

CONVERSION OF PRE-TREATED OIL PALM EMPTY FRUIT BUNCHES INTO BIO-OIL AND BIO-CHAR VIA FAST PYROLYSIS

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ABSTRACT

The empty fruit bunch (EFB) is a cumbersome biomass generated during the palm oil milling process. It is one of the most extensively researched biomass. This is due to its abundant availability from the palm oil industry – spread over Malaysia, Indonesia and to some extent Thailand. It is widely recognised as a potential fuel but its use faces much hurdle, mainly due to its high ash content. Converting EFB into valuable fuel resources such as bio-oil and bio-char, through the pyrolysis process, would be beneficial not only to support national energy security but also economic growth. In this study, the thermal conversion of the unwashed and washed EFB through fast pyrolysis was carried out using a fluidised bed reactor at 500°C with particle sizes ranging from <90 µm to 180 µm. Three types of pre-treatment were performed. These were washing with H₂SO₄ (0.1 M), NaOH (0.1 M), and distilled water. The aims were to investigate the impact of the different washings on the resulting pyrolysis products and the corresponding ash effects. The results indicated that the EFB washed with H₂SO₄, which gave the highest reduction in ash content i.e. ~56%, gave the maximum bio-oil yield (55.6 wt.%) while that washed using NaOH with ~50% ash increment produced the highest amount of bio-char (36.9 wt.%) and gas (38.8 wt.%). The resulting bio-oil and bio-char from the washed feedstock with much reduced ash had similar fuel characteristics with those from the unwashed feedstock, with the latter a better fuel in terms of calorific value, i.e. 19 -23 MJ kg⁻¹ vs. 20-25 MJ kg⁻¹, respectively.

Keywords: oil palm biomass, biofuel, pre-treatment, fast pyrolysis, bio-char.

Date received: 19 June 2017; **Sent for revision:** 20 June 2017; **Received in final form:** 24 October 2017; **Accepted:** 10 January 2018.

INTRODUCTION

The palm oil industry in Malaysia has contributed immensely to the socio-economic development of the nation. To date, the area under oil palm plantations have reached 5.74 million hectares (MPOB, 2016). With such rapid growth, the palm oil mills (453 mills) produce approximately 25.64 million tonnes of palm products. These include crude palm oil,

crude palm kernel oil, palm kernel cake and palm kernel as commodities, and more than 18.88 million tonnes of oil palm biomass comprising empty fruit bunches (EFB), palm kernel shell (PKS), and mesocarp fibres. All these come from 85.84 million tonnes of fresh fruit bunches processed. At the same time, the plantations also generate other types of oil palm biomass, mainly oil palm fronds (OPF) and oil palm trunks (OPT). Generally, the EFB is used as compost, soil mulch, and fuel in the palm oil mill boiler besides being processed into fibrous forms as feedstocks for multiple non-energy and energy applications. As a lignocellulosic biomass, the lignin in EFB presents the most complex structure

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compared to the other two components – cellulose and hemicellulose, making it recalcitrant to both chemical and biological conversions (Geng, 2013). Therefore, washing the EFB may be a promising pre-treatment method to reduce the lignin content and break the chains to facilitate thermal conversion such as pyrolysis (Misson *et al.*, 2009).

Washing is a practical pre-treatment method to improve the properties of biomass when deriving thermally-treated products. Washing the biomass with distilled water/acid can remove ash, sand, and other alkaline earth matters. According to Abdul Rahman *et al.* (2016), reducing the ash content in biomass can prevent slagging and fouling, which occur during thermal conversion. Davidsson *et al.* (2002) and Das *et al.* (2004) reported that acidic solution can effectively remove most of the ashes in the biomass. The rates of inorganic and metal ion removal via acid pre-treatment are much higher than that with other washing medium. However, acid washing causes negative effects such as the breakage of the hydrocarbon bonding and the erosion of the organic constituents in the biomass fibre structure (Sulaiman and Abdullah, 2014). By contrast, alkaline washing increases cellulose digestibility (Carvalho *et al.*, 2008). Mission *et al.* (2009) investigated and found that almost 100% lignin was degraded when EFB was firstly pre-treated with dilute NaOH and then H₂O₂.

Among the thermochemical biomass conversions, fast pyrolysis has received considerable attention recently due to the promising applications of the final products, especially the bio-oil and bio-char. The thermal decomposition of fast pyrolysis occurs at moderate temperature (400°C to 700°C) with rapid heating without oxygen or air (Mohamad Azri *et al.*, 2016). It effectively converts the bone-dry biomass into liquid products at ≈ 80 wt.% yield (Bridgewater, 2004). In fast pyrolysis of oil palm fronds using a fixed bed reactor, it was found that the maximum bio-oil yield was 47.4 wt.% at 400°C (Rahman *et al.*, 2014). Besides, Abnisa *et al.* (2013) pyrolysed oil palm residues (palm leaf and leaf rib, frond, trunk) in a fixed bed reactor at 500°C using a sweep gas flow rate of 2 litres min⁻¹ for 1 hr. The maximum bio-oil and bio-char yields were 43.5 wt.% and 36.75 wt.%, respectively. Another similar study pyrolysing EFB using a fluidised bed reactor at 400°C, 500°C and 600°C yielded a much lower bio-oil yield of 27 wt.% at 500°C (Sembiring *et al.*, 2015). To further improve the pyrolysis products, Amin *et al.* (2012) washed the EFB with NaOH before pyrolysing it in a semi-batch stainless steel reactor at 300°C for 20 min. The resulting bio-oil yield was much higher and the lignin content reduced. Interestingly, those biomass (PKS, OPT and OPF) washed with distilled water showed much reduced bio-oil yields after pyrolysing in a cylindrical stainless steel pyrolyser at 300°C for 2

hr (Sulaiman and Abdullah, 2014) but the bio-char yields significantly increased.

