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Physicochemical Property Changes and Volatile Analysis for Torrefaction of Oil Palm Frond

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Torrefaction is an upgrading technique for biomass properties which involves the heating of biomass to moderate temperatures typically between 200 and 300 °C in an inert condition. Torrefied biomass has darker colour, high energy density, high heating value and exhibits hydrophobic characteristic that makes it easier for grinding. Therefore, the aim of this work is to conduct an experimental work in order to study the torrefaction effects on the physicochemical properties of oil palm frond (OPF) as well as to identify the evolution of volatiles composition during the torrefaction. Torrefaction experiments were performed at four different temperatures (240 – 330 °C) and three different residence times (15, 30 and 60 min). The higher heating value of raw and torrefied biomass were measured to establish a relationship between energy loss and mass loss during torrefaction. Scanning electron microscope (for physical analysis) was used to study the structure of raw and torrefied OPF. Elemental analysis was carried out by using Carbon, Hydrogen. Nitrogen and Sulphur (CHNS) analyser and the proximate analysis were measured based on the method specified by American Society for Testing and Materials (ASTM). Condensable and non-condensable gases were analysed by using high performance liquid chromatography (HPLC) and gas chromatography thermal conductivity detection (GC-TCD) respectively. Higher torrefaction temperature and longer residence time leads to severe decomposition which reduces the mass yield of the torrefied oil palm frond but increases the heating value of torrefied OPF. The carbon content increases with the increasing of temperature and residence time, while hydrogen and oxygen contents are decreases. The values of fixed carbon and ash content increases, while volatile matter value decreases when the oil palm frond is torrefied for a longer time at high temperature. For volatile release, carbon monoxide and carbon dioxide are the major compounds presence in non-condensable gas and traces of methane was only identified when OPF was torrefied at 300 °C and 330 °C. Acetic acid and methanol are the major compounds of condensable gases with the presence of formic acid and lactic acid at 330 °C. It can be concluded that high temperature gives significant effect on the chemical reaction for formation of condensable and non-condensable gases.

1. Introduction

The role of sustainability in the heat and electricity production continues to increase worldwide. The use of biomass as renewable energy has become essential for alternatives to fossil fuel. In Malaysia, oil palm wastes are identified as the potential biomass sources. There are several wastes produced from the growing of oil palm and from the processing of palm oil. Example of these wastes are oil palm trunk (OPT), palm kernel shell (PKS), empty fruit bunch (EFB), palm mesocarp fibre (PMF) and oil palm frond (OPF). From the oil palm waste, the largest contributors come from OPF. This is the results from cutting the OPF regularly during harvesting and pruning of the oil palm trees. Mainly the OPF is left for rotten between the rows of palm trees for nutrient recycling purpose (Awalludin et al., 2015). One way to utilise OPF is using the OPF as alternative biofuel for palm oil mill. The OPF cannot be used directly as a fuel for palm oil mill due to low heating value and low bulk density. The high moisture content presents in biomass and their ability to absorb moisture from

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the surrounding atmosphere increase the costs of thermochemical conversion due to the drying process. In order to upgrade the properties of the biomass, torrefaction can be used as one of the pretreatment method.

Torrefaction is a process of converting biomass into a coal-like material at moderate temperature ranging from 200 - 300 °C under inert condition and atmospheric pressure. Torrefaction converts raw biomass to a material suitable for combustion and gasification applications. Torrified biomass have higher heating value, improved hydrophobicity, more compactable and grindable, and possesses lower oxygen-to-carbon (O/C) ratio compared to the raw biomass (Medic et al., 2011). In torrefaction process, the mass loss of the biomass is the result of the decomposition of hemicellulose and some lignin. By decomposition of these properties, different condensable and non-condensable products are produced.

The aim of this study is to evaluate the physicochemical and volatile analysis for torrefaction of OPF at temperatures of 240, 270, 300 and 330 °C with residence times of 15, 30 and 60 min. The evaluation is implemented by characterising mass yield, energy yield, higher heating value, ultimate analysis, proximate analysis and volatiles analysis.

2. Materials and methods

2.1 Oil palm frond preparation

Oil palm frond was obtained from Lepar Hilir Palm Oil Mills, Kuantan, Pahang. Before starting the experiment, the raw biomasses were dried in the oven at temperature of 105 °C for 4 h to lower its moisture content. Then the biomass is grinded and sieved into 0.5 to 1.0 mm particles sizes. The samples are then transferred into the air-tight containers until the torrefaction experiments were performed.

