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Modelling Multicomponent Devolatilization Kinetics of *Imperata Cylindrica*

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Biomass devolatilization is an important phenomenon in the thermochemical conversion of biomass into clean fuels through pyrolysis, gasification and combustion. In this paper multicomponent model fitting (MMF) was carried out to analyse the devolatilization kinetics of Imperata cylindrica using non-isothermal thermogravimetry (TG) to determine the pre-exponential factors (k_0), activation energies (E_a) and fractional contribution. The TGA of Imperata cylindrica was carried out in the temperature range of 30-1,000 °C at four heating rates of 5, 10, 15, and 20 K/min using Nitrogen at a flow rate of 20 mL/min as purge gas. Evaluation of the kinetic parameters involved the numerical regression of the non-isothermal TGA data in MATLAB 2013a based on the pseudocomponent modelling method. The pseudocomponents number used in the modelling was limited between 3 and 10, and the overall quality of fit (QOF) for eight pseudocomponents was found to be the lowest with the value of 1.89 %. The corresponding average values for pre-exponential factor, activation energy and fractional contribution were 791.63 s^{-1}, 12.13 kJ/mol and 0.13. The results proved that pseudocomponent reaction modelling method can be successfully employed to accurately predict the experimental devolatilization rates.

1. Introduction

Imperata cylindrica is a grass that grows widely and uncontrollably in South-East Asia and termed farmers nightmare weed. It is a weed that cost farmers' fortune to eliminate and most of the time impossible. However, Imperata cylindrica has a unique characteristic of burning even when green, making it a potential energy crop similar to Switchgrass (Balan et al., 2012) and Miscanthus (Hodgson et al., 2011) in the production of clean and green fuel.

The conversion of biomass to biofuel could be through thermochemical conversion processes such as combustion, gasification (Nyakuma et al., 2014) and pyrolysis (Basu, 2010). Pyrolysis is a very important thermochemical conversion process, it is the precursor of all the other processes. Pyrolysis uses heat to break down biomass to liquid (tar), gas and solid (char) products. In understanding the science of pyrolysis there is need to basically study biomass devolatilization which is the liquefying of biomass and showing possible ways of optimizing the process for the production of tar and char (Braza and Crnkovic, 2014).

Several researchers has worked on devolatilization process kinetics and mechanism and their works have provided many techniques for accurately predicting the devolatilization kinetic parameters (activation energies and pre-exponential factors) from non-isothermal thermogravimetric analysis (TGA) data using either "model free" or "model fitting" techniques (Sanchirico, 2014). The model free method includes Friedman (1964), Kissinger-Akahira-Sunose (KAS), Kissinger (Blaine and Kissinger, 2012), Flynn-Wall-Ozawa (Ozawa, 1992) and later by Starink (2003), which are also known as isoconversional methods.

However, the model fitting is more pertinent to this investigation. The application of this method to biomass decomposition and thermochemical conversion processes has been used extensively and recently found new use in coal and coal-biomass mixture kinetic studies (Várhegyi, 2007). Aboyade et al. (2011) found a hybrid application by combining model fitting and model free (Friedman method) in predicting the decomposition of kinetics of corn cobs and sugar. This hybrid method deconvoluted the TG data using 3

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pseudocomponents resulting in a poor quality of fit (QOF) (Aboyade et al., 2012). Therefore, finding the best fit Hattingh et al. (2014) applied the multicomponent model fitting (MMF)to a range of 3-8 pseudocomponents and found the best fit to be for 8 pseudocomponents for all the coal samples considered.

Presently, on I. cylindrica there is no work known to the authors on kinetic parameters prediction using model fitting or its exploitation as a possible green energy grass. Therefore, this research aims to apply the model fitting methods to I. cylindrica in predicting the kinetic parameters. The research will focus on finding the best fit considering 3-10 pseudocomponents and consequently predict the decomposition kinetics for each component. Furthermore, from the deconvoluted TGA data, the peaks for cellulose, hemicellulose and lignin would be identified using pyrolysis temperature range.

