Original

Kinetics of Biomass Decomposition in Pyrolysis and Torrefaction Process

Unchana Sae-Ueng,[1] Noppong Sritrakul[1], Nitipong Soponpongpiapat[1]

Received: 25 January 2012 ; Accepted: 11 April 2012

Abstract

This paper reviewed the mass loss kinetics of biomass in torrefaction process which is well-known as biomass's properties improving process. According to consideration of torrefaction process as mild pyrolysis process, this process was also reviewed. The weight loss prediction models, which are established from decomposition mechanisms of raw biomass, were reviewed. In addition, the experimental set up both isothermal and non-isothermal conditions in nitrogen atmospheres and oxidative atmospheres were presented in detail. Finally, parameters affecting kinetics of both torrefaction and pyrolysis such as particle size of raw biomass and heating rate were explained.

Keywords: Biomass, Kinetics, Mild pyrolysis, Thermogravimetric analysis, Torrefaction

Introduction

In recent years, the biomass is regarded as an interested renewable energy source because it is part of the neutral carbon cycle. In the world, there is a large quantity of biomass and it is environmentally friendly. However, the use of raw biomass is challenged by its poor properties such as low calorific value, low energy density, high moisture content, and low grindability index. These drawbacks result in many problems; for example, transportation, storage and application of raw biomass.[1-5] These problems can be solved by improvement of raw biomass's properties. There are several processes for biomass properties improvement such as densification, torrefaction, pyrolysis, and carbonization process. The pyrolysis process is general name of biomass thermal decomposition, and composes of carbonization, torrefaction and others process. The carbonization, which is known as slow pyrolysis, starts at temperature of 400^{0}C[6] while torrefaction, which is known as mild pyrolysis, starts at temperature of 200 - 300^{0}C.[1-3, 7] It is noted that both pyrolysis and torrefaction process is commonly used in practices. The understanding of biomass decomposition of both processes is need for developing of operation procedure and equipment design.

Pyrolysis Process

Generally, the pyrolysis is a thermo-chemical decomposition of biomass in inert atmosphere. Pyrolysis results in decomposition of complex hydrocarbon molecules biomass into simpler molecules of gas, liquid, and char.[6] The biomass pyrolysis compose of four procedures: moisture evolution at temperature of lower than 220^{0}C, hemicellulose decomposition in temperature range of 220-315^{0}C, cellulose decomposition in range of 315-400^{0}C, and decomposition of lignin in range of 160 - 900^{0}C.[8, 9]

The reaction mechanisms of pyrolysis

The study of biomass kinetics can be conducted by means of the reaction mechanism consideration. The reaction mechanism is defined as the sequence of chemical change. This mechanism is an important key for prediction of the weight loss of biomass due to decomposition reaction. The kinetics model of biomass decomposition was studied base on decomposition of hemicelluloses, cellulose, and lignin. The detail of each model can be described as follows.

[1] Department of Mechanical Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University (Sanam Chandra Palace), Nakhon Pathom 73000, Thailand. Email: N_ppong@yahoo.com,

One-step global model

A One-step global model shows the conversion of biomass to char and volatile matters as shown in Figure 1. According to literature,[10-12] it was found that the conversion prediction of this model was faster than that of the actual experiment, particularly at higher pyrolysis temperature regions. For one step model, the softening effect and formation of an intermediate were not taking into account.[10, 11]

Figure 1 One-step global model[11]

Two-step consecutive-reaction model

There are two reaction mechanisms of this model as shown in Figure 2. From the figure, raw biomass decomposes into intermediate and primary volatile. Intermediate, later, decomposes into finally char and secondary volatile. From previous researches,[10, 11, 13-15] the result shown that a two-step consecutive-reaction models provided excellent agreement between the experimental data and the conversion prediction.

