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Effect of Torrefaction on Palm Oil Waste Chemical Properties and Kinetic Parameter Estimation

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In Malaysia, palm oil wastes are identified as the potential biomass for renewable energy sources. However, biomass is more challenging to utilise as compared to coal. Usually palm oil wastes suffer from a low heating value, low bulk density and their ability to absorb moisture from the surrounding atmosphere increase the costs of thermochemical conversion due to the drying stage. One of the widely-used methods that can be applied as a pre-treatment step to improve biomass properties is torrefaction. Torrefaction involves heating of biomass to moderate temperatures typically between 200 °C and 300 °C in an inert condition. This study aims to investigate on how torrefied biomass properties exhibit on different torrefaction temperature. The effect of torrefaction at four different temperatures (240 °C, 270 °C, 300 °C and 330 °C) were evaluated in term of mass yield, energy yield and higher heating value on two different palm oil wastes which are empty fruit bunch (EFB) and palm kernel shell (PKS). The results show that temperature had significant effect on chemical properties of torrefied biomass as well as affecting the biomass degradation. In addition, the properties of biomass also affect the torrefaction. Overall, EFB shows higher decomposition percentages compared to PKS. PKS has a higher heating value compared to EFB due to the high carbon content of PKS. A two-step reaction in series namely Di Blasi and Lanzetta Model is used to model the anhydrous weight loss (AWL) of EFB and PKS. In the model, the kinetic parameters are estimated by using Arrhenius equation. It shows that the model mass loss data fit well with experimental data at 240 °C but not at 300 °C. This is due to the other factors such as heat transfer effect which is not included in the proposed model. The Di Blasi and Lanzetta model is reliable to be applied in predicting anhydrous weight loss (AWL) of EFB and PKS at lower temperature.

1. Introduction

Malaysia is blessed with an abundant of biomass resources due to the large scale cultivation of agricultural crops and palm oil. Currently Malaysia is the world second largest palm oil producer after Indonesia with production capacity of 18.75 Mt in 2015 (Basiron, 2015). The palm oil fruits produce only 10 % of oil whereas the other 90 % remains as biomass in the form of such as Empty Fruit Bunch (EFB), Palm Kernel Shell (PKS), Mesocarp Fibre (MF) and Oil Palm Trunk (OPT). EFB is used as organic fertiliser while OPF and OPT are left rotten at plantation area as mulch. PKS and MF are used as fuel for steam production at palm oil mills. The increasing in amount of biomass generated at palm oil mills may led to disposal problem. Therefore, one way to avoid the problem is by utilising and converting biomass into value-added product or alternative biofuel for co-firing process at palm oil mills. It is quite challenging to utilise biomass due to its unfavorable characteristics. Biomass contains high moisture level, low calorific value as well as inherits fibrous and hygroscopic nature. Biomass needs to undergo pre-treatment process in order to improve its properties.
One of the technologies used for upgrading biomass properties is torrefaction. Torrefaction is thermal treatment process known as mild pyrolysis where biomass is heated to a temperature range of 200 – 300 °C under inert condition. It's already proven that torrefaction is able to improve the characteristics of biomass. As a result of torrefaction, biomass exhibits brittle behavior and a reduction in mechanical strength thus eliminating poor grindability problem of raw biomass. Torrefaction increase energy yield of torrefied biomass due to the increase

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of carbon content. It also reduces the moisture content in biomass so that the shelf life of biomass is increased as no biodegradation occur during the storage (Sabil et al., 2013).

In this study, the main objective is to demonstrate the torrefaction of EFB and PKS at 240 °C, 270 °C, 300 °C and 330 °C. The effect of different torrefaction temperature on chemical properties of torrefied biomass especially on mass yield and high heating value (HHV) is investigated. Di Blasi and Lanzetta model is employed to model the anhydrous weight loss (AWL) of EFB and PKS torrefaction for the purpose of kinetic parameter estimation. The kinetic analysis is important in evaluating the torrefaction behavior throughout the process. From the kinetic parameter prediction, the dominant step in the torrefaction can be determined so that the desired properties of biomass can be achieved by controlling the AWL.

2. Experimental

2.1 Materials

The biomasses used in this study were Empty Fruit Bunch (EFB) and Palm Kernel Shell (PKS) which have been obtained from Lepar Hilir Palm Oil Mill, Kuantan, Pahang. Prior to the experimental study, the samples were oven-dried at 105 °C for 4 h to remove unbound water as well as avoiding biomass degradation that may affect the quality of the sample. Then, samples were grinded and sieved where only particles in the range of 0.5 – 1.0 mm were collected. All samples were stored in air-tight container until the experiments are carried out.

