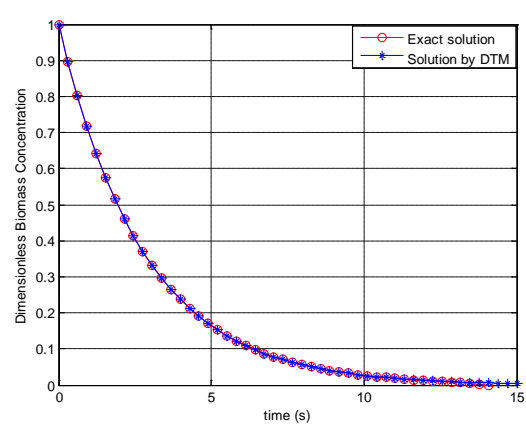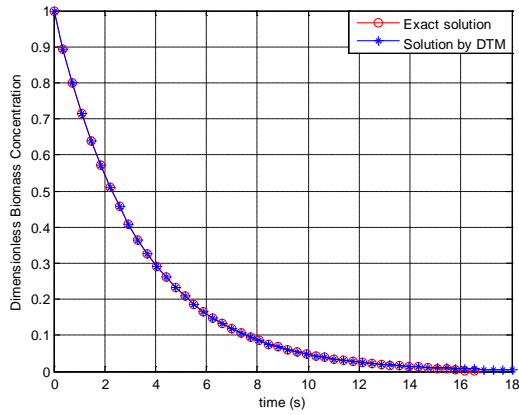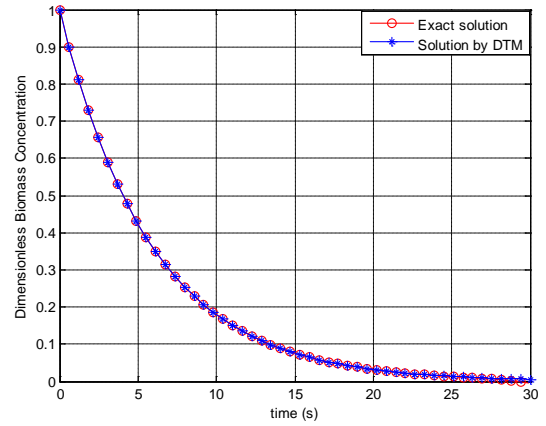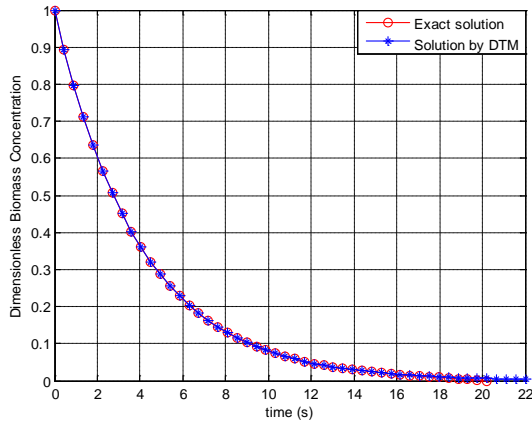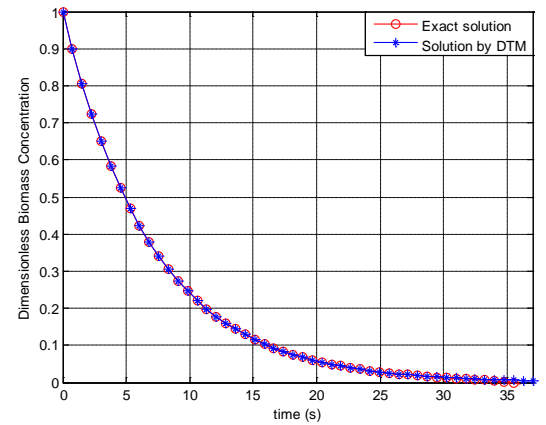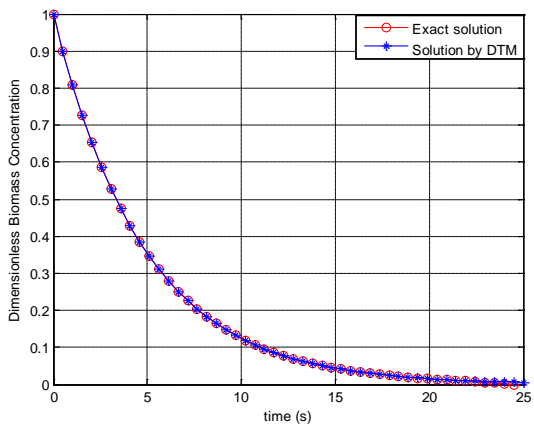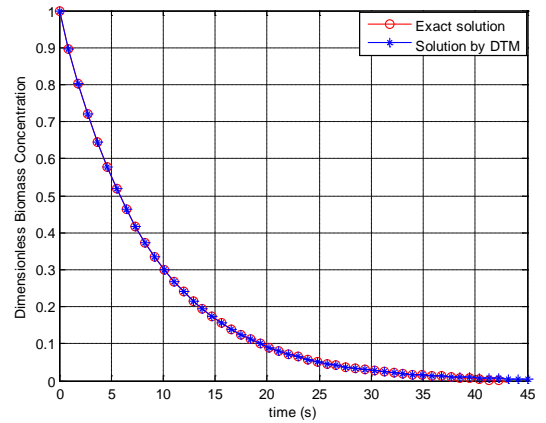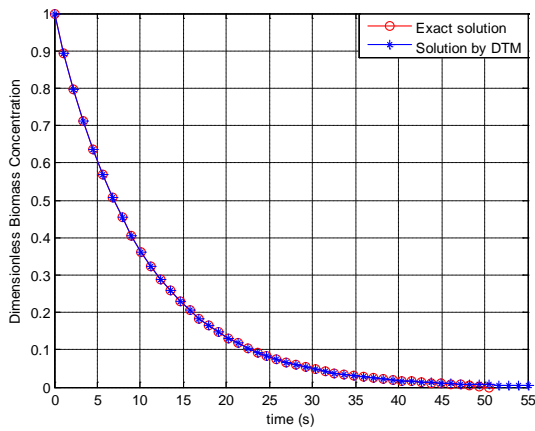*Fig. 5:* Biomass concentration against time at isothermal temperature of 973K