In the present study, the unwashed, and the (acid, alkaline and distilled water) washed EFB were pyrolysed under the previously optimised conditions (temperature: 500°C; particle size: 107–125 µm) (Mohamad Azri *et al.*, 2016) in a fluidised bed reactor. The effects of the employed pre-treatment methods on pyrolysis products and the resulting fuel characteristics were examined.

MATERIALS AND METHODS

Preparation of Raw Materials

The EFB was collected from a palm oil mill located in Selangor, Malaysia. It was milled and sieved using a test sieve shaker and subsequently separated into several different fractions with particle sizes ranging from <90 µm to 250 µm. The resulting EFB particles were dried at 103°C for 24 hr, until a constant weight was achieved. To perform the washing pre-treatment, firstly 10 g of EFB was immersed in 100 ml each of H₂SO₄ (0.1 M), NaOH (0.1 M) and distilled water for 24 hr followed by drying of the drained EFB in an oven at 60°C to a constant weight. Hexane, ethanol, sodium hydroxide, and concentrated H₂SO₄ (99.99%) were of analytical grade purchased from Fisher Scientific Sdn Bhd, Malaysia.

Characterisation of Unwashed and Washed EFB

The proximate analysis of unwashed and washed EFB was conducted using a thermogravimetric analyser (TGA) (LECO TGA-701) to determine the moisture content (MC), volatile matter (VM), fixed carbon (FC), and ash content according to ASTM D5142. The gross calorific value (CV) was determined using an isoperibolic system bomb calorimeter (LECO AC-600) according to ASTM D5865-07. The carbon (C), hydrogen (H), and nitrogen (N) contents of unwashed and washed EFB were determined with a CHNS analyser (LECO CHNS-628) according to ASTM D5373-93. The oxygen content (O) was determined from the difference between 100% and the total percentage of C, H, and N. The concentrations of trace elements [e.g. magnesium (Mg), aluminum (Al), silicon (Si), sulphur (S), chlorine (Cl), potassium (K) and calcium (Ca)] of the washed EFB were determined using a scanning electron microscopy energy dispersive x-ray (SEM-EDX) (Hitachi Bruker).

Structure Degradation of Unwashed and Washed EFB

The decomposition of the unwashed and washed EFB upon pyrolysis was investigated using

the TGA (Perkin Elmer-Pyris 6). The analyses were performed with sample masses of approximately 10 mg each; with linear heating rate of $20^{\circ}\text{C min}^{-1}$ within 30°C to 700°C , and under a flow of nitrogen at a rate of $0.1\text{ litres min}^{-1}$. The structure degradation of the unwashed and washed EFB was determined from the thermogravimetry (TG) and derivative thermogravimetry (DTG) curves.

