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MODEL FREE KINETICS ANALYSIS OF *IMPERATA CYLINDRICA* (LALANG)

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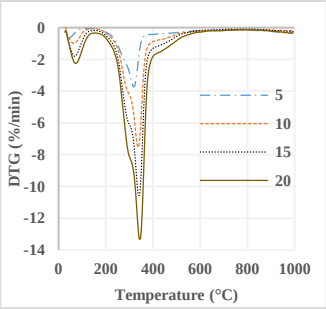
Graphical abstract



Abstract

This study is the first attempt at investigating the solid state decomposition and the devolatilization kinetics of Imperata cylindrica (lalang) grass termed the "farmer's nightmare weed" as a potential solid biofuel of the future. Biomass conversion technologies such as pyrolysis and gasification can be utilized for future green energy needs. However an important step in the efficient utilization and process optimizing of biomass conversion processes is understanding the thermal decomposition kinetics of the feedstock. Consequently, thermogravimetric analysis (TGA) of Imperata cylindrica was carried out in the temperature range of 30-1000 °C at four heating rates of 5, 10, 15, and 20 K min^{-1} using Nitrogen at a flow rate of 20 L min^{-1} as purge gas. Using the TGA results, the kinetic parameters activation energy (Ea) and pre-exponential frequency factor (k_o) of the grass were estimated via the model free or isoconversional methods of Kissinger and Starink. The results obtained for Kissinger model were 151.36 kJ mol^{-1} and 5.83 x 10^9 min^{-1} for activation energy and pre-exponential frequency factor respectively. However, Starink model activation energy and pre-exponential frequency factor were a function of conversion (α) with average values of 159.93 kJ mol^{-1} and 6.33 x 10^{22} min^{-1} respectively.

Keywords: Lalang; thermogravimetric; pyrolysis; kinetics; model free

Abstrak

Kajian ini adalah percubaan pertama pada Penyiasat penguraian keadaan pepejal dan kinetik Lalang devolatilization (lalang) rumput diistilahkan sebagai "mimpi ngeri rumpai petani" sebagai bahan api bio pepejal yang berpotensi di masa hadapan. Teknologi penukaran biojisim: seperti pirolisis dan penggasan boleh digunakan untuk keperluan tenaga hijau masa depan. Walau bagaimanapun langkah penting dalam proses dan penggunaan berkesan Proses Optimizing penukaran biojisim memahami kinetik penguraian terma bahan mentah itu. Oleh itu, analisis Termogravimetri (TGA) Imperata cylindrica telah dijalankan kepentingan di dalam lingkungan suhu 30-1000 ° C pada empat kadar pemanasan 5, 10, 15, dan 20 K min^{-1} menggunakan Nitrogen pada kadar aliran 20 L min^{-1} sebagai gas pembersihan. Menggunakan hasil TGA, parameter kinetik tenaga pengaktifan (*Ea*) dan faktor kekerapan pra-eksponen (*ko*) rumput Adakah Anggaran melalui model percuma atau kaedah isoconversional daripada Kissinger dan Starink. Keputusan Telah Mendapat untuk model Kissinger 151.36 kJ mol^{-1} dan 5.83 x 10^9 min^{-1} untuk tenaga pengaktifan dan faktor kekerapan pra-eksponen. Walau bagaimanapun, Starink pengaktifan model tenaga dan faktor kekerapan pra-eksponen Adakah fungsi penukaran (α) dengan nilai purata 159.93 kJ mol^{-1} dan masing-masing 6.33 x 10^{22} min^{-1}.

Kata kunci: Dendritic gels; tunable materials

1.0 INTRODUCTION

Perhaps this study is the first attempt at investigating the solid state decomposition and devolatilization kinetics of *Imperata cylindrica* (Lalang) as a potentially solid biofuel of the future. Lalang grows abundantly in South-East Asia with adverse effect on food crops, earning it the name "farmer's nightmare weed"[1]. This green grass (see Figure 1) grows readily with rice on farms, fallow lands and road side. It grows by an interconnected nodes of rhizomes with one node able to easily sprout and propagate an entire farmland making them difficult to eradicate [2]. The plant can grow to about two meters with pointed tip blade leaves of around 0.5 m with base of 2 cm and has been known to burn even when green (wet).