2.2 Torrefaction process

Torrefaction process was conducted by using a vertical-stainless steel reactor with 39.7 cm long and 1.9 cm internal diameter. The biomass is weighed approximately 2 - 3 g and then is inserted into the reactor. The reactor was flushed with 10 mL/min nitrogen for 5 min to ensure an inert condition is obtained. Next, the biomass was torrefied at temperatures of 240, 270, 300 and 330 °C for residence times of 15, 30 and 60 min by an electric furnace. The reactor is then cooled to room temperature before the torrefied biomass is taken out and weighed. In order to avoid contamination of the torrefied biomass before the analysis, it is transferred to air-tight containers. The experiment is then repeated for 3 times and the average of the reading is presented in this study.

2.3 Sample analysis

The analysis for the raw and torrefied biomass includes the ultimate, proximate and calorific analysis. The proximate analysis is according to ASTM E871 (2013), D1762 (2013) and E1755 (2015) for moisture content (MC), volatile matter (VM) and ash content. The MC for the OPF is found to be 15.95 %. For fixed carbon, it is calculated by subtracting 100 % with MC, volatile matter and ash content. Ultimate analysis was carried out by using the CHNS analyser while the calorific analysis was carried out by using Model 1341 bomb calorimeter. The condensable and non-condensable gases were analysed online using Agilent Technologies high performance liquid chromatography (HPLC) 1200 and Agilent 6890N gas chromatography with Thermal Conductivity Detector (GC-TCD) respectively. The non-condensable gases (NCG) were collected using gas bag and were directly injected to GC-TCD after the torrefaction experiment completed. Standard gas mixture was used as calibration standard while nitrogen was used as the carrier gas for the analysis. The condensable gases (CG) were collected in the Buchner flask where water acts as the trapper. Later, the CG was analysed with HPLC (Agilent Technologies 1200, California, USA) using Zorbax Eclipse Plus C18 column.

3. Results and discussions

3.1 Physical properties change of raw and torrefied oil palm frond

In this study, the OPF is torrefied at different temperatures and different residence times. Figure 1 shows the appearances of the raw OPF, torrefied OPF at mild (240 °C) and severe (300 °C) temperature at 30 min residence time. When the torrefaction temperature is increased, the OPF turned to the darker colour compare to the raw OPF. Similar observation has been made by Uemura et al. (2011) when using EFB, PMF and PKS.

Figure 2(a), (b) and (c) show the surface structure of raw and torrefied OPF at temperature of 240 and 300 °C respectively. The images were observed using Carl Zeis Evo 50 Scanning Electron Microscope (SEM). Figure 2(a) shows the structure of raw OPF before undergone torrefaction process. The surface structure of raw OPF shows a clear and rigid wall line. After torrefaction at 240 °C, the outer cell wall starts to experience structure destruction. The wall starts to decompose and the rigid cell wall line tends to diminished as shown in Figure

2(b). Figure 2(c) shows the image of torrefied OPF at 300 °C in which the surface is full with flat sheets of decomposed cell wall. It can be observed that the wall line is degraded and start to disappear.

Figure 1: Appearances of the raw and torrefied OPF: (a) Raw biomass (b) Torrefied at 240 °C (c) Torrefied at 300 °C

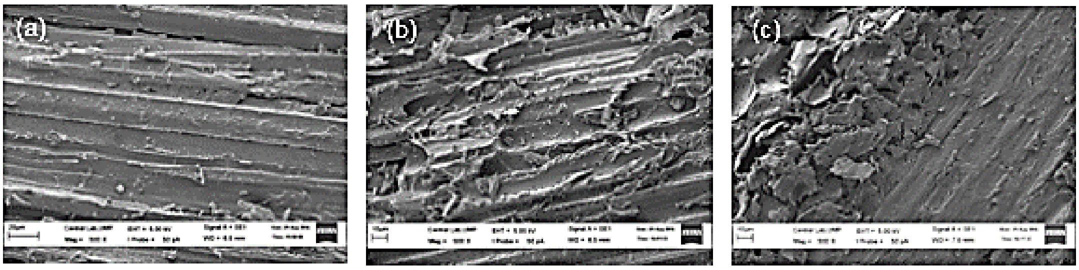


Figure 2: Scanning electron microscope of the raw and torrefied OPF: (a) Raw biomass (b) Torrefied at 240 °C (c) Torrefied at 300 °C