Fig. 8: Comparison of results of Biomass concentration against time at an isothermal temperature of 1273K

Fig. 9: Comparison of results of Biomass concentration against time at isothermal temperature of 1373K
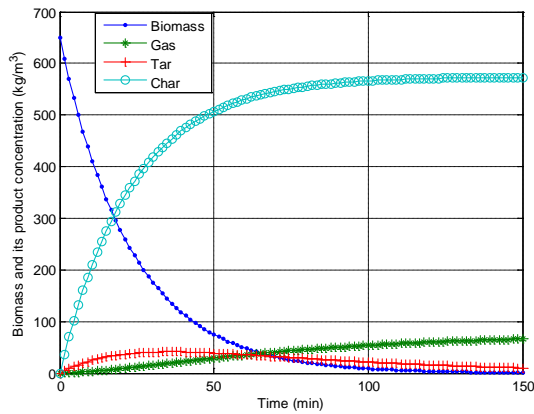

Fig. 12: Comparison of results of Biomass concentration against time at an isothermal temperature of 1673K

Fig. 10: Comparison of results of Biomass concentration against time at an isothermal temperature of 1473K

Fig.13: Comparison of results of Biomass concentration against time at isothermal temperature of 1773K

Fig. 11: Comparison of results of Biomass concentration against time at isothermal temperature of 1573K

Fig. 14: Comparison of results of Biomass concentration against time at an isothermal temperature of 1873K

Fig. 15: Comparison of results of Biomass concentration against time at isothermal temperature of 1973K

Fig. 16: Biomass concentration against temperature at an isothermal heating temperature of 573K
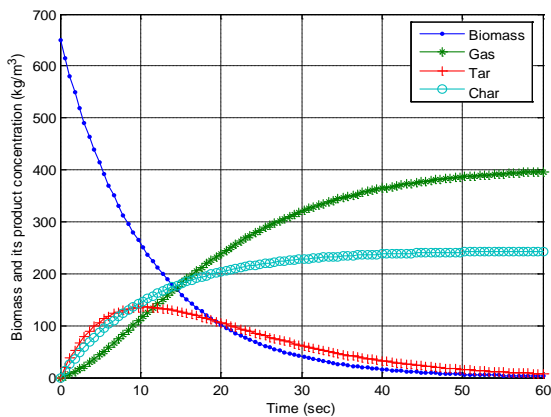
Fig. 17: Production and conversion rate against time at an isothermal heating temperature of 773K
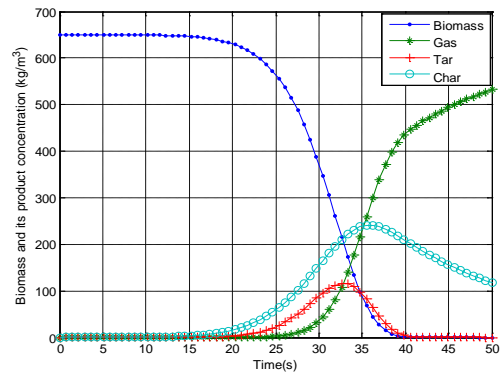

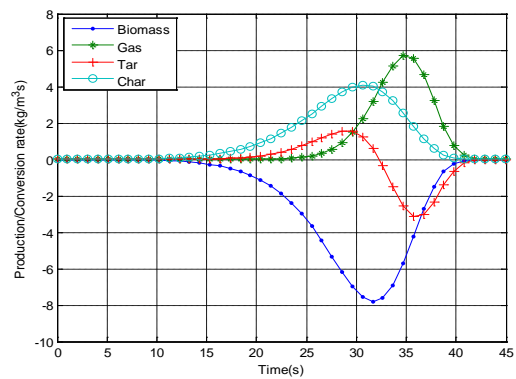*Fig. 18:* Biomass and its product concentration variation at heating rate of 10K/s

Fig. 19: Production/Conversion rate of Biomass and its Product with time at heating rate of 10K/s

Also, the results show that the tar rate yield increases first and then decreases and the gas yield increases as the pyrolysis temperature increases, but the char yield significantly decreases as the isothermal temperature increases to 573K and 673K. The decrease in the tar yield and sudden increase of gas yield observed at higher temperature may be due to secondary cracking of the pyrolysis liquid in to gaseous product at higher temperature. It could also be deduced from the results that the time required to obtain a certain conversion level decreases with increasing isothermal heating temperature. The trends obtained in this work as shown above are qualitatively the same as reported in literature [24] and [25].

b) *Effects of non-isothermal heating rates on biomass pyrolysis yields*

As pointed out in the previous section, heating rate is one of the important parameter for the yield of different products from the pyrolysis process. To determine the effects of heating rate on the yields of the biomass pyrolysis, simulations were carried out for different heating rates of as shown in Figs.26-41. The

14

effects of non-isothermal temperature on pyrolysis yields as functions of time are shown in Figs .26-37 while Figs. 38-41 show the effects of non-isothermal temperature on pyrolysis yields as a function of temperature at an initial particle temperature of 373 K. From the figures, the drying or pre-pyrolysis process are shown as zero rate of production and conversion of the products from 0-120 s and 303-473 K which validates the fact that pyrolysis process actually commenced at about 473K as stated in literatures [25]. It is surprising to see that at any heating rate, the production rate of char is higher than that of tar and gas. This may be due to the increase in the resistance for mass and heat transfers offered by the thick layer of the dried biomass i.e. for the gas and tar to evolve from the particle, they have to travel through a dried layer of the biomass which in consequence, comparably reduces their production rates. Also, it should be noted that increasing the heating rates reduces the particle residence time and as the heating rate are increased, the residence time of volatiles at low or intermediate temperatures decreases. Most of the reactions that favour tar conversion to gas occur at higher temperatures. At low heating rates, the volatiles have sufficient time to escape from the reaction zone before significant cracking can occur. Also, most of the decomposition takes place at temperatures lower than 500 K, and no more significant decomposition is produced above 750 K.