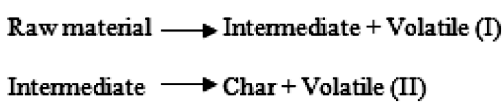

Figure 2 Two-step consecutive-reaction model[11]

Semi-global reaction model

There are three reaction mechanisms of this model as shown in Figure 3. From the figure, raw biomass decomposes into intermediate (I) and volatile (I). Next, intermediate (I) decomposes into intermediate (II) and volatile (II). Finally, intermediate (II) decomposes into finally char and volatile (III).[16]

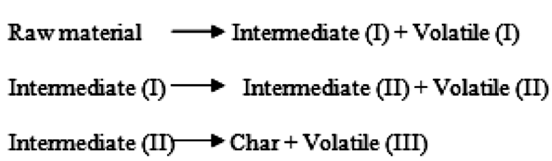

Figure 3 Semi-global reaction model[16]

Experimental setup

The experiment on pyrolysis kinetics can be conducted by several methods but the most popular technique is the thermogravimetric analysis (TGA).[10-15, 17-19] The TGA continuously measures and records the changes in weight of solid biomass on a high precision thermobalance. The typical TG curve is shown in Figure 4 for non-isothermal experimental setup and 5 for isothermal experimental setup.[20]

Figure 4 represents the weight loss of biomass in percentage versus temperature. The curves can be divided into three different ranges: drying, the releasing of some light volatiles, and the releasing of other heavy components[22] while Figure 5 represents the weight loss of biomass in percentage versus time. It is noted that there are difference between isothermal and non-isothermal TG curve on horizontal axis.

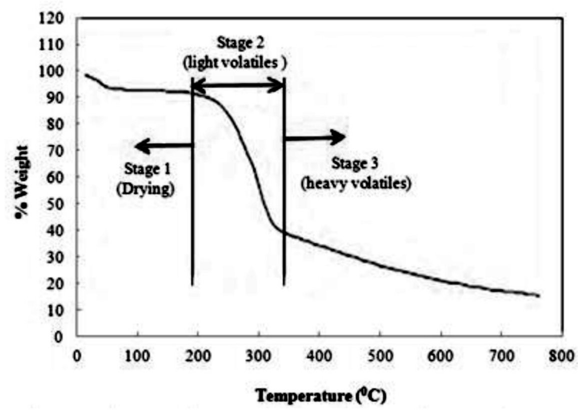

Figure 4 The non-isothermal TG curve for wheat straw[21]

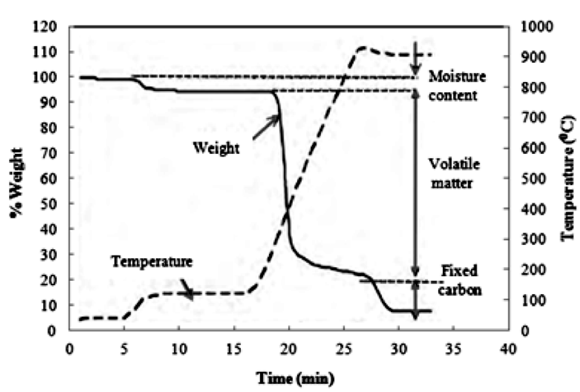

Figure 5 The isothermal TG curve for wheat straw[21]

The DTG is derivative thermogravimetry, which is conducted by TGA equipment. The typical DTG curve is shown in Figure 6. The peak of the DTG curves shows reactivity of main composition of biomass to volatile matters. Mostly, the TG and DTG technique were used together.[10, 11, 14, 23]

In addition, the experiment on pyrolysis can also be applied by laboratory pyrolysis reactor. As same as in TGA, the data gathering of weight loss is needed. *Branca* and *Blasi*[16] studied the decomposition of beech and willow at isothermal condition by quartz reactor. The experimental condition of previous researches was shown in Table 1.

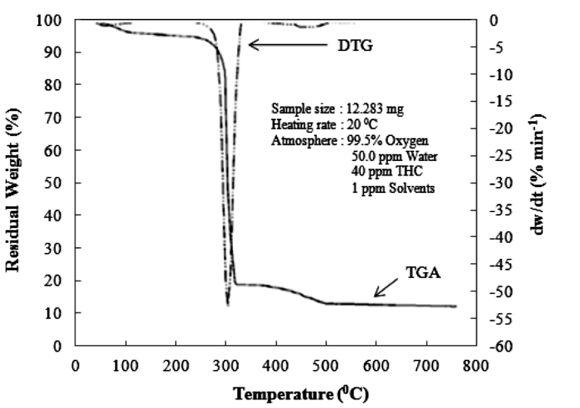

Figure 6 The DTG curve of rice husk[24]

