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A Study on Torrefaction of Oil Palm Biomass

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Abstract: Torrefaction is a thermal pre-treatment process to pre-treat biomass at temperature range of 200-300°C under an inert atmosphere. It was known that torrefaction process strongly depended on the decomposition temperature of the lignocellulosic constituents in biomass namely hemicellulose, cellulose and lignin. In this study, the torrefaction behaviour of Empty Fruit Bunches (EFB), Palm Mesocarp Fiber (PMF) and Palm Kernel Shell (PKS) were investigated. The study focuses on the relation between the lignocellulosic constituents with torrefaction process. Two different size ranges of 250-355 µm and 355-500 µm were used and then submitted to six final torrefaction temperatures of 200, 220, 240, 260, 280 and 300°C. The process was carried out in a thermogravimetric analyzer coupled with mass spectrometry (TGA-MS). The results implied that torrefaction was strongly depended on the thermal decomposition behaviour and composition of lignocellulosic constituents. The ultimate analysis showed that torrefaction increased the carbon content of torrefied solid, whilst decreased the hydrogen and oxygen content. Based on decomposition temperature, the TGA curves indicated that hemicellulose was more significantly decomposed than cellulose and lignin during torrefaction. Due to higher content of hemicellulose in EFB compared to others, EFB had been decomposed almost completely by torrefaction. From the mass spectrometry study, the percentile compositions of CO, CH₄, CO₂ and H₂ in the gases product were found to be 29-33, 20-23, 1.3-1.9 and 1.7-2.1%, respectively. It can be concluded that torrefaction of oil palm biomass affected by the chemical composition and decomposition temperature of hemicellulose, cellulose and lignin.

Key words: Torrefaction, lignocellulosic constituents, empty fruit bunches (EFB), palm mesocarp fiber (PMF), palm kernel shell (PKS)

INTRODUCTION

In the transition to a more sustainable renewable energy supply, energy from biomass has attracted wide attention across the world. Biomass is a promising alternative energy source to replace fossil fuels in the future, as it is abundant, clean and carbon dioxide neutral (Shuit *et al.*, 2009; Zhang *et al.*, 2010; Chen *et al.*, 2011). In fact, biomass from agricultural wastes is one of the most viable renewable energy. It is the third largest primary energy source after coal and oil (Zhang *et al.*, 2010). To develop energy from biomass, various conversion technologies such as physical, thermal, chemical and biological methods had been utilized. The thermal conversion is the most commonly technique applied namely direct combustion, pyrolysis, gasification and liquefaction (Zhang *et al.*, 2010; Uemura *et al.*, 2011).

However, many barriers occur in order to utilize raw biomass caused by its characteristics. The raw biomass is characterized as high moisture content, low energy density, hygroscopic behaviour, storage difficulty and poor grindability (Chen and Kuo, 2010; Arias *et al.*, 2008;

Deng *et al.*, 2009; Bridgeman *et al.*, 2008; Prins *et al.*, 2006a; Mohammed *et al.*, 2005). A pre-treatment method called 'torrefaction' is found to be effective process to improve the limitation properties of raw biomass. Torrefaction is a thermal pretreatment process to pre-treat biomass performed at temperature range within 200-300°C under an inert atmosphere. The products of torrefaction consist of dark colour solid, condensate including moisture and acetic acid and gases which are mainly CO₂, CO and small amounts of CH₄ and H₂ (Chen *et al.*, 2011; Chen and Kuo, 2010; Arias *et al.*, 2008; Deng *et al.*, 2009; Bridgeman *et al.*, 2008; Prins *et al.*, 2006b; Mohammed *et al.*, 2005).

Currently, the development to convert agricultural wastes such as oil palm wastes as energy resources are widely investigated in Malaysia. In 2008, Malaysia was the second largest producer of palm oil with 17.7 million tonnes, or 41% of the total world supply. By its plantation and milling, palm oil industry generates biomass including fronds, trunks, Empty Fruit Bunches (EFB), Palm Mesocarp Fiber (PMF) and Palm Kernel Shell (PKS) (Shuit *et al.*, 2009; Chen and Kuo, 2010).