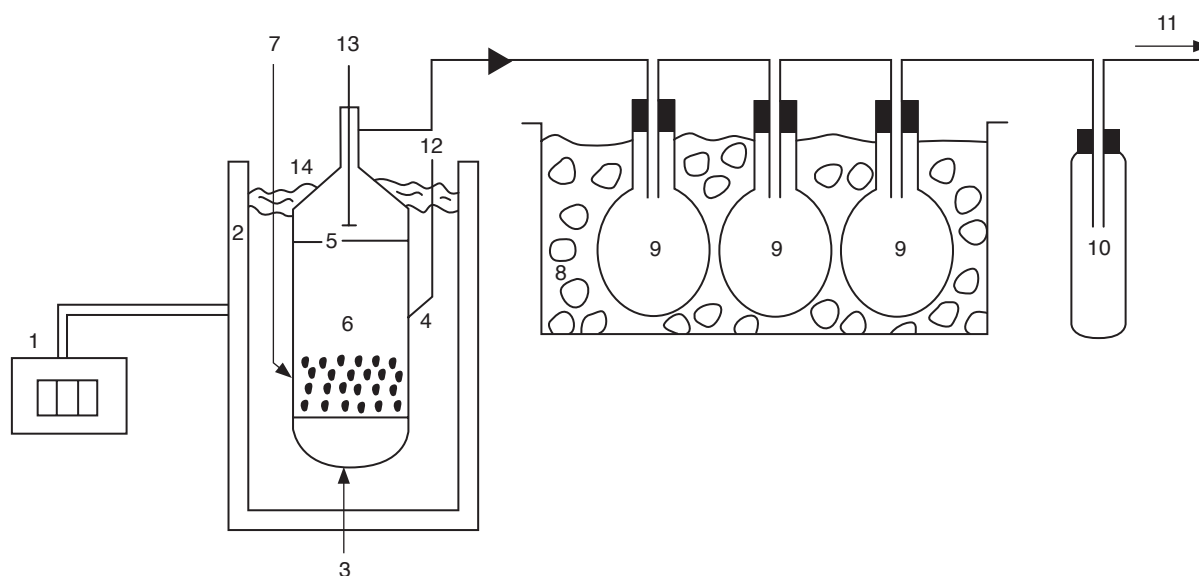
Fast Pyrolysis Experiment

The fast pyrolysis of the unwashed and washed EFB was performed using a fluidised fixed bed reactor (heated length: 135 mm, and inner diameter: 40 mm). The reactor temperature was determined by inserting a thermocouple to the upper fritz as near as possible. The experiment was performed to investigate the effect of different EFB pre-treatments on the pyrolysis products. Three types of pre-treated EFBs *i.e.* EFB washed with H_2SO_4 , EFB washed with NaOH , and EFB washed with distilled water were used. The pyrolysis of the unwashed EFB was conducted as an experimental control. All experiments were conducted at 500°C , and the particle size of feedstock was $107\text{--}125\ \mu\text{m}$. The whole experimental set-up consisting of the liquid and gas collection systems is illustrated in *Figure 1*. The sand bed was fluidised using argon at a rate of $0.5\text{ litres min}^{-1}$. Approximately 120 g of zircon sand ($180\text{--}250\ \mu\text{m}$) was used as the sand bed. For each experiment, 5 g of feedstock was fed into the reactor using argon at a rate of $2.5\text{ litres min}^{-1}$, and held for either a minimum of 20 min or until no further significant release of gas was observed. The connection tubes between the reactor and the

cooling system were heated using heating tape to avoid vapour condensation during pyrolysis. The reactor was weighed prior to the experiment. After a run, the cooled reactor was weighed again to determine the char yield from the difference in the weight of the reactor before and after usage. The char remaining in the reactor was elutriated by introducing argon to the sand bed. The bio-oil was collected in a series of flasks placed in a cold trap containing ice. The bio-oil accumulated in the flask was transferred to a small bottle, and the remaining liquid products retained in the flask and in all the connection tubes were dissolved with ethanol. The solvent from the bio-oil was removed with a rotary evaporator, and the resulting bio-oil was combined with the transferred bio-oil and its weight determined. Finally, the yield of the gas was calculated by subtracting the weight percentage of bio-oil and bio-char from the total of 100%. Each experiment was repeated twice, and the average yields of the pyrolysis products were recorded.

Characterisation of Bio-oil

The water contents of the bio-oils were determined by Karl Fischer titration method. The pH value and density of the bio-oils were measured with a pH meter (Eutech Instruments, pH Tutor) and a digital density meter (DE 40) according to ASTM D-4052, respectively. The total ash analysis was based on ASTM D 482. The sample contained in a suitable vessel was ignited and allowed to burn until only ash and carbon remained. The carbonaceous residue was reduced to ash by heating in a furnace at 775°C for 20 min, followed by cooling



Note: 1 - Temperature recorder, 2 - furnace, 3 - fluidising gas, 4 - reactor, 5 - quartz fritz, 6 - sand bed, 7 - feedstock inlet, 8 - water-ice bath, 9 - bio-oil collector, 10 - gas dryer, 11 - gas exit, 12 - sand feeder, 13 - thermocouple, 14 - glass wool.

Figure 1. Schematic diagram of the pyrolysis system.

and weighing. The functional groups of the bio-oil were detected using the Fourier transform infrared (FTIR) spectroscopy (Magna-IR550 Nicolet). A small amount of the bio-oil was mounted on a KBr disc that was scanned previously as a background. The CV was determined using an isoperobolic system bomb calorimeter (LECO AC-600) according to ASTM D5865-07.

Characterisation of Bio-char

The proximate analysis of bio-char was conducted using a TGA (LECO TGA-701) to determine the MC, VM, FC, and ash content according to ASTM D5142. The CV was determined using an isoperobolic system bomb calorimeter (LECO AC-600) according to ASTM D5865-07. The C, H, and N contents of bio-char were determined using a CHNS analyser (LECO CHNS-628) according to ASTM D5373. The difference between 100% and the total percentage of C, H, and N was the O concentration.