1.3 Parameters affecting pyrolysis kinetics

1.3.1 Heating rate

The effect of heating rate on decomposition of solid biomass in pyrolysis process was shown in Figure 7. It can be seen from the figure that residual weight fraction of raw biomass decreases with increasing of heating rate. The heating rate also affects kinetics parameters. When the heating rate increases, frequency factor (A) and rate constant (k) increase but the activation energy (E) decreases.[23] Moreover, the increasing of heating rate results in increasing of initial decomposition temperature.[10]

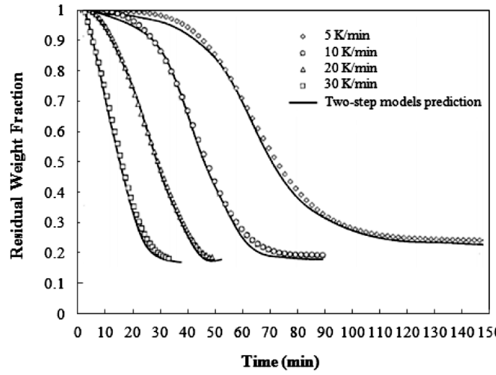

Figure 7 The effect of heating rate on palm shells decomposition[11]

Particle size of biomass

The effect of particle size on decomposition rate of solid biomass was shown in Figure 8. It was seen that, the decreasing of particle size of biomass results in the decreasing of residual weight fraction. *Guo* and *Lua,*[11] studied by isothermal TGA, they found that the pyrolysis temperature and the reaction rate is significantly increased when particle size is small. The non-isothermal experiment with the lager particle size was also conducted. It was found that the mass loss rate decreased due to decreasing of released volatile and increasing of residual solid state.[23] The high activation energy and difficult decomposition occurred with the large particle size; the decomposition was controlled by the kinetics and heat transfer mechanism. However, the less activation energy and easy decomposition occurred with small particle size; it was only controlled by kinetics mechanism.[10, 11, 17]

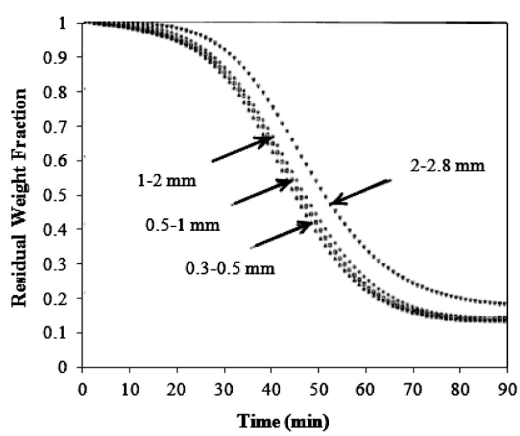

Figure 8 The effect of particle size on palm shells decomposition[11]

The data of pyrolysis kinetics parameters was summarized as shown in Table 2.

Torrefaction Process

The torrefaction is biomass's properties improvement technology. Torrefaction is also called mild pyrolysis.[1, 3, 7, 28] It was carried out at temperature range of 200-300^{0}C, in inert atmosphere, and low heating rate.[3, 7]

Reaction mechanisms of torrefaction

Generally, torrefaction process carried out at low temperature, thus, almost amount of hemicelluloses was decomposed while partial amount of celluloses was decomposed. The kinetics model can be described as follows.

One-step global model

A one-step global model describes the decomposition of biomass and the conversion to charcoal and volatile. This model is similar to one-step model of pyrolysis. The one-step global model is a simple model and suitable for applying with low temperature torrefaction. *Chen* and *Kuo*,[22] define the torrefaction at low temperature as light torrefaction process. The reaction mechanism of one-step global model is shown in Figure 9.

Figure 9 One-step global model[29]

Two-step consecutive-reaction model

This model[4, 29] assumes that the products of first step decomposition reaction of biomass are volatile (I) and intermediate. The second step decomposition of intermediate results in volatile (II) and charcoal. The reactant of the first step can be defined as hemicelluloses while the intermediate of the second step can be defined as residual substance inside biomass.[4] The reaction mechanism of two-step consecutive-reaction model is shown in Figure 10.