Table 1: Chemical composition of oil palm biomass (Mohammed *et al.*, 2005)

Component	Oil palm biomass (wt.%)		
	EFB	PMF	PKS
Hemicellulose	35.3	31.8	22.7
Cellulose	38.3	34.5	20.8
Lignin	22.1	25.7	50.7

Because of its availability, oil palm wastes seem to have a great potential to become alternative source of renewable energy.

In general, oil forms about 10% of the whole oil palm trees while the other 90% remains as biomass. Fresh fruit bunch contains only 21% palm oil, while the rest are 14-15% fiber, 6-7% palm kernel, 6-7% shell and 23% EFB which left as biomass. Lignocellulosic is another word for biomass that originates from plants. It generalises the structure of plants to the three main sugar-based polymeric structures namely hemicellulose, cellulose and lignin. For instance, Table 1 show the chemical composition of oil palm biomass (Mohammed *et al.*, 2005). Specifically, the hemicellulose breaks down firstly at the temperatures of 150-350°C and then does cellulose at the temperatures of 275-350°C, while lignin decomposition occurs between 250-500°C (Arias *et al.*, 2008). Due to variation of chemical composition and decomposition temperatures in biomass, it gives impact on the thermal decomposition behaviour during torrefaction.

Nowadays, torrefaction of lignocellulosic biomass has attracted interest of researchers because of its potential applications. Previously, research has revealed the influence of torrefaction on the chemical changes of biomass represented by the proximate and ultimate composition, mass and energy yields, added with composition of volatile products (Chen *et al.*, 2011; Chen and Kuo, 2010; Deng *et al.*, 2009; Bridgeman *et al.*, 2008; Prins *et al.*, 2006a). For instance, Arias *et al.* (2008) studied the torrefied woody biomass (eucalyptus) at 240-280°C and found that the grindability improved (Deng *et al.*, 2009). Prins *et al.* also proposed a kinetic model of torrefaction (Prins *et al.*, 2006b).

The main improvements properties of torrefied biomass are: the moisture is reduced which the energy density is increased; O/C ratio is reduced which increased the heating value; the strong fibrous of biomass become brittle, which improve grindability, reduces the cost and energy required for grinding; the ignitability and reactivity is improved so, it enhanced the efficiency during gasification or pyrolysis (Chen and Kuo, 2010; Deng *et al.*, 2009; Bridgeman *et al.*, 2008; Prins *et al.*, 2006a,b; Mohammed *et al.*, 2005).

Although, torrefaction seems to be one of the pre-treatment for biomass, less attention had been paid to torrefaction of oil palm biomass. Thus, in this study the

torrefaction characteristics of EFB, PMF and PKS will be explored by using a thermogravimetric analyzer coupled with mass spectrometry (TGA-MS). Specifically, study on the effect of temperatures during torrefaction was conducted. Besides, during torrefaction process, it can be divided into light torrefaction (i.e., 200, 220 and 240°C) and severe torrefaction (i.e., 260, 280 and 300°C).

MATERIALS AND METHODS

Materials: Three types of oil palm wastes which EFB, PMF and PKS were obtained from FELCRA Bota, Perak. All of the materials were oven dried at 105°C for 24 h to provide a basis of the tested materials. After drying, the raw materials were grinded and sieved into particle size ranges of 250-355 µm and 355-500 µm. Then, all the prepared raw samples were transferred into labeled sample bottle and stored in controlled moisture cupboard until the analyses were carried out.

Ultimate analysis: The ultimate analysis was carried out by CHNS analyzer (CHN-900/CHNS-932) by LECO which measured the elementary composition which were carbon, hydrogen, nitrogen and sulphur for torrefied biomass. Approximately, 2 mg of each biomass were tested. Oxygen content was a calculated value which determined by using Eq.:

$$\%O = 100 - \%C - \%H - \%N - \%S$$

Torrefaction process: The torrefaction behaviours of EFB, PMF and PKS at two particle size ranges of 250-355 µm and 355-500 µm were analyzed using a thermogravimetric analyzer (EXSTAR TG/DTA 6300-SII Japan) coupled with mass spectrometry (TGA-MS). A crucible loaded with samples (approximately 2 mg) was placed inside the TGA. The heating rate of 10°C min⁻¹ and nitrogen gas with flow rate of 100 mL min⁻¹ was applied. During torrefaction was performed, a temperature program consisting of a dynamic heating period and an isothermal heating period. Specifically, the TGA temperature was raised from 50°C to 120°C and hold for 10 min, then heated again to six final torrefaction temperature (i.e., 200, 220, 240, 260, 280 and 300°C). Once the TGA reached the torrefaction temperature, the samples were torrefied for 120 min.