RESULTS AND DISCUSSION

Feedstock Characterisation

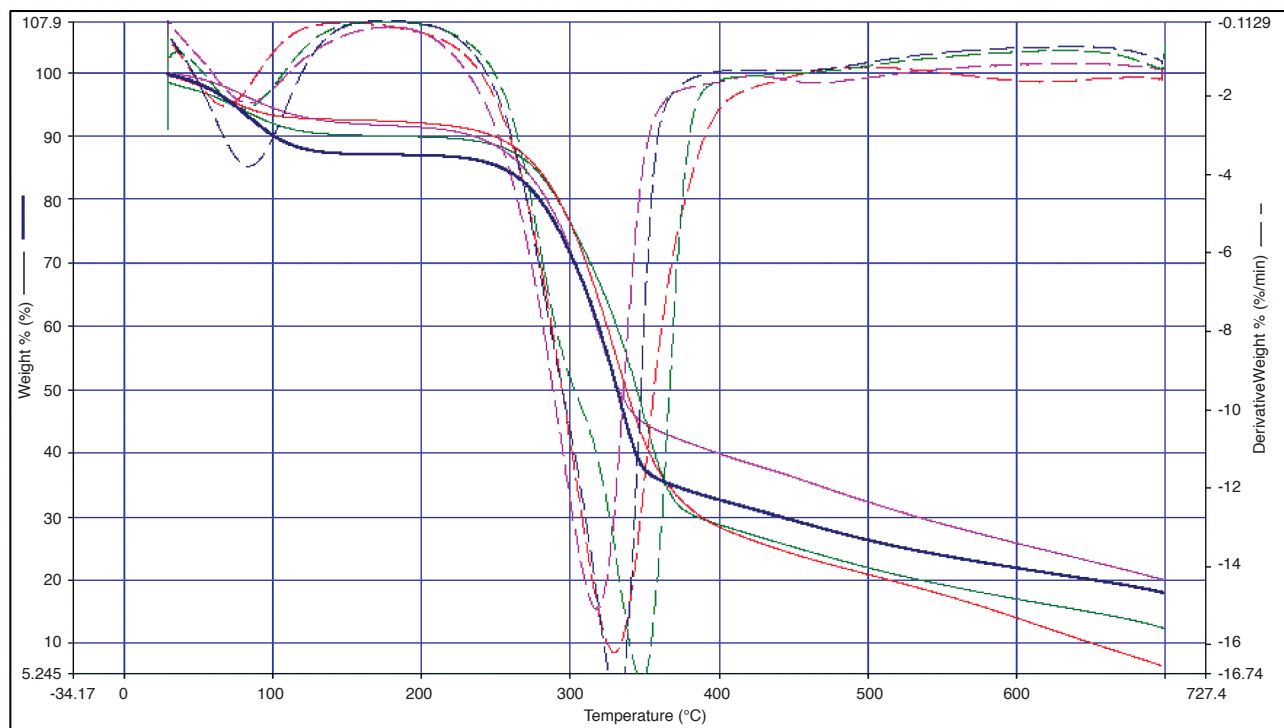
The results of the CV, proximate and ultimate analyses for the unwashed and washed EFB are presented in Table 1. The MC of the washed EFB (6.8%-7.6%) was lower than that of the unwashed EFB (12%). MC is an important characteristic of biomass fuel. High MC can influence the overall energy conversion during the thermochemical process. The washing technique applied had improved slightly the VM of EFB *i.e.* from the initial 71% to 76%-78%, which would favour the production of a larger amount of liquid product during pyrolysis (Abnisa *et al.*, 2013). By contrast, the FC of EFB decreased after pre-treatment and the ash content also reduced by approximately 42%-56% after washing with distilled water and H₂SO₄, but increased to 50% after washing with NaOH. After immersion in dilute acid, the ash content was reduced more than those in the

other washing medium. This result was similar to the findings of Abdullah and Sulaiman (2013) and Rahman *et al.* (2016) stating that washing using water/acid can remove potassium in biomass, which contributes to the ash reduction. However, if EFB is washed with dilute alkaline solution, the biomass tends to absorb ionic salts from the washing medium leading to an increased ash content. High ash content can reduce the CV of biomass (Xue *et al.*, 2014), as shown in Table 1. The highest CV was obtained from the EFB washed with H₂SO₄ (18.14 MJ kg⁻¹), with an ash reduction of approximately 56% from its initial raw biomass value. Contrarily, the CV of the EFB washed with NaOH was lower compared with that of unwashed EFB; mostly attributed to the higher ash content in the washed sample. These findings indicated that the presence of ash content in the feedstock will provide an indication of the CV. A biomass with high ash content will produce more char during pyrolysis (Abnisa and Wan Daud, 2014). The carbon content of EFB increased after washing, whereas the oxygen content decreased. The highest carbon content (44.8 wt.%) was obtained from the EFB washed with H₂SO₄. These two elements in the washed EFB influenced the CV; higher CV with higher carbon but lower oxygen contents (Mohamad Azri *et al.*, 2016). The TG and DTG curves (Figure 2) showed the thermal degradation behaviour of the unwashed and washed EFB at temperature ranged 30°C to 700°C. The two peaks at an approximate 280°C and 330°C in the DTG curves of all the EFB samples showed the beginning of biomass decompositions, which corresponded to the two main regimes of weight loss *i.e.* the low-temperature regime (200°C-300°C) correlated with hemicellulose decomposition, and the high-temperature regime (300°C-400°C) associated with cellulose decomposition (Rahman *et al.*, 2014; Hooi *et al.*, 2009). Their decomposition rates beyond 400°C were relatively slow, mainly attributed to lignin decomposition (Sulaiman and Abdullah, 2014). Finally, the remaining residues responsible for bio-char conversion were approximately 5-20 wt.% only from the original sample weights.