2. Methods

2.1 Experiment

Imperata cylindrica (Lalang) was collected from an open field in Skudai, Johor, Malaysia. The leaves were weighed, chopped and dried in an oven at 105 ^{o}C for 36 h. The dried leaves were milled and sieved to obtain particle size <125 µm. About 5-9 mg of I. cylindrica was placed in an aluminum crucible and heated from 30-1,000 °C at heating rates of 5, 10, 15 and 20 K/min in the Netzsch 209 F3 thermogravimetric (TG) analyser. Pure nitrogen (N_2) gas was used as a purge gas at a flow rate of 20 mL/min. The raw data from the thermogravimetric analyser was analysed using Proteus 6.1 Netzsch thermal analysis software to TG and Differential Thermal Gravimetric (DTG) data at their corresponding temperature, T, and time, t.

2.2 Kinetic Modeling

In developing the devolatilization kinetic model we made use of the Arrhenius rate of decomposition for solid state equation, which gives the relationship between fractional conversion, X (see Eq 1), pre-exponential constant, k_0 (s^{-1}), activation energy, E_a (J/mol), temperature, T (K), universal gas constant, R $(8.314\,J/molK)$ and time, t (s) as stated in Eq(2) (Hattingh *et al.*, 2014):

$$X = \frac{m_o - m_t}{m_0 - m_f} \tag{1}$$

$$\frac{dX}{dt} = k_0\, exp\left(-E_a/_{RT}\right) \cdot (1 - X) \tag{2}$$

The mass parameters in Eq(1) are sample masses, (mg) and defined as m_o- initial mass, m_t- mass at a specific time, and m_f- final mass after devolatilization, these values were obtained from TGA. The *I. cylindrica* multicomponent devolatilization kinetics assumes multiple independent pseudocomponents are decomposing in parallel reactions and in first order. Therefore, the devolatilization kinetics can be modelled for any component and the equation for all the pseudocomponents can be states as follows:

$$\frac{dX_i}{dt} = \xi_i k_{0,\mathrm{i}}\, exp\left(\frac{-E_a}{RT}\right) \cdot (1 - X_i) \tag{3}$$

$$\frac{dX_n}{dt} = \sum_{i=1}^{n} \frac{dX_i}{dt}, \qquad \Rightarrow X_n = \sum_{i=1}^{n} X_i \tag{4}$$

Since the TGA data is a function of heating rate, β (K/s), Eq(3) could be rearranged to reflect heating rate by using Eq(5) and integrating to give Eq(6), where ξ_i is known as the fractional contribution of component i.

$$\frac{dX}{dt} = \frac{dX}{dT} \cdot \beta \tag{5}$$

$$\int_0^{X_i} \frac{dX_i}{(1 - X_i)} = \xi_i \cdot \frac{k_{0,\mathrm{i}}}{\beta} \cdot \int_{T_0}^{T} exp\left(\frac{-E_a}{RT}\right) \cdot dT \tag{6}$$

Eq(6) could be solved analytically by integration by part and substitution to obtain Eq(7) for n, numbers of pseudo reactions.

$$X_n = \sum_{i=1}^{n} \xi_i \cdot \left(1 - exp\left\{\frac{k_{0,\mathrm{i}}}{\beta} \cdot \frac{E_{\mathrm{a,i}}}{R} \cdot \left[\frac{exp(-y_i)}{y_i} - \int_y^{\infty} \frac{exp(-y_i)}{y_i} dy\right]\right\}\right) \tag{7}$$

$where\ y_i = \frac{E_{a,i}}{RT}$

Kinetic parameters i.e $\xi_i, k_{0,i}$ and $E_a$for each pseudocomponent in the devolatilization of *I. cylindrica* was obtained by minimizing the objective function (OBF) - see Eq(8) using multidimensional nonlinear regression by means of MATLAB R2013a *lsqlcurvefit* function.

