



## Kinetic Modeling and Simulation of Pyrolysis of Shrinking Biomass Particle in Fixed Bed Gasifier

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### ABSTRACT

Pyrolysis plays an integrated role in the biomass conversion processes. The development of good mathematical models which in consequent leads to the design of pyrolysis reactors. The biomass gasifier is paramount in the scientific studies and understanding of the very important process in the thermochemical conversion of the solid fuels. However, due to the complexities of the biomass reaction scheme, the pyrolysis of biomass is generally modeled on the basis of apparent kinetics. Moreover, it is generally accepted that most important parameters affecting the process are temperature, concentration, residence time and heating conditions. This work presents the simulations of the pyrolysis kinetics of shrinking biomass particle under non-isothermal and isothermal heating conditions. The developed models were used to investigate the effects of shrinkage, heating conditions and heating rates on the pyrolysis of wood. There is a good agreement when the results of the developed models were compared to the experimental results. The results of this work could be used in estimating the optimum parameters in the pyrolysis of biomass and in the design of some pyrolysis reactors.

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### NOMENCLATURE

A1-A5	Frequency factor	1/s
C	concentration	kg/m <sup>3</sup>
E	activation energy	J/mol
$k_1$ - $k_5$	rate constants	1/s
$R_g$	universal gas constant	J/mol
t	time	s
T	temperature	K
V	Volume	m <sup>3</sup>
$\rho$	Bulk density of wood	Kg/m <sup>3</sup>
$\epsilon$	void fraction of particle	
Subscripts		
B	virgin biomass	
G	Gases	
C	Char	
T	Tar	
o	initial	

### INTRODUCTION

Pyrolysis is a process by which a solid fuel (biomass or coal) thermally decomposes in the absence or under limited supply of oxygen/air to char, tar and gaseous products. This process plays a vital role in the thermochemical conversion processes of biomass. Also, the study of biomass gasification processes requires a detail understanding of the pyrolysis process and the behaviour of the biomass particles in the reacting medium. On carrying out such studies, it is established that the 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. As a

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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°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 kinetics of the pyrolysis process can be studied under non-isothermal or isothermal conditions. During the non-isothermal condition, pyrolysis temperature is progressively increased with increasing heating time using a specified heating rate, while isothermal condition maintains a selected constant temperature in a pyrolyzing chamber. In describing pyrolysis behaviour of biomass particles under such conditions a number of pyrolysis kinetic models have been proposed [2-33]. Babu and Chaurasia [34] studied numerically the effects of heating conditions, heating rates and order of the kinetic reactions on wood pyrolysis using the two-step model of Koufopoulos et al. [18]. In the study of pyrolysis reaction temperature, Sheth and Babu [35] presented that pyrolysis of wood is typically initiated at 200°C and lasts till 450-500°C, depending on the species of wood. Yang et al. [36] presented that the major stage of biomass pyrolysis occurs between 250-450°C while Weerachanchai et al. [32] presented a study on the effects of biomass type (cassava pulp residue, palm kernel cake, palm shell, coconut shell and longan fruit seed), particle size (106-1325 μm) and heating rate (5-40°C/min) on the thermal decomposition behaviour and submitted that the major decomposition of all biomasses occurred in the range of 250-400°C. Recently, Katarzyna et al. [37], concluded in their studies of poplar wood, that the decomposition of hemicelluloses and cellulose take place in active pyrolysis in the temperature range of 473-653K and 523-623K, respectively. They then added that Lignin decomposes in both stages: active and passive pyrolysis in the range of 453-1173K without characteristic peaks.

Most of the past work cited above were based on the assumptions that there is no volume change during the pyrolysis. However, Ahmed and Clement [38] reported that the usual assumption made when setting up the balance equation describing pyrolysis is that particle size is constant through the pyrolysis process. This assumption is not correct since the kinetic parameters estimated by including the volume change represent experimental results better than those estimated assuming a fixed particle size. The same authors submitted that size

of cellulose decreased by 57% during the pyrolysis process. Lu et al. [39] reported that the size of wood particles reduced by 10% during pyrolysis. The reason for this volume reduction was put forward by Mayor and Sereno [40] as they stated that heating and water loss cause stresses in cellulose structure of the biomass material and lead to changes in shape and decrease in size. In laying the argument to rest, Babu and Chaurasia [41] reported that there is a negligible effect of shrinkage on the pyrolysis of a thermally thin particle and impact of shrinkage is pronounced in a thermally thick particle. Therefore, this work presents improved models of shrinking woodparticle (thermally thick particle) during pyrolysis process. The developed models are based on Shafizadeh and Chin's model [23] which has been stated to be the most classical models for wood pyrolysis [42]. The models were solved using the developed Runge-Kutta fifth-order for the simultaneous equations. In providing solutions for the pyrolysis kinetics of a thermally thin biomass particle as reported in literatures, recourse have been made to numerical methods (approximation methods) because of the non-linear nature of the developed models. 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 closed solutions of pyrolysis kinetics of biomass particle. Simulations were carried out to investigate the effects of both isothermal and non-isothermal heating conditions on the pyrolysis kinetics of biomass particle.

### Kinetic models and solutions

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; then the tar further decomposes into char and gases

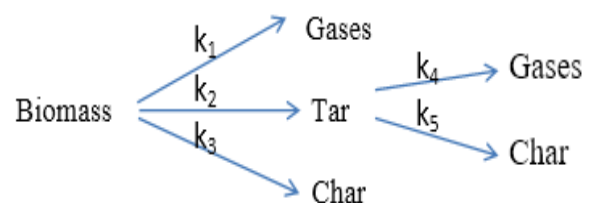


Figure. 1. Two-stage parallel reaction model of biomass pyrolysis

This two-stage parallel reaction model of biomass pyrolysis has previously been used by other researchers [8, 9, 10, 15, 23, 28, 36]. 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 has been stated to be the most classical models for wood pyrolysis [38].

In this work, the developed kinetic equations of pyrolysis of the shrinking biomass and the corresponding initial are given as follows:

$$\frac{dC_B}{dt} = -(k_1 + k_2 + k_3)C_B - \frac{C_B}{V_B} \frac{dV_B}{dt} \quad (1a)$$

$$\frac{dC_T}{dt} = k_2C_B - \varepsilon(k_4 + k_5)C_T - \frac{C_B}{V_B} \frac{dV_B}{dt} \quad (1b)$$

$$\frac{dC_C}{dt} = k_3C_B + \varepsilon k_5C_T - \frac{C_B}{V_B} \frac{dV_B}{dt} \quad (1c)$$

$$\frac{dC_G}{dt} = k_1C_B + \varepsilon k_4C_T - \frac{C_G}{V_G} \frac{dV_G}{dt} \quad (1d)$$

$$\frac{\partial V_B}{\partial t} = \left( \frac{\beta - 1}{C_{B_0}} \right) \left[ \sum_i^3 k_i C_B V_B \right] \quad (1e)$$

$$\frac{\partial V_G}{\partial t} = \left( \frac{\beta - 1}{C_{G_0}} \right) \left[ \sum_{i=1,4} k_i C_G V_G \right] \quad (1f)$$