In addition to saving and recouping millions of dollars spent every year on clearing and weeding the large amount of Lalang that grows on farms, thereby making available tons of biomass feedstock, the ability to burn readily are the major attractions in considering Lalang as a potential energy crops in the category of Switchgrass and Miscanthus for the production of green and clean biofuel through thermochemical processes [3, 4].

Figure 1 Field of growing *Imperata cylindrica* (Lalang) grass

Gasification, Combustion and Pyrolysis are major thermochemical processes where heat is used in converting biomass into biofuel, gas and chemicals [5]. Pyrolysis is the precursor of all thermochemical process, the reaction takes place in the absences of air and the bulky biomass feedstock are converted to energy packed products such as bio-oil (liquid), gas and char (solid). The proportion of the liquid, gas and solid products from pyrolysis are dependent on factors such as temperature, pressure, heating rate, particle size, residence time and biomass composition [6, 7]. Due to the importance of Pyrolysis in thermochemical processes and consequently the production of green, clean and sustainable energy from biomass, there is a need to understand the science of pyrolysis complex reactions.

The use of Thermogravimetric analysis (TGA) in the studying of thermal decomposition behavior of biomass, by researchers is a common technique in the determination of devolatilization kinetics parameters of biomass by means of either model fitting or model free methods [8]. The model free methods were used in this study due to its accuracy, reliability and computational easy as compare to any other method in predicting kinetic parameters [9]. There are several methods to choose from among model free techniques with all making use of graphical tool. The model free isoconversion categories includes Friedman[10] which is isothermal and the others which are non-isothermal namely Flynn-Wall-Ozawa (FWO) [11], Kissinger[12], Kissinger-Akahira-Sunose (KAS) [13, 14] and Starink[9] methods. This paper studied the possibility of exploiting Lalang as an energy grass, through pyrolysis and gasification processes by understanding the science of its decomposition and devolatilization kinetics using TGA data and two model free methods namely Kissinger and Starink.

2.0 EXPERIMENTAL

2.1 Experimental

Lalang was harvested from an open field in Skudai, Johor, Malaysia. The green leaves were chopped and weighed before dried at 105 °C for 36 hours in an oven. The dried leaves (brown) were milled and sieved to obtain particle size < 125 µm. A sample of the particle 5-9 mg was placed in an aluminum crucible and heated from 25-1000 °C using the heating rates of 5, 10, 15 and 20 K min^{-1} in the Netzsch 209 F3 thermogravimetric (TG) analyzer. The purge gas used was pure nitrogen at a flow rate of 20 mL min^{-1}. The mass loss data from Netzsch 209 F3 was converted to TGA and DTG data using Proteus 6.1 Netzsch thermal analysis software [15].

The sample composition was characterized using proximate and ultimate analysis and the results are presented in Table 1.

Table 1 Proximate and Ultimate Analysis of Imperata Cylindrica

	Imperata Cylindrica
Proximate analysis (wt.%)[a]	
Moisture	8.47
Volatiles	73.22
Fixed Carbon	14.27
Ash	4.04
Ultimate analysis (wt.%)[b]	
C	43.19
H	5.92
N	0.59
O	50.16
S	0.14

[a] As received basis
[b] Dry basis

2.2 Kinetic Model

The kinetic model was developed from first principle by considering the rate of biomass decomposition as first order and the rate equation of solid state biomass transformation is described in Eq 1.