TABLE 1. PROPERTIES OF THE UNWASHED AND WASHED EMPTY FRUIT BUNCHES (EFB)

Type of sample	Proximate analysis (wt.%)				Ultimate analysis (wt.%)				Calorific value (MJ kg ⁻¹)
	Moisture	Volatile matter	Fixed carbon	Ash	C	H	N	O ^a	
Unwashed EFB	11.86 ± 0.15	70.86 ± 0.23	14.92 ± 0.40	2.36 ± 0.03	40.98 ± 0.09	6.67 ± 0.04	0.16 ± 0.01	52.19 ± 0.11	16.83 ± 0.57
Washed EFB-distilled water	6.81 ± 0.06	77.59 ± 0.35	14.23 ± 0.32	1.37 ± 0.03	44.35 ± 0.14	6.56 ± 0.08	0.07 ± 0.01	49.02 ± 0.09	17.77 ± 0.20
Washed EFB-NaOH	7.62 ± 0.01	75.94 ± 0.56	12.89 ± 0.63	3.55 ± 0.06	42.24 ± 0.06	6.47 ± 0.02	0.18 ± 0.02	51.11 ± 0.08	16.97 ± 0.08
Washed EFB-H ₂ SO ₄	6.99 ± 0.01	76.54 ± 0.20	15.43 ± 0.21	1.04 ± 0.01	44.82 ± 0.03	6.71 ± 0.02	0.34 ± 0.01	48.13 ± 0.10	18.14 ± 1.27

Note: ^aBy difference.



Note: Weight loss: — unwashed EFB, — washed EFB-distilled water, — washed EFB-NaOH, — washed EFB-H₂SO₄, derivative weight loss: - - - unwashed EFB, - - - washed EFB-distilled water, - - - washed EFB-NaOH, - - - washed EFB-H₂SO₄.

Figure 2. Weight loss and derivative weight loss curves of the unwashed and washed empty fruit bunches (EFB).

Effect of EFB Pre-treatment Using Distilled Water, H₂SO₄, and NaOH on Pyrolysis Products

The EFB without washing pre-treatment gave 47.4 wt.% bio-oil, 22.3 wt.% bio-char and 30.3 wt.% gas when pyrolysed at 500°C for 30 min. The EFB washed with H₂SO₄ showed the highest bio-oil yield (55.6 wt.%) whereas EFB washed with NaOH gave the lowest yield (24.3 wt.%) (Figure 3). The acid removed the metal ions from the pre-treated EFB, hence the reduction of ash (56%); and a markedly increased bio-oil yield while that of bio-char and gas were significantly reduced. The elements found in EFB are Al, Si, K, Cl, Cu, Zn, Fe and Mg (Loh, 2017) (Table 2). The removal of some of these metal ions during acid pre-treatment (Table 2) affected the thermal decomposition of EFB leading to change in pyrolysis products distribution (Tan and Wang, 2009). Similarly, washing EFB with distilled water had reduced the ash content (42%) in EFB (Table 1), thus resulted in an increased yield of bio-oil (52.8 wt.%). Indirectly, the reduction of ash in EFB contributed to a substantial increase in its organic yield *i.e.* the bio-oil while others like reaction water, bio-char and gas yields declined (Abdullah and Gerhauser, 2008). According to Misson *et al.* (2009), the lignin degradation is approximately 65% when the EFB is pre-treated with NaOH. Intentionally, although pre-treating EFB with NaOH could

mean greater lignin removal, leading to greater degradation of lignocelluloses into bio-oil during pyrolysis, surprisingly, the NaOH-treated EFB in this study demonstrated a lower thermal degraded product (bio-oil) (24.3 wt.%) but higher bio-char yield (36.9 wt.%) (Figure 3). This might be due to the destruction of some important lignocellulose components during NaOH pre-treatment (Misson *et al.*, 2009). This also caused a higher gas production (38.8 wt.%) as compared to other pre-treated EFB. The lowest gas yield was 28.2 wt.% from the EFB washed with H₂SO₄. Probably, the catalytic effect of metal ion such as K⁺ in the acid-washed EFB (Table 2) was lost and refrained from fragmenting the lignocellulosic polymers into monomers and forming gas, thus less gases *i.e.* CO and CO₂ were produced (Tan and Wang, 2009).

Bio-oil Characterisation

All the bio-oils in this study from the unwashed and washed EFB were obtained at the same pyrolysis conditions, *i.e.* temperature of 500°C with particle size of 107-125 μm and heating rate of 30°C min⁻¹. The MC of bio-oil ranged from 22 wt.% to 27 wt.% (Table 3), depending on the pre-treatment condition. It was found that the MC of bio-oil derived from EFB washed with distilled water, NaOH, and H₂SO₄ reduced significantly as compared to the unwashed