The following dimensionless parameters were developed to non-dimensionalize equations

$$\tau = \frac{t}{t_f}, \quad \beta = \frac{RT_i^2}{E(T_0 - T_i)}, \quad \omega = \frac{V}{V_{B_0}}, \quad \alpha = \frac{C}{C_{B_0}}, \quad N = At_f e^{-\frac{E}{RT_i}}$$

and the resulting dimensionless equations are as follows:

$$\frac{d\alpha_B}{d\tau} = -(N_1 + N_2 + N_3)\alpha_B - \frac{\alpha_B}{\omega_B} \frac{d\omega_B}{d\tau} \quad (2a)$$

$$\frac{d\alpha_T}{d\tau} = N_1\alpha_B + \varepsilon N_4\alpha_T - \frac{\alpha_B}{\omega_G} \frac{d\omega_G}{d\tau} \quad (2b)$$

$$\frac{d\alpha_C}{d\tau} = N_3\alpha_B + \varepsilon N_5\alpha_T - \frac{\alpha_B}{\omega_B} \frac{d\omega_B}{d\tau} \quad (2c)$$

$$\frac{d\alpha_G}{d\tau} = N_1\alpha_B + \varepsilon N_4\alpha_T - \frac{\alpha_B}{\omega_G} \frac{d\omega_G}{d\tau} \quad (2d)$$

$$\frac{\partial \omega_B}{\partial \tau} = (\beta - 1) \left[ \sum_i^3 N_i \alpha_B \omega_B \right] \quad (2e)$$

$$\frac{\partial \omega_G}{\partial \tau} = (\beta - 1) \left[ \sum_{i=1,4} N_i \alpha_G \omega_G \right] \quad (2f)$$

If the volume change is neglected as in the case of hard wood, equations 1a to 1f become;

$$\frac{dC_B}{dt} = -(k_1 + k_2 + k_3)C_B \quad (3a)$$

$$\frac{\partial C_T}{\partial t} = k_2C_B - \varepsilon(k_4 + k_5)C_T \quad (3b)$$

$$\frac{\partial C_C}{\partial t} = k_3C_B + \varepsilon k_5C_T \quad (3c)$$

$$\frac{\partial C_G}{\partial t} = k_1C_B + \varepsilon k_4C_T \quad (3d)$$

Srivastava [26] 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 stated below:

$$T = T_0 + \beta t \quad (4)$$

Where  $T_0$  is the initial temperature in K,  $\beta$  is the heating rate in K/s and  $t$  is the time in s. also,

$$k_i = A_i \exp \left[ \left( \frac{-E_i}{RT} \right) \right] \quad (5a)$$

$$i = 1-5$$

The initial conditions for the kinetic equations are;

$$t = 0, C_B = C_{B_0}, C_C = C_G = C_T = 0 \quad V_B = V_{B_0} \quad (5b)$$

For the Isothermal condition,  $T = T_0$

$$k_i = A_i \exp \left[ \left( \frac{-E_i}{RT_0} \right) \right] \quad i = 1-5 \quad (5c)$$

While for the non-isothermal condition

$$k_i = A_i \exp \left[ \left( \frac{-E_i}{R(T_0 + \beta t)} \right) \right] \quad i = 1-5 \quad (5d)$$

Solving the resulting kinetic equation using Laplace transform, we arrived at

$$C_B = C_{B_0} \exp \{ -(k_1 + k_2 + k_3)t \} \quad (7a)$$

$$C_T = \frac{C_{B_0} k_2}{\{ \varepsilon(k_4 + k_5) - (k_1 + k_2 + k_3) \}} [\exp \{ -(k_1 + k_2 + k_3)t \} - \exp \{ -\varepsilon(k_4 + k_5)t \}] \quad (7b)$$

$$C_C = \frac{C_{B_0} k_3}{(k_1 + k_2 + k_3)} [1 - \exp \{ -(k_1 + k_2 + k_3)t \}] \quad (7c)$$

$$C_G = \frac{C_{B_0} k_1}{(k_1 + k_2 + k_3)} [1 - \exp \{ -(k_1 + k_2 + k_3)t \}] - \frac{\varepsilon C_{B_0} k_2 k_3}{\{ \varepsilon(k_4 + k_5) - (k_1 + k_2 + k_3) \}} \left[ \frac{1}{(k_1 + k_2 + k_3)} [1 - \exp \{ -(k_1 + k_2 + k_3)t \}] + \frac{1}{\varepsilon(k_4 + k_5)} [1 - \exp \{ -\varepsilon(k_4 + k_5)t \}] \right] \quad (7d)$$

$$C_G = \frac{C_{B_0} k_1}{(k_1 + k_2 + k_3)} [1 - \exp \{ -(k_1 + k_2 + k_3)t \}] - \frac{\varepsilon C_{B_0} k_2 k_4}{\{ \varepsilon(k_4 + k_5) - (k_1 + k_2 + k_3) \}} \left[ \frac{1}{(k_1 + k_2 + k_3)} [1 - \exp \{ -(k_1 + k_2 + k_3)t \}] + \frac{1}{\varepsilon(k_4 + k_5)} [1 - \exp \{ -\varepsilon(k_4 + k_5)t \}] \right]$$

TABLE 1. Values of the Parameters employed in this study

S/N	Parameter Description	Symbol	Value used	Source
1	Bulk density of wood	$\rho$	650Kg/m <sup>3</sup>	[41]
2	Radius of the particle	R	0.003m	[41]
3	Porosity of the wood particle	$\varepsilon$	0.4	[36]
4	Wood concentration	C	650Kg/m <sup>3</sup>	[41]
5	Tar, Gas and Char initial concentration	$C_T, C_G, C_C$	0Kg/m <sup>3</sup>	[41]

**TABLE 2.** Kinetic constants used in the simulations

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

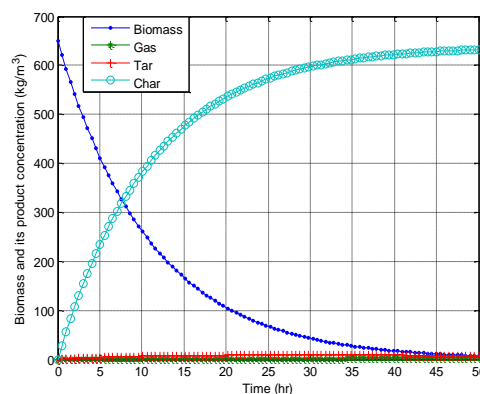
Tables 1 and 2 show the parameters used for the simulations of the kinetics and heat transfer during the pyrolysis of wood.