On comparing these results with that of isothermal heating conditions, it is shown that the amount of char produced in the non-isothermal heating conditions is lower than in the isothermal heating conditions. This is because the isothermal conditions were carried out at relative low temperature and the residual solid contains compounds that evaporate at higher temperatures. The tar yield was low at lower heating rate and slightly increases with increase in heating rate. The gas yield increases with increase in heating rate while the char yield decreases significantly with increase in heating rate. The increasing of the tar yield with the increase of heating rate may be due to some resistances to mass or heat transfer inside the particles of the biomass, but increasing the heating rate breaks the heat and mass transfer limitation in the pyrolysis and thereby increasing the tar yield and decreasing char formation.
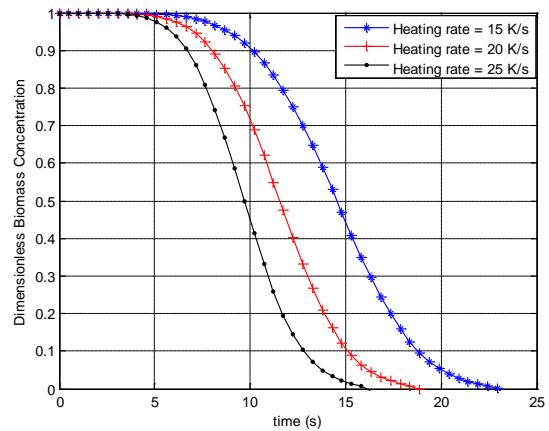

Fig. 20: Biomass concentration against time at non-isothermal condition at an initial temperature of 473K
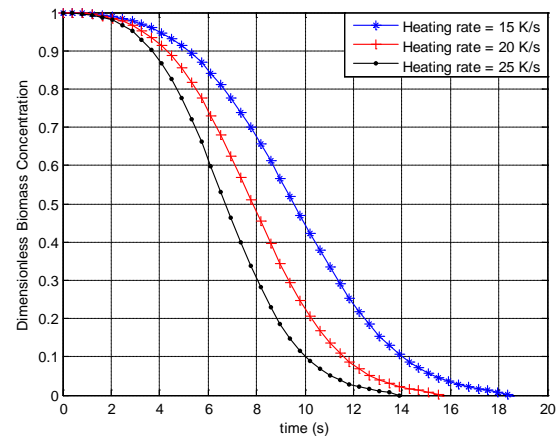

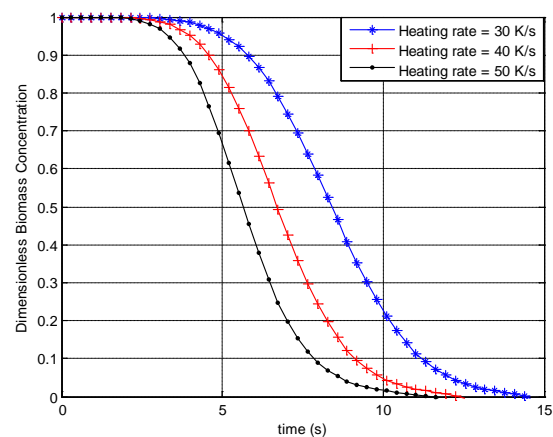*Fig. 21:* Biomass concentration against time at non-isothermal condition at an initial temperature of 573K

Fig. 22: Biomass concentration against time at non-isothermal condition at an preheating temperature of 473K
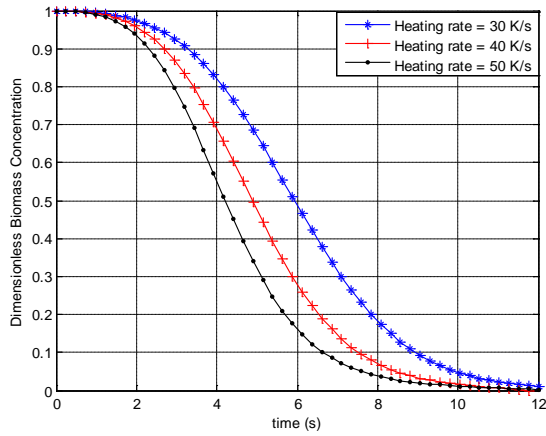
Fig. 23: Biomass concentration against time at non-isothermal condition at an preheating temperature of 573K
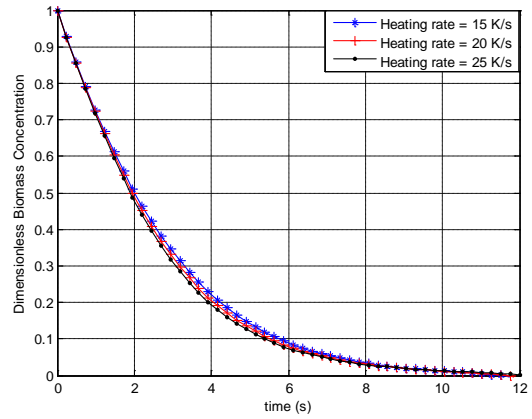

