COMPARISON OF PYROLYSIS KINETIC MODELS FOR THERMOGRAVIMETRIC ANALYSIS OF BIOMASS

Piyarat Weerachanchai [1], Chaiyot Tangsathitkulchai[1,*] and Malee Tangsathitkulchai [2]

Abstract

Pyrolysis kinetics of biomasses was studied in a thermogravimetric analyzer. Effects of biomass type (cassava pulp residue, palm kernel cake, palm shell, coconut shell and longan fruit seed), particle size (106-1,325 μm) and heating rate (5-40°C/min) on the thermal decomposition behavior were investigated and the pyrolysis kinetic data were tested with five different models to confirm their validities. The major decomposition of all biomasses occurred in the range of 250-400°C and their first derivative curves (DTG) showed different characteristics of one or two major peaks depending on the type of biomass. Differences in particle size gave almost no effect on the fractional weight remaining and its first derivative but heating rate influenced strongly the range of decomposition temperature and decomposition rate. On model fitting, the best fitting was observed for the two parallel reactions model. The one-step global model assuming n^{th} order reaction and the two-step consecutive reaction model with provision of stoichiometric coefficient gave satisfactory prediction. However, the one-step global model assuming 1st order reaction and the two-step consecutive-reaction model of Guo and Lua showed relatively large deviation between predicted and experimental results.

Keywords: Pyrolysis, biomass, TGA, DTG, pyrolysis kinetic parameters

Introduction

Pyrolysis is defined as a thermal degradation process of carbonaceous materials in the absence of oxygen. It is an important thermal conversion process being the first step of combustion and gasification (Bridgwater, 2003). In addition, it is widely applied in chemical industries, for example, for the preparation of char as a precursor for the production of activated carbon, for cracking medium weight hydrocarbons of petroleum oil to produce lighter fractions of gasoline, etc (Answers Corporation, 2009). Thus, fundamental knowledge on thermal behavior of pyrolysis is a prerequisite for the design and optimization of various thermal conversion processes.

Data on pyrolysis kinetics of lignocellulosic

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[1] *School of Chemical Engineering, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand. Tel.: 0-4422-4263, Fax: 0-4422-4609. E-mail: chaiyot@sut.ac.th*

[2] *School of Chemistry, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand.*

* *Corresponding author*

materials provides significant knowledge and understanding for the proper design of a pyrolysis reactor, especially for large-scale pyrolysis operation. The pyrolysis kinetics can be studied under dynamic or static conditions. During the dynamic condition, pyrolysis temperature is progressively increased with increasing heating time using a specified heating rate, while static condition maintains a selected constant temperature in a pyrolyzing chamber (Babu, 2008). Generally, studying thermal behavior of biomass can be carried out in various systems such as a tube furnace, an entrained-flow reactor, and a drop tube reactor but the most widely used and simplest system is a thermogravimetric analyzer (Di Blasi, 2008). Because of a large number of complex reactions involved caused by the variation of lignocellulosic compositions as well as the influences of heat and mass transfers during thermal decomposition, it is thus difficult to obtain the exact reaction mechanism to describe the pyrolysis reaction. The main problem of kinetic analysis is the combined effects of chemical reactions and transport phenomena. The important effects of heat and mass transfer could result from several factors. For example, the large size of pyrolyzed particle results in temperature gradient in the particle or the thermal lag occurring between the sample and the heating device due to the application of a high heating rate. To avoid these problems, most studies have employed small particle size and slow heating rate for pure kinetic control (Di Blasi, 2008). On simulation of the pyrolysis process, the reaction schemes are represented by mathematical equations. A number of pyrolysis models have been proposed for describing pyrolysis behavior of lignocellulosic materials. They can be classified into three types i.e., one-step global models, one-stage multireaction models and two-stage semi-global models (Di Blasi, 2008).

In this work, the kinetics of pyrolysis reaction of various biomasses were studied by using the thermogravimetric analysis (TGA) technique. The effects of biomass type, particle size and heating rate on the non-isothermal pyrolysis characteristics were investigated.

Furthermore, to enable the prediction of non-isothermal pyrolysis behavior of cassava pulp residue, five pyrolysis models were tested, namely the one-step global model with 1st order reaction, the one-step global model with nth order reaction, the two-step consecutive reaction model of Guo and Lua, the two-step consecutive reaction model with consideration of reaction stoichiometry and the two-parallel reactions model. Cassava pulp residue was studied in greater details in this work compared to other biomasses because it is generated as solid waste in large quantity from tapioca flour mills, with total annual discharge of approximately 1.7 million tons. This low cost biomass waste can be used as a potential raw material for producing a variety of valuable products including chemical feedstock and fuels in various forms through the application of pyrolysis process.

Kinetic Model Description

It is possible that the pyrolysis of a lignocellulosic material under different conditions could be described by different pyrolysis mechanisms. To check for the appropriate model for describing pyrolysis behaviors of cassava pulp residue for different heating rates, five models based on three pyrolysis schemes consisting of one-step global reaction, two-step consecutive-reactions and two parallel reactions were tested in this work. The model descriptions are presented as follows.