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

where a is the reacted fraction of the sample or conversion, f(a) the reaction model, t the time and k(T) the rate constant of reaction and could be expressed as Arrhenius equation in Eq 2.

$$k = k_0 \cdot exp\left[-\frac{E_a}{RT}\right] \tag{2}$$

where k0 (min-1) is pre-exponential factor, Ea (kJ.mol-1) is the activation energy, R (8.314 J.K-1.mol-1) is the Universal gas constant, T (K) is temperature and t (s) is time. It is worth noting that the conversion, a is expressed in Eq 3 and defined as the normalized weight loss.

$$\alpha = \frac{m_i - m_t}{m_i - m_f} \tag{3}$$

where mi is the initial mass of the sample, mf is the final mass of sample after devolatilization and mt is the time constraint mass of sample all obtained from TGA experiment.

Combination of the equations (1) and (2) is expressed in Eq 4 and is the basic TGA mathematical model for calculating kinetic parameters:

$$\frac{d\alpha}{dt} = A \cdot exp\left[-\frac{E_a}{RT}\right] f(\alpha) \tag{4}$$

Introducing the heating rate, β = dT / dt (K.min-1) into Eq. 4 for TGA non-isothermal experiment and and expressed as Eq. 5.

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \cdot f(\alpha) \cdot exp\left[-\frac{E_a}{RT}\right] \tag{5}$$

Equation 5 was analytical solved using the Doyle's method and a generalized equation for isoconversion model could be represented by Eq (6) [9].

$$ln\left(\frac{\beta}{T^{\kappa}}\right) = -A\frac{E_a}{RT} + C_w \tag{6}$$

where κ varies between 0 – 2 and Cw is the integral constant, both parameters depend on the method selected. The two methods considered are Kissinger and Starink and the values for κ are 2 and 1.8 respectively, their integral constant equations are stated in the full equations in section 2.2.1 and 2.2.2.

2.2.1 Kissinger Method

The Kissinger method is a model free non-isothermal model where the determination of the kinetic parameters are independent of the fractional conversions. A single activation energy and pre-exponential factor are obtained from the slope and intercepts of the plot of $\ln(\beta/T_m^2)$ and $1000/T_m$ on y and x axis respectively.

The plot is a single line with the points obtained at different heating rates, β and peak temperature, T_m of the DTG curve. The Kissinger equation is expressed below [13]:

$$ln\left[\frac{\beta}{T_m^2}\right] = -\left[\frac{E_a}{RT_m}\right] + ln\left[\frac{k_0 R}{E_a}\right] \tag{7}$$

From equation 7 the activation energy E_a and pre-exponential factor k_0 are computed from the following equations 8:

$$slope = -\left[\frac{E_a}{RT_m}\right] \; and \; intercept = ln\left[\frac{k_0 R}{E_a}\right] \tag{8}$$

2.2.2 Starink Method

Starink model-free non-isothermal method unlike Kissinger does not give a single kinetic parameter value but as many as the chosen conversions, a. The governing equation is expressed in Eq (9) [16]:

$$ln\left[\frac{\beta}{T_\alpha^{1.8}}\right] = -A\left[\frac{E_a}{RT_\alpha}\right] + C_5 \tag{9}$$

$$\text{with } A = 1.0070 - 1.2 \times 10^{-5} E_a \tag{10}$$

where T_α are the temperatures at chosen conversion, a and Coats-Redfern suggested the equation (11) for C_5 [17].

$$C_5 = ln\left[\frac{k_0 R}{\beta E_a}\right] \tag{11}$$

From the plot of $\ln(\beta/)T_{\alpha}^{1.8}$ and $1000/T_m$, the activation energy, Ea could be computed from the slope and the pre-exponential factor from intercept. The Equation (10) could be equated to the slope and use to obtain the first approximation of E_a.

3.0 RESULTS AND DISCUSSION

3.1 TGA and DTG analysis

The thermogravimetric analysis and differential thermogravimetric curves are shown in Figure 2 and Figure 3 respectively for the four different heating rates of 5, 10, 15 and 20 K.min^{-1}. The four heating rates profile follow the same pattern for the two profiles, however in Figure 2 the mass loss (%) at high temperature for the 5 K.min^{-1} heating rate drop sharply at 480 °C.