Fig. 26: Biomass concentration against time at non-isothermal condition at an initial temperature of 873K
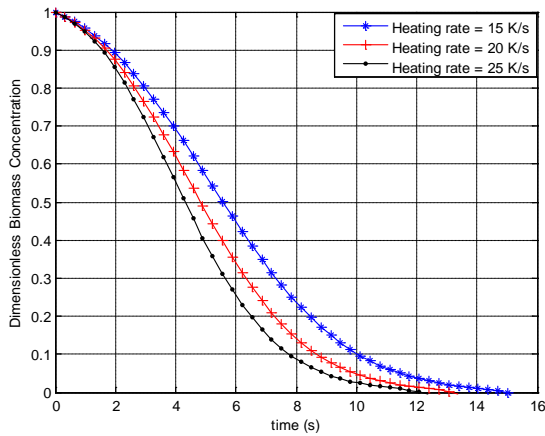

Fig. 24: Biomass concentration against time at non-isothermal condition at an initial temperature of 673K
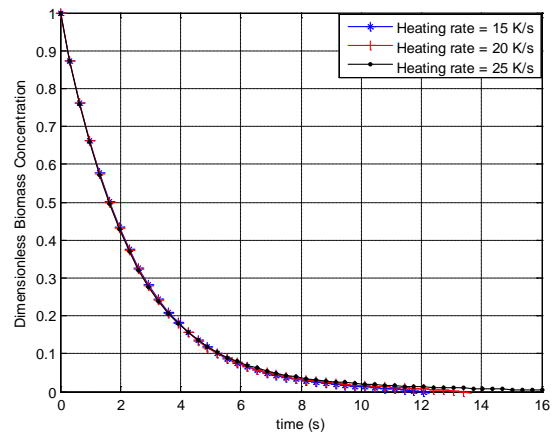

Fig. 27: Biomass concentration against time at non-isothermal condition at an initial temperature of 973K
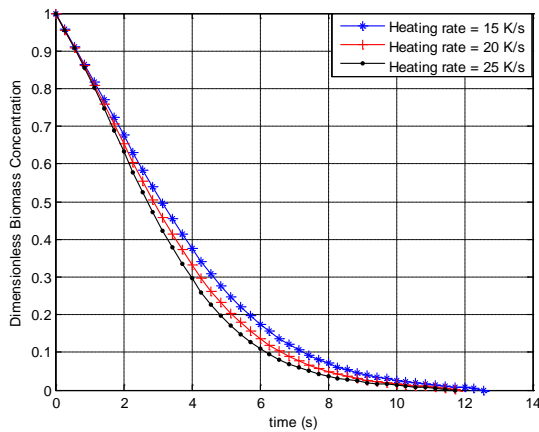

Fig. 25: Biomass concentration against time at non-isothermal condition at an initial temperature of 773K
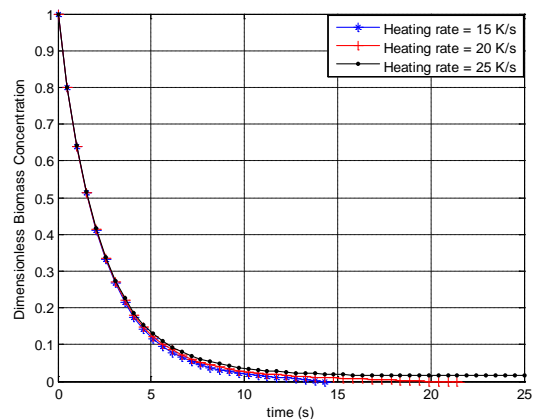

Fig. 28: Biomass concentration against time at non-isothermal condition at an initial temperature of 1073K
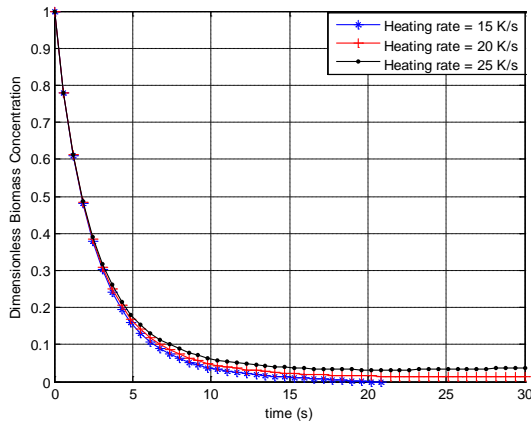
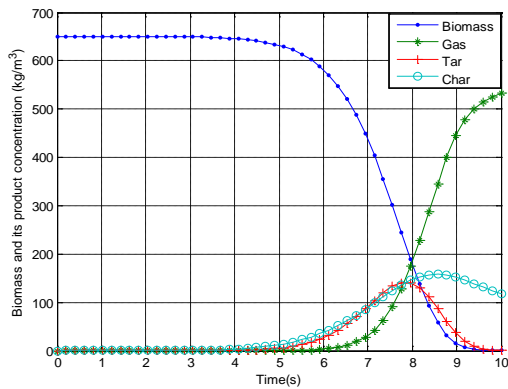Fig. 29: Biomass concentration against time at non-isothermal condition at an initial temperature of 1173K

Fig. 30: Biomass and its product concentration variation at heating rate of 50K/s
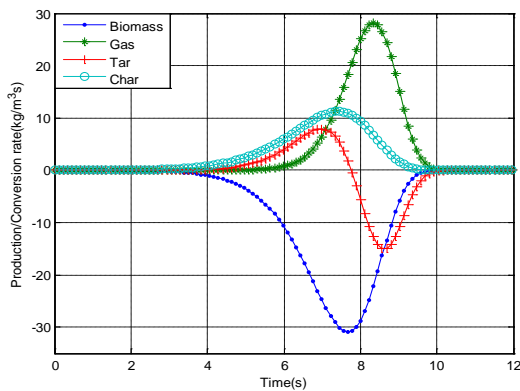

Fig. 31: Production/Conversion rate of Biomass and its Product with time at heating rate of 50K/s

Fig. 32: Biomass and its product concentration variation at heating rate of 10K/s