One-Step Global Model

The one-step global model is the simplest kinetics model which assumes that the decomposition rate of the pyrolysis process depends on an arbitrary reaction order. The reaction scheme can be represented as

$$\text{Raw material} \xrightarrow{\ k\ } \text{Char} + \text{Volatiles} \qquad (1)$$

where k is the rate constant of the reaction following the Arrhenius law. The rate of pyrolysis decomposition is defined in the following manner

$$\frac{d\alpha}{dt} = k(1-\alpha)^n = A\exp(-\frac{E}{RT})(1-\alpha)^n \quad (2)$$

where α is defined in terms of the fractional mass change of sample, $\alpha = \dfrac{W_0 - W}{W_0 - W_f}$, where W_0, W_f, and W represent initial, final and weight of sample at time t, respectively. A is frequency or pre-exponential factor, E is the activation energy of pyrolysis process, R is the universal gas constant, T is the absolute temperature and n is the order of reaction. The study of pyrolysis kinetics is usually performed at a constant heating rate, β, therefore

$$\beta = \frac{dT}{dt} \quad (3)$$

Thus, the decomposition rate as a function of temperature can be expressed as

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\exp(-\frac{E}{RT})(1-\alpha)^n \quad (4)$$

In this study, the weight remaining data (TG data) was tested by the one-step global model assuming both first-order and nth order reactions. The analytical solutions of 1st order reaction model and nth order reaction model are, respectively,

$$\alpha = 1 - \exp\{-\frac{ART^2}{\beta E}(1-\frac{2RT}{E})\exp(-\frac{E}{RT})\} \quad (5)$$

$$\alpha = 1 - \{1 - (1-n)(-\frac{ART^2}{\beta E})(1-\frac{2RT}{E})\exp(-\frac{E}{RT})\}^{\frac{1}{1-n}} \quad (6)$$

Two-Step Consecutive-Reaction Model

Guo and Lua (2001) have proposed the two-step consecutive-reaction model based on the consideration that all cellulosic components of biomass namely, lignin, cellulose and hemicellulose will decompose first to intermediates and then to the final solid char and volatiles. For example, cellulose converts to intemediates

of anhydrocellulose and levoglucosan, while hemicellulose decomposes to furanoses and furans and the intermediates of lignin are condensed aromatic and phenolic compounds. The kinetic rate of biomass based on this model can thus be represented as

$$\text{Raw material} \xrightarrow{k_1} \text{Intermediate + Volatile (I)} \quad (7)$$

$$\text{Intermediate} \xrightarrow{k_2} \text{Char + Volatile (II)} \quad (8)$$
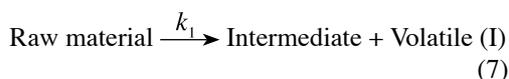
where k_1 and k_2 are reaction rate constants of the first and second steps of reaction, respectively. The model is simplified by assuming pure kinetic reaction control, no secondary reactions of the gaseous products and the pyrolytic reactions for low and high-temperature regimes following first-order reaction and contracting volume mechanism, respectively. The kinetic equations describing the pyrolysis process are presented as the following set of differential equations,

$$\frac{dU}{dT} = -\frac{2A_1}{\beta}\exp(-\frac{E_1}{RT})U \quad (9)$$

$$\frac{dZ}{dT} = \frac{A_1}{\beta}\exp(-\frac{E_1}{RT})U - \frac{6A_2}{\beta}\exp(-\frac{E_2}{RT})Z^{\frac{2}{3}} \quad (10)$$

$$\frac{dW}{dT} = \frac{3A_2}{\beta}\exp(-\frac{E_2}{RT})Z^{\frac{2}{3}} \quad (11)$$

where U, Z, and W are weight fractions of raw material, intermediate and solid char, respectively. The initial conditions for these three ordinary differential equations are $U = 1$, $Z = W = 0$, and $T = T_0$. The residual weight fraction of sample at any temperature and time should be equal to the summation of raw material, intermediate and char. The above set of ordinary differential equations can be solved, for example, using ODE solver of MATLAB program.

In addition, the data fitting by applying the modified two-step consecutive reaction was explored in the present work. This model was proposed by Luangkiattikhun (2007) by

adding the stoichiometric coefficients of the reactions, x and y, in the reaction schemes of the original two-step consecutive model. That is,

Raw material $\xrightarrow{k_1}$ x · Intermediate + Volatile(I)   (12)

Intermediate $\xrightarrow{k_2}$ y · Char + Volatile (II)   (13)
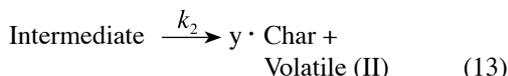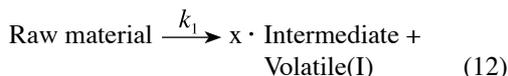
The assumptions are a pure kinetic controlled process, no secondary reactions among the gaseous products and the pyrolysis reactions following first-order reaction for the first step and n^{th} order for the second step, respectively. The decomposition rate of raw material and generation rates of intermediate and char are expressed as

$$\frac{dU}{dT} = -\frac{A_1}{\beta}\exp(-\frac{E_1}{RT})U \qquad (14)$$

$$\frac{dZ}{dT} = x\frac{A_1}{\beta}\exp(-\frac{E_1}{RT})U - \frac{A_2}{\beta}\exp(-\frac{E_2}{RT})Z^n \qquad (15)$$

$$\frac{dW}{dT} = y\frac{A_2}{\beta}\exp(-\frac{E_2}{RT})Z^n \qquad (16)$$

where n is the order of the second step of pyrolysis reaction and the relationship between x and y is correlated with the final char yield, m_f, by

$$x = \frac{m_f}{y} \qquad (17)$$

The residual weight fraction of sample at any time or temperature is the sum of weight fractions of raw material, intermediate and char. The differential equations are solved using ODE solver in MATLAB program with the initial values of $U = 1$, $Z = W = 0$ and $T = T_0$.