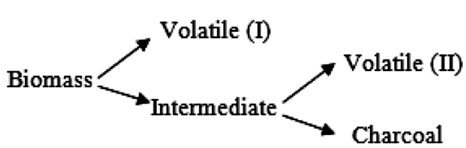

Figure 10 Two-step consecutive-reaction model[4]

Two-step reaction in series model

The decomposition reaction for this model can be divided into two groups, the fast and medium groups. The fast reaction group is defined as group of hemicelluloses decomposition. The medium reaction group is referred as the decomposition of cellulose and lignin. The reaction mechanism of two-step reaction in series model is shown in Figure 11.

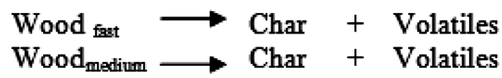

Figure 11 Two-step reaction in series model[30]

Experimental setup

The experimental setup of torrefaction for determination of kinetic parameters is similar to that of pyrolysis. The TGA/DTG technique is still used in thermal degradation analysis of biomass torrefaction.[1, 4, 5, 22]

Moreover, *Pe´trissans et al*.[31] creates special equipment for investigating kinetic parameters. This setup measures the weight loss in percentage during operation of torrefaction process as shown in Fig. 12. From the figure, the reactor size of 25 x 11 x 2.5 cm^3 is filled with Poplar of 269–280 g.

List experimental design and setup of previous works were summarized as shown in Table 3.

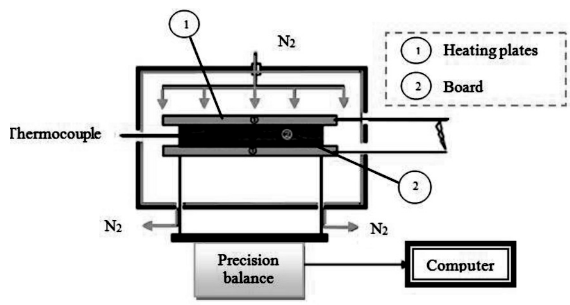

Figure 12 Torrefaction reactor[3]

Parameters affecting torrefaction kinetics

Peng et al.[31] considered the effect of particle size on torrefaction of by TGA and tubular fixed bed reactor. It was found that increasing of particle size results in decreasing of reaction constant rate.[30] The effect of heating rate on kinetic parameters of torrefaction process was not found in the literature review. The data of torrefaction kinetics parameter conducted by previous work was summarized as shown in Table 4.

Conclusion

This paper reviewed the weight loss kinetics studies of biomass in pyrolysis and torrefaction process. For a long time, the pyrolysis is known as biomass properties improvement process while the torrefaction is a new technology. The kinetic models of both processes are useful for determine to suitable operating conditions in industrial process. Nowadays, the information of biomass pyrolysis is sufficient but information of various biomasses in torrefaction process is needed.

Table 1 List of experimental design and setup of pyrolysis process

Technique	Atmospheres	Feedstock	References
Isothermal	Nitrogen	Xylan	(Lanzetta and Blasi, 1997)[13]
		Straw , corn stalks	(Blasi and Lanzetta, 1998)[15]
		Beech	(Branca and Blasi, 2003)[16]
		oil-shale	(Williams et al., 2000)[19]
		extracted oil palm fibers	(Guo and Lua, 2000)[17]
	Air	pine sawdust	(Bilbao et al., 1997)[25]
		Sweetener	(Conceio et al., 2005)[26]
Non-isothermal	Nitrogen	walnut shell	(Yuan and Liu, 2007)[14]
		corn cob	(Yu et al., 2008)[15]
		olive residue and sugar cane bagasse	(Ounas et al., 2011)[18]
		oil-palm solid wastes	(Luangkiattikhun et al., 2008)[23]
		oil-shale	(Williams et al., 2000)[19]
		cotton stalk, sugarcane bagasse, shea meal	(Munir et al., 2009)[27]
		extracted oil palm fibers	(Guo and Lua, 2000)[17]
	Air	Rice husk	(Mansaray and Ghaly, 1999)[24]
		cotton stalk, sugarcane bagasse, shea meal	(Munir et al., 2009)[27]
		pine sawdust	(Bilbao et al., 1997)[25]