Fig. 33: Production/Conversion rate of Biomass and its Product with temperature at heating rate of 10K/s
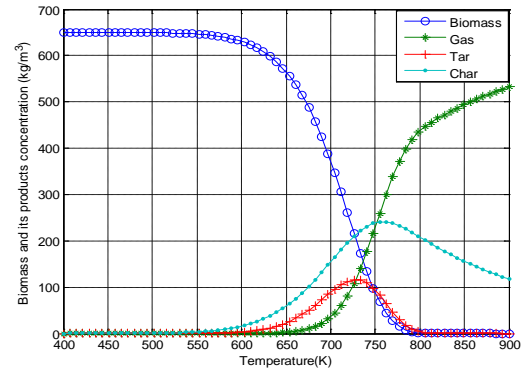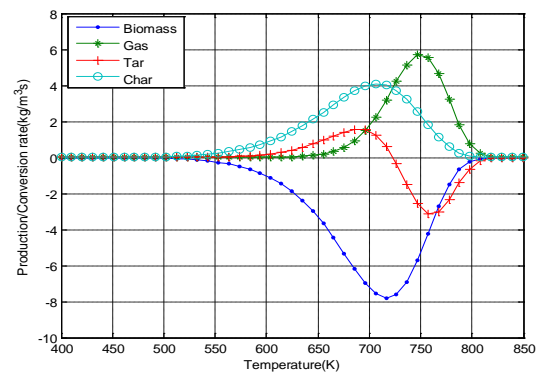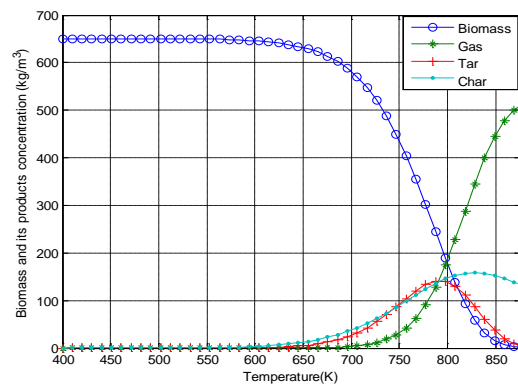

Fig. 34: Biomass and its product concentration variation at heating rate of 50K/s
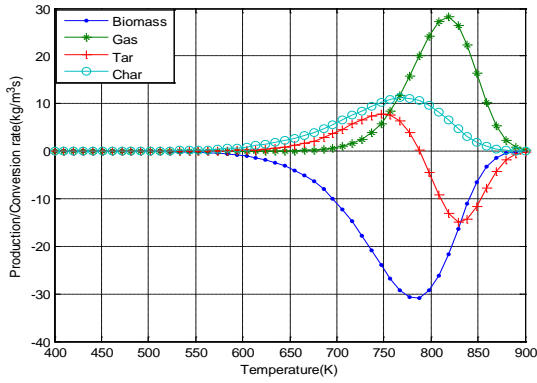
Fig. 35: Production/Conversion rate of Biomass and its Product with temperature at heating rate of 50K/s

From the Figs 38-41, the rate of char production increases gradually between the particle temperatures of 500 K and 573 K, and as the particle temperature increases, as gases and tar evolve from the biomass particle and consequently, the rate of char production increases rapidly from the particle temperature of 500 K to 723 K, after which there is a decrease in the production rate of char (due to the loss of H and O contents of the char at high temperatures) till the whole wood has been pyrolysed. This shows that pyrolysis process is slowed down from 723-873 K (depending on the heating rates). It could also be inferred from the results that the primary pyrolysis rate of tar production starts gradually from about 573 K till 753 K (depending on the heating rates) and then increases rapidly till the whole tar has been converted to char and gas at the final pyrolysis temperature. The extension of the rate-temperature figure to the negative portion of the graph depicts the conversion rate of tar to char and gas.

c) *Effects of heating rates on particle residence time*

Recently, Lédé' and Authier [32] advocated for the criteria for characterizing fast pyrolysis based on temperature and heating rate of solid particles that undergoes a thermal decomposition The effects of heating rates on the particle residence time are shown in Figs. 42-45. For the low heating rates of 0.01-0.1K/s in Figs. 42, it takes hours or days for the pyrolysis to occur and this will definitely enhance the production of charcoal as depicted in Table 4.
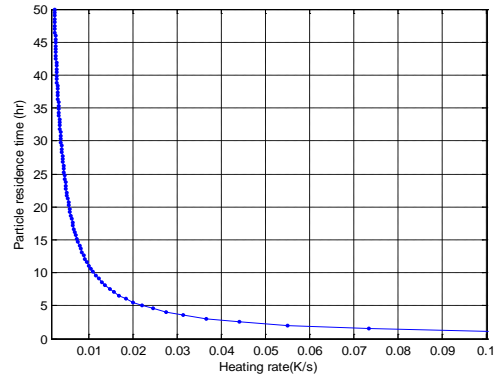

Fig. 36: Variations of biomass particle residence time very low heating rates
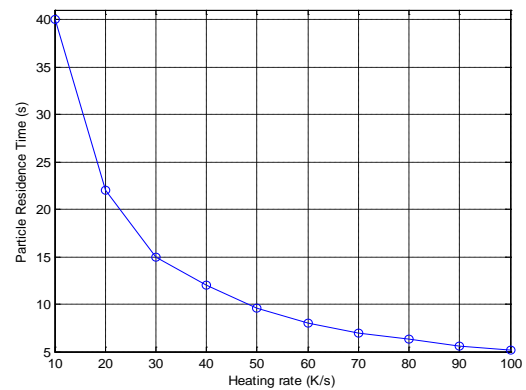