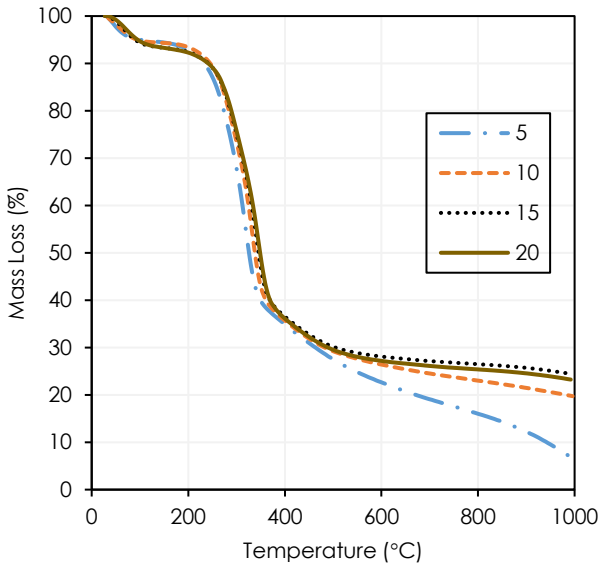


Figure 2 Lalang TGA profile for the four heating rates

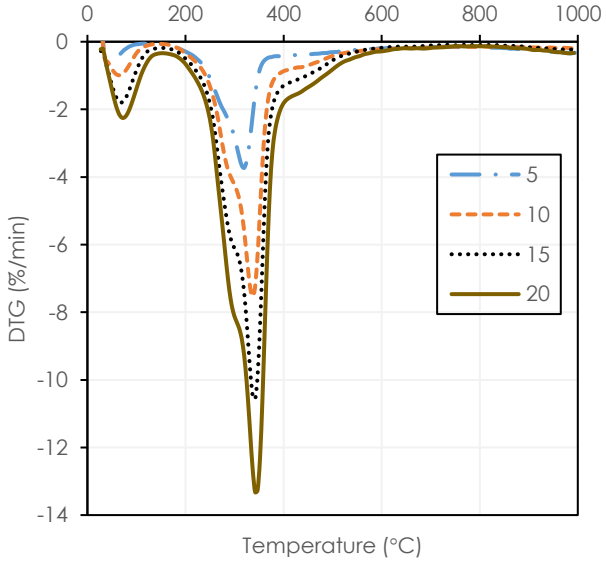


Figure 3 Lalang DTG profile for the four heating rates.

