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Modelling Anhydrous Weight Loss of Torrefied Wood Sawdust

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Abstract

Saw mill industries in Malaysia produce a large amount of biomass waste in the form of sawdust, especially from Cengal and Kulim wood species. One of the attractive options to utilize the available biomass is by converting it to an alternative biofuels via torrefaction process. During torrefaction process, biomass is thermally decomposed thus resulted in biomass weight loss which is known as an anhydrous weight loss (AWL). In this study, the kinetic parameters were predicted by two step reactions in series known as Di Blasi – Lanzetta model for both heating and isothermal phases to achieve the desired AWL of torrefied Cengal and Kulim sawdust at temperature of 240°C, 270°C, and 300°C. All kinetic parameters are estimated according to Arrhenius law and fitted to the experimental result. The mass yield results shows that at higher temperature of 300°C, the rate of degradation is higher compared to the lower torrefaction temperature for both Cengal and Kulim woods due to the hemicellulose and cellulose wood constituents. In conclusion, the Di Blasi – Lanzetta model is reliable to predict the AWL of Cengal and Kulim woods in achieving the desired torrefied biomass properties.

Keywords: Torrefaction; Wood Sawdust; Anhydrous Weight Loss; Parameter Estimation; Two Consecutive Reaction Model;

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1. Introduction

Renewable energy is a fundamental and growing part of the world ongoing energy transformation. A significant growth of urbanization leads to diminish fossil fuel reserves, serious environmental pollution and high greenhouse gas (GHG) emissions. Hence, the use of renewable energy is the prime choice for enhancing access to affordable, reliable and cleaner sources of modern energy services. According to International Energy Agency (IEA) report in 2016, nearly 60% of the power generated in 2040 is projected from renewable energy [1]. Among the renewable energy and alternative fuels under development, biomass is one of the promising resources to match the requirements of fossil fuels substitution. Malaysia known to have a luxuriant tropical forest and the saw mill industry from forestry sector have a significant contribution to the socio-economy in the country. The waste generated from saw mill industries contribute to one of the sources of biomass in Malaysia. Biomass can be transformed into gas or liquid fuels via variety of methods such as gasification, pyrolysis, anaerobic digestion, fermentation and transesterification [1]. However, biomass is characterized by its high moisture content, low calorific value, hygroscopic nature and large volume or low bulk density, which result in a low conversion efficiency as well as difficulties in its collection, grinding, storage and transportation. For those reasons, biomass needs to be pretreated before it can be converted into high-value-added products [2].

Among the explored biomass upgrading methods, torrefaction is a promising route for solid fuel production. Theoretically, torrefaction is an incomplete pyrolysis processor known as mild pyrolysis with reaction temperature between 200°C to 300°C, and residence time up to 60 minutes under inert condition. This process upgrades the solid fuel quality by reducing the moisture content, increase heating value, improve grindability, and increase carbon content as well as making the torrefied product become more brittle. Therefore, many studies and research on torrefaction process have been conducted in recent years and focused on the property changes of biomass [2-4]. However, less attention has been paid to the kinetic parameters study of biomass torrefaction. The kinetic study of torrefaction process is essential because it representing the kinetic reaction in torrefaction process which can be used to improve process control for continuous torrefaction reactor. Therefore, it is important to study and estimate the kinetic parameters of torrefaction process in order to determine the optimum condition for thermal degradation process in achieving the desired properties of torrefied product. Thermal degradation in torrefaction is described by anhydrous weight loss (AWL) of the biomass.

In the present work, the torrefaction of forestry residues from Cengal and Kulim wood sawdust being torrefied at three different temperatures (240°C, 270°C and 300°C) using thermogravimetric analysis (TGA) in order to determine the residual mass. For the kinetic modelling, Di Blasi-Lanzetta model was used to predict the residual mass of wood sawdust at all temperature. However, previous studies conducted on the torrefaction kinetic studies only considering the isothermal phase of torrefaction [3-4]. Therefore, in this study both heating (non-isothermal) and isothermal phases of torrefaction are taken into account when deriving the kinetic parameters. Based on both heating and isothermal phases, the kinetic parameters for all temperatures are estimated and fitted against the residual mass obtained from TGA and the applicability of these models in predicting residual mass as well as the mass yield were also discussed.