Fig. 37: Variations of biomass particle residence time with heating rates of 10-100K/s
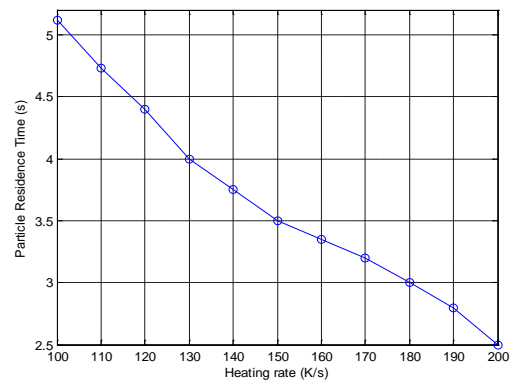

Fig. 38: Variations of biomass particle residence time heating rates of 100-200K,s
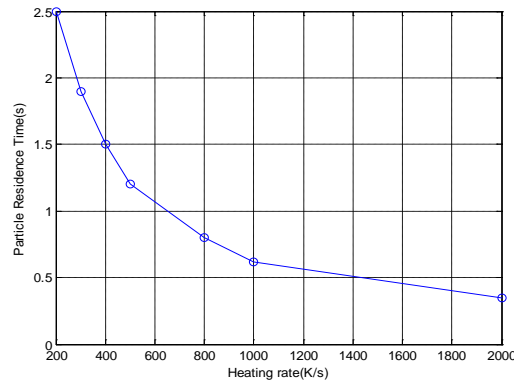
Fig. 39: Variations of biomass particle residence time with heating rates 200-200K/s
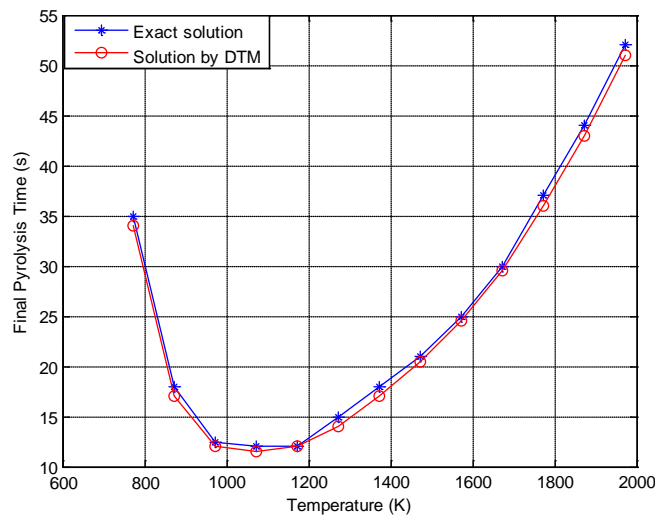
Fig. 40: Effects of heating rates on the particle residence/final pyrolysis time

Table 4: Pyrolysis conditions for different pyrolysis technologies

Pyrolysis technology	Residence time	Heating rate	Temperature (ºC)	Product
Carbonization	days	very low	400	charcoal
Conventional	5-30 min	low	600	oil, gas, char
Fast	0.5-5s	very high	650	bio-oil
Flash-liquid	< 1s	high	< 650	bio-oil
Flash-gas	< 1s	high	<650	chemicals, gas
Ultra	< 0.5s	very high	1000	chemicals, gas
Vacuum	2-30 s	medium	400	bio-oil
Hydro-pyrolysis	< 10s	high	< 500	bio-oil
Conventional	< 10s	high	< 700	chemicals

As the heating rates increases, the particle residence time in the reactor decreases and high heating rates favours the production of tar and gas. Therefore, as shown in the table, the length of heating and its intensity affect the rate and extent of pyrolytic reactions, the sequence of these reactions, and composition of the resultant products. Fig. 42-46 indicated the quantitative values of heating rates and residence time for different pyrolysis products. Such data as these are rarely found in open literatures.

V. Conclusion

In this work, differential transformation method has been applied to analyze pyrolysis kinetics of biomass particle under isothermal and non-isothermal heating conditions. The developed analytical solutions to the system of pyrolysis kinetic models were used to study the effects of heating conditions, heating rates on the pyrolysis residence time and technologies. Good agreements were established between the present results and the past works. It is therefore expected that this study will enhance the understanding of the pyrolysis process by giving physical insights into the various factors and the parameters affecting the phenomena.

Nomeclature

$A1; A2; A3; A4; A5$ frequency factor, 1/s
Bi_m Modified Biot number
C   concentration, kg/m^3
C_p specific heat capacity, J/kgK
E   activation energy, J/mol
h   convective heat transfer coefficient, W/m^2 K
K   thermal conductivity, W/mK
$k_1; k_2; k_3; k_4; k_5$ rate constants, 1/s
Q heat of pyrolysis, J/Kg
r   radial distance, m
R   radius for cylindrical particle, m
R_g universal gas constant, J/mol
t   time, s
T_f reactor final temperature, K
T   temperature, K
$R^{'}$ dimensionless radial distance

Greek letters

ρ   Bulk density of wood,   Kg/m^3
$ρ_∞$ Ultimate density of wood,   Kg/m^3
τ   dimensionless time
θ dimensionless temperature
ϵ   emissivity coefficient
ε   void fraction of particle
σ Stefan Boltzmann constant, W/m^2 K^4
α   Heat of reaction number

