

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

M . G. Sobamowo¹

¹ University of Lagos

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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, heating rates on the pyrolysis residence time and technologies. Also, as means verification, the developed solutions of the kinetic models using differential transformation method are compared with the results of the solutions of exact analytical method. 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.

Index terms— biomass particle; pyrolysis kinetics; isothermal temperature; non- isothermal heating rates; differential transformation method.

1 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 modeling of pyrolysis of biomass particle, particularly on the studies of the kinetic, thermal and heat transfer effects, Koufopoulos 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 o 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 o 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.

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 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(1a) (1b) (1c) (1d)

where

The initial conditions for the kinetic equations are;

For the Isothermal condition, $T = T_0$ (3) Srivastava [23] assumed that in the thermogravimetric 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; (4) where T_0 is the initial temperature in K, γ is the heating rate in K/s and t is the time in s.

2 Which makes (5)

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 nondimensionless forms of Eqs. (1a-1e) were not written out in this work.

3 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 [40] = = [8]

where U is called the spectrum of $u(t)$ (Expressing $u(t)$ in Taylor's series as $U = \sum_{k=0}^{\infty} \frac{u^{(k)}(t_0)}{k!} (t-t_0)^k$) (9)

where Equ. (9) is the inverse of U (denoting the differential transformation process and combining (8) and (9), we have $U = \sum_{k=0}^{\infty} \frac{u^{(k)}(t_0)}{k!} (t-t_0)^k$) (10) $U = \sum_{k=0}^{\infty} \frac{u^{(k)}(t_0)}{k!} (t-t_0)^k$ (11) $U = \sum_{k=0}^{\infty} \frac{u^{(k)}(t_0)}{k!} (t-t_0)^k$ (12) $U = \sum_{k=0}^{\infty} \frac{u^{(k)}(t_0)}{k!} (t-t_0)^k$ (13) $U = \sum_{k=0}^{\infty} \frac{u^{(k)}(t_0)}{k!} (t-t_0)^k$ (14) $U = \sum_{k=0}^{\infty} \frac{u^{(k)}(t_0)}{k!} (t-t_0)^k$ (15) $U = \sum_{k=0}^{\infty} \frac{u^{(k)}(t_0)}{k!} (t-t_0)^k$ (16) $U = \sum_{k=0}^{\infty} \frac{u^{(k)}(t_0)}{k!} (t-t_0)^k$ (17) $U = \sum_{k=0}^{\infty} \frac{u^{(k)}(t_0)}{k!} (t-t_0)^k$ (18) $U = \sum_{k=0}^{\infty} \frac{u^{(k)}(t_0)}{k!} (t-t_0)^k$ (19) $U = \sum_{k=0}^{\infty} \frac{u^{(k)}(t_0)}{k!} (t-t_0)^k$ (20) $U = \sum_{k=0}^{\infty} \frac{u^{(k)}(t_0)}{k!} (t-t_0)^k$ (21) $U = \sum_{k=0}^{\infty} \frac{u^{(k)}(t_0)}{k!} (t-t_0)^k$ (22) $U = \sum_{k=0}^{\infty} 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228 temperature increases to 573K and 673K. The decrease in the tar yield and sudden increase of gas yield observed
 229 at higher temperature may be due to secondary cracking of the pyrolysis liquid in to gaseous product at higher
 230 temperature. It could also be deduced from the results that the time required to obtain a certain conversion level
 231 decreases with increasing isothermal heating temperature. The trends obtained in this work as shown above are
 232 qualitatively the same as reported in literature [24] and [25].