2. Materials and Method

2.1 Materials and thermogravimetric analysis

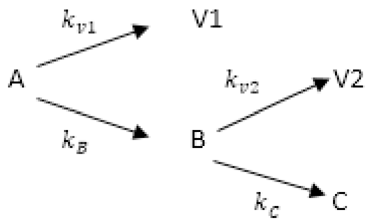
The samples used for the torrefaction process were Cengal and Kulim sawdust from logging residue. Prior to the thermogravimetric analysis (TGA), the samples were heated from 30°C up to 105°C at 10°C/min and were held for 5 minutes in order to remove all moisture that trapped inside the samples The samples weight were varied from 5 mg to 10 mg and the average sample particle is around 50 μm to 100 μm. A TGA/DSC 1 Mettler Toledo analyser was used in this study to evaluate the mass loss of biomass during the torrefaction process with nitrogen flow of 30ml/min. Cengal and Kulim sawdust were tested at three different temperatures : 240°C, 270°C and 300°C with heating rates of 10°C/min. The samples were heated at the desired temperature and were held for 90 minutes. The data obtained from TGA experiment were used to calculate the AWL for each sample at respective temperature and compared with the model prediction data from simulation work.

2.2. Kinetic Parameters Estimation

One specific approach to model torrefaction process is to develop equations around weight loss data. The well accepted model in literature for weight loss prediction is the two stage degradation of hemicellulose (xylans) developed by Di Blasi and Lanzetta [3]. It is a two stage model which first degrades to a solid intermediate through rate constant k_B and volatiles through k_{v1}. It is then followed by a sequential step to torrefied biomass through k_C and more volatiles products through k_{v2} as shown in Table 1. This two stage model predicts one stage of degradation at early times and later degradation over long processing times.

Torrefaction can be divided into two important stages namely as heating and isothermal stages [5]. Biomass is heated up to certain point at heating stage and the process was hold for certain time after achieving the torrefaction temperature. Fig. 1 shows the phases that involve in torrefaction for experimented and modelled result of Cengal sawdust at 240ºC. Heating phase started from 0th to 4th min while the later stage of isothermal occurred from 4th min until the end of torrefaction. However, many kinetic studies only considered the isothermal stages in their work because of the simplicity in deriving the isothermal kinetic parameters. It is important to note that there will be some weight loss during the heating phase which significantly contributing to the entire degradation process especially at high heating rate [5,6]. Thus, it is important to include the heating phase when deriving the kinetic parameters in predicting residual mass accurately. Table 2 shows the kinetic reaction equation for Di Blasi and Lanzetta model. There are two sets of equations for heating phase and isothermal phase. As shown in Table 2, the main different for heating phase model equations and isothermal phase model equations is the heating rate (β) is included in the heating phase model equations.

Table 1. Kinetic Reaction Equations for Di Blasi and Lanzetta Model

Two Series Reactions	Reaction Mechanism
Biomass A ➡ Intermediate [B]	
Biomass A ➡ Volatile [V1]	
Intermediate [B] ➡ Char [C]	
Intermediate [B] ➡ Volatile 2 [V2]	

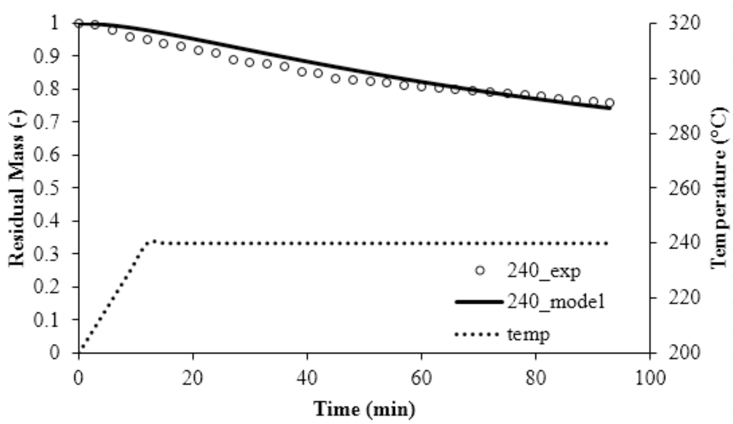


Fig. 1. Experimental and modeled result of Cengal sawdust torrefaction at 10ºC/min heating rate