Two-Parallel Reactions Model

The two parallel reactions model proposed by Luangkiattikhun (2007) was also tested for describing the reaction of biomass pyrolysis

in the present study. It is assumed that a raw material consists of two components, M_1 and M_2, which decompose simultaneously according to Equations (18) and (19), respectively. The reaction is controlled by kinetic process only and there are no secondary reactions among the gaseous products and char.

$M_1 \xrightarrow{k_1}$ Volatile + char   (18)

$M_2 \xrightarrow{k_2}$ Volatile + char   (19)
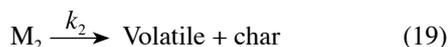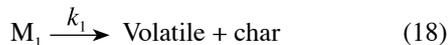
where k_1 and k_2 represent the rate constant of reaction occurring from the first and the second fractions, respectively. The first fraction is assumed to decompose via first-order reaction and the second fraction obeys n^{th} order reaction. The decomposition rates of the two parallel reactions are presented as follows,

$$\frac{d\alpha_1}{dT} = -\frac{A_1}{\beta}\exp(-\frac{E}{RT})\alpha_1 \qquad (20)$$

$$\frac{d\alpha_2}{dT} = -\frac{A_2}{\beta}\exp(-\frac{E}{RT})\alpha_2^{\ n} \qquad (21)$$

The residual weight fractions of solid product are defined as follows

$$\alpha = \frac{M - m_f}{1 - m_f}; \ \alpha_1 = \frac{M_1 - m_{f1}}{1 - m_f}; \ \alpha_2 = \frac{M_2 - m_{f2}}{1 - m_f} \qquad (22)$$

where m_f is the final yield of char and m_{f1} and m_{f2} are the final mass fractions of the first and second components, respectively. M, M_1 and M_2 are mass fractions of total residual weight, residual weight of the first and second components present at time t, respectively, and their relationships are

$$m_f = m_1 + m_2 \qquad (23)$$

$$M = M_1 + M_2 \qquad (24)$$

By integrating Equations (20) and (21), the solutions of the remaining mass of the first and second components at any temperature, α_1 and α_2, can be obtained as the following equations

$$\alpha_1 = \exp\left[-\frac{A_1 RT^2}{\beta E_1}\left(1-\frac{2RT}{E_1}\right)\exp\left(-\frac{E_1}{RT}\right)+\ln(a)\right] \quad (25)$$

$$\alpha_2 = \left[\frac{(n-1)A_2 RT^2}{\beta E_2}\left(1-\frac{2RT}{E_2}\right)\exp\left(-\frac{E_2}{RT}\right)+b^{(1-n)}\right]^{\frac{1}{1-n}} (26)$$

where a and b are the initial weight fractions of the first and second components. The total remaining mass at any temperature is the sum of each residual fraction, that is

$$\alpha = \exp\left[-\frac{ART^2}{\beta E_1}(1-\frac{2RT}{E_1})\exp(-\frac{E_1}{RT})+\ln(a)\right]$$

$$+\left[\frac{(n-1)A_2 RT^2}{\beta E_2}(1-\frac{2RT}{E_2})\exp(-\frac{E_2}{RT})+b^{(1-n)}\right]^{\frac{1}{1-n}} \quad (27)$$

All models were fitted with the experimental data (TG data) to determine their kinetic parameters. The derived kinetic parameters were estimated by minimizing the sum of square of relative error *(SSRE)*, defined as

$$SSRE = \sum_{i=1}^{N}\left[\frac{(\alpha_{\exp})_i - (\alpha_{cal})_i}{(\alpha_{\exp})_i}\right]^2 \quad (28)$$

where $(\alpha_{\exp})_i$ and $(\alpha_{cal})_i$ are the experimental and calculated values, respectively, and N is the total number of data points.

Materials and Methods

Feedstock Characterization

Biomass feedstocks including cassava pulp residue, palm kernel cake, palm shell, coconut shell and longan fruit seed were milled and sieved to obtain an average particle size of 106 μm for biomass characterization and study of pyrolysis kinetics. In addition, four particle sizes of cassava pulp residue including 106, 431, 750, and 1,325 μm were also used for studying particle size effect on the pyrolysis kinetics. The sieved biomasses were dried at 120°C for 24 h in an oven. The dried biomass samples were characterized for bulk density, true density (Helium pycnometer, AccuPyc 1330 Micromeritics), proximate analysis (moisture content (ASTM D2867-95), volatile content (ASTM D5832-95), ash content (ASTM D2866-94) and fixed carbon content (by difference)), elemental analysis (CHNS/O analyzer, Perkin Elmer PE2400 series II) and heating values (ASTM D3286-96).

Study of Pyrolysis Kinetics

Thermal decomposition behavior of various biomasses was studied using a thermogravimetric analyzer (SDT 2960 simultaneous DSC-TGA model, TA instruments). For this analysis, a sample of 10-15 mg was heated from room temperature to 650°C with a heating rate varying from 5 to 40°C/min under a nitrogen flow rate of 100 cm^3/min. All test conditions are summarized in Table 1. The fractional weight remaining (TG data) and its first derivative (DTG data) as a function of increasing temperature were recorded continuously. The weight remaining TG data derived under varying heating rates (5-40°C/min) of cassava pulp residue pyrolysis were fitted with the previous proposed five models (detailed in Kinetic Model Description) to simulate the kinetics of pyrolysis process using optimization function of MATLAB program based on Equation (28). It should be noted that each type of biomass was prepared once in large enough quantity and randomly sampled for thermogravimetric analysis under varying studied conditions. The repeatability of TGA data, when the analysis was performed on two samples at a fixed heating rate and a constant flow rate of purge gas, was found to be excellent with the maximum deviation being less than 3%.