233 As pointed out in the previous section, heating rate is one of the important parameter for the yield of different
 234 products from the pyrolysis process. To determine the effects of heating rate on the yields of the biomass
 235 pyrolysis, simulations were carried out for different heating rates of as shown in Figs. 26 38-41 show the effects of
 236 non-isothermal temperature on pyrolysis yields as a function of temperature at an initial particle temperature of
 237 373 K. From the figures, the drying or pre-pyrolysis process are shown as zero rate of production and conversion
 238 of the products from 0-120 s and 303-473 K which validates the fact that pyrolysis process actually commenced
 239 at about 473K as stated in literatures [25]. It is surprising to see that at any heating rate, the production rate
 240 of char is higher than that of tar and gas. This may be due to the increase in the resistance for mass and heat
 241 transfers offered by the thick layer of the dried biomass i.e. for the gas and tar to evolve from the particle, they
 242 have to travel through a dried layer of the biomass which in consequence, comparably reduces their production
 243 rates. Also, it should be noted that increasing the heating rates reduces the particle residence time and as the
 244 heating rate are increased, the residence time of volatiles at low or intermediate temperatures decreases. Most of
 245 the reactions that favour tar conversion to gas occur at higher temperatures. At low heating rates, the volatiles
 246 have sufficient time to escape from the reaction zone before significant cracking can occur. Also, most of the
 247 decomposition takes place at temperatures lower than 500 K, and no more significant decomposition is produced
 248 above 750 K.

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

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

268 5 c) Effects of heating rates on particle residence time

269 Recently, Lédé , and Authier [32] advocated for the criteria for characterizing fast pyrolysis based on temperature
 270 and heating rate of solid particles that undergoes a thermal decomposition The effects of heating rates on the
 271 particle residence time are shown in Figs. ??2-45. For the low heating rates of 0.01-0.1K/s in Figs. 42, it takes
 272 hours or days for the pyrolysis to occur and this will definitely enhance the production of charcoal as depicted in
 273 Table 4. As the heating rates increases, the particle residence time in the reactor decreases and high heating rates
 274 favours the production of tar and gas. Therefore, as shown in the table, the length of heating and its intensity
 275 affect the rate and extent of pyrolytic reactions, the sequence of these reactions, and composition of the resultant
 products. ^{1 2}

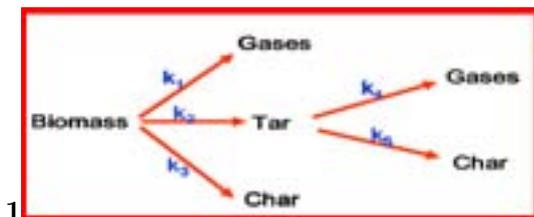


Figure 1: Fig. 1 :

3

S/N	Function	properties of differential transformation method	Differential Transform
1	$() () u t v t \pm$		
2	?	$() u t$	
3	$() du t$	dt	
4	$() () u t v t$		
5	$() u t m$		
6	$() d u t n$	dx	n
7	$(\sin t ? ? +$)
8		$()$	

Figure 2: Table 3 :

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Figure 3:

2

Figure 4: Table 2 :

3

[Note: IV.]

Figure 5: Table 3 :

Pyrolysis technology	Residence time	Heating rate	Temperature (° C)	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

Figure 6: Table 4 :

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²Analyzing the differential transform in Eq. (11a), we have Applying the inverse differential transform, © 2017 Global Journals Inc. (US)

276 .1 Global

277 A study the effects of heating conditions, heating rates on the pyrolysis residence time and technologies. Good
 278 agreements were established between the present results and the past works. It is therefore expected that this
 279 study will enhance the understanding of the pyrolysis process by giving physical insights into the various factors
 280 and the parameters affecting the phenomena.

281 V.

282 .2 Conclusion

283 In this work, differential transformation method has been applied to analyze pyrolysis kinetics of biomass particle
 284 under isothermal and non-isothermal heating conditions. The developed analytical solutions to the system of
 285 pyrolysis kinetic models were used to Nameclature A1; A2; A3; A4; A5 frequency factor, 1/s Bi m Modified Biot
 286 number C concentration, kg/m³ C p specific heat capacity, J/kgK E activation energy, J/mol h convective heat
 287 transfer coefficient, W/m² K K thermal conductivity, W/mK k 1 ; k 2 ; k 3 ; k 4 ; k 5 rate constants, 1/s Q heat
 288 of pyrolysis, J/Kg r radial distance, m R radius for cylindrical particle, m R g universal gas constant, J/mol t
 289 time, s T f reactor final temperature, K T temperature, K R '

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5 C) EFFECTS OF HEATING RATES ON PARTICLE RESIDENCE TIME

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