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Evaluation of Non-Isothermal Kinetic Parameters for Pyrolysis of Teak Wood using Model-Fitting Techniques

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Abstract

Teak wood is one of the prominently used raw material in the construction industry, thus contributing extremely to the biomass waste available in Nigeria. These wastes are usually used for energy generation that requires upgrade into better fuel before application. Hence, the present study evaluates the non-isothermal kinetic parameters for pyrolysis of teak wood using model-fitting techniques. Teak wood dust was subjected to proximate, ultimate and calorific value analyses based on different ASTM standards. The thermal degradation and decomposition behaviour of the teak wood dust was examined using a thermogravimetric analyzer. Pulverized teak (6.5 mg) was heated from 30 to 800 ºC at varying heating rates (5, 10 and 15 ºC) in an environment where 100 mL/min of nitrogen gas was charged in continuously to maintain an inert condition. Avrami-Erofeev, Ginstling-Broushtein (GB) and Mampel models were used to evaluate the kinetic parameters of the pyrolysis of teak wood dust. The teak wood dust contained 7.25 % moisture, 79.26 % volatile matter (VM), 1.74 % ash and 11.75 % fixed carbon. The calorific value of the wood dust was 18.72 MJ/kg. The results of the thermogravimetric analyses depicted that heating rate has no effect on weight loss during the reactive drying zone. However, as the thermal treatment progressed into the active pyrolysis and passive pyrolysis zones, the weight loss decreased with increase in heating rate. The devolatilization parameters also increased with heating rates except for the maximum conversion. The results of the kinetic parameters evaluation revealed that the GB model was best fit to evaluate the kinetic parameters of teak in the active pyrolysis zone while GB and Mampel models were considered most appropriate for the evaluation of the kinetic parameters in the passive pyrolysis zone. Model-fitting method has the capacity to capture a wide range of fractional conversion at a glance.

Keywords: Model-fitting techniques, Teak wood dust, Thermogravimetry, Frequency factor, Activation energy

Introduction

Climate change and its adverse effect on man and the environment are as a result of overdependence on the use of fossil fuel as energy source for human activities. This has necessitated numerous researches into the use of alternative energy sources such as biomass. These biomasses are readily available at low cost and are environmental friendly [1-4]. This energy source has been classified as a renewable energy because of its potential for sustainability and environmental friendliness [5,6]. The level of SO_x and CO_2 emissions can be reduced by blending biomass with fossil fuel such as coal, but the heating value of the fuel are often lowered due to rich oxygen and hydrogen content of the biomass [7,8]. This is however compensated for by the low activation energy of the blend due to the presence of oxygen in the biomass which aids combustion. Biomass can be converted into useful products by thermochemical processing through pyrolysis. During pyrolysis, biomass is changed to gases, liquid and char [9]. Pyrolysis is the thermal degradation of biomass which occurs in the absence of oxygen and other gasses [10]. The pyrolysis kinetics of biomass can be examined through time-based thermal dissociation [11]. Non-isothermal kinetic evaluation is a suitable thermal analysis method that has been deployed in the study of pyrolysis kinetics of woody biomass [12].

Pradhan *et al.* [13] explained various models for the pyrolysis of biomass. Isoconversional model is the most commonly used model for explaining the kinetic behaviour of lumped biomass. It takes into cognizance kinetic parameters like frequency factor and activation energies during pyrolysis [9]. These factors can be investigated using model-fitting models [14]. Thermogravimetric analysis (TGA) has been adopted by many researchers as a reliable method for studying thermal behaviour of biomass [1,15,16]. TGA deploys the use of non-isothermal methods which requires that change in weight be measured as a function of temperature [17]. Model fitting methods assume that the reaction mechanism and specific rate constant fit suitably with the results obtained from the TGA [12]. The mineral composition of feedstock affects its torrefaction behaviour and heating value of biomass [17]. Also, the architecture and specific gravity of different tree species vary [18], hence the need to examine their non-isothermal kinetic parameters prior to use. Teak wood dust is considered the most important deciduous plant in tropic region, due to the ease of conversion into timber. The broad leaves tree is native to many tropical countries like Brazil, Thailand, India and Nigeria [18,19]. Due to its high usefulness, a lot of wastes are generated from the plant which can be converted into useful forms through thermochemical processes [14,20].