Subscripts

B   virgin biomass
G   gases
C   char
T   tar
G   gas
0   initial
f   final

References Références Referencias

1. D. L. Pyle, C. A. Zaror. Heat transfer and kinetics in the low temperature pyrolysis of solids. Chemical Engineering Science 39(1984.), 147-158.
2. C. H. Bamford, J. Crank, D. H. Malan. The combustion of wood. Part I. Proceedings of the Cambridge Philosophical Society 42 (1946)., 166-182.
3. A. F. Roberts, G. Clough. Thermal degradation of wood in an inert atmosphere. In: Proceedings of the ninth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh,. 1963. 158-167.
4. E. J. Kansa, H. E. Perlee and R. F. Chaiken, R. Mathematical model of wood pyrolysis including internal forced convection. Combustion and Flame 29(1977), 311–324.
5. W. R. Chan, M. Kelbon and B. B. Krieger, Modeling and experimental verification of physical and chemical processes during pyrolysis of large biomass particle. Fuel 64(1985.), 1505–1513.
6. C. A. Koufopanos, N. Papayannakos, G. Maschio and A. Lucchesi. Modelling of the pyrolysis of biomass particles. Studies on kinetics, thermal andheat transfer e4ects. The Canadian Journal of Chemical Engineering 69(1991.), 907–915.
7. K. Miyanami, L. S. Fan, L. T. Fan and W. P. Walawender. A mathematical model for pyrolysis of a solid particle-effects of the heat of reaction. The Canadian Journal of Chemical Engineering 55(1977)., 317–325.
8. L. T. Fan, L. S. Fan, K. Miyanami, T. Y. Chen, and W. P. Walawender. A mathematical model for pyrolysis of a solid particle-effects of the Lewis number. The Canadian Journal of Chemical Engineering 55(1977)., 47-53.
9. J. Villermaux,B. Antoine., J. Lede, F. Soulignac. A new model for thermal volatilization of solid particles undergoing fast pyrolysis. Chemical Engineering Science 41(1986),, 151–157.
10. C. Di Blasi. Analysis of convection and secondary reaction effects within porous solid fuels undergoing pyrolysis. Combustion Science and Technology 90(1993), 315–340.
11. R. K. Jalan and V. K. Srivastava.. Studies on pyrolysis of a single biomass cylindrical pellet-kinetic and heat transfer effects. Energy Conversion and Management 40 (1999), 467-494.
12. M. R. Ravi, A. Jhalani., S. Sinha and A. Ray. "Development of a semi-empirical model for pyrolysis of an annular sawdust bed". Journal of Analytical and Applied Pyrolysis, 71(2004): 353-374.
13. B. V. Babu andA. S. Chaurasia. Modeling for pyrolysis of solid particle: kinetics and heat transfer

effects. Energy Conversion and Management 44(2003), 2251–2275.

14. P. N. Sheth and B. V. Babu. Kinetic Modeling of the Pyrolysis of Biomass National Conference on Environmental Conservation, Pilani, India; 2006, 453-458.

15. P. Weerachanchai, C. Tangsathitkulchai and M. Tangsathitkulchai. Comparison of Pyrolysis Kinetic Model for Thermogravimetric analysis of Biomass. Suranree Journal of Tecnologies 17(4) (2010), 387-400.

16. K. Slopiecka, P. Bartocci and F. Fantozzi. Thermogravimetric analysis and Kinetic study of poplar wood pyrolysis, 3rd International Conference on Applied Energy, Perugia, Italy; 2011, 1687-1698.

17. S. J. Ojolo, C. A. Osheku and M. G. Sobamowo. Analytical Investigations of Kinetic and Heat Transfer in Slow Pyrolysis of a Biomass Particle. Int. Journal of Renewable Energy Development 2 (2) 2013: 105-115

18. B. H. Dizaji, M. Bidabadi. Analytical study about the kinetics of different processes in pyrolysis of lycopodium dust [J]. Journal of Fuel and Combustion, 2014, 6(2): 13-20. (in Persian)

19. R. Font., A. Marcilla., E. Verdu and J. Devesa,, Kinetics of the pyrolysis of almond shells and almond shells impregnated with $COCl_2$ in a Fluidized bed reactor and in a Pyroprobe 100. Industrial and Engineering Chemistry Research 29 (1990)., 1846-1855.

20. F. Thurner and U. Mann. Kinetic investigation of wood pyrolysis. Industrial and Engineering Chemical Process Design and Development 20 (1981), 482-488.

21. C. K. Liden, F. Berruti., D. S. Scott. "A kinetic model for the production of liquids from the flash pyrolysis of biomass". Chem. Eng. Commun. 65(1988), 207–221.

22. N. Prakash and T. Karunanithi. "Kinetic Modelling in Biomass pyrolysis – a review". Journal of applied sciences research, 4(12) (2008), 1627-1636.

23. C. Branca and C. Di Blasi. Kinetics of the isothermal degradation of wood in the temperature range, 528-708 K. Journal of Analytical and Applied Pyrolysis, 67(2003), 207-219.

24. G. Gauthier, T. Melkior, S. Salvador, M. Corbetta, A. Frassoldati, S. Pierucci, E. Ranzi, H. Bennadji, E. M. Fisher. Pyrolysis of Thick Biomass Particles: Experimental and Kinetic Modelling. Chemical Engineering Transactions Vol. 32, 2013.

25. D. V. Suriapparao and R. Vinu. Effects of Biomass Particle Size on Slow Pyrolysis Kinetics and Fast Pyrolysis Product Distribution. Waste Biomass Valorization, 2017.

26. H. Bennadji. Low-Temperature Pyrolysis of Woody Biomass in the Thermally Thick Regime. Energy & Fuels, 27(3), 1453-1459, 2013.

27. Ranzi, E., et al., Comprehensive and Detailed Kinetic Model of a Traveling Grate Combustor of Biomass. Energy and Fuels, 25(9), 4195-4205, 2011.

28. Park, W.C., A. Atreya, and H.R. Baum, Experimental and theoretical investigation of heat and mass transfer processes during wood pyrolysis. Combustion and Flame, 157(3), 481-494, 2010.

29. Norinaga, K., et al., Detailed chemical kinetic modelling of vapour-phase cracking of multi-component molecular mixtures derived from the fast pyrolysis of cellulose. Fuel, 103, 141-150, 2013.

30. Ranzi, E., et al., Hierarchical and comparative kinetic modeling of laminar flame speeds of hydrocarbon and oxygenated fuels. Progress in Energy and Combustion Science, 2012. 38(4): p. 468-501.