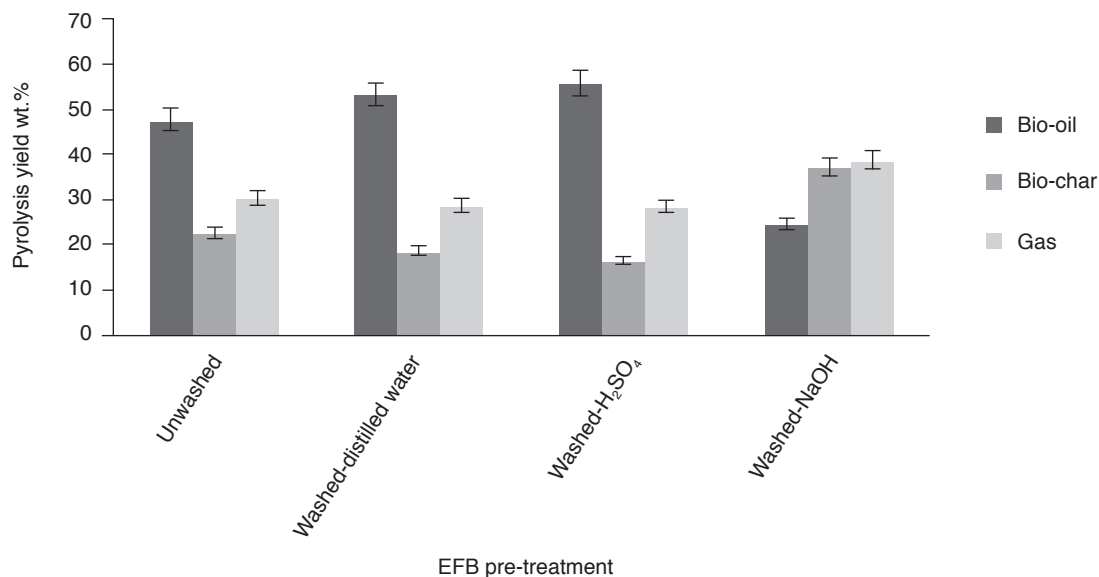


Figure 3. Product yields of different pre-treated empty fruit bunches (EFB) at pyrolysis conditions: temperature: 500°C; particle size: 107-125 μm; argon flow rate: 2.5 litres min⁻¹.

TABLE 2. ELEMENTAL CONTENT (wt. %) OF THE UNWASHED AND WASHED EMPTY FRUIT BUNCHES (EFB)

Element	Unwashed EFB ^a	Washed EFB - distilled water	Washed EFB - NaOH	Washed EFB - H ₂ SO ₄
Mg	0.13	0.08 ± 0.01	ND	ND
Al	0.26	0.37 ± 0.14	0.46 ± 0.21	1.77 ± 1.27
Si	0.66	0.36 ± 0.23	0.22 ± 0.05	ND
P	0.09	ND	ND	ND
S	0.05	0.07 ± 0.01	ND	1.51 ± 1.17
Cl	0.25	ND	0.09 ± 0.01	ND
K	2.10	3.03 ± 1.03	0.84 ± 0.16	0.04 ± 0.02
Ca	0.22	1.61 ± 0.05	ND	ND
Fe	0.12	ND	ND	ND
Cu	0.48	ND	ND	ND
Zn	0.16	ND	ND	ND
Na	ND	ND	4.36 ± 1.82	ND

Note: ^aSingle measurement. ND – not detected.
Source: ^{*}Loh (2017).

TABLE 3. PHYSICO-CHEMICAL PROPERTIES OF BIO-OILS

Type of bio-oil ^a	Physico-chemical property				
	pH	Water content (wt.%)	Total ash, (wt.%)	Density (kg m ⁻³)	Calorific value (MJ kg ⁻¹)
Unwashed empty fruit bunches (EFB)	2.4 ± 0.1	27.5 ± 1.32	0.55 ± 0.05	0.95 ± 0.02	21.5 ± 0.70
Washed EFB-distilled water	2.2 ± 0.3	21.7 ± 2.45	0.39 ± 0.10	0.92 ± 0.03	21.8 ± 0.62
Washed EFB-NaOH	3.5 ± 0.1	24.5 ± 3.35	0.42 ± 0.08	0.96 ± 0.03	19.4 ± 0.52
Washed EFB-H ₂ SO ₄	3.7 ± 0.1	23.7 ± 1.14	0.67 ± 0.05	0.94 ± 0.02	22.5 ± 0.80

Note: ^aObtained at temperature of 500°C with particle size of 107-125 μm and heating rate of 30°C min⁻¹.

EFB with the highest MC. The MC in bio-oils mainly originated from the >20% initial water in the feedstock used which was then retained through condensation during pyrolysis and other secondary reactions affected by the process parameters. As the water present in bio-oil commonly reduces the

viscosity and CV of the bio-oils produced (Zhang *et al.*, 2007), the energy density of the fuel will be lowered, thereby causing ignition difficulties. The pH of the bio-oils ranged from 2.2 to 3.7, with the highest (3.7) obtained when the EFB washed with H₂SO₄ was used as a feedstock. The result obtained

