Journal of Physical Science, Vol. 25(2), 73–84, 2014

Pyrolytic Product of Washed and Unwashed Oil Palm Wastes by Slow Thermal Conversion Process

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ABSTRACT: *In Malaysia, there are presently 4.3 million hectares of oil palm plantation, which produce over 100 million tonnes of biomass, such as empty fruit bunches (EFB), kernel shells (oil palm shell or OPS) and pressed fruit fibres (PPF) from mills, as well as oil palm fronds (OPF) and oil palm trunks (OPT) from fields. In this work, proximate, ultimate, hydrolysis and heating value analyses were carried out on EFB, OPS and OPF. The results demonstrated that dried unwashed EFB, OPS and OPF have a moisture content of 7.01 mf wt%, 3.44 mf wt% and 8.01 mf wt%, respectively, with high volatile matter of approximately 75–82 mf wt% and ash content of approximately 4 mf wt%. The higher heating values (HHV) of the samples were determined using a bomb calorimeter technique. A simple water washing pre-treatment was also employed to study ash reduction in EFB, OPS and OPF. A high char yield was obtained by slow pyrolysis while minimising liquid and gas yields. It was determined that the carbon content was high for samples with low ash content. Furthermore, the washed and unwashed samples were analysed by thermogravimetric analysis to determine their thermal degradation behaviour.*

Keywords: Oil palm wastes, water washing pretreatment, ash content, slow pyrolysis, empty fruit bunches

1. INTRODUCTION

Presently, there are approximately 4.3 million hectares of oil palm plantation in Malaysia, which produce over 100 million tonnes of biomass, such as empty fruit bunches (EFB), kernel shells (oil palm shell [OPS]) and pressed fruit fibres (PPF) from mills, as well as oil palm fronds (OPF) and oil palm trunks (OPT) from fields.[1] Large quantities of biomass are produced every day, and almost 80% can be used as fuel for boilers to generate heat and power.

Pyrolysis is the thermal degradation of waste material in the absence of oxygen and produces carbonaceous char, oils and combustible gases. Different proportions of the products (char, oils and gases) are produced depending on the pyrolysis technology used and the process parameters.

In this study, EFB, OPS and OPF were pyrolysed by slow pyrolysis. Slow pyrolysis, which has a heating rate of up to 100°C min^{-1} and a maximum temperature of 600°C, produces approximately equal yields of char, liquid and gas.[2] However, biomass heated slowly at a relatively low temperature of approximately 400°C over an extended period of time will maximise char formation. Sukiran et al.[3] have studied bio-char yields by varying the pyrolysis temperature. They determined that the highest bio-char yield (42%) was obtained at 300°C by using argon as a fluidising gas at a rate of 1.5 l min^{-1}. However, the biochar yield significantly decreased as the pyrolysis temperature was raised from 300°C to 700°C, which could be due to the secondary decomposition of the biochar residues.

The properties of EFB, OPS and OPF were characterised by proximate, elemental and hydrolysis analyses, whereas the heating value was determined using the bomb calorimeter technique. The biomass properties, such as moisture, ash, elemental content (C, H, N, S and O) and volatile matter, will considerably influence the suitability of the biomass for yield production. Therefore, a simple washing pre-treatment was performed to improve the quality of biomass that has low ash content. The ash content of biomass has been found to influence the yield of organics, as indicated in prior research.[4] The study demonstrated the impact of varying ash content in EFB through different water washing techniques. Lowering the ash content from 2.04 mf wt% to 1.03 mf wt% produced an increase in organics yield on a dry basis from 44.32% to 61.34%. Meanwhile, the yield for the unwashed EFB was approximately 34.71% under the same conditions.

Thermogravimetric analysis (TGA) was carried out on each sample to determine their hemicelluloses, cellulose and lignin content along with their thermal degradation behaviour. A study by Sulaiman and Abdullah[5] on the thermal degradation behaviour of EFB used thermogravimetry (TG) and differential thermogravimetry (DTG) analyses. They determined that between 100°C and 200°C, weight loss mainly occurred through the evaporation of extractives. They also found a single peak in the DTG curve of the cellulose and hemicelluloses of EFB with the maximum rate of weight loss occurring at 354°C. These trends are in agreement with previous studies conducted by Ravendran et al.[6] and Meszaros et al.[7] for high mineral matter ligno-cellulosic feedstock.