There are numerous studies on non-isothermal kinetic parameters evaluation for various biomass and solid fuels [11,21,22]. These works laid a solid foundation to obtain the kinetic parameters of biomass especially teak wood with the aim of producing biofuel from it through pyrolysis process. Thus, the objective of the present study is to obtain Arrhenius parameters in terms of activation energy and pre-exponential factor for the pyrolysis of teak wood while comparing 4 different model-fitting techniques

Materials and methods

Sample preparation

The biomass used in this study was teak wood. The wood was obtained from Benin, Nigeria. It was transformed into fines below 6.35 mm using a saw wood cutting machine (Model No: CS33EB). The wood chips and fines were sun-dried for 5 days (6 h/day). A Laboratory Mill (Thomas Wiley, Model 4) was then use to further pulverize the wood chips and screened to < 0.5 mm.

Sample characterization and thermogravimetric experiment

The ultimate, proximate and calorific analyses (higher heating value (HHV)) of the teak wood dust were determined based on different ASTM and BS standards. Moisture content (MC) was determined based on ASTM E871-81 standard while the VM content was obtained using BS EN 15148 standard. The ash content (AC) was determined in accordance with the ASTM E1755-01 standard. Fixed carbon of the sample was then determined by difference (100 – (MC + AC + VM)). The ultimate analyses (CHN) was obtained in a LECO-CHN 628 analyzer using ASTM D5373 while Sulphur content was obtained based on ASTM D4239-11 techniques. The oxygen content was evaluated by difference (100 – (C + H + N + S + AC)). The calorific values of the teak wood dust was gotten from a Par 6200 oxygen bomb calorimeter following ASTM D5865-04 method. A thermogravimetric analyser (Model No: STA7300) was used for the observation of the thermal degradation and decomposition behaviour of teak wood dust, where the approximate test sample loaded into the crucible for analysis was 6.5 mg. An inert environment with 100 mL/min nitrogen gas continuous flow was used for the experiment. The samples were heated from 30 to 800 ºC at different heating rates of 5, 10, and 15 ºC/min.

Evaluation of kinetic parameters using model-fitting techniques

The reaction scheme for thermal decomposition of teak wood dust is expressed by Eq. (1) [23]:

$$\alpha A_{solid} \rightarrow bB_{solid} + cC_{gas} \tag{1}$$

The mass loss during this process of decomposition follows the solid-state reaction rate law as presented in Eq. (2) [23]. The heating rate was incorporated into it since the thermogravimetry was done with a constant heating rate under non-isothermal condition thereby the rate reaction was described as a function of temperature as given in Eq. (3) [23]:

$$\frac{d\alpha}{dt} = A\, exp^{-E_a/RT} \mathrm{f}(\alpha) \tag{2}$$

$$d\alpha/dT = d\alpha/dt \times dt/dT \tag{3}$$

where $d\alpha/dT$ is the non-isothermal reaction rate, α is the conversion fraction, $dT/dt = \beta$ is the heating rate, E_a is the activation energy, A is the frequency factor/pre-exponential factor, T is the temperature in K, $f(\alpha)$ is the reaction model and R is the gas constant. Eq. (4) which is the differential form of the non-isothermal rate law, was obtained by substituting Eq. (2) into Eq. (3).

$$\frac{d\alpha}{dT} = A/\beta \; exp^{-E_a/RT} \mathrm{f}(\alpha) \tag{4}$$

By separating variables and integrating Eq. (4), the integral form of the non-isothermal rate law was obtained and it is presented as Eq. (5):

$$\mathrm{g}(\alpha) = \frac{A}{\beta}\int_0^T e^{-E_a/RT}\, dt \tag{5}$$

where $\mathrm{g}(\alpha)$ is the integrated form of the conversion dependence which is without a specific analytical solution. Let x replace $\frac{-E_a}{RT}$, Eq. (5) becomes Eq. (6) by transforming the limits:

$$\mathrm{g}(\alpha) = \frac{AE_a}{\beta RT}\int_x^\infty \frac{e^{-x}}{x^2}\, dx \tag{6}$$

Replacing the integral part with $p(x)$ which is a standard one, we have Eq. (7):

$$\mathrm{g}(\alpha) = \frac{AE_a}{\beta RT}\, p(x) \tag{7}$$

The Coats and Redfern [24] method is a prevailing approximation proposed for solving $p(x)$, which does not have an exact solution. The solution proffer by Coats and Redfern [24] was adopted for this study and it leads to Eq. (8):

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E_a}\left(1 - \frac{2R\bar{T}}{E_a}\right)\right] - \frac{E_a}{RT} \tag{8}$$