Table 2. Kinetic Reaction Equation for Di Blasi and Lanzetta Model [6]

Heating Phase	Isothermal Phase
$\frac{d[A]}{dt} = \frac{1}{\beta}\cdot\{-(k_B + k_{v1})[A]\}$	$\frac{d[A]}{dt} = -(k_B + k_{v1})[A]$
$\frac{d[B]}{dt} = \frac{1}{\beta}\cdot\{k_B[A] - (k_c + k_{v2})[B]\}$	$\frac{d[B]}{dt} = k_B[A] - (k_c + k_{v2})[B]$
$\frac{d[C]}{dt} = \frac{1}{\beta}\cdot\{k_C[B]\}$	$\frac{d[C]}{dt} = k_C[B]$

3. Results and Discussion

3.1. Kinetic Parameters Estimation

For the kinetic parameter estimation, the initial conditions used for this two step in series reactions are [A]=1; [B]=0; [C]=0 where [A] is the biomass (Cengal or Kulim wood), [B] is the intermediate compononet and [C] is the char. The mathematical model for heating phase and isothermal phase as shown in Table 2 was developed in MATLAB (R2014a). The iterations to estimate the necessary kinetic parameters were done using MATLAB (R2014a) and 'lsqcurvefit' routine was used for nonlinear optimization. The 'lsqcurvefit' routine was used to minimize the variance between experimental and simulated data to find the best suited data. Firstly, the calculations were done using heating phase model equations from 0^{th} to 4^{th} minutes and followed by isothermal phase model equations from 4^{th} minutes onwards. Based on the calculated *k* values, the pre-exponential factors (A) and activation energies (Ea) for every temperature were calculated by using Arrhenius Law formula (k =A exp(-Ea/RT) where k is the rate reaction constant expressed in s^{-1}, T is the temperature in K and R is the universal gas constant which is 8.3142 J $mol^{-1}K^{-1}$. The iteration was repeated until stable values of both A and Ea were reached. The kinetic parameters obtained by fitting the experimental data at 240°C, 270°C and 300°C using Di Blasi and Lanzetta model for both types of Cengal and Kulim wood sawdust are shown in Table 3 and Table 4.

Table 3. Kinetic parameters for two consecutive reaction model at temperature of 240°C, 270°C and 300°C for Cengal wood

Parameters	A (s^{-1})	Ea ($Jmol^{-1}$)	Parameters	A (s^{-1})	Ea ($Jmol^{-1}$)
k_B	*0.5 x 10^{1}*	*4.2 x 10^{4}*	k_{v1}	*9.80 x 10^{8}*	*9.8 x 10^{5}*
k_C	*2.44 x 10^{4}*	*9.07 x 10^{4}*	k_{v2}	*1.37 x 10^{8}*	*1.28 x 10^{5}*

Table 4. Kinetic parameters for two consecutive reaction model at temperature of 240°C, 270°C and 300°C for Kulim wood

Parameters	A (s^{-1})	Ea ($Jmol^{-1}$)	Parameters	A (s^{-1})	Ea ($Jmol^{-1}$)
k_B	*0.48 x 10^{1}*	*4.2 x 10^{4}*	k_{v1}	*8.00x 10^{8}*	*1.08 x 10^{6}*
k_C	*2.39 x 10^{4}*	*9.04 x 10^{4}*	k_{v2}	*1.29 x 10^{8}*	*1.28 x 10^{5}*