Table 2 Summary of pyrolysis kinetic parameters

Feedstock	Technique	Conditions	Reaction mechanisms	Kinetic parameter
oil-palm shell 0.3-0.5, 0.5 -1, 1-2 and 2-2.8 mm[11]	non-isothermal TG-DTG	nitrogen 50 cm^3/min	One-step global model Raw material → Char + Volatiles two-step consecutive-reaction model Raw material → Intermediate + Volatile (I) Intermediate → Char + Volatile (II)	One-step; $A=9.74\ X10^{3}\ s^{-1}$ E=54.8 kJ/mol Two-step; $A1 = 6.85\ X10^{7}\ s^{-1}$ E1=110.3 kJ/mol $A2=9.82\ X10^{12}\ s^{-1}$ E1=168.4 kJ/mol

Table 2 Conclusion of the kinetic parameters in pyrolysis process (Cont.)

Feedstock	Technique	Conditions	Reaction mechanisms	Kinetic parameter
corn cob 0.5, 1, and 2 mm[10]	non-isothermal TG-DTG	373-1073 K 10, 20, and 30 K/min nitrogen 4.0 ml/min	One-step global model Corn cob ⟶ Char + Volatiles two-step consecutive-reaction model Corn cob → Intermediate + Volatile ↓ Volatile + Char	One-step; A1=6.4 $X10^{-3}$ s^{-1} E1=27.64 kJ/mol Two-step; A1 = 1.49 $X10^{16}$ s^{-1} E1=210.71 kJ/mol A2=3.76 $X10^{36}$ s^{-1} E2=459.8 kJ/mol
Spruce, Pine, Fir[12]	non-isothermal TGA	Nitrogen 100 ml/min	One-step global models Wood $\xrightarrow{k}$ Char + Volatiles	Spruce; 262.4kJ/mol Pine; 197.14 kJ/mol Fir; 139.94 kJ/mol
Xylan[13]	isothermal TGA	473-613 K 40-70 K/ s	Two-step consecutive model Biomass → Volatile (I) Biomass → Intermediate Intermediate → Volatile (II) Intermediate → Char	A1=3.62 $X10^{5}$ s^{-1} E1=18.3 kcal/mol A2 = 3.83 $x10^{2}$ s^{-1} E2=13.1 kcal/mol
walnut shell 0.154 mm[14]	non-isothermal TGA	Nitrogen 20 ml/min 5,10, 20, 30 and 40 K /min	Two-step consecutive model Raw material ⟶ Intermediate + Volatile (I) └⟶ Char + Volatile (II)	A1=5.3$X10^{7}$ s^{-1} E1=120.158 kJ/mol A2 = 6.19$x10^{12}$ s^{-1} E2=154.414 kJ/mol
Straw, Corn stalks 100 μm[15]	isothermal TGA	400–648 K.	Two-step consecutive model Biomass → Volatile (I) Biomass → Intermediate Intermediate → Volatile (II) Intermediate → Char	Straw; A1=2.43 $X10^{4}$ s^{1} E1=15.44 kcal/mol A2 = 5.43 $x10^{1}$ s^{-1} E2=11.3 kcal/mol
Beech particle sizes below 80 μm[16]	isothermal quartz reactor	528–708 K	Semi-global reaction mechanism Raw material ⟶ Intermediate (I) + Volatile (I) Intermediate (I) ⟶ Intermediate (II) + Volatile (II) Intermediate (II) ⟶ Char + Volatile (III)	ln A1=10.2 s^{-1} E1=76.2 kJ/mol ln A2 = 22.5 s^{-1} E2=142.8 kJ/mol ln A3= 2.3 s^{-1} E2=43.8 kJ/mol

Table 3 List of experimental design and setup of torrefaction process

Technique	Atmospheres	Feedstock	References
isothermal	Nitrogen	bamboo, willow, coconut shell and wood	(Chen and Kuo, 2010)[22]
		spruce and beech	(Vincent et al., 2010)[29]
		beech, willow , larch, straw	(Prins et al., 2006)[4]
		hemicelluloses, cellulose and lignin	(Chen and Kuo, 2011)[5]
	Air	Eucalyptus grandis wood	(Rousset et al., 2012)[32]
Non-isothermal	Air	Eucalyptus	(Arias et al., 2008)[1]