2.2 Torrefaction Experiment

Torrefaction of EFB and PKS was carried out using a vertical-stainless steel reactor with 39.7 cm long and 1.9 cm internal diameter. Approximately, 2 – 3 g of biomass sample was placed in the reactor for the torrefaction process. The reactor was flushed with 10 mL/min nitrogen for 5 min to create inert atmosphere. Afterwards, the biomass was heated to the desired torrefaction temperature (240 °C, 270 °C, 300 °C and 330 °C) for 30 min by an electric furnace. Various temperatures were used for studying the effect between low temperature and high temperature on physical and chemical changes of EFB and PKS. As the experiment finished, the furnace was switched off and reactor is allowed to cool to ambient temperature. Then, the torrefied sample was weighed to measure the mass loss of torrefied biomass. The torrefied biomass was stored in air-tight container to avoid moisture getting into the sample. For each temperature, the experiments were repeated for three times to enhance the data reliability.

2.3 Thermogravimetric Analysis

For kinetic parameter analysis, a TGA/DSC 1 Mettler Toledo analyser was used to evaluate the mass loss of biomass during the torrefaction process with respect to time. Prior to the analysis, all the sample was heated from 30 °C up to 105 °C at 10 °C/min and were held for 5 min to remove unbound moisture in the sample. Next, sample was heated to the torrefaction temperature (240 °C, 270 °C, 300 °C and 330 °C). Once the desired temperature is achieved, the analysis was held for 90 min. Finally, the TGA data were used to calculate the kinetic parameters for determining the AWL of the samples.

2.4 Mass Yield and Energy Yield

The mass yield and energy yields were calculated by using Eq(1) and Eq(2) respectively.

$$\text{Mass yield (\%)} = \frac{\text{Mass of torrefied biomass}}{\text{Mass of raw biomass}} \text{x}100\% \tag{1}$$

$$\text{Energy yield (\%)} = \text{Mass yield x} \frac{\text{Higher heating value of torrefied biomass}}{\text{Higher heating value of raw biomass}} \tag{2}$$

2.5 Proximate and Ultimate Analysis

For the analysis of torrefied biomass, the proximate and ultimate analyses were conducted according to American Society for Testing and Material (ASTM) standards. The moisture, volatile matter and ash content are calculated using Eq(3) – Eq(6) by referring to ASTM E871 (2013), E872-82 (2013) and E1755-01 (2015) respectively while the fixed carbon content was calculated using Eq(7).

$$\text{Moisture content (\%)} = \frac{m_i - m_f}{m_i - m_c} \text{x}100\,\% = B \tag{3}$$

$$\text{Mass loss (\%)} = \frac{m_{initial} - m_{final}}{m_{initial} - m_{crucible}} x100\,\% = A \quad (4)$$

$$\text{Ash content (\%)} = \frac{m_{ash} - m_{crucible}}{m_{initial} - m_{crucible}} \times 100\,\% \quad (5)$$

$$\text{Volatile matter (\%)} = A - B \quad (6)$$

$$\text{Fixed carbon} = 100\,\% \text{ - Volatile matter - Ash content - Moisture content} \quad (7)$$

3. Kinetic Model

A two-step in series model named as Di Blasi and Lanzetta model as shown in Table 1 is used to study the kinetics of EFB and PKS torrefaction.Only data at 240 °C, 270 °C and 300 °C were chosen for the kinetic analysis to represent the mild torrefaction (240 °C), medium torrefaction (270 °C) and severe torrefaction (300 °C). Here, the decomposition of biomass comprises of two important reactions. The first reaction is the decomposition of biomass into intermediate compound and volatile whereas the second reaction is the formation of char and volatile from the intermediate compound (Prins et al., 2006). As the overall heating process of torrefaction is depending on the two different phases which are non-isothermal (considering the heating rate, *β*) and isothermal phase, therefore different equations should be employed in deriving the kinetic parameters as shown in Table 1. The example EFB mass loss data with respect to the heating profile is shown in Figure 1.