Generally, the term $2R\bar{T}/E_a$ is much less than unity for thermal decomposition of polymeric materials. Therefore, the plots of $\ln\left[\frac{\mathrm{g}(\alpha)}{T^2}\right]$ against $\frac{1}{T}$for different models gives straight lines with $\frac{-E_a}{R}$ as slopes and $\ln\left[\frac{AR}{\beta E_a}\right]$ as intercepts from which A was determined for APZ and PPZ. For thermogravimetric data, α was calculated via Eq. (9):

$$\alpha = \frac{m_o - m_t}{m_o - m_f} \tag{9}$$

where m_o and m_f are the initial and final mass of the reactant respectively, and m_t is the mass at a temperature.

The 4 models adopted for g(α) are given in Eqs. (10) (Avrami-Erofeev), (11) (Ginstling-Broushtein model (GB), (12) (Mampel) and (13) (SSS):

$$\mathrm{g}(\alpha) = [-\ln(1-\alpha)]^{1/2} \tag{10}$$

$$\mathrm{g}(\alpha) = \left(1 - {}^{2\alpha}/_{3}\right) - (1-\alpha)^{2/3} \tag{11}$$

$$\mathrm{g}(\alpha) = -\ln(1-\alpha) \tag{12}$$

$$\mathrm{g}(\alpha) = 1 - (1-\alpha)^{1/3} \tag{13}$$

Results and discussion

Characterization, decomposition changes and degradation mechanism of the teak wood dust

The results of the proximate, ultimate and calorific value analyses of the teak wood dust in the present study compared with results of previous research works are presented in **Table 1**. It is revealed that the moisture content, VM and ash content are 7.25, 79.26 and 1.74 %, respectively. The fixed carbon content of teak wood dust is 11.75 % which is slightly higher than of melina as reported by Adeleke *et al.* [19]. The ultimate analysis showed that the woody biomass is composed of carbon (47.84 %), hydrogen (6.09 %), nitrogen (0.39 %), oxygen (45.42 %) and sulphur (0.26 %) with a calorific value of 18.72 MJ/kg. The ranges of value obtained for these properties are common for tropical woody biomass [19,26]. **Figure 1** shows the thermogravimetric curves for the teak wood dust at different heating rates. The curves in **Figure 1** shows 3 distinct zones; a moisture evolution and drying zone (A), active pyrolysis zone (B) and passive pyrolysis zone (C) which is line with the findings of Kamble *et al.* [27]. The 3 zones were identified by Kothandaraman and Somasundaram [11] as cellulose, hemicellulose and lignin degradation zones, respectively. In zone A (50 to 200 ºC), as temperature rises, the moisture content of the wood was lost due to evaporation. The temperature at which this occurs and weight loss are independent of the heating rate. However, as the heating proceeds into zones B (200 to 400 ºC) and C (> 400 ºC), a variation in the weight loss due to the various heating rates was observed. The sample exposed to 5 ºC/min heating rates experienced the most weight loss while the sample with 15 ºC/min heating rate showed the least weight loss in both zones. This shows that weight loss decreases with increase in heating rate. According to Guida *et al.* [15], heating rate plays an important role in the pyrolysis of biomass as maximum decomposition rate increases with higher heating rates. **Figure 2** represents the DTG for the teak wood dust at the 3 heating rates. The maximum DTG peak temperature for the teak wood dust ranges from 321 to 341 ºC at the different heating rates (**Table 2**). This was linked to cellulose degradation [4,25]. The lignin content of teak wood dust degraded around 341 - 550 ºC. **Figure 2** revealed that above 550 ºC, there was a continuous mild weight loss, which was suggested to be fractional thermal cracking of some chemical bonds possibly formed at the initial devolatilization [25,26]. The temperature at which devolatilization begins (T_{onset}) was slightly affected by change in heating rates as shown in **Table 2**. This was mirrored by the temperature that showed the termination of degradation of cellulose (T_{offset}). $T_{burnout}$ that represent the temperature at which weight loss of the sample remain constant/relatively unchanged increased with heating rates. The maximum cellulose decomposition (DTG_{peak}) increased from 0.3824 to 0.9210 mg/min. The maximum conversion ($\propto_{max}$) reduced from 50.21 % at 5 ºC/min to 47.46 % at 15 ºC/min. The result trend was similar to what was reported by Adeleke *et al.* [25] for decomposition parameters of melina wood dust. The implication is that lower heating rates results in higher weight loss that was encouraged by mass diffusion mechanism. Thus, better pyrolysis process ensues using lower heating rates.