## RESULTS AND DISCUSSION

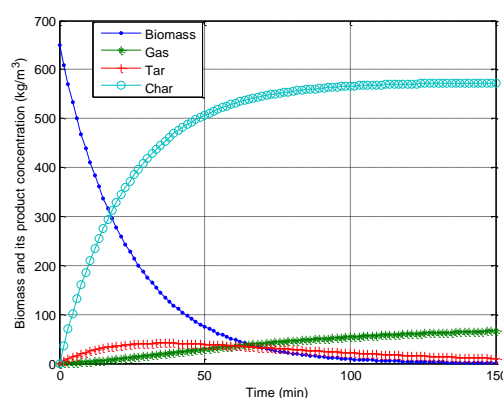
According to the two-stage parallel reaction model used in this work, as the pyrolysis zone temperature increases, the biomass undergoes thermal degradation according to primary reactions giving gases, tar and char as products. Tar also undergoes secondary reactions to give char and gases. Since the amounts of each of these products vary depending mainly on the zone temperature, rate of heating and the size of the particle, the parametric studies of these factors were carried out.

### Effects of isothermal heating temperature on pyrolysis yields.

Figs. 2a to 2d show effects of isothermal heating temperature on the pyrolysis yield as predicted from the developed model in this study. From the results, a lower isothermal heating temperature of 474K and 573K take more time for thermal decomposition than that of higher isothermal heating temperature of 673K and 773K for the biomass particle of the same size. It clearly depicted from the figures that low temperature pyrolysis produces more char and high temperature pyrolysis enhances the production of gas and tar i.e. an increase in isothermal heating temperature increases the yield of gaseous products and decreases char production. The impeding 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 rate of char production becomes constant.



**Figure 2a.** Biomass concentration against temperature at an isothermal heating temperature of 473K



**Figure 2b.** Production and conversion rate against time at an isothermal heating temperature of 573K

Also, the results show that the tar 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 of tar yield and sudden increase of gas yield are observed at higher temperature, this may be due to secondary cracking of the pyrolysis liquid into 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.

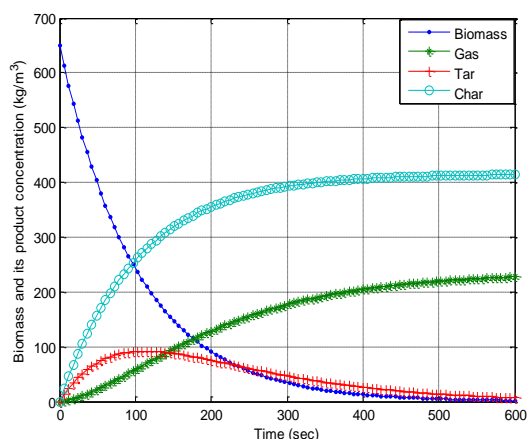


Figure 2c. Biomass concentration against temperature at an isothermal heating temperature of 673K

### 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 10, 20, 30, 40, 50K/s as

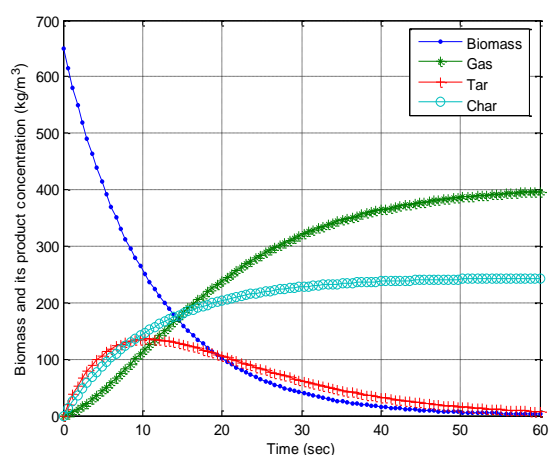


Figure 2d. Production and conversion rate against time at an isothermal heating temperature of 773K

shown in Figs. 3a to 3j and Figs. 4a to 4j. The effects of non-isothermal temperature on pyrolysis yields as functions of time are shown in Figs.2a to 2j while Figs. 3a to 3j show the effects of non-isothermal temperature on pyrolysis yields as a function of temperature at an initial particle temperature of 373K. From the figures, the drying or pre-pyrolysis process are shown as zero rate of production and conversion of the products from 0-120s and 303-473K validates the fact that pyrolysis process actually commenced at about 473K as stated in literatures. 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 noted that the increasing the heating rates reduce the particle residence time and as the heating rate are increased, the residence time of volatiles at low or intermediate temperatures decreases.

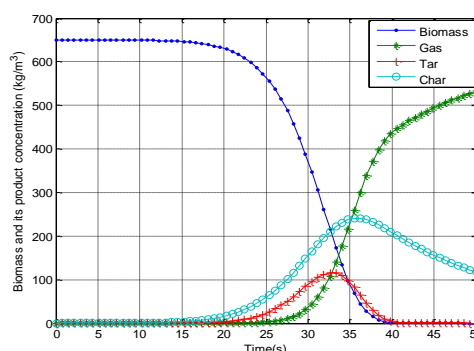


Figure 3a. Biomass and its product concentration variation at heating rate of 10K/s

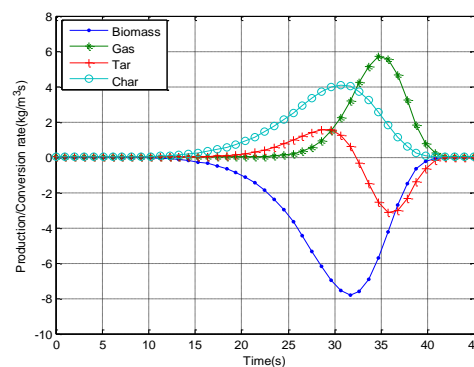


Figure 3b. Production/Conversion rate of Biomass and its Product with time at heating rate of 10K/s

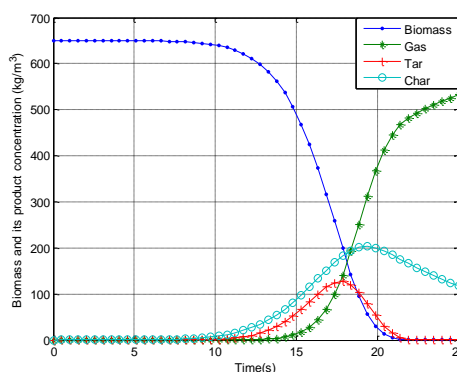
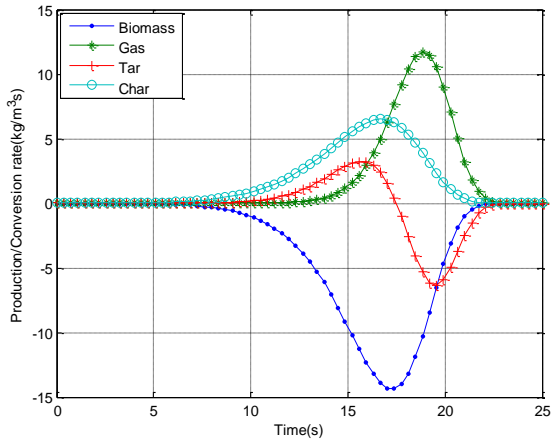
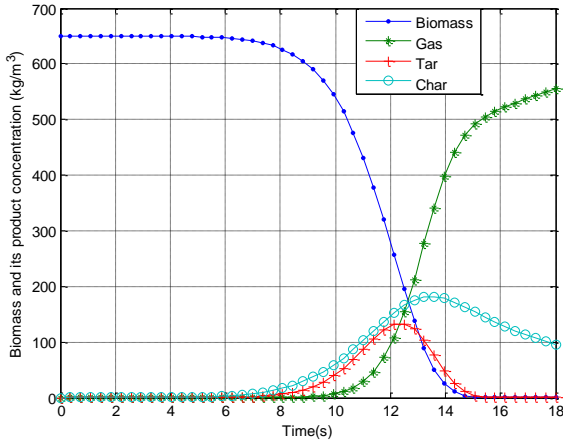