Results and Discussions

Feedstock Properties

Table 2 shows basic physical properties and compositions of the biomasses studied. Bulk densities of the various biomasses at average particle size of 106 μm are in the range

Table 1. Pyrolysis conditions for pyrolysis kinetics studies

Parameters affecting pyrolysis kinetics	Fixed conditions	Studied parameters	Run No.
Biomass type	Particle size of 106 μm, heating rate of 20°C/min	Cassava pulp residue	1
		Palm kernel cake	2
		Palm shell	3
		Coconut shell	4
		Longan fruit seed	5
Particle size (μm)	Cassava pulp residue, heating rate of 20°C/min	106	1
		431	6
		750	7
		1325	8
Heating rate (°C/min)	Cassava pulp residue, particle size of 106 μm	5	9
		10	10
		20	1
		40	11

Table 2. Biomass properties and chemical compositions

Properties	Biomass type				
	Cassava pulp residue	Palm kernel cake	Palm shell	Coconut shell	Longan fruit seed
Bulk density (g/cm³)					
particle size of 106 μm	0.362	0.711	0.786	0.797	0.789
particle size of 431 μm	0.341	-	-	-	-
particle size of 750 μm	0.332	-	-	-	-
particle size of 1325 μm	0.320	-	-	-	-
True density (g/cm³)	1.507	1.385	1.416	1.421	1.470
Proximate analysis (Dry basis) (wt%)					
Volatiles	81.98	79.57	75.69	82.38	84.51
Fixed carbon	11.83	16.74	19.20	16.33	14.80
Ash	6.19	3.69	5.11	1.29	0.70
Elemental analysis (wt%)					
C	35.89	47.19	48.74	49.76	43.75
H	5.47	6.38	4.99	5.60	6.30
O	58.27	43.28	45.63	44.30	48.81
N	0.36	3.15	0.64	0.35	1.14
H/C (mole ratio)	1.829	1.622	1.229	1.727	1.350
O/C (mole ratio)	1.218	0.688	0.702	0.837	0.668
Gross heating value (MJ/kg)	22.41	21.91	22.29	21.28	21.16

of 0.36-0.80 g/cm³ The bulk density of cassava pulp residue is lowest being about half of the other biomasses. For cassava pulp residue, increasing particle size from 106 to 1,325 μm gives a slight decrease of solid bulk density. The true densities of all biomasses are not so greatly different varying in the range from 1.385-1.507 g/cm³. Proximate and elemental analyses show that the main composition of biomasses is volatile contents and carbon and oxygen are the major elements. The gross heating values of all biomasses are approximately the same with the value of about 22 MJ/kg.

Non Isothermal Pyrolysis of Biomass

Non-isothermal thermogravimetric analysis of various biomasses was conducted and the effects of particle size and heating rate were examined using cassava pulp residue as a test material. Figures 1-3 show the obtained results presented as weight percent remaining (TG curves) and the corresponding first derivative (DTG curves). Generally, the TG curves showed sigmoid shape and DTG curves exhibited one or two major peaks depending on the type of biomass. For the effect of biomass type, Figure 1(a) shows that the TG curves almost superimposed on one another, except the cassava pulp residue, where its curve shifted downward at temperatures higher than 350°C. From DTG curves in Figure 1(b), it was noted that the main pyrolysis

decomposition of all biomasses occurred roughly in the range of 250-400°C. Obviously, the thermal decomposition of these biomasses will result from contributions of their lignocellulosic components (hemicellulose, cellulose and lignin), which generally decompose over the temperature range of 200-400°C (Antal, 1983). Lignin usually decomposes first at the lowest temperature and continues up to the temperature around 900°C. Hemicellulose and cellulose decompose over the temperature range of 160-360°C and 240-390°C, respectively (Vamvuka et al., 2003). At pyrolysis temperature of 350°C cassava pulp residue gave the lowest weight remaining with its final weight at 650°C being 19.9 wt%, whereas that of the other biomasses was about 26.2 wt% at the same pyrolysis conditions (Figure 1(a) and Table 3). This may imply that cassava pulp residue may contain larger fractions of cellulose and hemicellulose, thus contributing to the releasing of more volatile components, while other biomasses could contain higher lignin content that is responsible for the production of higher char yield (McGinnis, 1971; Koufopanos et al., 1989; Williams and Besler, 1994). It can be also noted that there are three distinct characteristics of DTG curves as displayed in Figure 1(b). Cassava pulp residue and longan fruit seed had only one distinct peak of DTG curve, while palm shell and coconut shell gave two peaks of decomposition and the
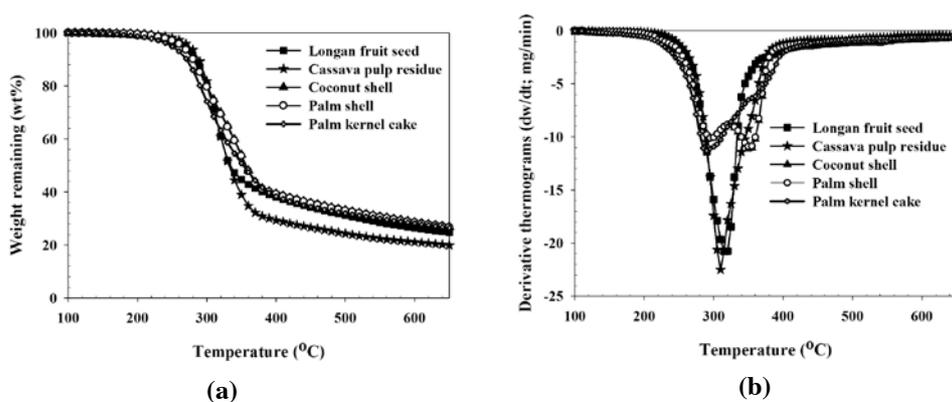