3.2 Ultimate and proximate analysis

The ultimate and proximate analysis for raw and torrefied OPF are listed in Table 1. The carbon content is increased up to 27 % when it is exposed to the higher torrefaction temperature (300 °C), while for oxygen and hydrogen shows a decreasing trend. The decrease for oxygen and hydrogen are up to approximately 25 % and 14 % respectively when the temperature is higher. The decreased of oxygen and hydrogen composition mainly due to the release of volatile gases during the torrefaction (Sabil et al., 2013). For proximate analysis, the values of fixed carbon and ash content show an increase from 12.02 % (raw OPF) to 33.75 % (torrefied OPF at 300 °C) and 2.87 % (raw OPF) to 4.76 % (torrefied OPF at 300 °C) respectively. Volatile matter for raw OPF is 69.16 % and it decreased to 45.54 % when OPF was torrefied at 300 °C. Degradation of OPF during torrefaction process contributes to the release of volatiles and moisture from OPF and thereby, decreased the value of volatile matter (Acharya et al., 2015).

Table 1: Ultimate and proximate analysis for raw and torrefied oil palm frond

	Raw	240 °C	300 °C
Ultimate analysis (wt%)			
C	43.94	48.33	55.72
H	6.94	6.50	5.96
N	3.52	4.14	4.32
O	44.88	40.77	33.78
S	0.72	0.26	0.22
Proximate analysis (wt%)			
Volatile matter	69.16	64.86	45.54
Fixed carbon	12.02	15.99	33.75
Ash content	2.87	3.20	4.76

Figure 3 shows the Van Krevelen plot for different types of biomass, mainly the oil palm wastes. When the temperature of torrefaction is increased from 240 °C to 300 °C both the ratio of H/C and O/C decreases. The ratio for OPF in this study shows the same trend as the other torrefied biomass. When comparing with other oil palm wastes, the values of both ratios are higher mainly due to the hydrogen content of torrefied OPF are higher compared to the torrefied biomass used by Uemura et al. (2011), as well as Sabil et al. (2013).

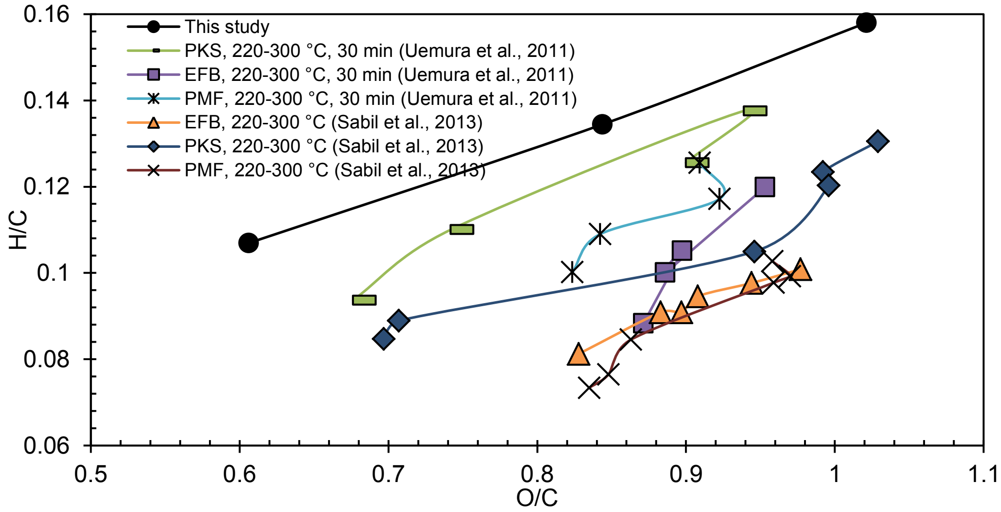


Figure 3: Van Krevelen plot of torrefied biomass sample

3.3 Mass yield and energy yield

The equations used to calculate mass and energy yields are listed in Eq(1) and Eq(2).