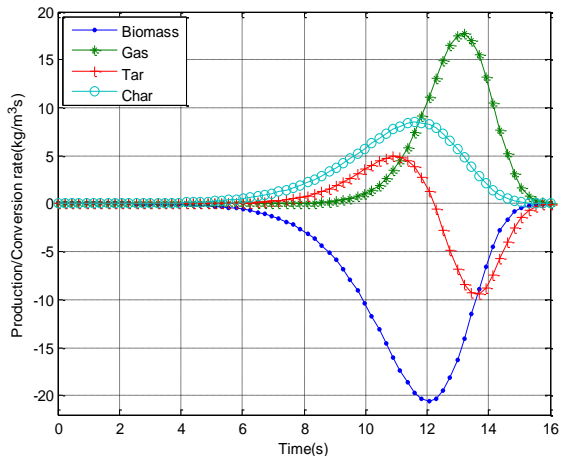
Figure 3c. Biomass and its product concentration variation at heating rate of 20K/s



**Figure 3d.** Production/Conversion rate of Biomass and its Product with time at heating rate of 20K/s



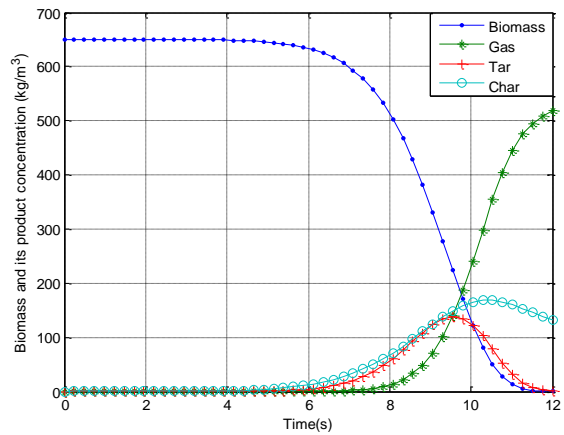
**Figure 3e.** Biomass and its product concentration variation at heating rate of 30K/s



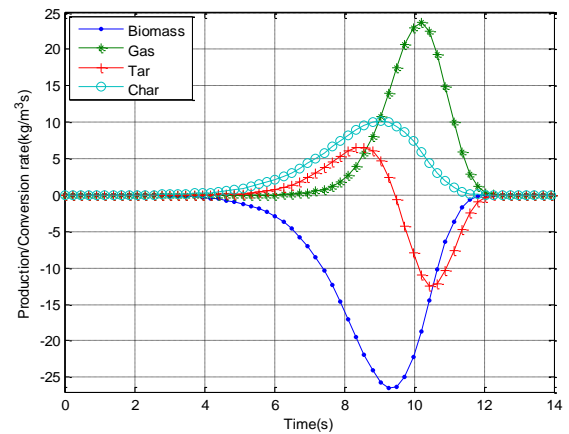
**Figure 3f.** Production/Conversion rate of Biomass and its Product with time at heating rate of 30K/s

Most of the reactions that favour tar conversion to gas occur at higher temperatures. At low heating rates, the

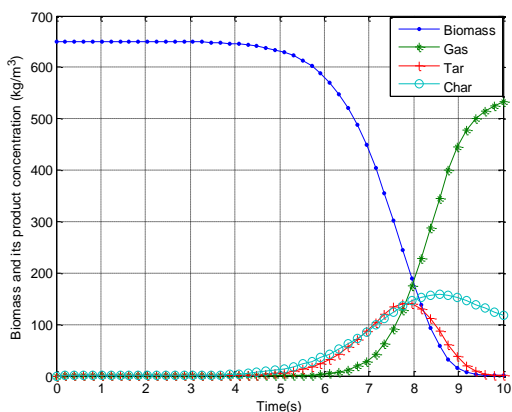
volatiles have sufficient time to escape from the reaction zone before significant cracking can occur. Also, most of the decomposition takes place at temperatures lower than 500K, and no more significant decomposition is produced above 750K. On comparing these results with that of isothermal heating conditions, it is shown that 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. Also, it was found that the tar yield is low at lower heating rate and slightly increases with the increase of heating rate. The gas yield increases with increase in heating rate while the char yield decreases significantly with the 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.



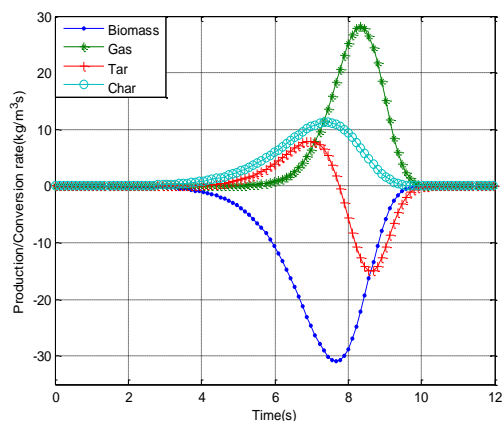
**Figure 3g.** Biomass and its product concentration variation at heating rate of 40K/s



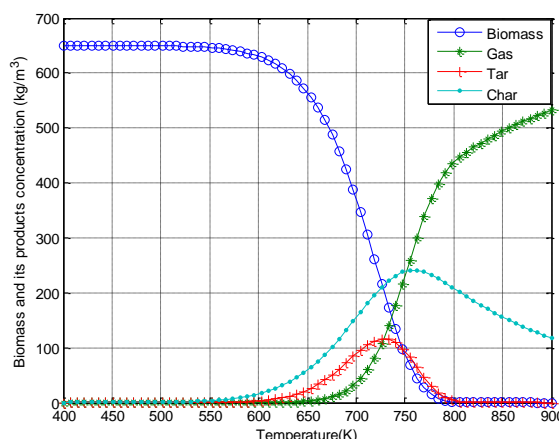
**Figure 3h.** Production/conversion rate of biomass and its product with time at heating rate of 40K/s