$$OBF = \sum_{k=1}^{N_k}\sum_{m=1}^{N_m}\left[\left(\frac{dX_n}{dt}\right)_{exp,k,m} - \left(\frac{dX_n}{dt}\right)_{cal,k,m}\right] \quad (8)$$

For Eq(8) to be minimized Eq(7) was evaluated using MATLAB R2013a expint function and the calculated values were consequently differentiated numerically using Eq(5). The values for $\mathrm{N_k}$ and $\mathrm{N_m}$ which correspond to the number of heating rates and amount of TGA measured are 4 and 194. The differential TG (DTG) data was used in Eq(8) because of its ability to magnify small changes or peaks in TGA curves. Considering, the fact that different number of pseudocompenents used was from 3 to 10 for the simulation in order to finding the best fit, the quality of fit (QOF) of the model predicted values to the experimental data was determined by Eq(9) for each heating rate and the overall process (Aboyade et al., 2011).

$$\sqrt{\left[\left(\frac{dX_n}{dt}\right)_{exp,m} - \left(\frac{dX_n}{dt}\right)_{cal,m}\right]^2}\Big/ N_m \quad (9)$$

$$QOF = 100 \times \sum_{m=1}^{N_m} \frac{}{max\left|\frac{dX}{dt}\right|_{exp,m}}$$

The MATLAB R2013a lsqlcurvefit function is generally used for curve or data fitting problems and could make use of either Trust-region-reflective or Levenberg-Marquardt algorithm. However, the trust-region-reflective was used because of its ability to handle bound constraints in order for the predicted values of $E_{a,i}, k_{0,i}$ to be between 1 and infinity and ξ_i to be between 0 and 1.

3. Results and Discussion

3.1 TG and DTG Curves

The TG plots for the four heating rates are shown in Figure 1(a), the shape of curves are similar for all the heating rates. For easy identification of the peaks a combined plot of TG and DTG for 20 K/min are shown in Figure 1(b). Figure 1(b) showed five (5) notable distinct peaks at 77 °C, 307 °C, 347 °C, 427 °C and 612 °C.

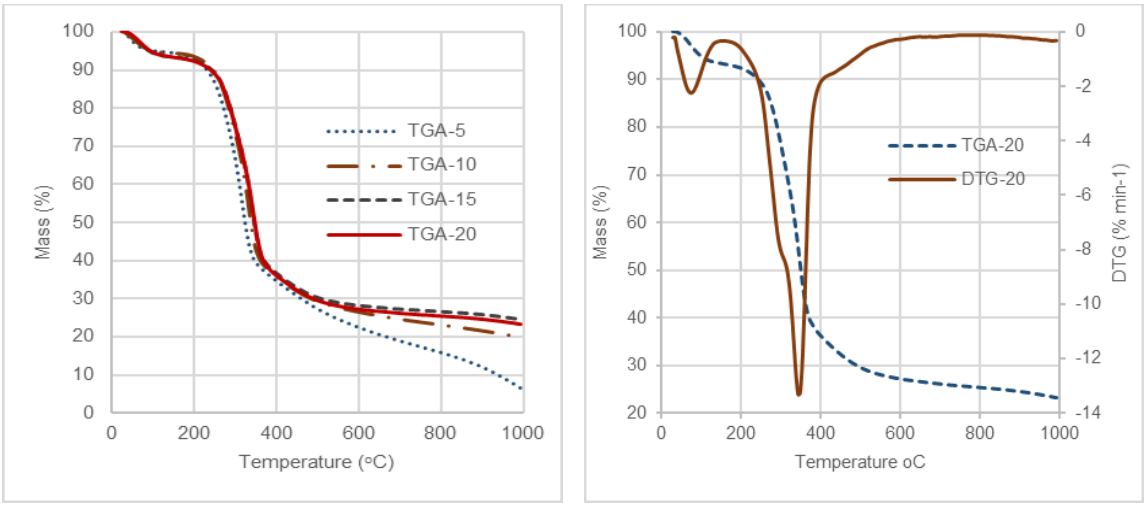

Figure 1: (a) TG curves I. cylindrica at different heating rates. (b) TG and DTG curves at 20 K/min

Furthermore, the mass loss could be separated into three regions (see Fig 1b), region (I) represents drying, occurring between 35 – 150 °C and essentially water moisture was removed. Region (II)

characterized by rapid mass loss and temperature range 150 – 450 °C is known as the region of active pyrolysis. In this region biomass constituent mainly cellulose and hemicellulose decomposes. The third region (III) is governed by temperatures above 450 °C and known as passive pyrolysis with the decomposition of Lignin.