Table 1 Proximate, ultimate and calorific value analyses of the teak wood dusts compare to some other biomass.

Proximate (%)				**Ultimate (%)**					**HHV (MJ/kg)**	**Type of Biomass**
MC	**VM**	**AC**	**FC**	**C**	**H**	**N**	**O**	**S**	**HHV**	
7.25	79.26	1.74	11.75	47.84	6.09	0.39	45.42	0.26	18.72	Teak wood ++
7.52	81.42	2.15	8.92	47.09	6.65	0.38	43.54	0.19	18.72	Melina wood+
8.60	95.5	0.70	3.80	49.60	6.30	0.40	43.70	-	19.80	Teak wood*
9.40	70.40	3.50	26.10	43.90	5.30	0.40	46.90	-	16.59	Iroko wood**

*MC (Moisture content), VM (Volatile matter), AC (Ash content), FC (Fixed carbon content,) C (Carbon), H (Hyrogen), N (Nitrogen), O (Oxygen), S (Sulphur), HHV (Higher heating value (calorific value)), ++This study, +Adeleke *et al.* [25], *Balogun *et al.* [26] and **Azeez *et al.* [28].

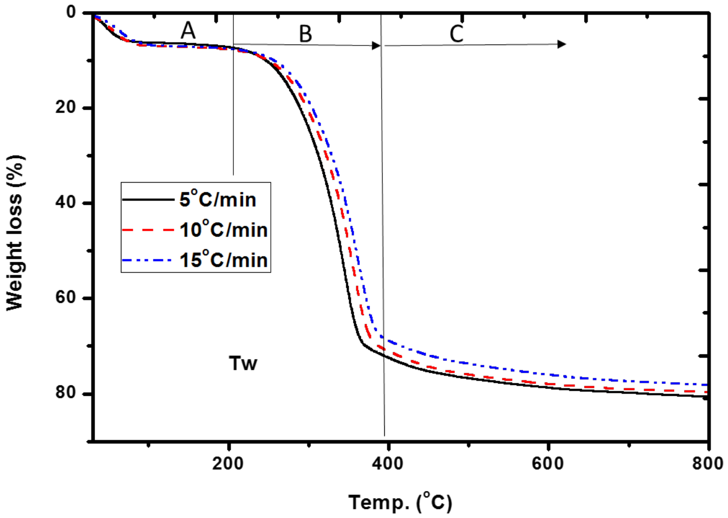

Figure 1 Thermogravimeteric curves for teak wood at different heating rates showing; (A) moisture evolution and reactive drying zone, (B) active pyrolysis zone and (C) passive pyrolysis zone.

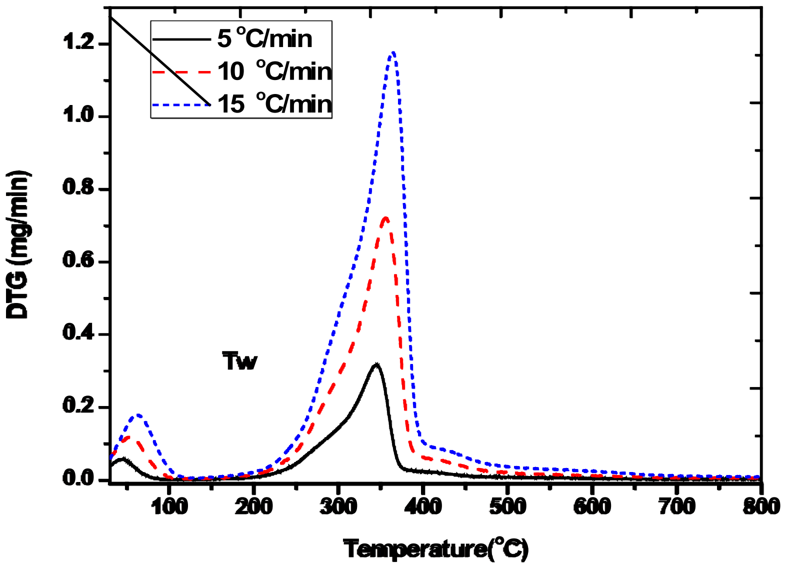

Figure 2 DTG curves for teak wood dust at different heating rates.