Figure 1. Thermal analysis of various biomasses: TG and (b) DTG (average particle size of 106 μm, heating rate of 20°C/min and nitrogen flow rate of 100 cm³/min)

palm kernel cake showed one major peak with a small shoulder. In addition, the temperature that gives the maximum decomposition rate depends on the biomass type. Two maximum of decomposition rates of palm shell and coconut shell occurred at approximately the same temperatures of 295 and 350°C, while the maximum decomposition rate of palm kernel cake, cassava pulp residue and longan fruit seed occurred at the temperature of 290, 310, and 320°C, respectively. Table 3

shows characteristic data of maximum decomposition rate from DTG curves for all test runs.

Cassava pulp residue was also used to study the effects of particle size and heating rate on the pyrolysis characteristics. Figure 2 indicates that cassava pulp residue pyrolysis at different particle sizes in the range of 106-1325 μm gave no specific trend on the weight remaining and relatively no effect on its 1st derivative. The main decomposition occurred

Table 3. First and second maximum decomposition rates $((\frac{dw}{dt})_{1,\,max}$ and $(\frac{dw}{dt})_{2,max})$ at corresponding temperatures ($T_{1,max}$ and $T_{2,max}$) and final residual weights (m_f) of various biomasses

Run No.	$T_{1,max}$ (°C)	$(\frac{dw}{dt})_{2,max}$ (wt%/min)	$T_{2,max}$ (°C)	$(\frac{dw}{dt})_{2,max}$ (wt%/min)	m_f (wt%)
1	310	-23.00	-	-	19.89
2	290	-11.98	-	-	26.42
3	295	-10.30	350	-11.09	26.81
4	295	-10.80	350	-11.13	26.65
5	320	-21.05	-	-	24.73
6	290	-24.18	-	-	19.35
7	290	-26.59	-	-	20.90
8	290	-27.11	-	-	19.16
9	283	-5.06	-	-	23.84
10	288	-9.97	-	-	20.77
11	290	-45.77	-	-	19.09
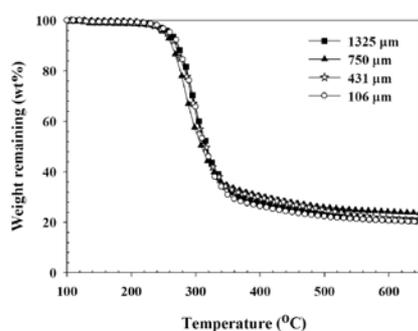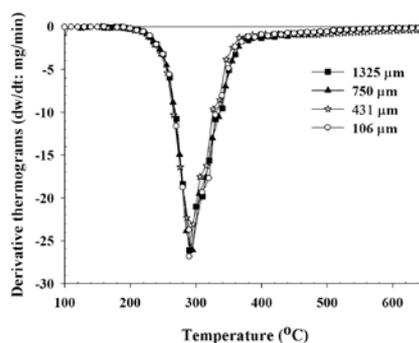
(a)   (b)

Figure 2. Thermal analysis of cassava pulp residue for various particle sizes: (a) TG and (b) DTG (heating rate of 20°C/min and nitrogen flow rate of 100 cm³/min)

between 210 and 380°C and the final weight remaining was about 19.6 wt%. The insensitivity of the thermograms with respect to changes in particle size tends to indicate that the particle size studied is small enough to cause no effects of heat and mass transfer resistance inside the particle. This agrees with the work of Guo and Lua (2001) that pyrolysis is controlled by pure reaction kinetics for the sample particle sizes of smaller than 2 mm. On the effect of heating rate, Figure 3(a) shows that pyrolysis at the heating rate of 5-40°C/min exhibited almost no effect on the TG curves at temperatures less than 350°C. However, at higher temperatures, pyrolyzing at higher heating rate gave systematically lower value of weight remaining. It is probable that rapid heating could impose faster rate of decomposition; the plot of DTG curve indicated that the pyrolysis at higher heating rate provided higher rate of decomposition and wider temperature ranges of decomposition (Figure 3(b)). However, the temperature giving maximum rate of decomposition was shifted to a higher temperature when higher heating rate was applied (Figure 3(b) and Table 3). This may be explained that the increase of heating rate could cause larger temperature gradient between the surface and inside the particles which would cause a lower average temperature inside the particle for the same pyrolysis temperature and thus shifting the maximum decomposition rate to a higher

temperature. Furthermore, a small shoulder was observed at heating rates greater than 20°C/min and this may result from the effect of heat transfer lag that could prolong the decomposition of some biomass components.

Model Fitting and Estimation of Kinetic Parameters

In this section, the TG data of cassava pulp residue pyrolysis at different heating rates were further tested with the five kinetics models and pyrolysis kinetic parameters determined from the model fitting.