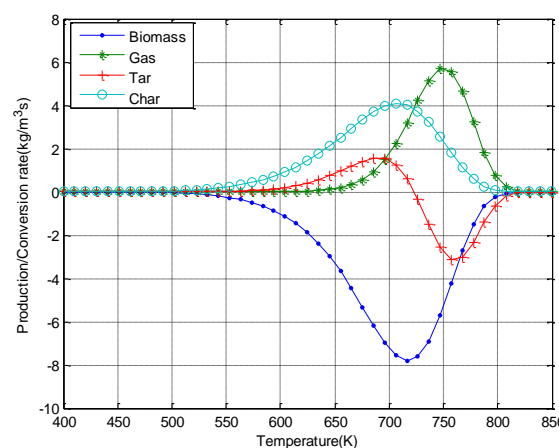
**Figure 3i.** Biomass and its product concentration variation at heating rate of 50K/s



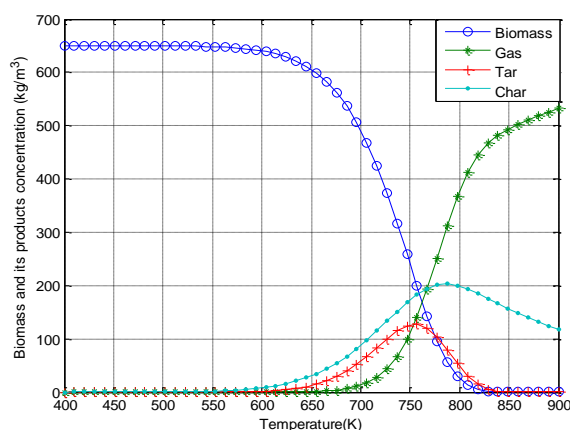
**Figure 3j.** Production/Conversion rate of Biomass and its Product with time at heating rate of 50K/s



**Figure 4a.** Biomass and its product concentration variation at heating rate of 10K/s

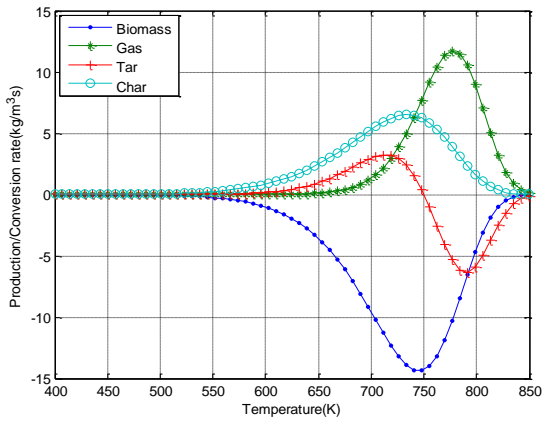


**Figure 4b.** Production/Conversion rate of Biomass and its Product with temperature at heating rate of 10K/s

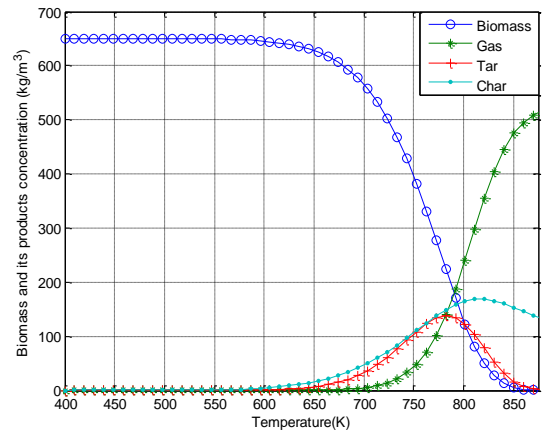


**Figure 4c.** Biomass and its product concentration variation at heating rate of 20K/s

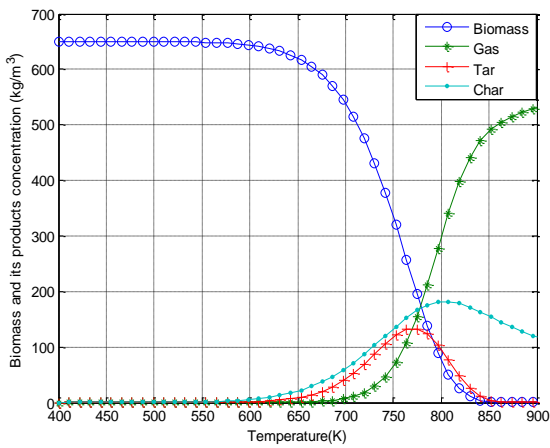
From the Figs. 4a to 4j as shown below, the rate of char production increases gradually between the particle temperatures of 500K and 573K, and as the particle temperature increases, gases and tar evolve from the biomass particle and consequently, the rate of char production increases rapidly from the particle temperature of 500K to 723K, after which there is 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 pyrolyzed. This shows that pyrolysis process slows down from 723-873K (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 573K till 753K (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.



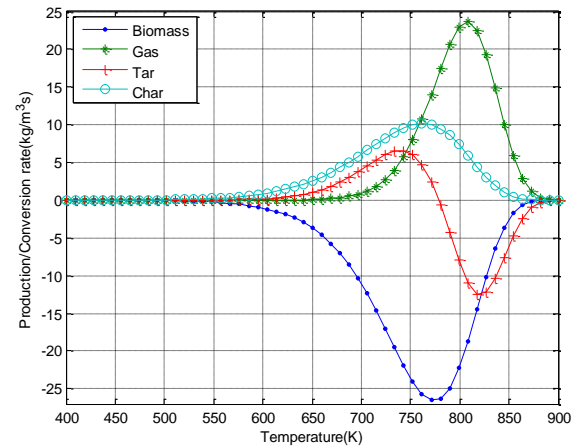
**Figure 4d.** Production/Conversion rate of Biomass and its Product with temperature at heating rate of 20K/s



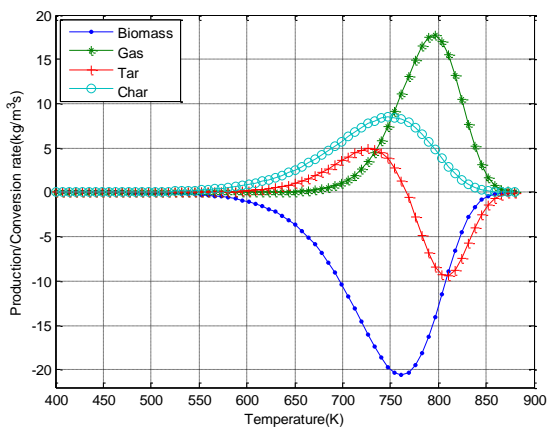
**Figure 4g.** Biomass and its product concentration variation at heating rate of 40K/s



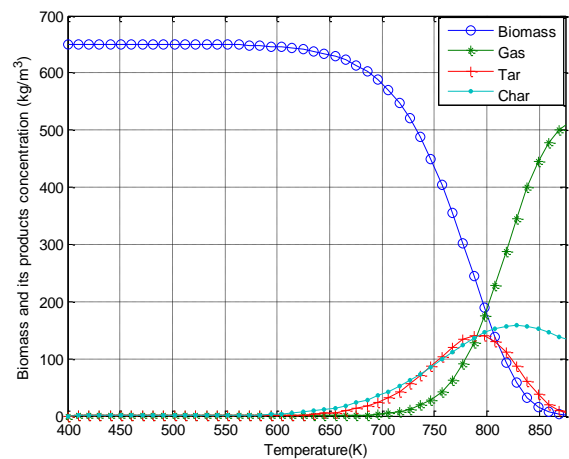
**Figure 4e.** Biomass and its product concentration variation at heating rate of 30K/s