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

$$\text{Energy yield (\%)} = \text{Mass yield} \times \frac{\text{HHV of torrefied biomass}}{\text{HHV of raw biomass}} \tag{2}$$

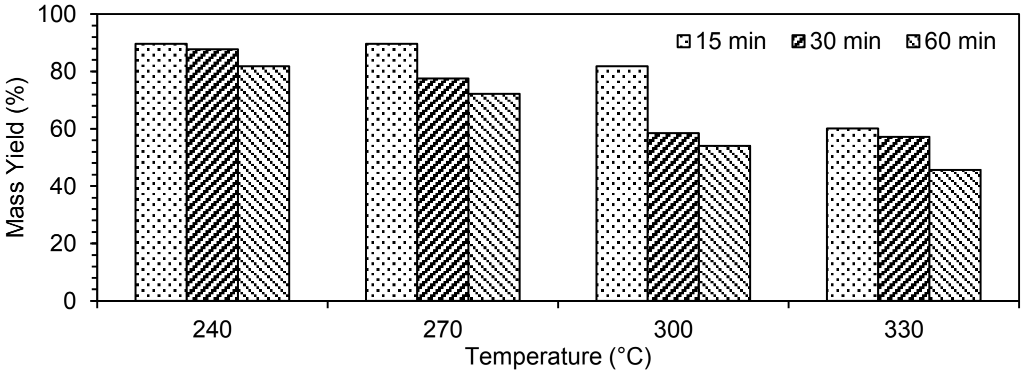


Figure 4: Mass yield of torrefied OPF at different temperatures and residence times

The mass yield for each experiment are calculated and presented as shown in Figure 4 to study the effects of temperatures and residence times. It is observed that the percentage of mass yield at higher torrefaction temperature (particularly at 300 °C and 330 °C) shows decreasing trends. This is because the moisture and volatile matter in the OPF is liberated. Decomposition of hemicellulose also contributes to the mass loss. Usually the decomposition of hemicellulose and lignin took places at temperature range of 220 - 315 °C and 160 - 900 °C (Chew and Doshi, 2011). Torrefaction of OPF at different residence times (15, 30 and 60 min) shows the mass yield is decreased as the residence time is increased. The longer heating process increases the decomposition of OPF thus resulting in lower mass yield.

Table 2: HHV for raw and torrefied OPF at different temperatures and residence times

Treatment	High heating value (MJ/kg)				
	Raw	240 °C	270 °C	300 °C	330 °C
Raw	17.74	-	-	-	-
15 min	-	15.78	17.86	19.79	21.58
30 min	-	19.82	21.60	23.79	25.83
60 min	-	20.00	21.91	23.96	25.68

Higher heating value (HHV) of the raw and torrefied OPF at different temperatures and residence times are shown in Table 2. From the results obtained, the HHV is increased as the temperature and residence time increased. The highest HHV value (25.83 MJ/kg) is obtained when the OPF is torrefied for 30 min at 330 °C. The HHV value consequently affects the value of energy yield calculated. Higher value of HHV can lead to the higher energy yield thus overcome the problem of low calorific value in raw biomass. As shown in Figure 5, the energy yield at residence time 30 min shows the highest yield at temperature of 240, 270 and 330 °C. This indicates the most suitable time to torrefied OPF is at 30 min which in accordance with the residence time should be lesser than or equal to 1 h (Chew and Doshi, 2011).

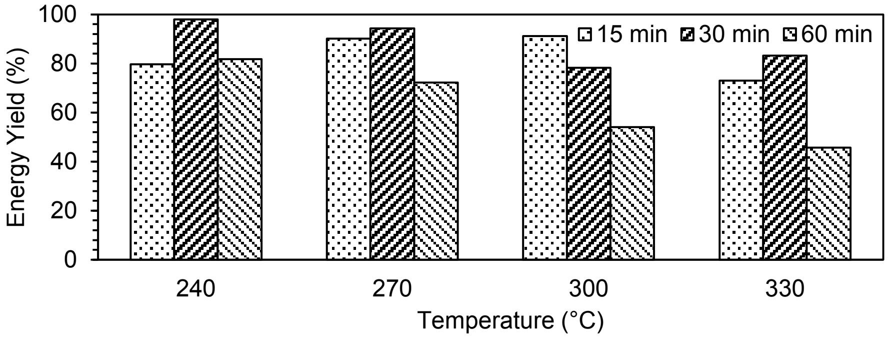
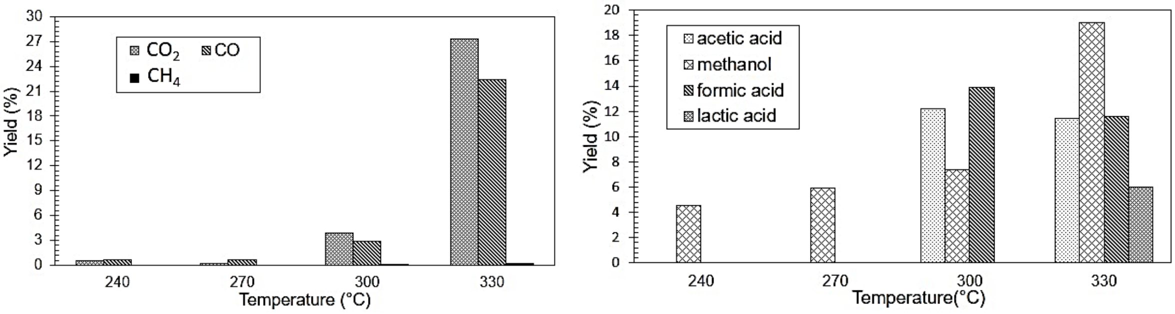