2. EXPERIMENTAL

2.1 Oil Palm Wastes Preparations

EFB, OPS and OPF were studied in this work. These oil palm wastes were obtained from a local palm oil mill in the northern region of the Peninsular Malaysia. EFB, OPS and OPF were dried in the oven until their moisture content was less than 10 mf wt% to prevent growth of fungus and microorganisms.[5] In this study, EFB, OPS and OPF samples were cut into 2–3 cm pieces before washing pre-treatment and pyrolysis.

Proximate analysis for moisture, ash and volatile contents were completed according to ASTM E 871-82, E 872-82 and E 830-87, respectively, on each of the samples. The fixed carbon content for each sample was then calculated by determining the difference. Elements such as carbon, hydrogen, nitrogen and sulphur were analysed using a CHNS Analyser, Perkin Elmer 2400. Oxygen levels were determined by subtracting the summation of the other percentages from 100%. The higher heating value (HHV) for each sample was determined according to the ASTM E 711-87 standard test method, and the lower heating value (LHV) was calculated by Equation 1:[8]

$$LHV_{dry}\left(\frac{MJ}{kg}\right) = HHV_{dry} - 2.442\left(\frac{8.936H}{100}\right) \quad (1)$$

where H is the mass of hydrogen in wt% on a dry basis.

In addition, a TGA study was also performed on the samples to analyse their thermal characteristics using a Perkin Elmer Pyris 1 that was set at 0^{o} to 600°C at a heating rate of 10°C min^{-1}, utilising 100 ml min^{-1} of N_2 purging. The ignition and peak temperature of pyrolysis were determined by the DTG curve.

As for the washing pre-treatment, approximately 100 g of each sample were soaked in 5 l of distilled water for 10 min and drained. These washed samples were then dried in the oven until their moisture content reached below 10 mf wt%.

2.2 Experimental Procedure

The slow pyrolysis experiments were performed on EFB, OPS and OPF. Samples were packed inside a cylindrical stainless steel pyrolyser with an internal diameter of 6.5 cm and a length of 15 cm. The pyrolyser was placed in a muffle furnace (Type F62700-33-80, Barnstead International) at a constant temperature of 300°C for two hours with a heating rate of 30°C min^{-1}. Gas emission from the pyrolysis process was condensed using a liquid collecting system, as shown in Figure 1, which was adapted from Khor et al.[9] The yields of char and liquid are calculated using Equation 2, as suggested by Abnisa et al.[8] The gas product was then calculated by determining the difference.

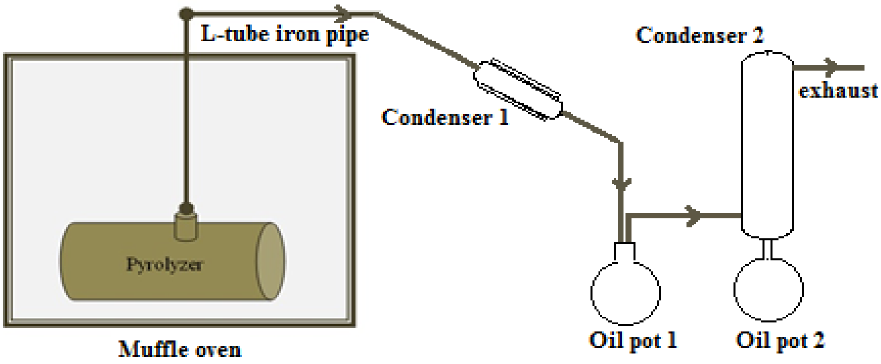


Figure 1: Slow pyrolysis unit with a liquid collecting system.

$$\text{Yield (wt\%)} = \frac{\text{Desired Product (g)}}{\text{Oil Palm Wastes Feed (g)}} \times 100\% \qquad (2)$$