**Figure 4h.** Production/conversion rate of biomass and its Product with temperature at heating rate of 40K/s

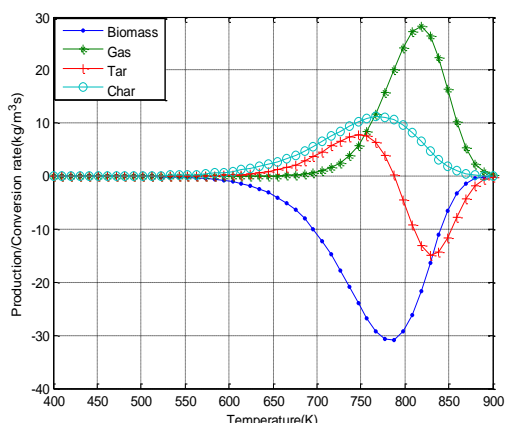


**Figure 4f.** Production/Conversion rate of Biomass and its Product with temperature at heating rate of 30K/s



**Figure 4i.** Biomass and its product concentration variation at heating rate of 50K/s



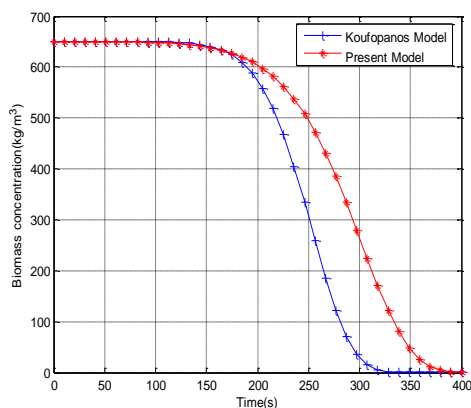


**Figure 4j.** Production/Conversion rate of Biomass and its Product with temperature at heating rate of 50K/s

**TABLE3.** Comparison of Results with literature

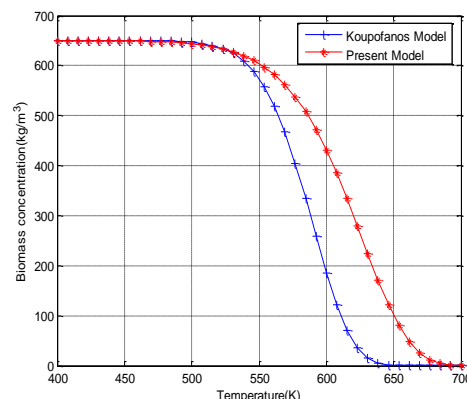
Heating rate	Order of reactions 1 and 1.5 [26]	Order of reactions 1 and 1.5 [34]	Present work, 1 <sup>st</sup> order reaction rate
40 K/s	9.65	9.707	11.52
50 K/s	9.43	9.532	9.57

A good agreement was obtained when the results in this work were compared with the other results reported in literatures as shown in Table 3.

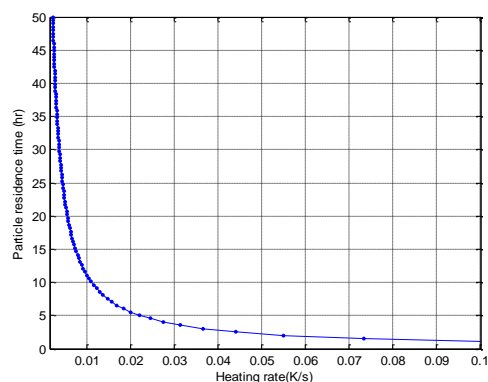


**Figure 5a.** Comparison of Results of biomass pyrolysis against time Babu and Chaurasia [34] used the Koufopoulos’s model [18] for the pyrolysis of wood but in this work, Shafizadeh and Chin’s model [23] which has been stated to be the most classical models for wood pyrolysis [43] is used and the results of their closed form solutions as provided in this work are compared.

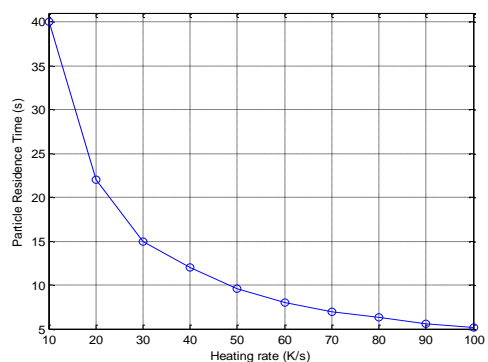
**Effects of heating rates on particle residence time**



**Figure 5b.** Comparison of Results of biomass pyrolysis against time The effects of heating rates on the particle residence time are shown in Figs. 6a to 6d. For the low heating rates of 0.01-0.1K/s in Fig. 6a, it takes hours or days for the pyrolysis to occur and this will definitely enhance the production of charcoal as depicted in Table 4. 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.



**Figure 6a.** Variations of biomass particle residence time very low heating rates



**Figure 6b.** Variations of biomass particle residence time with heating rates of 10-100K/s

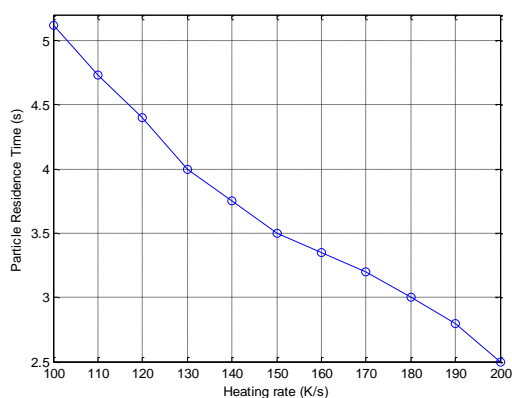


Figure 6c. Variations of biomass particle residence time heating rates of 100-200K/s

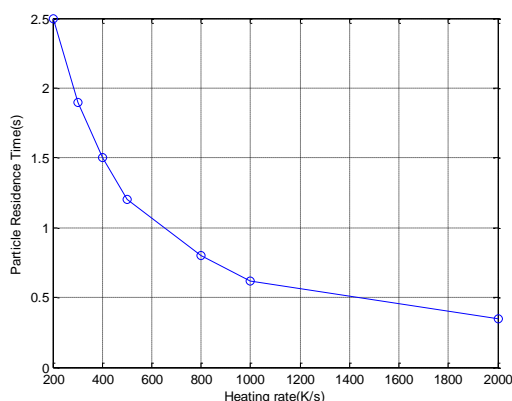


Figure 6d. Variations of biomass particle residence time with heating rates 200-2000K/s