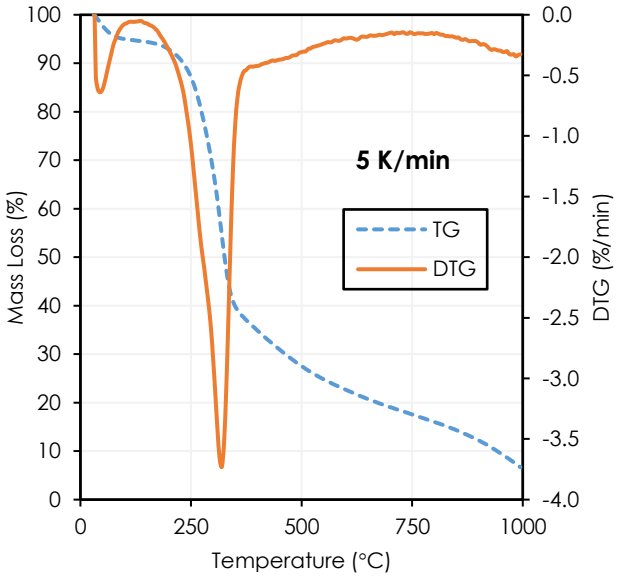


Figure 4 TGA and DTG profile for 5 K min^{-1}

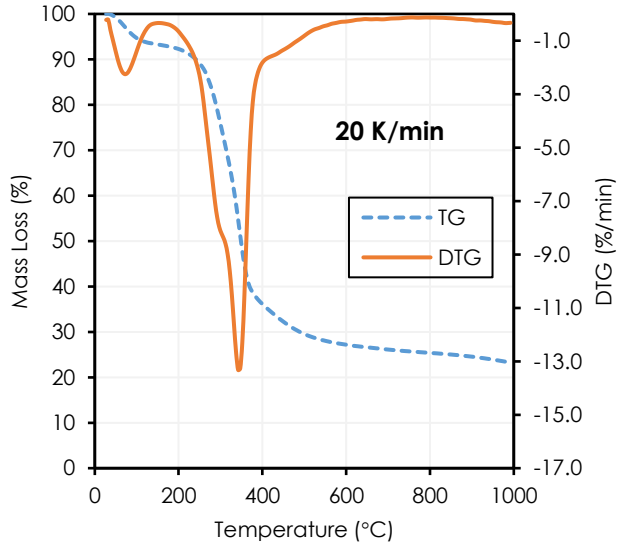


Figure 5 TGA and DTG profile for 20 K min^{-1}

Furthermore, the TGA and DTG shows three distinct mass loss regions and the combine profiles for 5 K.min^{-1} and 20 K.min^{-1} are shown in Figure 4 and Figure 5 respectively. Using Figure 5, Region (I) occurs between 35 – 150 °C essentially drying and water moisture was removed. Region (II) is region of active pyrolysis and is characterized by rapid mass loss at 150 – 450 °C. Also biomass constituent mainly Cellulose and Hemicellulose decomposes in region (II). The Region (III) is known for passive pyrolysis and is governed by

temperatures above 450 °C and Lignin decomposition occurs.

The DTG normally pronounce the peaks [8] and for 20 K.min^{-1} five notable distinct peaks at 77 °C, 307 °C, 347 °C, 427 °C and 612 °C were observed. This signifies the presence of five distinct components which are probably Cellulose, Hemicellulose, Lignin, Water and Char [7, 8].

3.2 Kinetic Analysis

The Kissinger and Starink models were applied to the thermogravimetric analysis data in other to compute the kinetic parameters i.e the activation energy (E_α) and the pre-exponential factor (k_0). Figure 6 shows the Kissinger model profile of $\ln(\beta/T_m^2)$ against $1000/T_m$, the peak temperature T_m corresponding to the maximum weight loss for the four heating rates of 5, 10, 15 and 20 K.min^{-1} with values of 318.8, 332.0, 340.4 and 344.3 °C respectively (Figure 3).

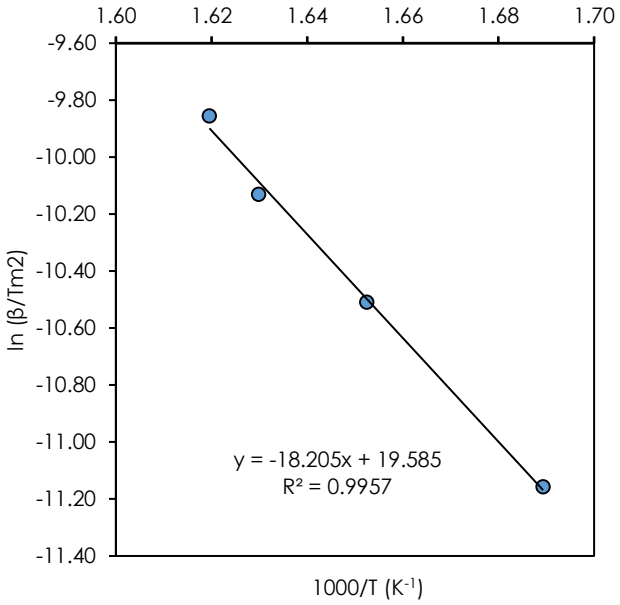


Figure 6 Kissinger model for Lalang

However, for Starink model the profiles of the regression line for various conversions are shown in Figure 7, where $\ln(\beta/T_\alpha^{1.8})$ was plotted against $1000/T_\alpha$. The reaction conversions, a, selected were 5 – 75 % and their corresponding temperatures were used in the model calculations.