corresponded well with published data (Czernik and Bridgwater, 2004), indicating that the bio-oil contains substantial amounts of organic acids, mostly acetic and formic acids, which lower the bio-oil pH (2-3). The presence of acids in the bio-oil causes corrosiveness to the materials used during storage and application. The low pH also makes bio-oil considerably unstable. The density of bio-oils from the washed and unwashed EFB ranged from 0.92 kg cm⁻³ to 0.96 kg cm⁻³, thus indicating that the washing technique employed in this study did not affect the bio-oil density. According to Mohamad Azri *et al.* (2009), density is a fundamental physical property that can be used in combination with other properties to characterise the mass and volumetric energy density of bio-oil products relative to petroleum liquids. The ash content in the bio-oils ranged from 0.39 wt.% to 0.67 wt.% which was much reduced compared to that in the feedstock. Ash represents the residue after the combustion of a fuel. A high ash content in liquids fuels such as bio-oil can cause high wear in pumps and injectors, deposits and corrosion in combustion equipment due to the presence of alkali metals in ash (Mohamad Azri *et al.*, 2016). The CV of bio-oils ranged from 19 MJ kg⁻¹ to 23 MJ kg⁻¹, with the highest obtained from the EFB washed with H₂SO₄. This range of CV was remarkably lower than that of conventional fuel oils, such as gasoline (47 MJ kg⁻¹), diesel fuel (43 MJ

kg⁻¹), and petroleum (42 MJ kg⁻¹) (Sensöz *et al.*, 2000). Probably, the combined effect of high MC and high oxygen content had resulted in the poorer CV of the bio-oils. The presence of oxygenated compounds in bio-oil, as elucidated by the FTIR (Figure 4 and Table 4) e.g. the phenol (3200-3400 cm⁻¹), carboxylic acid (1650-1750 cm⁻¹) and esters (1000-1100 cm⁻¹), could have lowered the CV of the produced bio-oil. These potential specialty chemicals (fine chemicals) should be extracted before the bio-oils are used as a fuel (unpublished data).

Bio-char Characterisation

The bio-char properties, including those obtained from the proximate and ultimate analyses and calorific value, are presented in Table 5. The VM and FC were in the range of 44 wt.%-49 wt.% and 27 wt.%-39 wt.%, respectively. The ash content of bio-char ranged from 8 wt.% to 15 wt.% due to the inherited amounts in the raw material; the highest from the bio-char derived from the NaOH-washed EFB. Conversely, the bio-char from the EFB washed with distilled water contained the lowest ash (8 wt.%). The resulting ash could influence the bio-char properties, especially the CV to a certain extent but was not as great as the MC in influencing the CV of the bio-oil. The CV of bio-char from the unwashed and washed EFB was in the range of 20-25 MJ kg⁻¹.