3.2 Kinetic Model fitting and Parameters

The TGA was converted to rate of mass loss data by means to kinetic model Eqs(1)-(7). The simulation was carried out between 3 and 10 pseudocomponents, the calculated quality of fits (QOF) for the four heating rates (5 – 20 K/min) and with their objective function (OBF) values are shown in Table 1.

Table 1: Kinetic Model Quality of Fit for each Pseudocomponent reactions

Heating Rates (K/min)	QOF (%) (Number of Pseudocomponent reactions)							
	3	4	5	6	7	8	9	10
5	7.66	5.08	6.15	5.63	4.22	4.40	4.52	4.19
10	3.67	2.31	2.23	1.97	1.35	1.30	1.61	1.37
20	3.40	2.12	1.57	1.33	1.12	0.97	1.20	1.14
Overall	4.47	2.86	2.84	2.55	1.94	1.89	2.11	1.93
OBF (x 10^{-6})	8.42	4.82	1.84	1.39	1.09	1.06	1.40	1.46

The lower the quality of fit the closer the predicted values to the experimental data. From Table 1 the quality of fit decreases with increase in heating rates and also decreases with increase in number of pseudocomponents for each heating rates until 9 pseudocomponents where slight increase was noticed before decreasing again for 10 pseudocomponents. Therefore, 8 pseudocomponents with 1.89 % overall quality of fit had the best predictions. The plot of the devolatilization kinetics of the 8 pseudocomponents in comparison to the experiments data are shown in Figure 2.