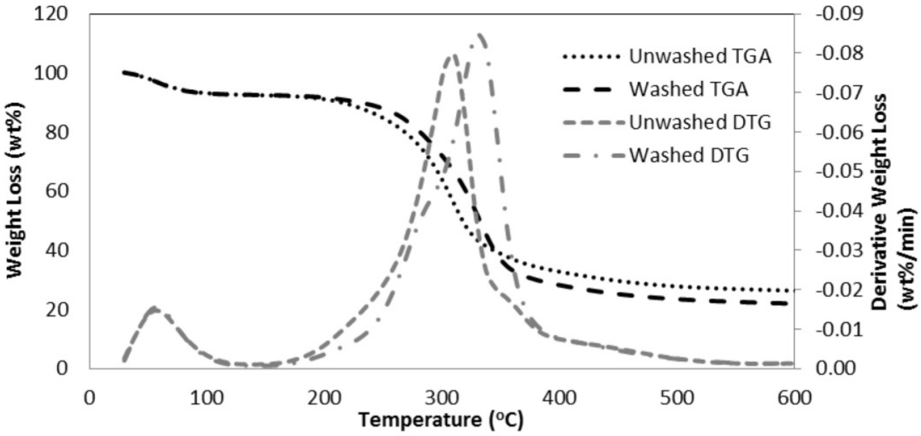
3. RESULTS AND DISCUSSION

The proximate and elemental analyses along with the heating values of EFB, OPS and OPF are presented in Table 1. As a comparison, the properties of hardwood are also presented. Both EFB and OPF have higher volatile matter compared to that of OPS. High volatile matter may contribute to greater efficiency for burning during the combustion process.[10] In this study, the carbon content in the unwashed EFB, OPS and OPF are approximately 43–46 wt%, but increased approximately 3%–5% after undergoing a water washing pre-treatment. The unwashed OPF has a higher hydrogen content of approximately 5.73 wt% compared to EFB and OPS. However, the hydrogen content of EFB and OPS decreased approximately 1% after being washed. This decrease is due to the leaching process, which removed dirt and other particulates that existed in the unwashed biomass, thus decreasing the overall weight. The washing process did not leach the carbon but may have leached some of the hydrogen content. Overall, the washed elemental components of OPF are quite similar to that of hardwood except for nitrogen.[11] In addition, these analyses indicated that all samples are environmentally friendly, with the exception of nitrogen and sulphur, which were considerably low in amounts.

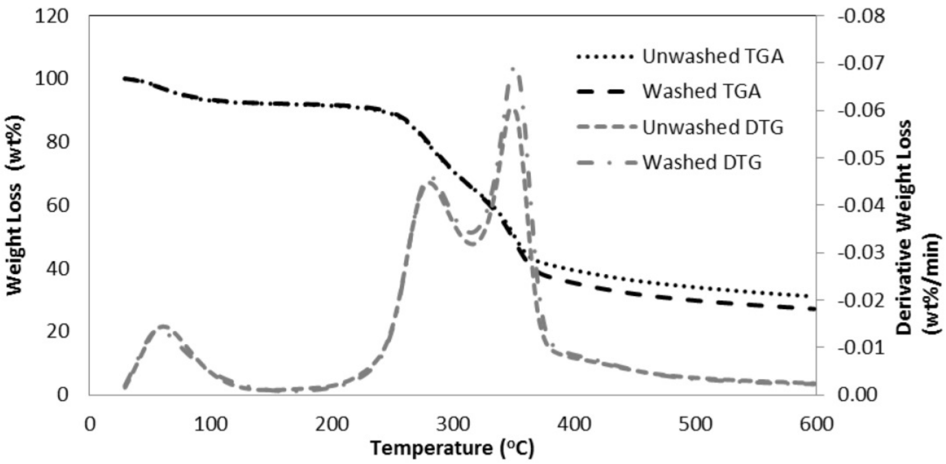
Table 1: Characteristics of EFB, OPS and OPF.

Component/ property (dry basis)	EFB		OPS		OPF		Hardwood[14]
	Un-washed	Washed	Un-washed	Washed	Un-washed	Washed	
Proximate analysis (mf wt%)							
Moisture	7.01	3.47	3.44	3.11	8.01	3.21	7.8
Ash	3.65	2.63	4.28	2.47	4.20	2.08	2.7
Volatiles	81.81	76.85	75.31	74.63	81.03	78.70	72.3
Fixed Carbon	14.54	20.52	20.41	22.90	14.77	19.22	25.0
Elemental analysis (mf wt%)							
Carbon	45.29	48.09	43.65	49.05	45.47	48.50	48.6
Hydrogen	5.06	4.67	3.27	2.00	5.73	5.02	6.2
Nitrogen	1.20	1.63	1.54	1.47	1.29	1.14	0.4
Sulphur	0.35	0.27	0.10	0.15	0.36	0.42	–
Oxygen	48.10	45.34	51.44	47.33	47.15	43.92	41.1
Component (mf wt%)							
Cellulose	38.3[15]	–	20.8[15]	–	49.8[15]	–	45.2
Hemicellulose	35.3[15]	–	22.7[15]	–	23.5[15]	–	31.3
Lignin	22.1[15]	–	50.7[15]	–	20.5[15]	–	21.7
Heating values (MJ kg^{-1})							
HHV	13.94	14.82	10.20	10.94	15.14	17.17	18.8
LHV	12.84	13.81	9.49	10.50	13.89	15.85	–