Table 1: Di Blasi and Lanzetta kinetic model

Kinetic Model	Non-Isothermal Phase	Isothermal Phase
Biomass $[A] \rightarrow$ Intermediate $[B]$	$\frac{d[A]}{dt} = \frac{1}{\beta} \cdot \{(k_B + k_{V1})[A]\}$	$\frac{d[A]}{dt} = -(k_B + k_{V1})[A]$
Biomass $[A] \rightarrow$ Volatile $[V1]$	$\frac{d[B]}{dt} = \frac{1}{\beta} \cdot \{k_B [A] - (k_C + k_{V2})[B]\}$	$\frac{d[B]}{dt} = k_B [A] - (k_C + k_{V2})[B]$
Intermediate $[B] \rightarrow$ Char $[C]$	$\frac{d[C]}{dt} = \frac{1}{\beta} \cdot \{k_C [B]\}$	$\frac{d[C]}{dt} = k_C [B]$

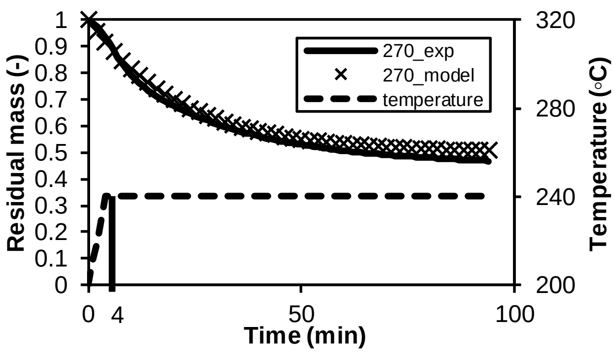

Figure 1: Experimental and modeled result of EFB at 270 °C using heating rate of 10 °C/min

4. Results and Discussion

4.1 Properties of Raw Biomass

The summary of ultimate and proximate analysis of raw PKS and EFB is shown in Table 2 while the higher heating value is listed in Table 3. For ultimate analysis, it shows that the percentage of carbon and sulphur in PKS are higher than EFB. The percentage of H, N and O are vice versa. For proximate analysis, both of the biomass had almost similar value of volatile matter which is 65.56 % and 65.0 % for PKS and EFB respectively. The value of fixed carbon and ash content for PKS is higher than EFB which are 20.44 % and 3.85 %, contributing to the higher value of higher heating value (HHV) as shown in Table 3. This is due to the fact that the carbon content in PKS is higher than EFB. Meanwhile higher carbon and hydrogen composition increases the heat in combustion thus increasing the calorific value of the biomass. Although oxygen composition in biomass is great for fuel burning, the heating value of the biomass is reduces as higher oxygen composition in biomass usually comes with lower carbon composition (Chen et al., 2015).

Table 2: Ultimate and proximate analysis for raw PKS and EFB

	Palm kernel shell	Empty fruit bunch
Moisture content (%)	11.87	15.77
Ultimate analysis (wt%)		
C	49.91	43.53
H	6.94	7.20
N	3.52	1.73
O	38.2	47.09
S	0.72	0.46
Proximate analysis (wt%)		
Volatile matter	65.56	65.00
Fixed carbon	20.44	15.37
Ash content	3.85	2.13

Table 3: Higher heating values (HHV) of raw and torrefied EFB and PKS

	HHV (MJ/kg)	
	Empty fruit bunch	Palm kernel shell
Raw	15.49	16.25
240 °C	15.59	19.68
270 °C	17.99	21.91
300 °C	19.60	23.64
330 °C	22.07	25.46

4.2 Properties of Torrefied Biomass

Biomass that undergone torrefaction process will loss the moisture, oxygen that contained organic compound and volatiles. Mass yield is calculated by using Eq(1) to know how much the biomass remains after torrefaction. Study done by Chen et al. (2015) stated some biomasses are not suitable for torrefaction as the mass yield is lower than 25 %. From Figure 2, the mass yields of both PKS and EFB shows decreasing in value when the torrefaction temperature is higher. Comparing these two biomasses, EFB recorded lower mass yield at each torrefaction temperature. Aziz et al. (2011) reported that hemicellulose and cellulose composition in EFB is higher compared to PKS thus contribute to the lower mass yield EFB.