31. Koufopanos, C. A., Maschio, G. and Lucchesi, A. (1989). "Kinetic modeling of the Pyrolysis of Biomass and Biomass Components", The Canadian Journal of Chemical Engineering, 67, pp 75-83.

32. Koufopanos, C. A., Papayannanos, N., Maschio, G. and Lucchesi, A. (1991) "Modeling the pyrolysis of biomass particles: studies on kinetics, thermal and heat transfer effects", The Canadian Journal of Chemical Engineering, 69, pp 907–915.

33. G. Gentile, P. Eduardo A. Debiagi, A. Cuoci, A. Frassoldati, E. Ranzi, T. Faravelli. A computational framework for the pyrolysis of anisotropic biomass particles. Chemical Engineering Journal . Article in press, 2017.

34. C. Di Blasi, Modeling chemical and physical processes of wood and biomass pyrolysis, Progress in Energy and Combustion Science 34 (2008) 47-90.

35. A. Anca-Couce, Reaction mechanisms and multi-scale modelling of lignocellulosic biomass pyrolysis, Progress in Energy and Combustion Science 53 (2016) 41-79.

36. M.S. Mettler, D.G. Vlachos, P.J. Dauenhauer, Top ten fundamental challenges of biomass pyrolysis for biofuels, Energy & Environmental Science 5 (2012) 7797-7809.

37. K. Davidsson, J. Pettersson, Birch wood particle shrinkage during rapid pyrolysis, Fuel 81 (2002) 263-270.

38. C. Di Blasi, Heat, momentum and mass transport through a shrinking biomass particle exposed to thermal radiation, Chemical engineering science 51 (1996) 1121-1132.

39. M.J. Hagge, K.M. Bryden, Modeling the impact of shrinkage on the pyrolysis of dry biomass, Chemical engineering science 57 (2002) 2811-2823.

40. J. Larfeldt, B. Leckner, M.C. Melaaen, Modelling and measurements of the pyrolysis of large wood particles, Fuel 79 (2000) 1637-1643.

41. B. Babu, A. Chaurasia, Pyrolysis of shrinking cylindrical biomass pellet, at International symposium & 56th annual session of IIChE (CHEMCON-2003), 2003, pp. 19-22.

42. B. Babu, A. Chaurasia, Heat transfer and kinetics in the pyrolysis of shrinking biomass particle, Chemical engineering science 59 (2004) 1999-2012.

43. A. Cuoci, A. Frassoldati, T. Faravelli, E. Ranzi, A computational tool for the detailed kinetic modeling of laminar flames: Application to C2H4/CH4 coflow flames, Combustion and Flame 160 (2013) 870-886.

44. Cuoci, A. Frassoldati, T. Faravelli, E. Ranzi, Open SMOKE++: An object-oriented framework for the numerical modeling of reactive systems with detailed kinetic mechanisms, Computer Physics Communications 192 (2015) 237-264.

45. T. Maffei, G. Gentile, S. Rebughini, M. Bracconi, F. Manelli, S. Lipp, A. Cuoci, M. Maestri, A multiregion operator-splitting CFD approach for coupling microkinetic modeling with internal porous transport in heterogeneous catalytic reactors, Chemical Engineering Journal 283 (2016) 1392-1404.

46. J. Blondeau, H. Jeanmart, Biomass pyrolysis at high temperatures: Prediction of gaseous species yields from an anisotropic particle, Biomass and bioenergy 41 (2012) 107-121.

47. M. Gronli, A theoretical and experimental study of the thermal conversion of biomass, PhD thesis, NTNU, Trondheim, 1996.

48. H. Bennadji, K. Smith, S. Shabangu, E.M. Fisher, Low-temperature pyrolysis of woody biomass in the thermally thick regime, Energy & Fuels 27 (2013) 1453-1459.

49. M. Corbetta, A. Frassoldati, H. Bennadji, K. Smith, M.J. Serapiglia, G. Gauthier, T. Melkior, E. Ranzi, E.M. Fisher, Pyrolysis of centimeter-scale woody biomass particles: Kinetic modeling and experimental validation, Energy & Fuels 28 (2014) 3884-3898.

50. G. Gauthier, Syntesis of second generation biofuels: study of pyrolysis of centimeter-scale wood particles at high temperature, Univerisite de Toulouse, 2013.

51. G. Gauthier, T. Melkior, M. Grateau, S. Thiery, S. Salvador, Pyrolysis of centimetre-scale wood particles: New experimental developments and results, Journal of Analytical and Applied Pyrolysis 104 (2013) 521-530.

52. A.D. Paulsen, B.R. Hough, C.L. Williams, A.R. Teixeira, D.T. Schwartz, J. Pfaendtner, P.J. Dauenhauer, Fast pyrolysis of wood for biofuels: spatiotemporally resolved diffuse reflectance in situ spectroscopy of particles, ChemSusChem 7 (2014) 765-776.

53. E. Ranzi, A. Cuoci, T. Faravelli, A. Frassoldati, G. Migliavacca, S. Pierucci, S. Sommariva, Chemical kinetics of biomass pyrolysis, Energy & Fuels 22 (2008) 4292-4300.

54. P.E.A. Debiagi, C. Pecchi, G. Gentile, A. Frassoldati, A. Cuoci, T. Faravelli, E. Ranzi, Extractives extend the applicability of multistep kinetic scheme of biomass pyrolysis, Energy & Fuels 29 (2015) 6544-6555.

55. P.E.A. Debiagi, G. Gentile, M. Pelucchi, A. Frassoldati, A. Cuoci, T. Faravelli, E. Ranzi, Detailed kinetic mechanism of gas-phase reactions of volatiles released from biomass pyrolysis, Biomass and bioenergy 93 (2016) 60-71.

56. Milosavljevic, E.M. Suuberg, Cellulose thermal decomposition kinetics: global mass loss kinetics, Industrial & Engineering Chemistry Research 34 (1995) 1081-1091.

This page is intentionally left blank