Generally, it can be assumed that biomass has three major components: cellulose, hemicelluloses and lignin. The TG and DTG profiles for the washed and unwashed samples are shown in Figure 2. A slight drop in the first weight loss of the samples occurred at 100°C due to moisture evaporation. However, this could be considered an insignificant change in weight loss at the early stage of devolatisation (0°C–200°C).[12] Thermal degradation of raw samples occurs at approximately 200°C–400°C. It is well known that hemicellulose breaks down at a lower temperature compared to cellulose.[13] This regime of weight loss was also explored by Khor et al.,[9] where a lower temperature range (200°C–300°C) could be correlated with the decomposition of hemicelluloses. Meanwhile, cellulose decomposition occurred in the upper temperature range (300°C–400°C).

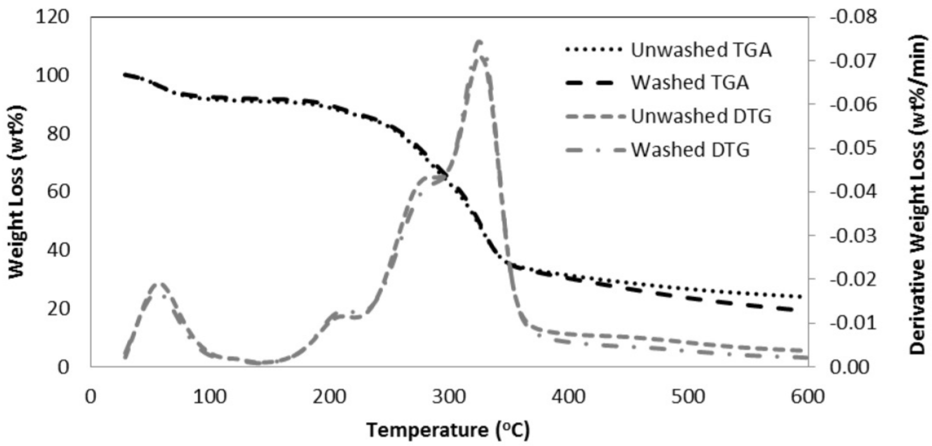


(a)



(b)

Figure 2: TG and DTG curves for (a) EFB, (b) OPS and (c) OPF (*continued on next page*).



(c)

Figure 2: (*continued*).

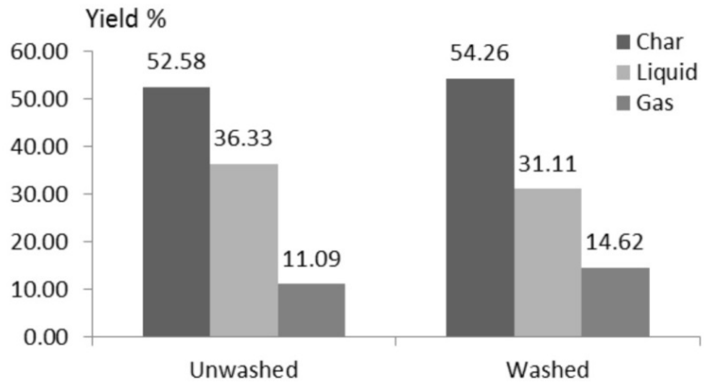
Two peaks observed at approximately 280°C and 320°C for both the washed and unwashed samples in the DTG curve could be the beginning of hemicelluloses and cellulose decomposition. A peak shifting to the right that occurred between the washed and unwashed samples was due to the reduction of ash content, which is more obvious in the EFB samples. Figure 2 shows that the peak maxima shifted to a higher temperature (i.e., shifted to the right) as ash content in the feedstock was reduced by washing. It is well known that ash containing minerals exerted a catalytic action during the thermal decomposition of polymer blocks and eased hemicellulose/cellulose decomposition to lower temperatures. As ash is reduced, the decomposition of hemicellulose/cellulose occurs at a higher temperature. As for the DTG peaks, the increases in the peaks of the washed samples are due to increased combustion of the biomass with less ash. The decomposition rates above 400°C for all samples were relatively slow, which was mainly due to the decomposition of lignin. At the end, the residues that were left were approximately 20% of the sample weight, which contributed to the high yield of char, especially in OPS.