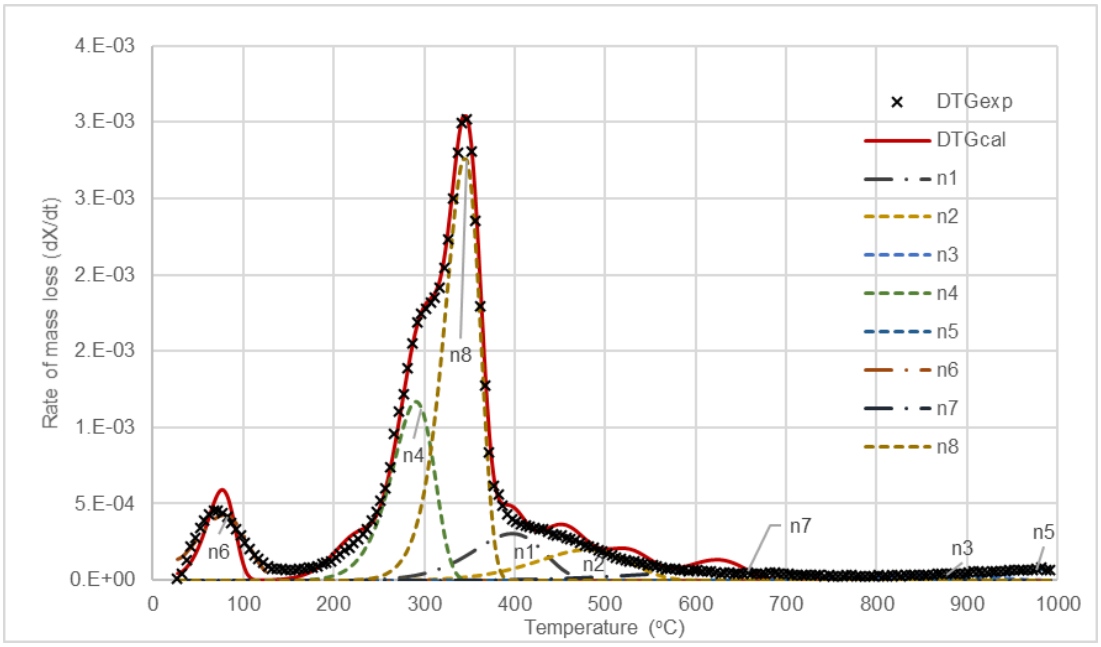

Figure 2: I. cylindrica simulated devolatilization curve for 8 pseudocomponents

Furthermore, Figure 2 shows that some components correspond to some identified peaks from the experimental data. Based on the three regions partitioning used earlier it was noted that component 6 is in Region (I), the components in Region (II) are 4, 8, 1 and part of component 2. Region (III) the tail part of the plot is made up of components 2, 7, 3 and 5. Therefore, for biomass lignocellulosic components of cellulose, hemicellulose and lignin the identified peaks and their corresponding model component number are 8, 4 and 1.

The kinetic parameters ($E_{a,i}, k_{0,i}$ and ξ_i) predicted from the multicomponent kinetic analysis for 8 pseudocomponents (the lowest quality of fit) with their corresponding region of influence is supplied in

Table 2. All pseudocomponents from Table 2 with factors of contribution (< 0.05) are classified as spurious and negligible components, which include components 3, 5 and 7 (Hattingh *et al.*, 2014). Therefore, the components with significant contribution to the overall TG profile in ascending order are component 2, 1, 6, 4 and 8.

Table 2: Kinetic Parameters for 8 Pseudocomponents

n	$k_{0,\mathrm{i}}\ (s^{-1})$	$E_{\mathrm{a,i}}\ (kJ/mol)$	ξ_i	Region
1	8.59 x 10^{-4}	9.02	0.09	II
2	6.59 x 10^{-5}	8.70	0.08	II and III
3	5.74 x 10^{-3}	17.61	0.02	III
4	2.47	11.06	0.21	II
5	3.43 x 10^{-1}	24.33	0.04	III
6	1.44 x 10^{-5}	3.44	0.09	I
7	2.66 x 10^{-7}	6.84	0.04	III
8	6.33 x 103	16.05	0.43	II
Average	791.63	12.13	0.13	

Region: I- Drying, II- Active Pyrolysis and III- Passive Pyrolysis

From Table 2, the average activation energy for all the pseudocomponents was 12.13 kJ/mol, with range 3.44-24.33 kJ/mol. The lowest activation energy (3.44 kJ/mol) was for the component, 6 in region (I) and characterized by drying or the evolution of moisture. The highest activation energy was for one of the identified spurious components, however, the highest value among the significant components was 16.05 kJ/mol and component, 8. Comparing the activation energies of the components fully in region (II) i.e component 1, 4 and 8 the values are 9.02, 11.06 and 16.05 kJ/mol and are identified as Lignin, Hemicellulose and Cellulose. Although, the range of values predicted for activation energies are lower than literature suggested values by Bradbury *et al.* (1979) and Miller and Bellan (2010), however they showed similar order of magnitude.

4. Conclusions

The model fitting method was successfully applied to deconvolute the TGA data for I. cylindrica. The simulation was carried out for varying pseudocomponents of 3 – 10 for the purpose of determining the best fit. The 8 pseudocomponents simulation gave the best overall quality of fit of 1.89 %. The kinetic parameters of pre-exponential factor, activation energy and fractional contribution gave a good range with the average values of 791.63 s^{-1}, 12.13 kJ/mol and 0.13 respectively. Furthermore, the deconvolution identified components 8, 4 and 1 as cellulose, hemicellulose and lignin with activation energies of 16.05 kJ/mol, 11.06 kJ/mol and 9.02 kJ/mol, showing a good and similar order of magnitude with literature. However, some components contribution where assumed insignificant to the global TG curve, the possible effect of these components values on the identified significant components could be of interest for future investigations.

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