RESULTS AND DISCUSSION

In order to discuss elementary composition, the carbon, oxygen, hydrogen, nitrogen and sulphur content were plotted in Fig.1-5 for torrefied EFB, PMF and PKS, respectively. It revealed that the alteration occur in the

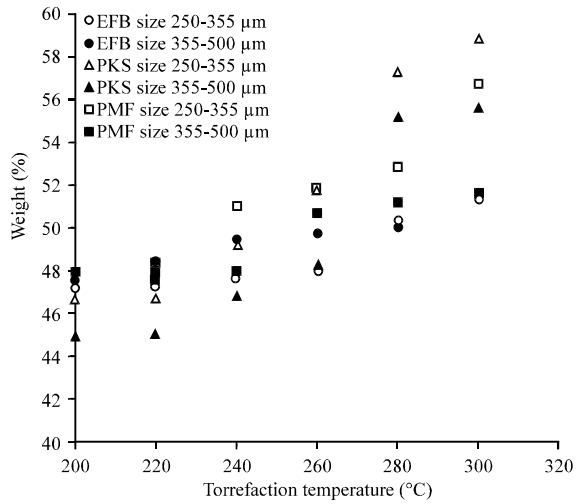


Fig. 1: Carbon content of different torrefied biomass as a function torrefaction temperature

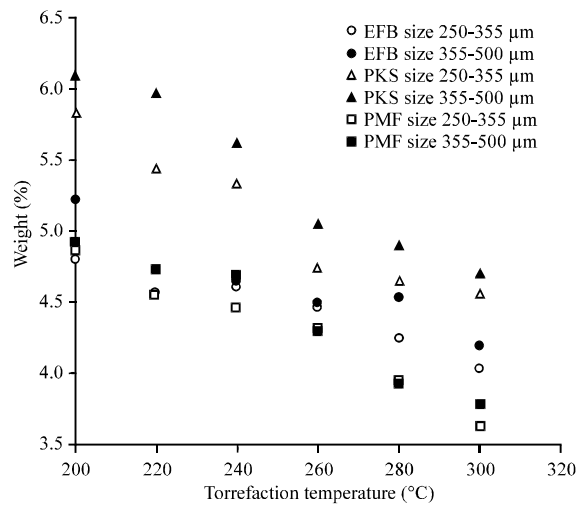


Fig. 3: Hydrogen content of different torrefied biomass as a function torrefaction temperature

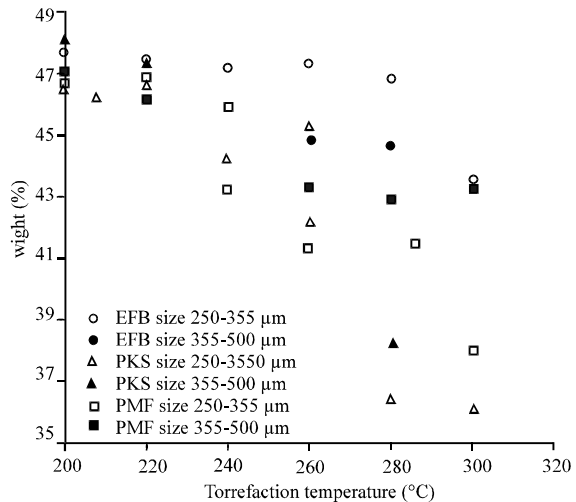


Fig. 2: Oxygen content of different torrefied biomass as a function torrefaction temperature