The effectiveness of water washing pre-treatment can be determined from the percentage of ash reduction. The percentage of ash reduction in OPF was approximately 50.48%. The minerals taken up and retained by plants when growing are classified as ash, and the most common elements in ash are calcium, potassium and sodium. The ash, which is loosely bound to the cell, is easily removed using water. However, both the ash, which is bound to the cell walls, and the hemicellulose are not easy to remove. Therefore, removal may require more severe agents, such as acid, and more aggressive removal techniques. High ash reduction in OPF is most likely due to its structural surface, which makes the removal of sand, mineral and silica content easier. Ash may correspond to a reduction in organics yield due to its behaviour, as it is catalytically active and favours secondary reactions.[16]

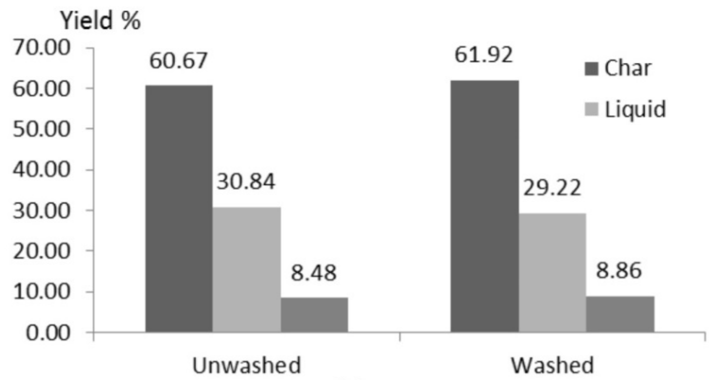
In this study, all samples had lower HHV compared to hardwood (~18.8 MJ kg^{-1}), as shown in Table 1. Jenkins et al.[17] reported that a 1% increase in ash yields a significant decrease in the heating value (approximately 0.2 MJ kg^{-1}). This decrease occurs because ash does not substantially contribute to the overall heat released by combustion, although elements in ash might be catalytic to the thermal decomposition. The washing pre-treatment applied to samples may contribute to low ash content but increase their heating value.

The yield percentage obtained from EFB, OPS and OPF is shown in Figure 3. At 300°C, the yield percentage of char produced was higher compared to the liquid and gas yields. The char yield obtained from the unwashed EFB, OPS and OPF were 52.58%, 60.67% and 50.86%, respectively. The large ratio weight of OPS to the volume of cylindrical pyrolyser (approximately 0.276 g cm^{-3}) most likely contributed to these significant results. The high density of OPS inside the pyrolyser made the combustion process more comprehensive due to its compactness. The char yield increased for all washed samples most likely due to the decreased amount of volatile matter in the samples. According to these results, the volatility of the unwashed samples was better than that of the washed samples. The burning of volatiles is generally quite rapid and follows as soon as volatiles are released; the oxidation of the char occurs much more slowly.[17] Accordingly, the samples combusted well and produced higher char yields.

From experimental observations, a greater amount of gas emissions occurred in OPF compared to other samples. More vapour was produced in maximising liquid yield during the condensation process in the liquid collecting system. The high cellulose component in OPF was most likely causing high differences in the gaseous products. Atnaw et al.[15] found cellulose to be the most preferable chemical component in biomass gasification. The product gas composition in cellulose is reported to have higher carbon monoxide composition compared to the hemicellulose and lignin components.



(a)



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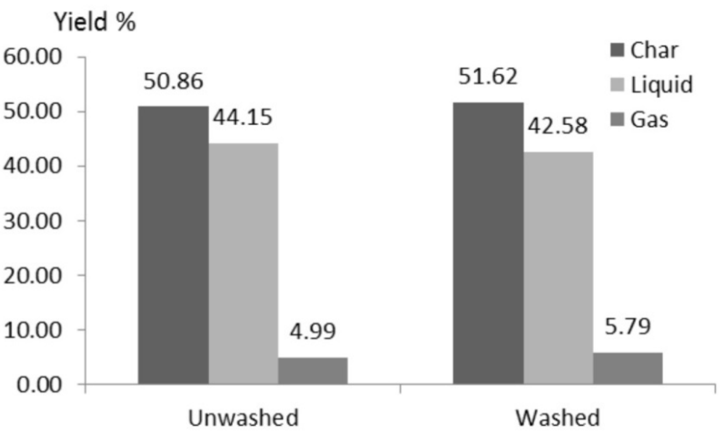

(c)

Figure 3: Yield percentage of (a) EFB, (b) OPS and (c) OPF.