Using the Kissinger model free equation (7) comparing to the regression equation in Figure 6 and using equation (8) the estimated value of activation energy (E_α) and pre-exponential factor (k_0) are 151.36 kJ.mol^{-1} and 5.83 x 10^9 min^{-1} respectively.

The estimation of kinetic parameters by Starink model for a specific conversion, a, was evaluated by comparing the conversions regression line equations in Figure 7 to equations (9), (10) and (11). The activation energies and the pre-exponential factors obtained for each conversion and the averages are given in Table 2.

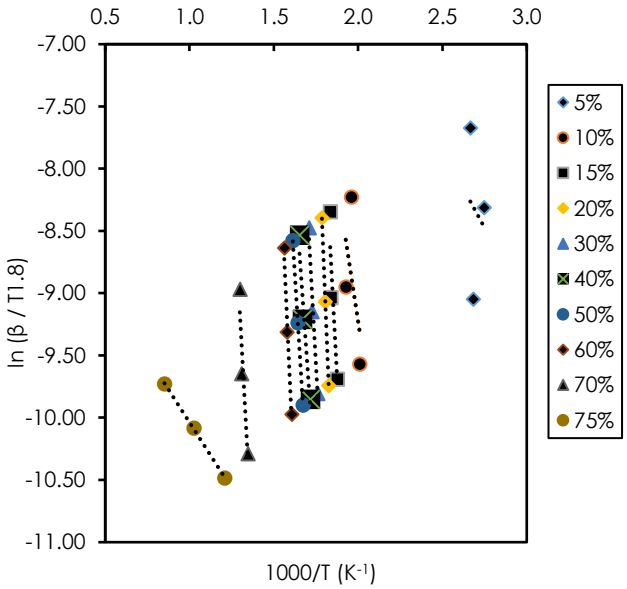


Figure 7 Starink plot of Lalang for different percent conversion

The profile of the activation energies and pre-exponential factors with conversion are presented in Figure 8 and it shows that apparent activation energy varies with conversion indicating the presence of complex multi-step reaction mechanism [18].

The range of apparent activation energy value is 17.54 – 277.02 kJ mol^{-1} meaning the decomposition of the biomass Lalang is dependent on conversion and the reaction mechanism varies during the process of decomposition. This shows the advantage of model free isoconversion method such as Starink over Kissinger which predicted a single activation energy (E_α) of 151.36 kJ.mol^{-1} and given an inaccurate description as single-step rather than multi-step kinetic mechanism as evident in the varying value of E_α with conversion by Starink. However, the activation energy computed from Kissinger method is comparable to the average of the apparent activation energies with values of 151.36 kJ mol^{-1} and 159.93 kJ mol^{-1} respectively.

Table 2 E_a and k_o for Lalang obtained by Starink method

a	E_a (kJ mol^{-1})	k_o (min^{-1})
0.05	20.73	5.07 x 10^{1}
0.10	74.08	5.13 x 10^{4}
0.15	212.03	1.12 x 10^{18}
0.20	277.02	6.33 x 10^{23}
0.30	204.47	9.78 x 10^{15}
0.40	159.99	2.36 x 10^{11}
0.50	181.37	8.78 x 10^{12}
0.60	246.31	7.15 x 10^{17}
0.70	205.73	2.65 x 10^{11}
0.75	17.54	7.65 x 10^{4}
Average	**159.93**	**6.33 x 10^{22}**