### Effects of shrinkage inclusion on biomass decomposition

Figs. 7a and 7b show the effects of the developed kinetic pyrolysis number on the biomass concentration and volume. As it is shown in the figures, the rate of kinetic of pyrolysis of the shrinking particle increases with the increase in the kinetic pyrolysis number while the particle residence time decreases with the kinetic pyrolysis number. The effects of kinetic pyrolysis number represent the effects isothermal heating temperature on the pyrolysis yield. From the results, a low isothermal heating temperature (low kinetic pyrolysis number) take more time for thermal decomposition than that of higher isothermal heating temperature (high kinetic pyrolysis number) for the biomass particle of the same size. The low isothermal heating temperature pyrolysis will produce more char and high temperature pyrolysis will enhance the production of gas and tar i.e. an increase in isothermal heating temperature increases the yield of gaseous products and decreases char production. Also, it could also be deduced from the results that the time required to obtain a certain conversion level decreases with increasing isothermal heating temperature. Figs 7a-7l shows the comparison of numerical simulation of the

TABLE 4. Pyrolysis conditions for different pyrolysis process

Pyrolysis Technology	Residence time	Heating rate	Temperature (°C)	Products
Carbonization	Days	Very low	400	Charcoal
Conventional	5-30 min.	low	600	Oil, gas, char
Flash-liquid	0.5-5 s	Very high	<650	Bio-oil
Flash gas	<1 s	High	<650	Bio-oil
Ultra	<1 s	High	1000	Chemicals
Vacuum	<1 s	High	400	, gas
Hydro-pyrolysis	<0.5 s	Very high	<500	Chemicals
Methano-pyrolysis	2-30 s	high	>700	, gas
	<10 s	Medium		Bio-oil
	<10 s	High		Bio-oil
		High		Chemicals

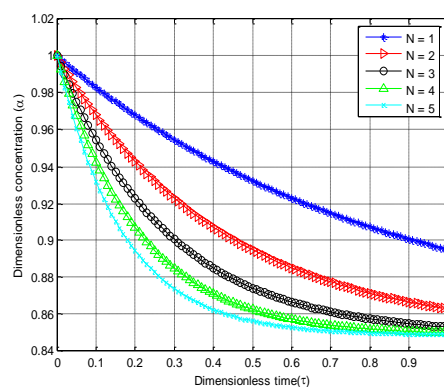


Figure 7a. Effects of the developed pyrolysis kinetic number on the biomass concentration

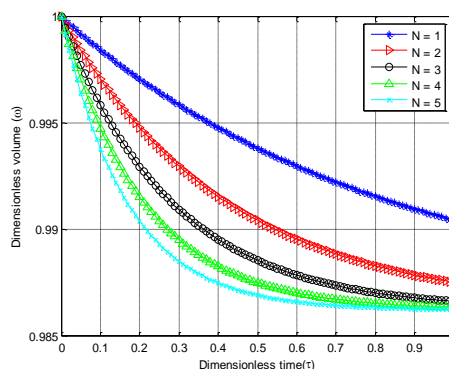
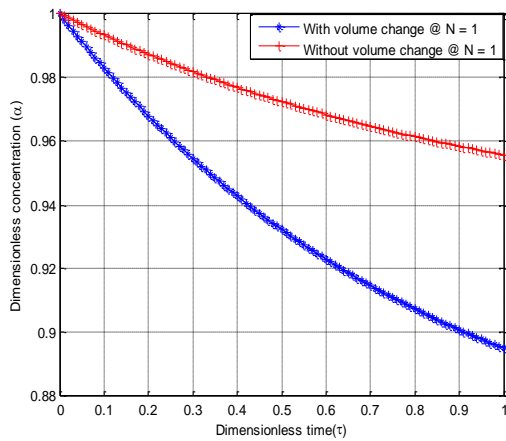
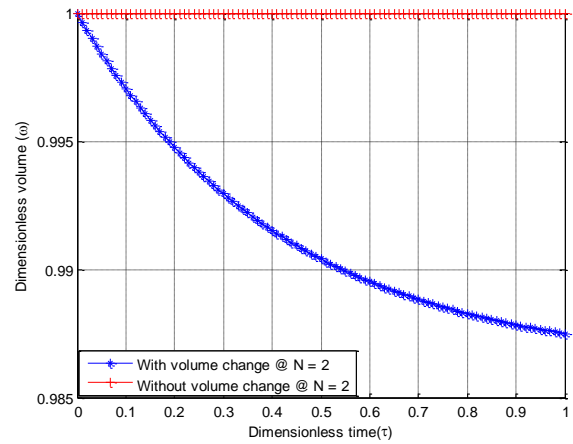


Figure 7b. Effects of the developed pyrolysis kinetic number on the biomass volume

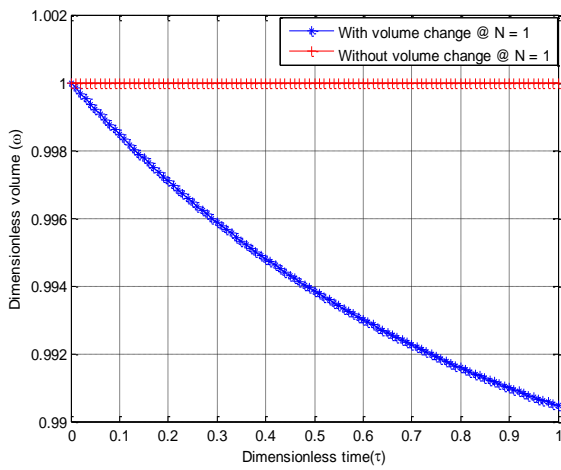
inclusion of volume change in the model with one of without volume change at different new pyrolysis number developed in this model. The wide variation in the two results in the dimensionless form justified and established that, the assumption of volume constancy during the modeling and analysis of biomass drying process is incorrect. Therefore, a better thermochemical models for the analysis of biomass gasification processes



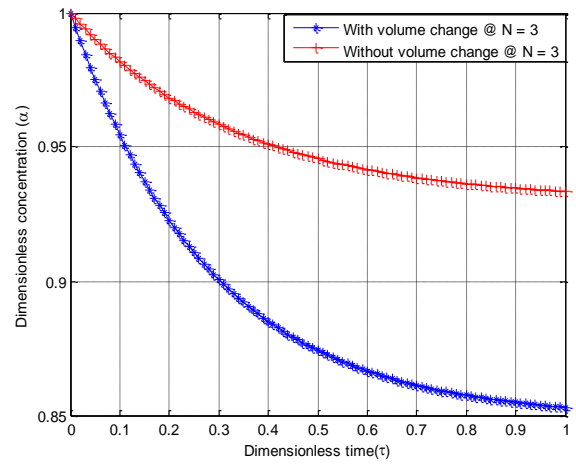
**Figure 7c.** Effects of shrinkage on the concentration of biomass particle at N=1