Comparison of the models

The α-temperature plot that describes solid-state reactions for teak wood dust is a bell shape which implied that it follows sigmoidal model as shown in **Figures 3**(**a**) and **3**(**b**). Skrdla and Robertson [29] suggested that nucleation and nuclei growth models can best describe the acceleratory and deceleratory region of the sigmoidal α-temperature curves of which Avrami-Erofeev model is a major type, thus the rationale behind its adoption for the present study. Thermal decomposition of biomass is a heterogeneous reaction and thus Ginstling-Broushtein model [29], a diffusion mechanism was also adopted to fit the heterogeneous solid-state reactions during thermal decomposition of biomass. **Figure 4** represents a typical plot of $\ln g(\alpha)/T^2$ against $1/T$ for the active pyrolysis zone (APZ) and **Figure 5** represents passive pyrolysis (PPZ) at 5 ºC/min heating rate for teak wood dust. For the different models employed to fit the thermogravimetric data, negative slopes were obtained for the APZ though with varying correlation factors (R^2). However, at PPZ, positive slopes were obtained for Avrami-Erofeev and SSS models which implied that negative activation energy values will be interpolated from the linear fit functions. For the 3 heating rates, consistent negative slopes were obtained for APZ (area of major mass loss took place) for the nucleation, diffusion, geometric contraction and reaction order models with relatively high correlation factor (R^2). However, Ginstling-Broushtein model consistently yield high correlation factor for the 3 heating rates compared to others. The highest correlation factor 0.9993 was obtained with 10 ºC/min heating rate compared to 0.9802, 0.9905 and 0.9859 of Avrami-Erofeev, SSS and Mampel models, respectively, as shown in **Table 3**. It implied that diffusion mechanistic assumptions could predominantly explain what take place within the primary pyrolysis zone of the thermal decomposition/degradation of teak wood dust. Khawam and Flanagan [30] explained that in diffusion-controlled reaction, the rate of product formation decreases proportionally with the thickness of product barrier layer. Kinetic parameters obtained via GB model is fitted for adoption during the APZ or the major mass loss arena of teak wood dsut. The GB and Mampel models yielded negative slopes as against the positives slopes of Avrami-Erofeev and SSS models at different heating rates for PPZ. The positive values obtained for the slopes could be as a result of the inability of the models to capture the overlapping multiple reactions that were taking place simultaneously within this zone [6,31] or simply put that the mechanistic assumptions of these models did not fit for the PPZ. Therefore, GB and Mampel model could be used to obtain the kinetic parameters during the PPZ. However, Mampel model has higher correlation factor (R^2) than GB at every heating rate as shown in **Table 3**. The R^2 values of 0.991, 0.9714 and 0.9876 for Mampel compared to 0.9787, 0.9568 and 0.9731 of GB for 5, 10 and 15 ºC/min evidently showed that during the further degradation of cellulose-lignin polymers of teak wood dust (PPZ), Mampel 1st order reaction model is better fit to determine kinetic parameters. Okoroigwe [2] reported that reaction order model adequately correlates the experimental data for thermal decomposition at the passive pyrolysis zone and the stage was referred to as char combustion in his study. The results suggested that prevailing mechanism changes depending on the temperature zone or region of the decomposition process.

Table 2 Devolatilization parameters based on different heating rates.

Sample	β (°C/min)	T_{onset} (°C)	T_{peak} (°C)	DTG_{peak} (mg/min)	T_{offset} (°C)	α_{max} (%)	$T_{burnout}$ (°C)	References
Teak	5	193	321	0.3824	515	50.21	602	This study
	10	196	330	0.5732	518	48.21	606	This study
	15	198	341	0.9210	524	47.46	610	This study
Melina	5	191	318	0.3577	444	49.96	560	[25]
	10	197	326	0.4706	502	49.91	607	[25]
	15	197	336	0.9194	504	48.55	645	[25]