One-Step Global Model

The simplest model of one-step global model was expected to give reasonable fitting for single peak of DTG curves derived from cassava pulp residue decomposition. However, as Figure 4(a) shows the one-step global model assuming first-order reaction underpredicted the experimental value at the upper and lower inflection points. Maximum errors resulting from the mismatch were in the range of 22.51-27.01% (Table 4). The fitting parameters including frequency factor, A and activation energy, E were in the range of 1.05×10^3-2.28×10^4 s^{-1} and 6.84×10^1-7.65×10^1 kJ/mol, respectively, with no definite trend for the effect of heating rate (Table 4). On the other hand, the fitting by one-step global model assuming n^{th} order reaction provided improved


(a)   (b)
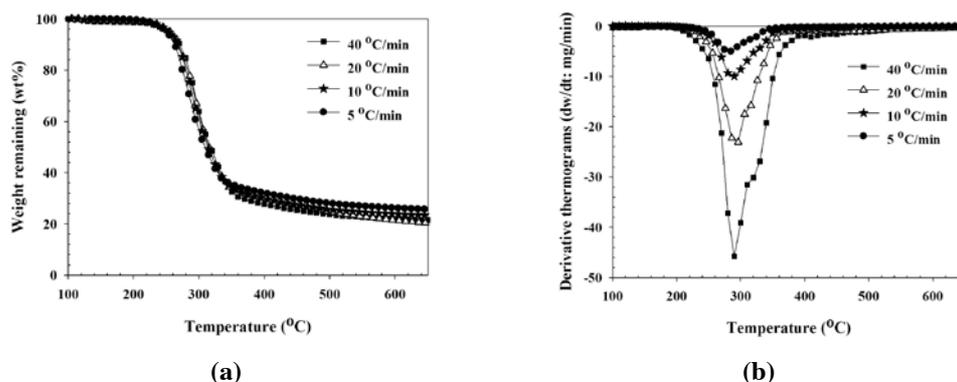
Figure 3. Thermal analysis of cassava pulp residue at various heating rates: (a) TG and (b) DTG (particle sizes of 106 μm and nitrogen flow rate of 100 cm³/min)

fitting but a relatively large error in the range from 7.96-13.98% was still observed (Figure 4(b) and Table 4). The estimated reaction order and the frequency factor for cassava pulp residue pyrolysis tended to decrease with increased heating rate varying in the range of 3.97-5.60 and 1.13×10^{19}-8.72×10^{21} s^{-1}, while the activation energy, E, was considered relatively constant varying between 1.99×10^2-2.53×10^2 kJ/mol (Table 4). Concerning the fitted results, great deviations were still obtained from applying the one-step global model especially at the inflection points of the TG curves. Next, the two-step consecutive reaction model and the two parallel reactions model were further applied to test their validities in describing the actual pyrolysis kinetic of the test biomasses.

Two-Step Consecutive-Reaction Model

The fitting of experimental TG data by using the two-step consecutive reaction model of Guo and Lua (Guo and Lua, 2001) revealed reasonable agreement between the experimental and the predicted values. However, the predicted values for cassava pulp residue pyrolysis at heating rates higher than 20°C/min were satisfactory up to the weight remaining of about 30% at which the main decomposition period had been passed (Figure 5(a)). Afterwards, the weight remaining of cassava

pulp residue pyrolysis decreased slowly but the predicted value from the model approached a constant value. This results in the maximum error lying between 3.53-17.31% and the maximum errors tended to increase with increased heating rate (Table 4). The frequency factor and activation energy of the first reaction (A_1 and E_1) remained relatively constant independent of heating rate, with the average values being about 2.37×10^8 s^{-1} and 1.11×10^2 kJ/mol, respectively (Table 4). For the frequency factor and activation energy of the secondary reaction (A_2 and E_2), they did not give a definite trend with respect to changes in heating rate, varying in the range of 2.11×10^2-3.90×10^2 s^{-1} and 1.23×10^1-3.73×10^1 kJ/mol, respectively.

The limitation of applying Guo and Lua model is that it cannot describe the pyrolysis kinetics of cassava pulp residue after the main decomposition period. The modified Guo and Lua model, the two-step consecutive reaction with the allowance for reaction stoichiometry, was then attempted to overcome this shortcoming. Figure 5(b) showed that using the modified Guo and Lua model can improve the fitting results considerably for all conditions. The maximum errors were in the range of 3.06-8.34%. The stoichiometric coefficients for the primary (x) and secondary reactions (y) derived from the model fitting were 0.44
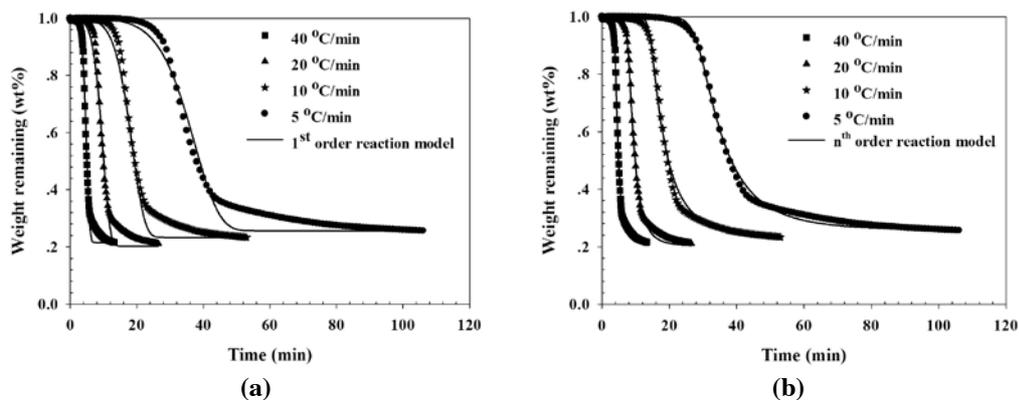

Figure 4. Comparison of experimental data with the fitted results using the one-step global model assuming (a) first-order reaction and (b) nth order reaction for cassava pulp residue pyrolysis at different heating rates

Table 4. Kinetic parameters derived from fitting the TG data of cassava pulp residue pyrolysis at different heating rates with various kinetic models