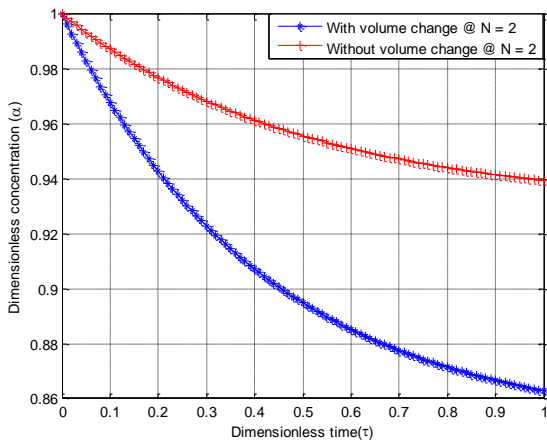
**Figure 7f** Effects of shrinkage on the volume of biomass particle at N=2



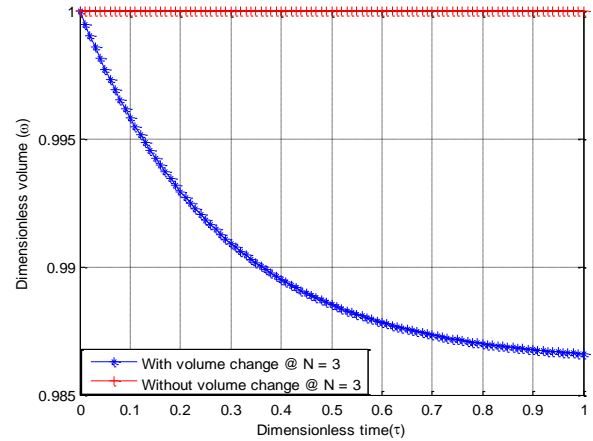
**Figure 7d.** Effects of shrinkage on the volume of biomass particle at N=1



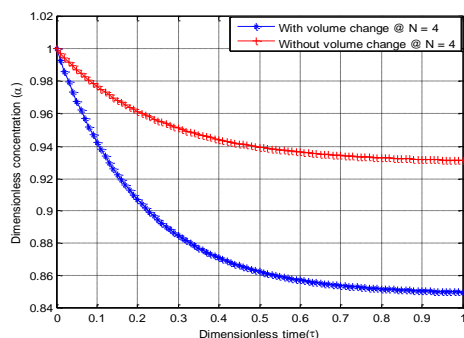
**Figure 7g.** Effects of shrinkage on the concentration of biomass particle at N=3



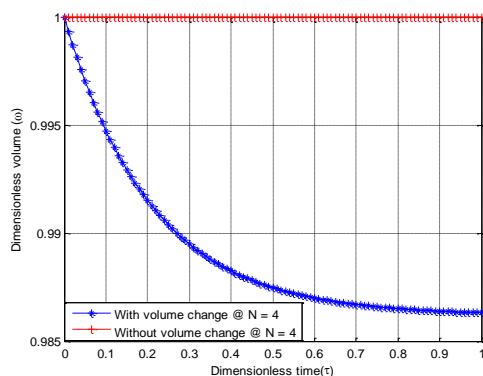
**Figure 7e** Effects of shrinkage on the concentration of biomass particle at N=2



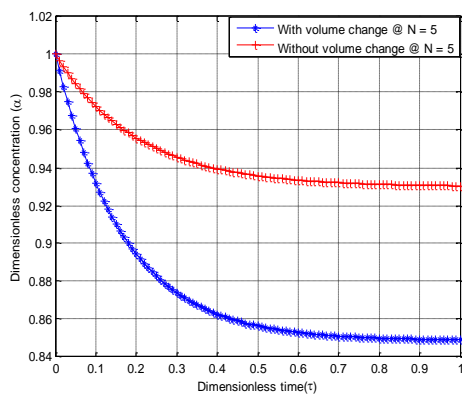
**Figure 7h** Effects of shrinkage on the volume of biomass particle at N=3



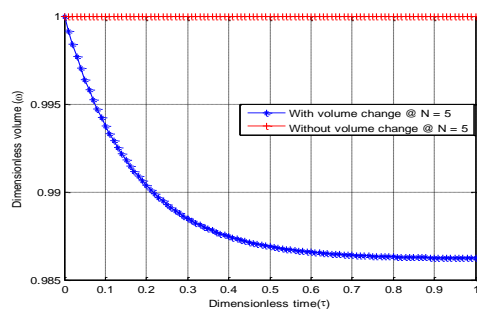
**Figure 7i.** Effects of shrinkage on the concentration of biomass particle at N=4



**Figure 7j.** Effects of shrinkage on the volume of biomass particle at N=4



**Figure 7k.** Effects of shrinkage on the concentration of biomass particle at N=1



**Figure 7l.** Effects of shrinkage on the volume of biomass particle at N=1

or biomass pyrolysis will be obtained if the biomass shrinkage effects are considered. Moreover, the developed model is based on Shafizadeh and Chin's model [23] which has been stated to be the most classical models for wood pyrolysis [42].

## CONCLUSION

In this work, mathematical models of the pyrolysis kinetics of shrinking biomass particle under non-isothermal and isothermal heating conditions were developed and the numerical simulations carried out. The developed models were used to investigate the effects of shrinkage on the pyrolysis of wood. Also, closed form solutions were developed for the pyrolysis of wood particle for the previously developed pyrolysis kinetic models in literatures which were solved numerically. The effects of heating conditions and heating rates on the pyrolysis temperature and residence time were investigated. A good agreement was obtained when the results in this work were compared with the other results reported in literatures. This work could be used in estimating the optimum parameters in the pyrolysis of biomass and in the design of some pyrolysis reactors.

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#### Persian Abstract

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#### چکیده

پیرولیز نقش جامعی در فرایندهای تبدیل بیومس ایفا می کند. توسعه مدل های ریاضی مناسب که در نتیجه، منجر به طراحی راکتورهای پیرولیز می شود. گازی فایر بیومس نقش برجسته ای در مطالعات علمی و درک فرایندهای خیلی مهم در تبدیل ترموشیمیایی سوخت های جامد دارد. اگرچه بدلیل پیچیدگی های طرحواره واکنش بیومس، پیرولیز بیومس بطور کلی براساس سینیتیک ظاهری مدل می شود. علاوه بر این بطور کلی پذیرفته شده است که مهمترین پارامترهای تاثیرگذار بر فرایند دما، غلظت، زمان اقامت و شرایط گرمایش هستند. این کار شبیه سازی سینیتیک پیرولیز ذرات بیومس کم حجم را تحت شرایط گرمایش همدما و غیرهمدما ارائه می دهد. مدل های توسعه یافته برای بررسی اثرات افت حجمی، شرایط گرمایش، شدت های گرمایش بر روی پیرولیز چوب استفاده شده است. یک توافق خوب موجود است زمانی که نتایج مدل های توسعه یافته با نتایج آزمایشگاهی مقایسه شده است. نتایج این کار توانسته در تخمین پارامترهای بهینه در پیرولیز بیومس و در طراحی بعضی از راکتورهای پیرولیز استفاده شود.

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