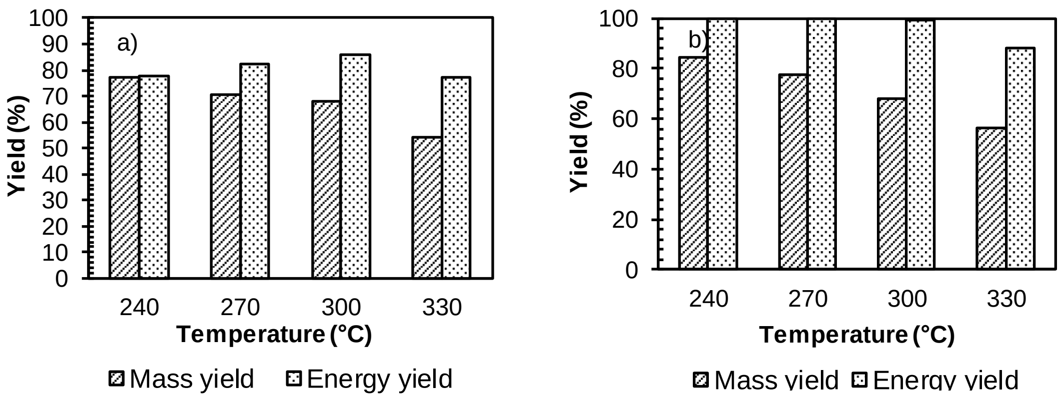

Figure 2: Mass and energy yield of (a) empty fruit bunch and (b) palm kernel shell

As shown in Eq(2), the energy yield is depending on the value of mass yield and HHV. Increasing the torrefaction temperature definitely increases the HHV of EFB and PKS in the ranges of 15 - 22 MJ/kg and 16 - 25 MJ/kg, thus increasing the value of energy yield calculated. Ben and Ragauskas (2012) explained that because of more C-C and C-H interacts with aromatics molecules, the heating value of torrefied biomass increases. The trends for both mass and energy yields obtained from torrefied EFB and PKS was in accordance to the other studies done by Uemura et al. (2011) and Sabil et al. (2013). As stated in section 4.1, due to the carbon content of PKS is higher compared to EFB, the higher heating value at each temperature shows PKS has higher HHV than EFB. This result illustrated that torrefied PKS will show better performances if used as biofuel.

4.3 Torrefaction kinetics modeling

In the kinetic modelling, it is assumed only solid was present at the initial condition of torrefaction and the kinetic rates as shown in Table 1 are represented by Arrhenius equation where it consists of two parameters namely the pre-exponential factor (A) and activation energy (Ea). These parameters were predicted using MATLAB 'lsqcurvefit' routine. The method was repeated until a constant value of A and Ea was obtained. The kinetic parameters for EFB and PKS are shown in Table 4 and Table 5 respectively.

Table 4: Kinetic parameters for EFB

Parameters	A (s^{-1})	Ea ($J.mol^{-1}$)	Parameters	A (s^{-1})	Ea ($J.mol^{-1}$)
k_B	4.26×10^1	3.40×10^4	k_C	5.18×10^{10}	3.94×10^4
k_{V1}	5.97×10^6	8.75×10^4	k_{V2}	1.26×10^{-3}	2.56×10^4

Table 5: Kinetic parameters for PKS

Parameter	A (s^{-1})	Ea ($J.mol^{-1}$)	Parameter	A (s^{-1})	Ea ($J.mol^{-1}$)
k_B	5.86×10^1	3.40×10^4	k_C	4.55×10^{10}	3.45×10^4
k_{V1}	3.97×10^6	8.74×10^4	k_{V2}	2.43×10^{-3}	2.44×10^4

Figure 3 shows the experimental and modeled anhydrous weight loss (AWL) of EFB during the torrefaction process. Figure 3 (a) shows the modeled data fit the experimental data well at 240 °C and 270 °C but not at 300 °C. It is clearly shown the biomass degraded faster at high temperature (300 °C) compared to low temperature (240 °C). At 300 °C, EFB experienced a huge reduction of weight loss at the beginning and fully decomposed at the end of the reaction compared to 240 °C. It is due to hemicellulose degradation that occurs faster at high temperature (Sabil et al., 2013). Figure 3 (b) shows the variation of the reactions took part in the torrefaction. It indicates the evolution for solid products which are A (EFB), B (intermediate) and C (char). It shows that, at higher temperature, formation of intermediate from biomass is faster compared to the lower temperature. This situation is caused by the rapid biomass degradation at high temperature (Anca-Couce et al., 2014).