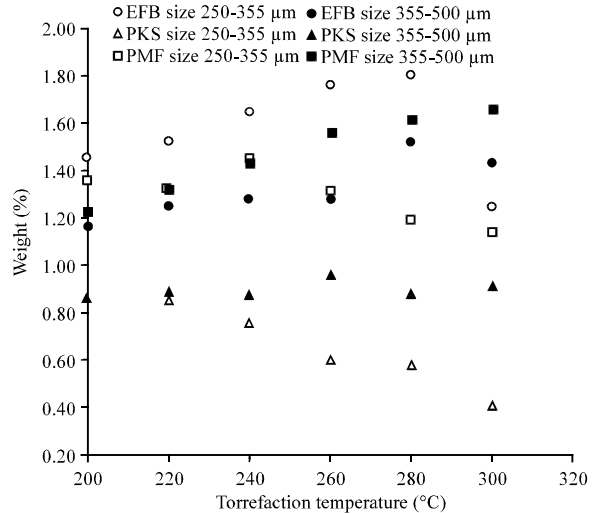


Fig. 4: Nitrogen content of different torrefied biomass as a function torrefaction temperature

composition of oil palm wastes as it was exposed to torrefaction temperature. As the torrefaction temperature increased, the carbon content was increased, whilst the hydrogen and oxygen content were decreased respectively. The exception was nitrogen content, because at any temperature it remained almost constant, below than 2%. Meanwhile, sulphur content for torrefied biomass approximately to zero. These results seem to be in line with the reported in literatures (Chen and Kuo, 2010; Prins *et al.*, 2006a).

The hydrogen and oxygen contents were decreasing due to the formation of CO, CO₂, CH₄ and H₂. During torrefaction, the liberated volatiles contained higher

proportions of oxygen and hydrogen than carbon, thus reducing these elements in the torrefied solid (Chen and Kuo, 2010; Prins *et al.*, 2006b). It was due to the decomposition of hemicellulose via devolatilisation and carbonisation process.

The distributions of thermogravimetric analysis (TGA) of the oil palm wastes at six torrefaction temperatures were displayed in Fig. 6-7. In this study, torrefaction process can be divided into light torrefaction (i.e., 200, 220 and 240°C) and severe torrefaction (i.e., 260, 280 and 300°C). It can be seen that the weight loss of biomass was influenced by the torrefaction temperature.

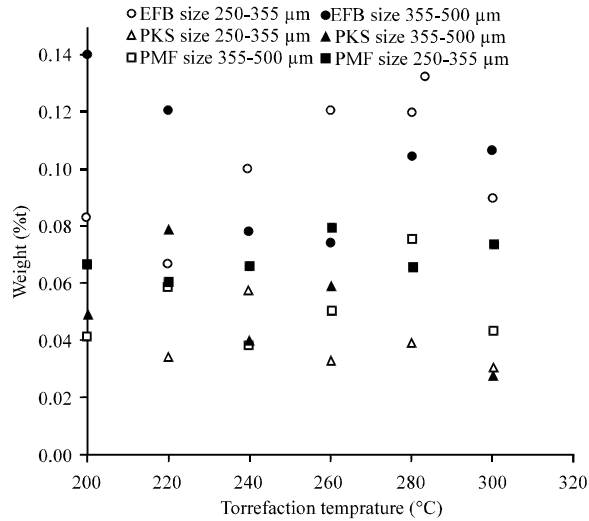


Fig. 5: Sulphur content of different torrefied biomass as a function torrefaction temperature

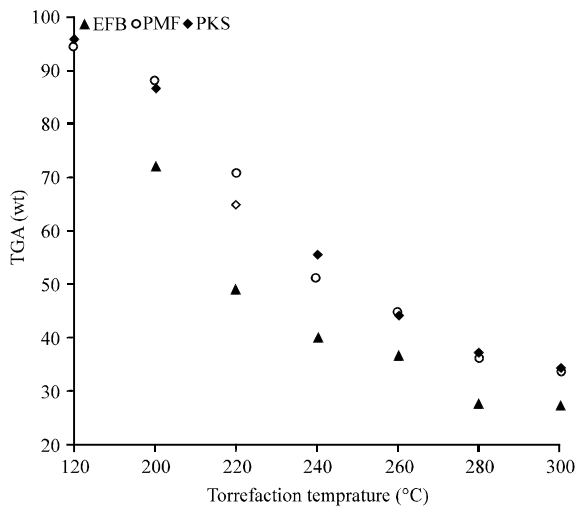


Fig. 6: Thermogravimetric analyses (TGA) at torrefaction temperature for size 250-355 μm

During torrefaction, at the first stage (below than 200°C), the weight loss occurred was due to moisture loss (dehydration) and thermal decomposition reactions to form volatiles and organic molecules (Bridgeman *et al.*, 2008).