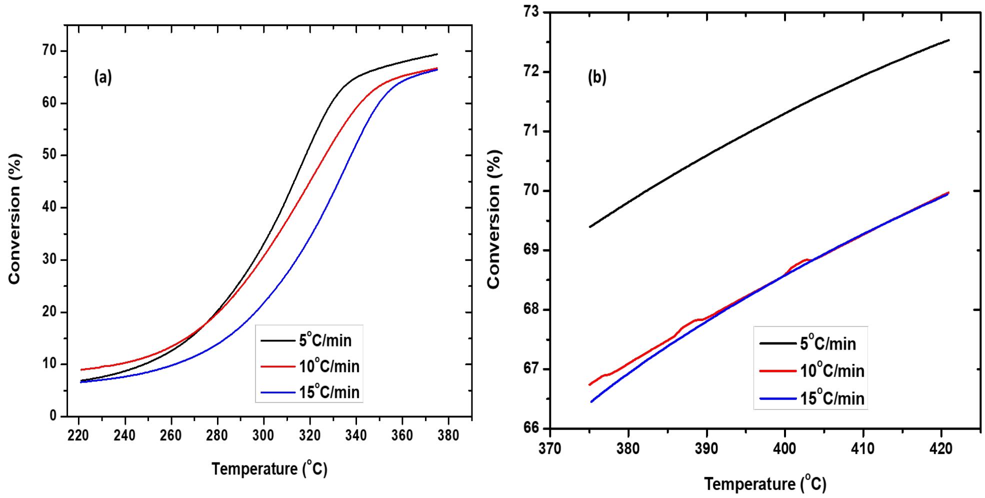

Figure 3 Conversion versus temperature at the different heating rates for (a) active pyrolysis zone (APZ) (b) passive pyrolysis zone (PPZ).

The kinetic parameters of the pyrolysis process of teak wood dust: Activation energy and pre-exponential factors

The activation energy (E_a) and pre-exponential factors (A) for APZ and PPZ are shown in **Figure 6** and **Table 3**, respectively. The activation energy and pre-exponential factor varies for different models as well as heating rates. This could be as a result of different assumptions upon which each model was developed as previously established. Ginstling-Broushtein is appropriate in reporting the activation energy and pre-exponential factor for APZ as shown in **Figure 6** and **Table 3**. The activation energy is approximately averaged to be 120.45 kJ/mol for the 3 heating rates. The activation energy at this stage agrees closely to 125.1 kJ/mol that was reported by Okoroigwe [2] for devolatilization kinetics of teak wood dust in a synthetic air environment. Consistent low activation energy values were obtained for all models at passive pyrolysis zone. However, for the high correlation factor (R^2) of Mampel model, the activation energy at PPZ is 2.67 kJ/mol. Essentially, the major devolatilization and degradation of teak wood dust polymers took place at the APZ which accounts for the higher activation energy with the 10 - 80 % fractional conversion. One advantage of model-fitting method is the ability to capture wide range of fractional conversion at a glance. According to Varhegyi *et al.* [12], ‘a good empirical model should provide a good fit between experimental and calculated data’. The activation energy for PPZ significantly showed that above 80 % conversion, minimum external energy input is required to maintain and further the decomposition and degradation of cellulose and lignin. The pre-exponential factors of approximately 2.0E + 10/min showed that the reaction was slow during APZ. Conversely, with A of 7.13E - 1/min during PPZ as shown in **Table 3**, the reaction was swift compared to the APZ. Mortari *et al.* [32] reported the activation energy of 2 steps thermal decomposition kinetics of bagasse and stated that at passive pyrolysis stage, it was lower compared to the active pyrolysis stage. As discussed earlier, the temperature profile (**Figure 6**) of APZ and PPZ showed that with less external supply of energy, it is possible to obtain maximum devolatilization and conversion into various bio-energy and gases from teak wood dust.

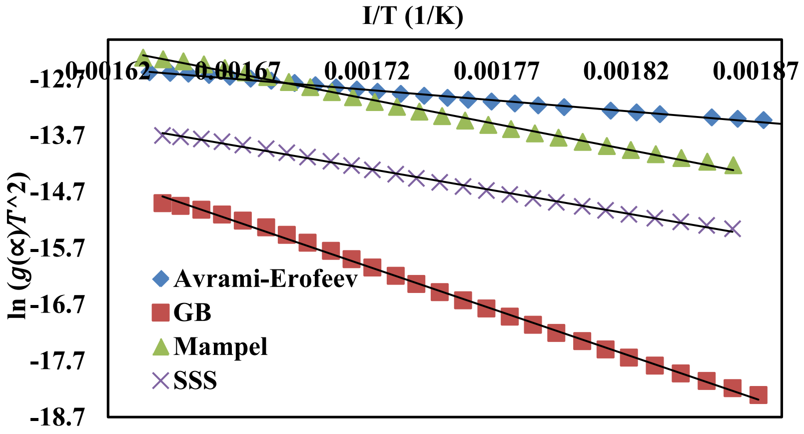

Figure 4 Typical plot for comparing different g(α) at APZ of teak wood dust at different heating rates (at 5 ºC/min.