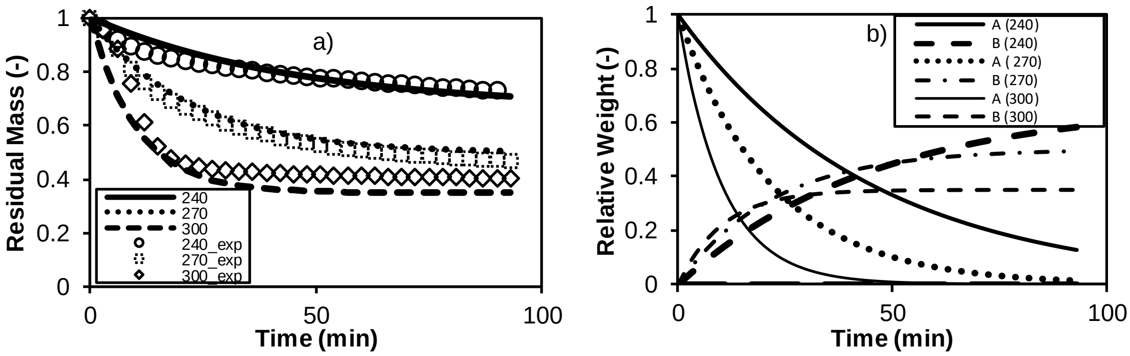

Figure 3: a) AWL and b) mass yield of EFB during torrefaction at three different temperatures

Figure 4 shows the experimental and modeled anhydrous weight loss (AWL) as well as the mass yield of solid product of PKS torrefaction process. Figure 4 (a) shows the degradation of PKS at 240, 270 and 300 °C. The same trend of mass loss is observed from PKS degradation. PKS encountered a low mass loss percentage compared to EFB. At 300 °C, almost 60 % EFB degraded during the torrefaction whereas only 48 % of PKS degraded. This is due to the high composition of hemicellulose in EFB compared to PKS (Aziz et al., 2011). It is well known that the decomposition of hemicellulose occurs actively in the range of 220 – 315 °C. The product yield for PKS torrefaction is shown in Figure 4 (b).

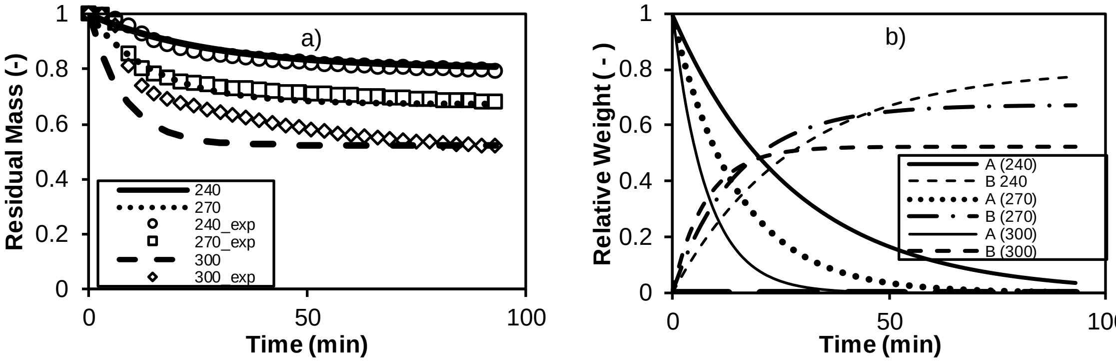

Figure 4: a) AWL and b) mass yield of PKS during torrefaction at three different temperature

5. Conclusions

In this study, the effect of different torrefaction temperatures on chemical properties of empty fruit bunch (EFB) and palm kernel shell (PKS) is evaluated. The temperature effect is assessed based on mass yield and high heating value (HHV) of both biomass samples. The result shows that the mass yield of torrefied PKS and EFB are lower than raw samples as an effect of mass loss due to heating process. Both torrefied biomasses recorded a high amount of HHV compared to raw biomasses. Both PKS and EFB recorded highest value of HHV at high temperature (330 °C) which is 22.07 MJ/kg and 25.46 MJ/kg respectively. As PKS has higher carbon content (49.91 %) compared to EFB (43.53 %), therefore PKS exhibits higher HHV, indicating its suitability to be used as biofuel compared to EFB. It is proven that the properties of biomass can be improved by applying torrefaction. For the kinetic analysis, the result shows that the residual mass obtained from simulation model using the kinetic parameters are in good agreement with the experimental data for EFB and PKS except at 300 °C. It can be concluded that the Di Blasi and Lanzetta model is reliable to predict the AWL of EFB and PKS in achieving desired torrefied biomass properties.

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