At the second stage, a significant drop in weight was observed for all biomass. In brief, after experiencing light torrefaction, 41.45, 49.06 and 56.98% of EFB, PMF and PKS remained respectively at 240°C. Meanwhile, after severe torrefaction, only 28.80% of EFB, 32.76% of PMF and 36.42% of PKS remained. After a prolonged

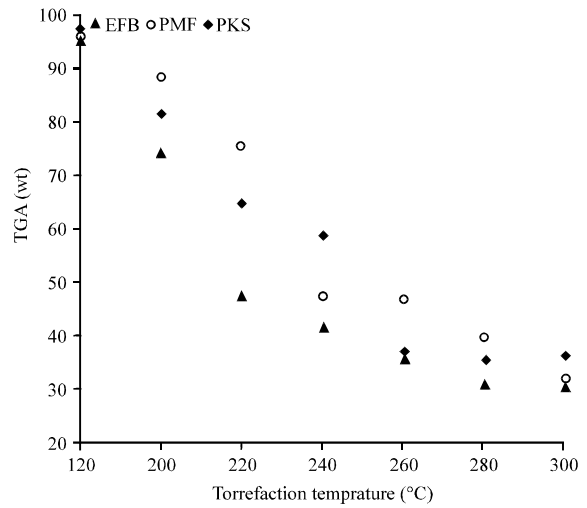


Fig. 7: Thermogravimetric analyses (TGA) at torrefaction temperature for size 355-500 μm

torrefaction time, the curve remains constant which representing no more weight loss occurred in the biomass. Therefore, it can be assumed that the decomposition of the biomass had been completed.

Based on the weight loss percentage, EFB was the most significantly decomposed by torrefaction followed by PMF and PKS. It was due to high content of hemicellulose in EFB rather than in PMF and PKS (Prins *et al.*, 2006a). So, during torrefaction of EFB, it had been decomposed almost completely. The results also revealed that PKS was the most difficult to be decomposed during torrefaction due to its high content of lignin rather than EFB and PMF (Prins *et al.*, 2006a).

Generally, hemicellulose breaks down firstly at the temperatures ranging from 150- 350°C and then does cellulose at 275-350°C, whereas, lignin being the last component to decompose between 250-500°C (Arias *et al.*, 2008). From the variation of decomposition temperatures as stated above, only hemicellulose was more significantly decomposed because of the decomposition temperature was within the range of torrefaction temperature. The weight loss during torrefaction for EFB, PMF and PKS also related to the changes in their structure. It involved the decomposition of hemicellulose, partial depolymerization of lignin and cellulose (shortening of cellulose macro-fibrils). Moreover, during torrefaction, biomass were undergoes dehydration, decarboxylation and deacetylation of xylan in hemicellulose (Bridgeman *et al.*, 2008; Prins *et al.*, 2006a).

The mass spectrometry (MS) was employed to analyse the composition of gases produced. During torrefaction, the thermal decomposition of biomass yields a number of different gases products. Table 2 and 3 displayed the percentage for composition of CO,

Table 2: Gas composition for torrefied biomass size of 250-355 µm as function torrefaction temperature