Pyrolysis models	Run No. (heating rate)	A_1* (s^{-1})	E_1* (kJ/mol)	A_2 (s^{-1})	E_2 (kJ/mol)	n	Maximum error (%)
One-step global model assuming 1st order reaction	9 (5°C/min)	1.42×10^4	7.54×10^1	-	-	-	22.51
	10 (10°C/min)	2.28×10^4	7.53×10^1	-	-	-	25.17
	1 (20°C/min)	9.06×10^3	6.84×10^1	-	-	-	27.01
	11 (40°C/min)	1.05×10^3	7.65×10^1	-	-	-	23.14
One-step global model assuming nth order reaction	9 (5°C/min)	8.72×10^{21}	2.53×10^2			5.34	7.96
	10 (10°C/min)	5.65×10^{19}	2.31×10^2			5.60	13.98
	1 (20°C/min)	9.15×10^{19}	2.32×10^2			4.62	10.82
	11 (40°C/min)	1.13×10^{19}	1.99×10^2		-	3.97	8.32
Two-step consecutive reaction model based on Guo and Lua concept	9 (5°C/min)	2.76×10^8	1.10×10^2	2.54×10^2	1.23×10^1	-	3.53
	10 (10°C/min)	2.07×10^8	1.09×10^2	2.78×10^2	1.28×10^1	-	6.43
	1 (20°C/min)	2.14×10^8	1.10×10^2	2.11×10^2	3.73×10^1	-	17.31
	11 (40°C/min)	2.52×10^8	1.13×10^2	3.90×10^2	3.42×10^1	-	16.96
Two-step consecutive reaction model with provision of stoichiometric coefficients	9 (5°C/min)	1.76×10^{10}	1.29×10^2	4.34×10^{24}	2.71×10^2	7.72	3.06
	10 (10°C/min)	1.89×10^{10}	1.31×10^2	6.78×10^{23}	2.63×10^2	8.76	8.34
	1 (20°C/min)	1.10×10^{10}	1.30×10^2	1.02×10^{24}	2.70×10^2	6.98	7.87
	11 (40°C/min)	1.19×10^{10}	1.27×10^2	1.05×10^{24}	2.69×10^2	6.55	5.15
Two parallel reactions model	9 (5°C/min)	1.08×10^8	1.13×10^2	9.31×10^{20}	2.27×10^2	6.78	3.09
	10 (10°C/min)	3.54×10^8	1.26×10^2	2.06×10^{20}	2.47×10^2	8.24	3.15
	1 (20°C/min)	2.90×10^8	1.14×10^2	8.02×10^{17}	1.99×10^2	5.47	3.43
	11 (40°C/min)	1.03×10^8	1.06×10^2	2.05×10^{16}	1.80×10^2	4.91	3.09

Note: * A_1 and E_1 for one-step global model assuming 1st or nth order reaction are A and E in Equations (5) and 6)

and 0.49, respectively. The kinetic parameters including frequency factor (A), activation energy (E) and reaction order (n) seems to be insensitive to the changes in heating rate (Table 4). The A_1 and E_1 of the primary reaction assuming first-order reaction were approximately constant of about 1.49×10^{10} s^{-1} and 1.29×10^2 kJ/mol, respectively, while the average values of A_2 and E_2 of the secondary reaction were 1.77×10^{24} s^{-1} and 2.68×10^2 kJ/mol, respectively, and the orders of reaction varied widely in the range 6.55 to 8.76 (Table 4). The higher values of the fitting parameters, A_2 and E_2 compared to A_1 and E_1 indicate that the decomposition rate of the secondary reaction is greater than that of the primary reaction but the decomposition of the secondary reaction is more difficult to proceed.

Two-Parallel Reactions Model

The fitting by the two-parallel reactions model gave excellent agreement between experimental data and predicted results for all pyrolysis conditions (Figure 6) with maximum errors varying between 3.09-3.43%. The model fitting gave the fractions of the first and second fractions to be 0.51 and 0.49, respectively. The reaction order of the second component varied in the range of 4.91-8.24. The frequency factor of the first component

(A_1) provided no definite trend, while A_2 tended to decrease with increasing heating rate. A_1 and A_2 varied in the range of 1.03×10^8-3.54×10^9 s^{-1} and 2.05×10^{16}-9.31×10^{20} s^{-1}, respectively (Table 4). The activation energy of the first and second components were almost constant varying in the narrow range of 1.06×10^2-1.26×10^2 kJ/mol and 1.80×10^2-2.47×10^2 kJ/mol, respectively (Table 4). It is noted that A_1 and E_1 are lower than A_2 and E_2 which implies that the first component of cassava pulp residue could decompose at a slower rate than the second component as well as easier to decompose than the second component. Since values of E_1 and E_2 fall in the range of activation energy for the pyrolysis of hemicellulose (80-116 kJ/mol) and cellulose (195-286 kJ/mol) (Gronli, *et al.*, 2002), it may be inferred that the first component is decomposed at a lower temperature than the second component. In addition, the first and the second components should represent the lighter compound of hemicellulose and heavier compound of cellulose, respectively.

Since there are many model parameters to be searched for, it is suggested that a sensitivity analysis on each optimized parameter should be performed to assess its significance on the model predictive capability.