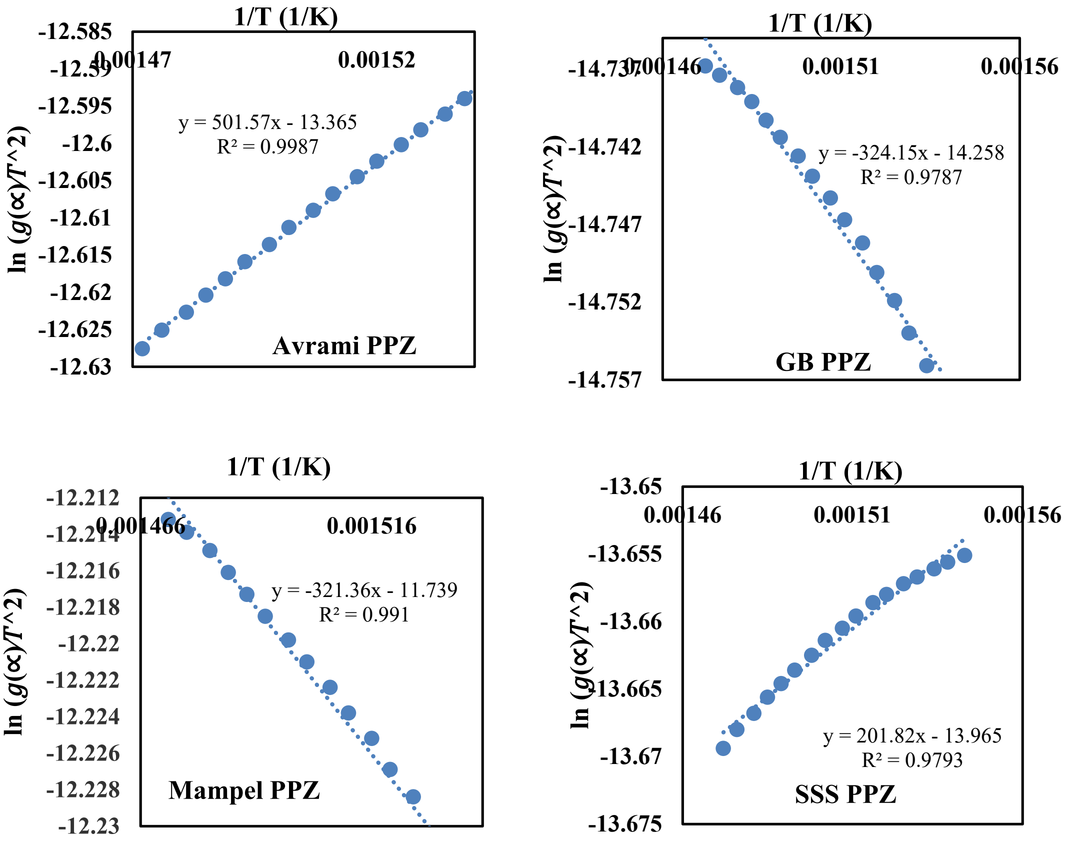

Figure 5 Typical plots for comparing different g(α) at PPZ of teak wood dust at different heating rates (5 ºC/min).

Table 3 Kinetic parameters obtained via the different solid-state reaction models for the 2- pyrolysis zone (active and passive zones).

		β (ºC/min)					
		APZ			**PPZ**		
g(α)		**5**	**10**	**15**	**5**	**10**	**15**
Avrami-Erofeev	**E_a (kJ/mol)**	31.97	25.15	27.98	–4.17	–5.06	–3.71
	A (min^{-1})	2.11E + 3	3.52E + 2	6.38E2	–2.19E – 1	–2.23E – 1	–2.16E – 1
	R^2	0.9933	0.9802	0.9703	0.9987	0.9977	0.9926
GB	**E_a (kJ/mol)**	122.70	119.75	118.91	2.70	2.14	4.21
	A (min^{-1})	2.57E + 11	1.71E + 10	1.02E + 10	5.78E – 2	3.99E – 2	1.21E – 1
	R^2	0.9981	0.9993	0.9893	0.9787	0.9568	0.9731
SSS	**E_a (kJ/mol)**	65.57	53.31	58.40	–1.68	–2.73	–1.40
	A (min^{-1})	1.06E + 6	5.71E + 4	1.48E + 5	–4.83E – 2	6.36E - 2	–4.33E – 2
	R^2	0.9971	0.9905	0.9835	0.97930	0.9835	0.9484
Mampel	**E_a (kJ/mol)**	74.36	59.81	64.03	2.67	1.61	3.97
	A (min^{-1})	2.13E + 8	8.35E + 5	1.71E + 6	7.13E – 1	3.4E – 1	1.36
	R^2	0.9959	0.9859	0.9770	0.9910	0.9714	0.9876