3.2. Anhydrous weight loss (AWL) modelling

Fig. 2(a) and (b) shows the experimental and modeled AWL of Kulim and Cengal sawdust at all temperatures. Based on Fig. 2, Di Blasi and Lanzetta model is able to describe the reaction for Cengal and Kulim wood sawdust accurately. Kinetic parameters were predicted by two step reaction in series known as Di Blasi – Lanzetta Model for both heating and isothermal phases to achieve the desired properties of biomass in terms of AWL of torrefied Cengal and Kulim sawdust at temperature of 240°C, 270°C, and 300°C. All kinetic parameters are estimated according to Arrhenius law and fitted to the experimental result. The results show that parameters obtained by this way are in better accordance with the experimental results. By using Di Blasi and Lanzetta model, the kinetic parameters gave good prediction of AWL at the end of the reaction for both types of Cengal and Kulim wood sawdust.

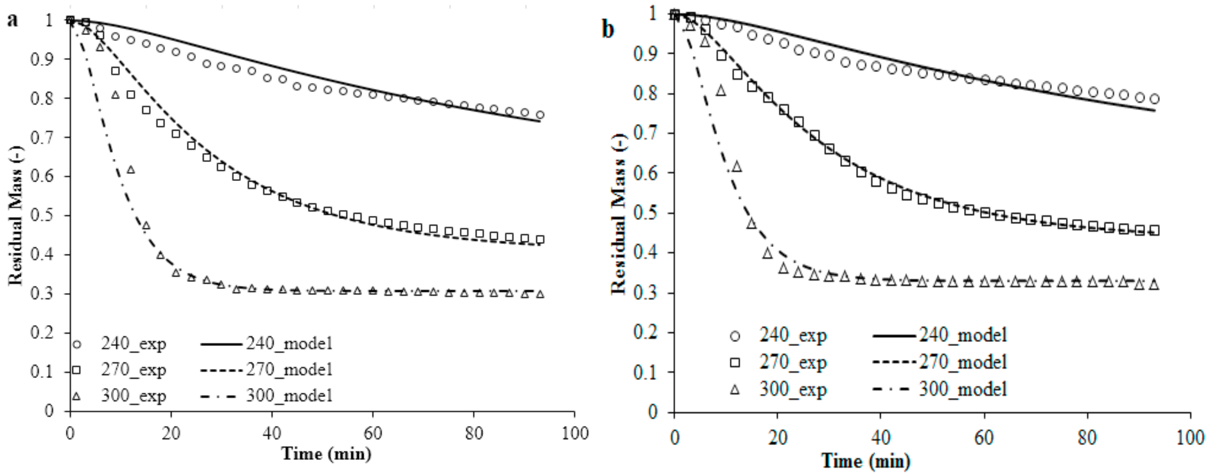


Fig. 2. AWL modelling for (a) Cengal ; (b) Kulim wood sawdust at all temperature with heating rate 10°C/min during torrefaction

Figs. 3 and 4 show the changes of biomass (A), intermediate compound (B), and char (C) of Cengal and Kulim sawdust during torrefaction process. According to Figs. 3(a) and 4(a), biomass (A) degraded faster at 300°C for both Cengal and Kulim which experienced a huge reduction of weight loss at the beginning and fully decomposed at earlier time compared to 240°C and 270°C which show a lower degradation rate of biomass. Based on the Figs. 3 and 4, the highest mass yield of intermediate (B) and lowest char (C) generated for both types of wood sawdust recorded at temperature 240°C. This is due to the slower degradation rate of biomass at 240°C compared to the higher torrefaction temperature. At 300°C, the intermediate (B) is at the lowest and the char (C) generated rapidly for the first 20 minutes process. This is due to the strong decrease of hemicellulose and cellulose content which attributed to the thermal degradation of carbohydrate polymers into volatile compounds and the evaporation of water and carbon dioxide [7]. This shows that Cengal and Kulim both have a higher composition of hemicellulose and cellulose, thus need a higher temperature to degrade into char while at 270°C, the char (C) generated at the highest value because hemicellulose decomposition and volatiles releases are escalated in the range of 235°C - 275°C [8].