Gas percentage (%)												
Torrefaction	EFB size 250-355 µm				PMF size 250-355 µm				PKS size 250-355 µm			
Temperature (°C)	CO	CH ₄	CO ₂	H ₂	CO	CH ₄	CO ₂	H ₂	CO	CH ₄	CO ₂	H ₂
200	29.14	20.06	1.97	2.06	32.84	22.74	1.43	2.16	32.43	23.20	1.42	2.16
220	32.88	23.86	1.27	2.05	30.55	22.45	1.45	1.83	30.40	20.70	1.63	1.83
240	32.56	22.78	1.51	2.10	33.13	23.90	1.38	2.10	32.51	23.59	1.32	2.10
260	31.41	22.86	1.37	1.98	29.68	21.03	1.61	1.76	31.63	22.81	1.40	1.76
280	31.30	21.76	1.60	1.90	33.14	23.38	1.39	2.09	29.65	20.93	1.58	2.09
300	32.52	24.28	1.42	1.97	30.81	21.98	1.74	1.88	32.88	22.69	1.48	1.88

Table 3: Gas composition for torrefied biomass size of 355-500 µm as function torrefaction temperature

Gas percentage (%)												
Torrefaction	EFB size 355-500 µm				PMF size 355-500 µm				PKS size 355-500 µm			
Temperature (°C)	CO	CH ₄	CO ₂	H ₂	CO	CH ₄	CO ₂	H ₂	CO	CH ₄	CO ₂	H ₂
200	31.63	21.22	1.47	1.78	29.63	20.85	1.68	1.80	32.85	23.13	1.31	2.09
220	29.59	19.98	1.75	1.66	31.83	22.38	1.42	1.95	32.65	22.61	1.40	2.10
240	33.10	22.44	1.43	1.85	31.76	22.87	1.40	1.99	29.82	20.81	1.63	1.94
260	32.25	22.16	1.51	1.96	32.10	23.07	1.37	1.99	33.18	23.55	1.40	2.20
280	30.53	20.96	1.62	1.80	30.78	21.12	2.00	1.89	30.70	21.33	1.53	1.99
300	33.12	23.02	1.54	2.00	32.67	22.98	1.42	2.01	32.83	23.06	1.43	2.15

CO₂, CH₄ and H₂ yields at each of torrefaction temperature for EFB, PMF and PKS, respectively. The percentile compositions main gases; CO and CH₄ were found to be approximately 29-33 and 20-23%, respectively. Besides, small amount of CO₂ and H₂ were formed. Specifically, 1.3-1.9% of CO₂ and 1.7-2.1% of H₂ were produced. In contrast, from previous torrefaction studies it was reported that the main gas product was CO₂ with small amounts of CH₄ (Bridgeman *et al.*, 2008; Prins *et al.*, 2006a). It seems to be that for torrefaction of oil palm biomass, CO was significantly the main gas formed rather than formation of CO₂.

During torrefaction, the most reactive fraction decomposed was the hemicellulose fraction. Hemicellulose decomposition can be summarized as a two-step reaction. First step was the formation of light volatiles (mono and polysaccharide fractions and dehydrosugars. Then, it was followed by their catalytic degradation (mineral matter) resulting in the formation of CO and CO₂. The formation of CO₂ may result from decarboxylation and depolymerization reaction while CH₄ may form from depolymerization reaction and oxides of carbon (Bridgeman *et al.*, 2008).

CONCLUSION

Torrefaction behaviours of three types of oil palm biomass namely Empty Fruit Bunches (EFB), Palm Mesocarp Fiber (PMF) and Palm Kernel Shell (PKS) have been studied by thermogravimetric analyzer coupled with mass spectrometry (TGA-MS). The ultimate analysis revealed as the torrefaction temperature increased, the

carbon content was increased, whilst hydrogen and oxygen content were decreased respectively. The results from TGA curves indicated that hemicellulose decomposition was more significant compared to cellulose and lignin decomposition during torrefaction. Due to the high content of hemicellulose in EFB compared to PMF and PKS, EFB had been decomposed almost completely by torrefaction.

From the variation of decomposition temperatures of lignocellulosic constituents, only hemicellulose was more significantly decomposed because its decomposition temperature was within in the range of torrefaction temperature. The results also revealed that PKS was the most difficult to decompose during torrefaction due to its high content of lignin rather than EFB and PMF. From mass spectrometry study, the gases products in oil palm biomass were mainly consisted of approximately 29-33 of CO and 20-23% of CH₄, respectively. Furthermore, small amount of CO₂ (1.3-1.9%) and H₂ (1.7-2.1%) were produced.

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