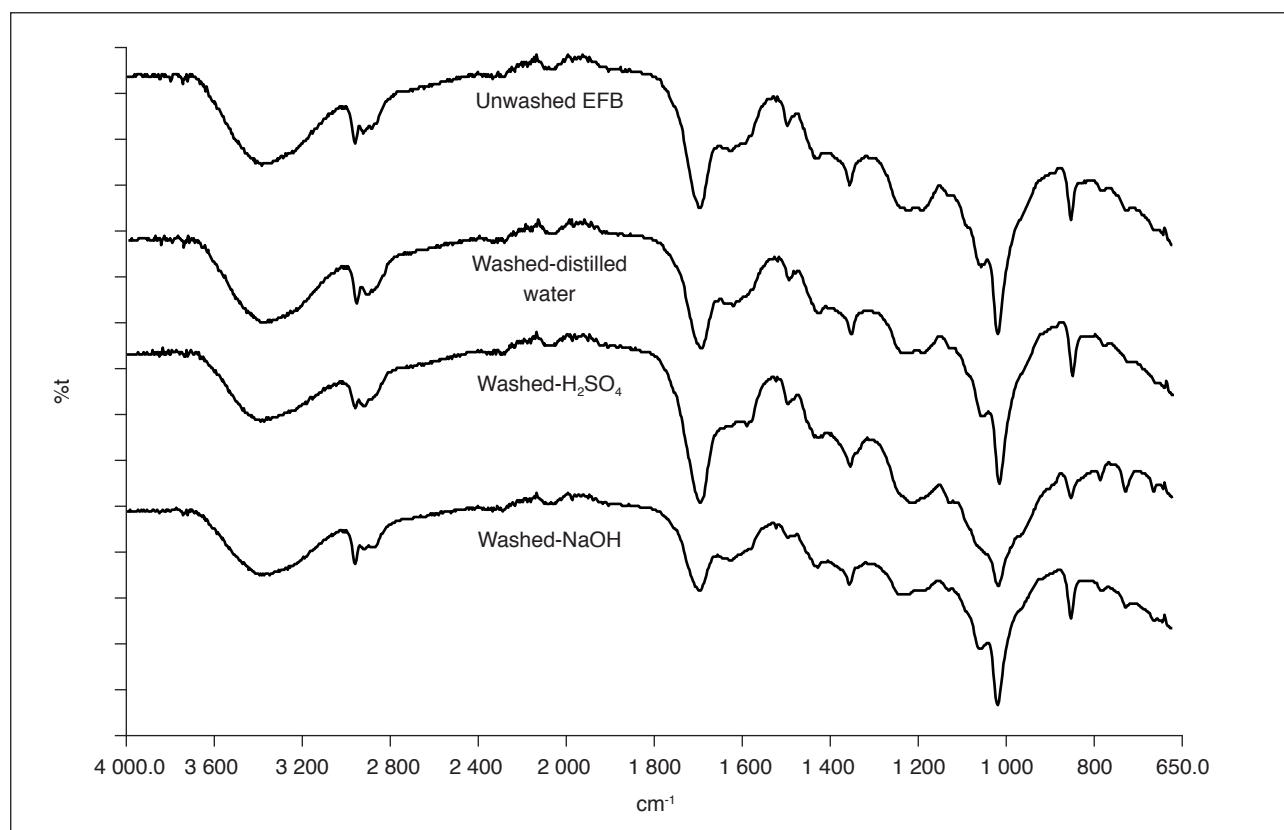


Figure 4. Fourier transform infrared spectroscopy (FTIR) spectra of bio-oils obtained through fast pyrolysis of the unwashed and washed empty fruit bunches (EFB).

TABLE 4. FTIR ABSORPTION BANDS AND FUNCTIONALITIES OF BIO-OILS

Wavenumber (cm ⁻¹)	Functional group	Compound
3 400-3 200	O–H stretching	Phenols, alcohols, and acids
3 000-2 800	C–H stretching	Alkenes
1 750-1 650	C=O stretching	Ketones, aldehydes, carboxylic acids, and their derivatives
1 600-1 500	C=C stretching	Alkenes and aromatics
1 100-1 000	C–O stretching	Alcohols, esters, carboxylic acids, or ethers
950-850	C–H bending	Aromatic compounds

Note: FTIR – Fourier transform infrared.

TABLE 5. PROPERTIES OF BIO-CHAR OBTAINED FROM THE UNWASHED AND WASHED EMPTY FRUIT BUNCHES (EFB)

Type of bio-char ^a	Proximate analysis (wt. %)				Ultimate analysis (wt. %) ^b				Calorific value (MJ kg ⁻¹)
	Moisture	Volatile matter	Fixed carbon	Ash	C	H	N	O ^c	
Unwashed EFB	7.13 ± 0.08	43.59 ± 1.22	38.64 ± 2.32	10.64 ± 0.10	69.69	4.11	2.95	23.25	24.34 ± 0.81
Washed EFB-distilled water	8.35 ± 0.06	46.12 ± 2.48	37.70 ± 0.66	7.83 ± 0.08	74.75	4.15	2.74	18.36	24.76 ± 0.55
Washed EFB-NaOH	9.78 ± 0.11	48.72 ± 1.36	26.55 ± 1.17	14.95 ± 1.21	59.72	3.09	2.96	34.23	20.33 ± 0.62
Washed EFB-H ₂ SO ₄	8.95 ± 0.09	45.63 ± 2.20	36.23 ± 0.55	9.19 ± 0.15	65.60	2.50	2.79	29.11	23.89 ± 0.60

Note: ^aObtained at temperature of 500°C with particle size of 107–125 µm and heating rate of 30°C min⁻¹. ^bSingle measurement.

^cBy difference.

Similar to the bio-oil, the bio-char obtained from the EFB washed with NaOH exhibited a much lower CV compared with those bio-chars derived via different EFB washing approaches. The highest CV was observed in the bio-char from the EFB washed with distilled water, whereas the lowest value from the EFB washed with diluted alkaline. The carbon in bio-char ranged from 60 wt.% to 75 wt.%, with the highest from the EFB washed with distilled water. The oxygen content of bio-char ranged from 18 wt.% to 34 wt.%, with the lowest from the EFB washed with distilled water. In particular, the bio-char produced had much higher CV than the bio-oil, hence a better fuel. This together with higher carbon and lower oxygen contents of bio-char are desirable as a solid fuel. In this study, distilled water can serve as a good washing medium for EFB pre-treatment to get rid of the cumbersome ash inferior for biomass thermal conversion.

CONCLUSION

The unwashed and washed EFB with particle size of 107-125 µm were pyrolysed at an optimum temperature *i.e.* 500°C. The EFB washed with H₂SO₄ with a reduced ash content gave the maximum bio-oil yield (55.6 wt.%) while that washed with NaOH with an increased ash content produced the highest amount of bio-char (36.9 wt.%) and gas (38.8 wt.%). The pre-treated EFB with distilled water could be a potential and practical source to get the most pyrolysis product yields and quality. Other pre-treatment methods employed could also be promising but are more costly, affecting both

the upstream and downstream operation. The produced bio-oil showed moderate CV ranging from 19 MJ kg⁻¹ to 23 MJ kg⁻¹ and contained many chemical constituents that could be valuable as specialty chemicals. The bio-char exhibited a high carbon content (60 wt.%-75 wt.%) and a much higher CV (20-25 MJ kg⁻¹) than those of the bio-oil. In future, an integrated fuel (bio-oil, bio-char and gaseous products harnessing) and chemical (bio-oil) production through pyrolysis would be one of the potentially feasible solutions for the management of oil palm biomass.

ACKNOWLEDGEMENT

The authors would like to thank the Director-General of MPOB for permission to publish the article.

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