Table 4 Summary of the torrefaction kinetic parameters

Feedstock	Technique	Conditions	Reaction mechanism	Kinetic parameters
spruce and beech[29]	isothermal TGA	473-613 K 40-70 K/s	One-step global model Wood → Char + Volatiles two-step consecutive model Wood → Intermediate compound Wood → Volatile (I) Intermediate compound → Char Intermediate compound → Volatile (II)	Two step (spruce); k1 = 2.47 X10^4 s^{-1} E1=76 kJ/mol A2 = 1.1x10^{10} s^{-1} E2=151.7 kJ/mol
beech and willow 0.7–2.0 mm[4]	isothermal TGA	225–300 ^{0}C nitrogen 20 ml /min. 10 ^{0}C/min	two-step reaction in series model Biomass → Volatile (I) Biomass → Intermediate Intermediate → Volatile (II) Intermediate → Charcoal	Willow; A1=2.48X10^4 s^{-1} E1=76 kJ/mol A2 = 1.1x10^{10} s^{-1} E2=151.7 kJ/mol
Pine 125 μm[30]	isothermal TGA, bench- scale fixed bed	T=553 K nitrogen 50 ml/min 50 K/min	two-step reaction in series model $Wood_{fast}$ → Char + Volatiles $Wood_{medium}$ → Char + Volatiles	k1 =1.48 x $10^{-3}s^{-1}$ k2 =4 x $10^{-5}s^{-1}$

Acknowledgement

The authors would like to thank Energy Policy and Planning Office, Ministry of Energy, Thailand for supporting research fund.

References

1. Arias B, Pevida C, Fermoso J, Plaza M G, Rubiera F, Pis JJ. Influence of torrefaction on the grindability and reactivity of woody biomass. Fuel Processing Technology 2008;89:169-75.
2. Chen, W-H and Kuo P-C. Torrefaction and co-torrefaction characterization of hemicellulose, cellulose and lignin as well as torrefaction of some basic constituents in biomass. Energy 2011;36: 803-11.
3. Medic D, Darr M, Shah A, Potter B, Zimmerman J. Effects of torrefaction process parameters on biomass feedstock upgrading. Fuel 2012;91:147-54.