(a)   **(b)**
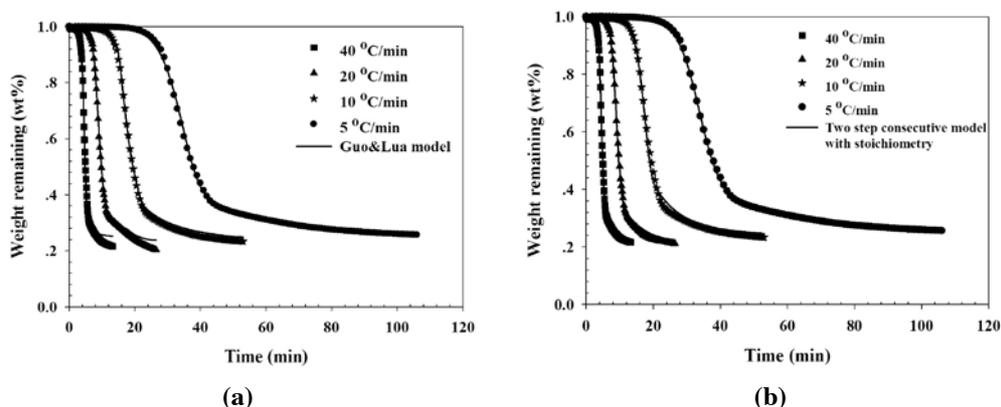
Figure 5. **Comparison of experimental data with the fitted results using the two-step consecutive reaction model based on (a) Guo and Lua concept and (b) provision of stoichiometric coefficient for cassava pulp residue pyrolysis at different heating rates**

Conclusions

The studies of non-isothermal pyrolysis characteristics of various biomasses in a thermogravimetric analyzer indicated that all biomasses showed different characteristics of their first derivative curves (DTG) but gave the same temperature range of main decomposition at 250-400°C. Biomass type and heating rate (5-40°C/min) had significant effects on TG and DTG curves but thermograms derived from pyrolysis of cassava pulp residue at different particle sizes (106-1,325μm) were not greatly different. On fitting TG data by different kinetic models, the best fitting for describing pyrolysis behavior of cassava pulp residue for different heating rates was obtained from the two-parallel reactions model (3.43% in maximum error). The optimized parameters derived from model fitting at different conditions were relatively constant or did not give a definite trend, varying in range of 1.03×10^8-3.54×10^9 s^{-1} for A_1, 1.06×10^2-1.26×10^2 kJ/mol for E_1, 2.05×10^{16}-9.31×10^{20} s^{-1} for A_2, 1.80×10^2-2.47×10^2 kJ/mol for E_2 and 4.91-8.24 for reaction order of the second component (n). Weight fraction of the first and second fractions which could represent lighter component of hemicellulose and heavier component of cellulose were found to be 0.51 and 0.49, respectively.

Acknowledgment

References

Answers Corporation (2009). Pyrolysis. New York: Answers Corporation. Available from: http://www.answers.com/topic/pyrolysis. Accessed date: Oct 19, 2010.

Antal, M.J. (1983). Biomass pyrolysis: a review of the literature: part 1 carbohydrate pyrolysis. In: Advances in Solar Energy. American Solar Energy Society. Boer, K.W., and Duffie, J.A. (eds.). Boulder, CO, p. 61-111.

Babu, B.V. (2008). Biomass pyrolysis: a state-of the-art review. Biofuels, Bioprod. Bioref. 2:393-414.

Bridgwater, A.V. (2003). Renewable fuels and chemicals by thermal processing of biomass. Chem. Eng. J. 91 (2-3):87-102.

Di Blasi, C. (2008). Modeling chemical and physical processes of wood and biomass pyrolysis. Prog. Energy Combust. Sci. 34 (1):47-90.

Gronli, M.G., Varhegyi, G., and Di Blasi C. (2002). Thermogravimetric analysis and devolatilization kinetics of wood. Ind. Eng. Chem. Res. 41 (17):4201-4208.

Guo, J., and Lua, A.C. (2001). Kinetic study on pyrolytic process of oil-palm solid waste using two-step consecutive reaction model. Biomass Bioenergy 20 (3):223-233.

Koufopanos, C.A., Maschio, G., and Lucchesi, A. (1989). Kinetic modeling of the pyrolysis of biomass components. Can. J. Chem. Eng. 67 (1):75-84.

Luangkiattikhun, P. (2007). Activated carbon from oil-palm solid wastes: preparation and CFD simulation of spouted bed activator, [Ph.D. thesis]. School of Chemical Engineering, Institute of
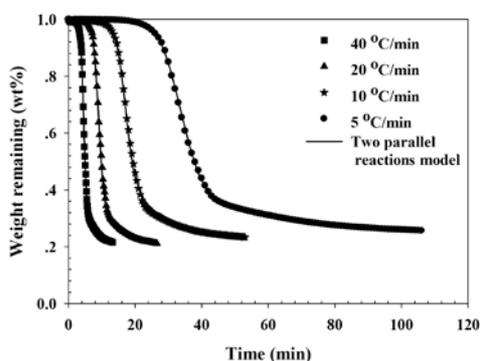

Figure 6. Comparison of experimental data with the fitted results using the two parallel reactions model for cassava pulp residue pyrolysis at different heating rates

Engineering, Suranaree University of Technology. Nakhon Ratchasima, Thailand, 19p.

Shafizadeh, F., and McGinnis, G.D. (1971). Chemical composition and thermal analysis of cotton wood. Carbohydr. Res. 16 (2):273-277.

Vamvuka, D., Kakaras, E., Kastanaki, E., and Grammelis, P. (2003). Pyrolysis characteristics of biomass residuals mixture with lignite. Fuel 82 (15-17): 1,949-1,960.

Williams, P.T., and Besler, S. (1994). Thermogravimetric analysis of the components of biomass. In: Advances in thermochemical biomass conversion. Bridgwater A.V. (ed.). Blackie Academic & Professional, London, p. 771-783.