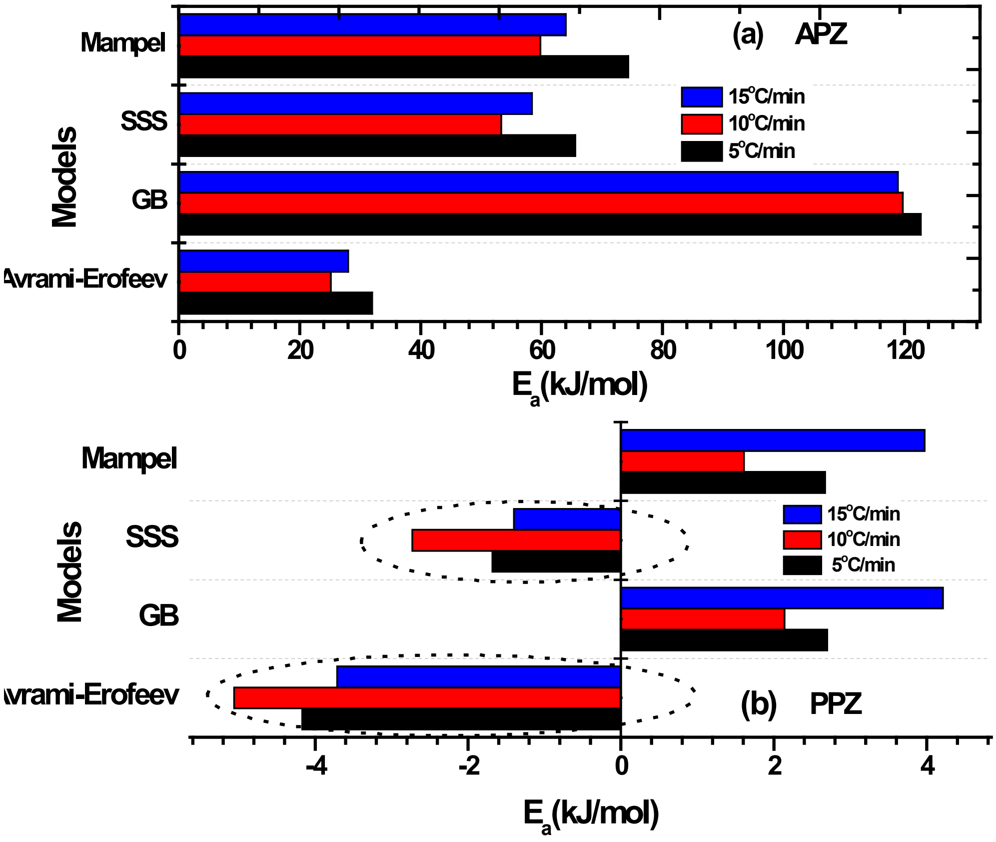

Figure 6 Activation energy obtained via the different solid-state reaction models for (a) active pyrolysis zone (b) passive pyrolysis zones.

Conclusions

The evaluation of non-isothermal kinetic parameters for pyrolysis of teak wood using model-fitting techniques was carried out in this study. Teak wood dust contained 7.25 % moisture, 79.26 % VM, 1.74 % ash and 11.75 % fixed carbon. The calorific value of the teak wood dust was 18.72 MJ/kg. The weight loss of teak wood dust decreased with increase in heating rate. The maximum cellulose decomposition (DTG_{peak}) increased from 0.3824 to 0.9210 mg/min. The maximum conversion ($\propto_{max}$) reduced from 50.21 % at 5 ºC/min to 47.46 % at 15 ºC/min. The α-temperature plot for solid state reaction of teak wood dust was a bell-shape (sigmoidal model). The Avrami-Erofeev and SSS models were unable to capture the overlapping multiple reactions that took place simultaneously at the active pyrolysis zone. Higher energy input is needed for devolatilization of teak wood dust to give 10 - 80 % conversion due to higher activation energy at the active pyrolysis zone. Reaction rate is low at the active pyrolysis zone but speedy at the passive zone based on the pre-exponential factor. Ginstling-Broushtein was found to be the best model for evaluating the kinetic parameters at the active pyrolysis zone as it had the highest R^2 value.

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