4. Prins MJ, Ptasinski KJ, Janssen FJJG. Torrefaction of wood Part 1. Weight loss kinetics. Journal of Analytical and Applied Pyrolysis 2006;77:28-34.
5. Chen W-H, Kuo P-C. Isothermal torrefaction kinetics of hemicellulose, cellulose, lignin and xylan using thermogravimetric analysis. Energy 2011.
6. Basu P. Biomass gasification and pyrolysis. Oxford: Elsevier; 2010.
7. Chew JJ, Doshi V. Recent advances in biomass pretreatment – torrefaction fundamentals and technology. Renewable and Sustainable Energy Reviews 2011;15:4212–22.
8. Yang H, Yan R, Chen H, Zheng C, Lee DH, Liang DT. In-depth investigation of biomass pyrolysis based on three major components: hemicellulose, cellulose and Lignin. Energy & Fuels 2006;20:388-93.
9. Yang H, Yan R, Chen H, Lee DH, Zheng C. Characteristics of hemicellulose, cellulose and lignin pyrolysis. Fuel 2007;86:1781-8.
10. Yu F, Ruan R, Steele P. Consecutive reaction model for the pyrolysis of corn. American Society of Agricultural and Biological Engineers 2008;51(3):1023-8.
11. Guo J, Lua AC. Kinetic study on pyrolytic process of oil-palm solid waste using two-step consecutive reaction model. Biomass and Bioenergy 2001;20:223-33.
12. Harun NY, Afzal MT. Thermal decomposition kinetics of forest residue. Journal of Applied Sciences 2010;10(12):1122-7.
13. Blasi CD, M. Lanzetta M. Intrinsic kinetics of isothermal xylan degradation in inert atmosphere. Journal of Analytical and Applied Pyroiysis 1997;40-41:287-303.
14. Yuan HR, Liu RH. Study on pyrolysis kinetics of walnut. Journal of Thermal Analysis and Calorimetry 2007;89(3):983-986.
15. Lanzetta M, Blasi CD. Pyrolysis kinetics of wheat and corn straw. Journal of Analytical and Applied Pyrolysis 1998;44:181-92.
16. Branca C, Blasi CD. Kinetics of the isothermal degradation of wood in the temperature range 528–708 K. Journal of Analytical and Applied Pyrolysis 2003;67:207-19.
17. Guo J, Lua AC. Kinetic study on pyrolysis of extracted oil palm fiber: Isothermal and non-isothermal conditions. Journal of Thermal Analysis and Calorimetry 2000;59:763-74.
18. Ounas A, Aboulkas A, El harfi K, Bacaoui A, Yaacoubi A. Pyrolysis of olive residue and sugar cane bagasse: non-isothermal thermogravimetric kinetic analysis. Bioresource Technology 2011;102:11234-8.
19. Williams PT, Ahmad N. Investigation of oil-shale pyrolysis processing conditions using thermogravimetric analysis. Applied Energy 2000;66(2):113-33.
20. Plante AF, Fernández JM, Leifeld J. Application of thermal analysis techniques in soil science. Geoderma 2009;153:1-10.
21. Mani T, Murugan P, Abedi J, Mahinpey N. Pyrolysis of wheat straw in a thermogravimetric analyzer: Effect of particle size and heating rate on devolatilization and estimation of global kinetics. Chemical Engineering Research and Design 2010;88:952-8.
22. Chen W-H, Kuo P-C. A study on torrefaction of various biomass materials and its impact on lignocellulosic structure simulated by a thermogravimetry. Energy 2010;35:2580-6.
23. Luangkiattikhun P, Tangsathitkulchai C, Tangsathitkulchai M. Non-isothermal thermogravimetric analysis of oil-palm solid wastes. Bioresource Technology 2008;99:986-97.
24. Mansaray KG, Ghaly AE. Determination of kinetic parameters of rice husks in oxygen using thermogravimetric analysis. Biomass and Bioenergy 1999;17:19-31.
25. Bilbao R, Mastral JF, Aldea ME, Ceamanos J. Kinetic study for the thermal decomposition of cellulose and pine sawdust in an air atmosphere. Journal Analytical and Applied Pyrolysis 1997;39:53-64.
26. Conceio MM, Fernandes Jr. VJ, Sinfrônio FSM, Santos JCO, Silva MCD, Fonseca VM, Souza AG. Evaluation of isothermal kinetic of sweetener. Journal of Thermal Analysis and Calorimetry 2005;79:263-6.

27. Munir S, Daood SS, Nimmo W, Cunliffe AM, Gibbs BM. Thermal analysis and devolatilization kinetics of cotton stalk, sugar cane bagasse and shea meal under nitrogen and air atmospheres. Bioresource Technology 2009;100:1413-8.
28. Chen W-H, Hsu H-C, Lu K-M, Lee W-J, Lin T-C. Thermal pretreatment of wood (Lauan) block by torrefaction and its influence on the properties of the biomass. Energy 2011;36:3012-21.
29. Repellin V, Govin A, Rolland M, Rene´Guyonnet. Modelling anhydrous weight loss of wood chips during torrefaction in a pilot kiln. Biomass and Bioenergy 2010;34:602-9.
30. Peng JH, Bi HT, Sokhansanj S, Lim JC. A study of particle size effect on biomass torrefaction and densification. Energy Fuels 2012;26:3826-39.
31. Pe´trissans A, Ge´rardin P, Younsi R, Pe´trissans M, Chaouch M. Experimental and numerical analysis of wood thermodegradation: mass loss kinetics. Journal of Thermal Analysis and Calorimetry 2011.
32. Rousset P, Macedo L, Commandré J-M, Moreira A. Biomass torrefaction under different oxygen concentrations and its effect on the composition of the solid by-product. Journal of Analytical and Applied Pyrolysis 2012;96:86-91.