Highly condensable gas from OPF contributed to the high yield in liquid production. Non-homogeneous liquid has only been observed in unwashed EFB as two fractions, one fraction consisting of insoluble tar and the other of a less oily aqueous fraction. Meanwhile, other samples were observed to be quite homogeneous. Moisture content in the sample most likely distinguished the homogeneity of the liquid.[18] However, there are methods to remove the water content in the pyrolytic liquid such as a hydrotreating-hydrocracking process to make the liquid suitable to be used as fuel.[8] Lower gas yields were obtained from the total pyrolysis yield at this temperature for all samples. Most gaseous products were condensed to liquid in the liquid collecting system, which also had an outlet for non-condensable gas to escape.

The HHV of the raw samples and the char products for EFB, OPS and OPF are shown in Table 2. The char derived from washed EFB yielded the highest HHV (28.73 MJ kg^{-1}). There were significant increases in HHV (approximately 10–15 MJ kg^{-1}) for each sample in the char product. The effectiveness of the washing pre-treatment could also be distinguished, especially in EFB. In this work, the char product from the washed samples has better HHV compared to the unwashed samples. In addition to ash, the elemental composition of each sample contributed to any differences in the heating values.

In this study, a high carbon content (approximately 60–65 mf wt%) was obtained from each sample. The washed samples have higher carbon content compared to the unwashed samples in this work. This relationship showed that the carbon content in biomass can be influenced by water washing pre-treatment. It was reported that carbon concentration could also be correlated with heating values.[17] Each increment of 1% carbon content produced an increase in the heating value of approximately 0.39 MJ kg^{-1}. High carbon content contained in char product could characterise it as high quality fuel. Heating values are proportional to the carbon content and hydrogen content present in the biomass. Biomass with a higher proportion of carbon content compared to hydrogen and oxygen may have increased energy value. Furthermore, hydrogen is also one of the parameters that has a high influence on gross calorific value, as shown in Equation 1. In this study, the char products from EFB, OPS and OPF can be categorised as carbon rich with high amounts of HHV that have high potential as solid fuels.

Table 2: HHV comparison between the raw sample and both the char product and the char product elemental composition of EFB, OPS and OPF.

Sample/ properties		HHV ($MJ\ kg^{-1}$)		Char product elemental composition (mf wt%)				
		Raw sample	Char product	Carbon	Hydro-gen	Nitro-gen	Sulphur	Oxygen (by difference)
EFB	U	13.94	26.34	62.47	5.92	1.08	< 1	29.53
	W	14.82	28.73	64.86	5.94	0.93	< 1	27.27
OPS	U	10.20	24.61	60.39	4.09	0.37	< 1	34.15
	W	10.94	24.93	62.36	5.27	0.49	< 1	30.88
OPF	U	15.14	26.51	63.35	4.71	0.38	< 1	30.56
	W	17.17	26.72	64.64	4.79	0.31	< 1	29.26

Note: U = unwashed, W = washed.

4. CONCLUSION

The pyrolytic products of washed and unwashed oil palm wastes via a slow pyrolysis process were studied in this paper. It was determined that the carbon content in the unwashed EFB, OPS and OPF increased approximately 3%–5%, while the hydrogen content of EFB and OPS decreased approximately 1% after undergoing a water washing pre-treatment. A peak shifting to the right of the DTG curve occurred between a washed and an unwashed sample, which was due to the reduction of ash content. All samples had lower HHV compared to hardwood. The volatility of the unwashed samples was better than that of the washed samples. Only non-homogeneous liquid has been observed in unwashed EFB; meanwhile, other samples were observed to be quite homogeneous. The char product from the washed samples has better HHV compared to the unwashed samples. The washed samples have higher carbon content compared to the unwashed samples, demonstrating that the carbon content in biomass can be influenced by water washing pre-treatment. The high carbon content contained in char product is a sign of high quality solid fuel; therefore, char products from EFB, OPS and OPF can be categorised as carbon rich with high amounts of HHV and have high potential for use as solid fuels.

5. ACKNOWLEDGEMENT

The authors would like to acknowledge the research grants provided by Universiti Sains Malaysia (1001/PFIZIK/814087, 304/PFIZIK/6310087 and 304/PFIZIK/6310073), which made this research possible.

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