Figure 5: Energy yield of torrefied OPF at different temperatures and residence times

3.4 Volatile analysis

During the torrefaction, some of the condensable and non-condensable gases were released. Figure 6(a) shows the composition of non-condensable gases obtained from torrefaction of OPF at 240 °C, 270 °C, 300 °C and 330 °C. From Figure 6(a), it can be seen that temperature gives significant effect on the gases yield. As the temperature increases, the formation of CO and CO_2 also increases. This scenario can be explained by the fact that, higher temperature enriches the decomposition of hemicellulose. During thermolysis (thermal degradation in inert environment) of biomass, the degradation of uronic acid of xylan contributes to the CO_2 formation and CO. However, the formation of methane (CH_4) can only be observed at higher temperature (300 °C and 330 °C). In pyrolysis reaction, CH_4 is formed during methanation or methane formation reaction. Methanation is a reaction whereby CO reacts with H_2 to form CH_4 and H_2O. In the case of inert condition applied, the formation of CH_4 is more likely to follow the CH_4 formation in which C reacts with H_2O to produce CH_4. As shown in Figure 6(a), at 300 °C, a huge amount of CO_2 produced during torrefaction, an amount that is more than enough to trigger the reaction with H_2O that acted as condenser hence producing CH_4. At low temperature, the amount of CO_2 produced is not enough to produce CH_4 due to reaction of 1 mole of C and H_2O only produced 0.5 CH_4. Figure 6(b) shows the compounds detected in condensable gas obtained from torrefaction of OPF in this study. Overall, methanol present as early as 240 °C while formic acid, acetic acid and lactic acid started to appear at 300 °C and 330 °C respectively. The hemicellulose in biomass samples are mainly made up of carbohydrates which are polysaccharides structure which composes of glucose, xylose, galactose, arabinose, mannose and certain amount of methylglucuronic acid and galacturonic acid residues. As the hemicellulose is thermally responsive and active at the range of 220 – 315 °C, therefore the formation of condensable gases is dependent on the decomposition of hemicellulose. Hemicellulose decomposition may occur in two steps which are decomposition of the polymer into soluble fragments as well as degradation of monomer units. Acetic acid and methanol are formed due to the degradation of acetoxy- and methoxy-groups that attached to xylose (Chen et al., 2015).



(a) (b)

Figure 6: (a) Non-condensable and (b) condensable product of torrefied OPF

4. Conclusion

Torrefaction process of OPF at temperature of 240, 270, 300 and 330 °C and residence time of 15, 30 and 60 min were successfully carried out. As the temperature and residence time are increases, the mass and energy yields decreases. Meanwhile carbon composition of torrefied OPF is increased by 27 % but hydrogen and oxygen composition are decreased to 14 % and 25 %. Fixed carbon and ash content are increased in the range 33 - 232 % and 11 - 79 %, while volatile matter is decreased in the range 6 - 43 %. In terms of volatile evolution, more CO_2 and CO for non-condensable product are released as temperature is increased and the CH_4 was detected only at temperature of 300 and 330 °C. For condensable gases, the major product formed is methanol where it has been detected at temperature as early as 240 °C. The presence of acetic acid, lactic acid and formic acid are detected at temperature of 300 and 330 °C.

Acknowledgments

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