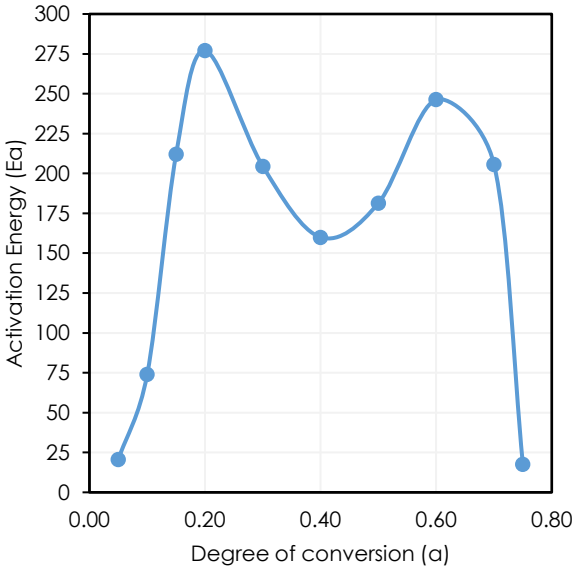


Figure 8 The activation energy as a function of conversion

Several biomass devolatilization kinetic have been investigated using thermogravimetric analysis. Kissinger was used to determine the kinetic parameter for poplar wood and the values of activation energy and pre-exponential factor obtained were 153.92 kJ mol^{-1} and 2.14 x 1012 min^{-1} [18]. Switchgrass and Miscanthus are grasses a characteristic share by Lalang and thermogravimetric analysis was used in the Literature to estimate their kinetic parameter. Yat *et al.*[19] determined the activation energy and pre-exponential factor of Switchgrass treated with dilute sulphuric acid and obtained 49-180 kJ mol^{-1} and 7.5 x 10^{4} to 2.6 x 10^{20} min $^{-1}$ respectively and Jeguirim *et al.*[20] found Miscanthus activation energy range of 86.6- 199.1 kJ mol^{-1}. The value of activation energy and pre-exponential factor from the literatures for these lignocellulosic biomass are comparable with the values predicted by the Kissinger and Starink methods used for Lalang in this study.

The kinetic parameters estimated from the model free methods for the devolatilization of Lalang in this work could be used in modelling, simulating and optimization study of thermochemical processes such as pyrolysis and gasification. It is useful in mass and energy balance for computation of the required overall rate of reaction (*ko*) from Arrhenius equation using the activation energy and pre-exponential factor estimated in this study.

4.0 CONCLUSION

The two model free methods Kissinger and Starink were successful applied in the prediction of Lalang kinetic parameters (activation energy and pre-exponential factor). The thermogravimetric analysis (TGA) data used were from heating rates of 5, 10, 15 and 20 K.min^{-1}. The TGA and DTG shows a good profile which agrees with the literature by the existing of three (3) regions i.e drying, active pyrolysis and passive pyrolysis with the active pyrolysis occurring at about 150 - 450 °C .

The activation energy and pre-exponential factor for Kissinger model are 151.36 kJ.mol^{-1} and 5.83 x 10^{9} min^{-1}. The Kissinger model gave a constant value for the entire process contrary to Starink model. The Starink model predicted kinetic parameters as a function of conversion. The average activation energy and pre-exponential factor are 159.93 kJ.mol^{-1} and 6.33 x 10^{22} min^{-1} respectively.

The results from the two models are consistent by comparing their average values (151.36 kJ.mol^{-1} and 159.93 kJ.mol^{-1}) and show good agreement with literature. Furthermore, the fact that activation energy varies with conversion from Starink method indicate the complexity of devolatilization process.

The kinetic parameters of Lalang from model free methods are not available in the literature, therefore, the results obtained could be used in modelling, simulation and optimization of thermochemical process such as pyrolysis and gasification. Computational fluid dynamics (CFD) software mass and energy balance routine for biomass devolatilization process can utilize the activation energy and pre-exponential factor in routine rate of reaction computation.

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