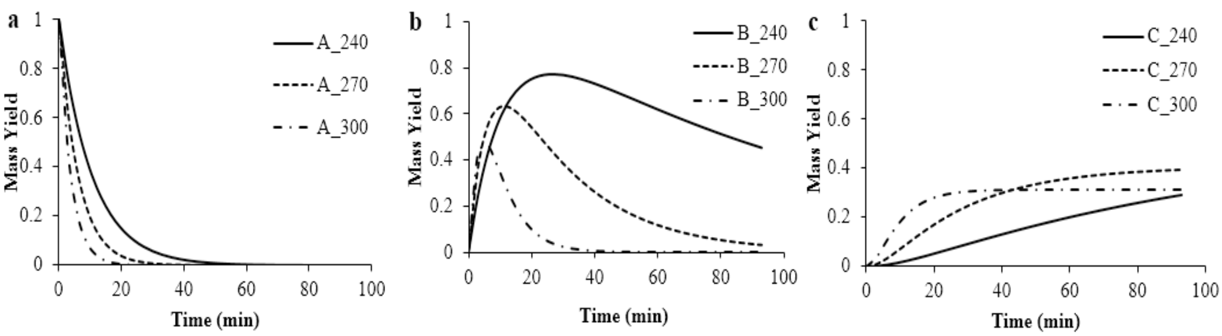


Fig. 3. Mass yield of (a) A (Biomass); (b) B (Intermediate); (c) C (Char) for Cengal wood sawdust at all temperature

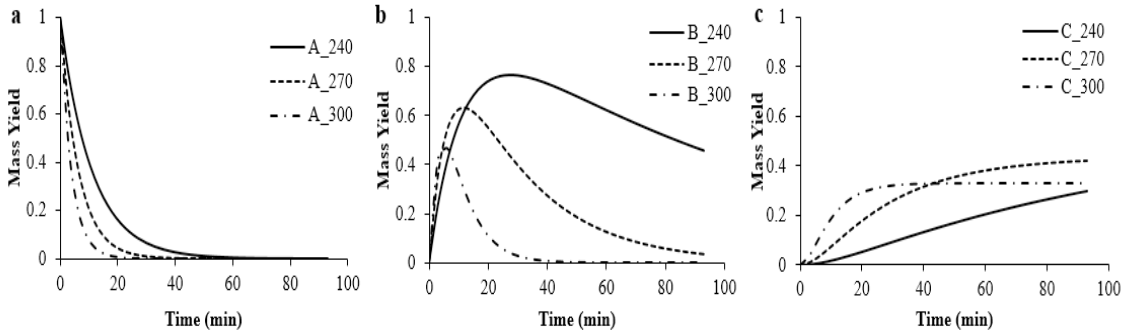


Fig. 4. Mass yield of (a) A (Biomass); (b) B (Intermediate); (c) C (Char) for Kulim wood sawdust at all temperature

4. Conclusions

In this study, a two-step first order reaction in series model known as Di Blasi and Lanzetta model was used to evaluate the anhydrous weight loss of Kulim and Cengal wood sawdust torrefaction in TGA setup. As compared to other studies which normally neglecting the heating phase during the torrefaction process, this study takes into account the mass loss during the heating period as well as the isothermal period when deriving the parameters. The results show that parameters obtained in this way are in better accordance with the experimental results. By using Di Blasi and Lanzetta model, the kinetic parameters gave good prediction of residual mass at the end of the reaction for both types of Cengal and Kulim wood sawdust. The mass yield results shows that at higher temperature, 300°C, the rate of degradation is higher compared to lower torrefaction temperature due to the hemicellulose and cellulose wood constituents. At high temperature, a strong decrease of hemicellulose and cellulose content attributed to the thermal degradation of wood into volatile compounds and the evaporation of water and carbon dioxide occurred. Literally, the hemicellulose decomposition and volatiles releases are escalated in the range of 235°C - 275°C. It means that the anhydrous weight loss and mass yield in the real torrefaction facility can be predicted by simply knowing the temperature history of the sample. In conclusion, the kinetic parameters estimated using Di Blasi and Lanzetta model can be employed for sawdust residues from Cengal and Kulim wood, and the mass yield can be predicted to optimize the torrefaction process in the pilot and industrial scales.

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