Production of Bio-oil from Fast Pyrolysis of Oil Palm Biomass using Fluidised Bed Reactor

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Abstract

Biomass is a renewable resource that can potentially be used to produce biofuels via the fast pyrolysis process. Oil palm biomass are a rich biomass resource in Malaysia, and it is therefore very important that they be utilized for more beneficial purposes, particularly in the context of the development of biofuels. The use of this pyrolysis technique can significantly contribute to reduce the biomass volume because more biomass can be consumed as raw material for bio-oil production. In this study, the thermal conversion of oil palm biomass via fast pyrolysis was carried out using a fluidised bed reactor. Several process parameters i.e types of oil palm biomass, pyrolysis temperature and particle size that can affect the yield of the pyrolysis products were investigated. EFB, trunk, frond and palm kernel shell (PKS) were used to investigate the effect of different oil palm biomass on pyrolysis products. The temperature used was in the range of 400-600 ℃ and particle size of EFB was < 90 – 180 µm. The results indicated that the optimum yield of bio-oils (47.4 wt.%) was obtained using EFB having a particle size of 107-125 µm at pyrolyzed temperature of 500 ℃. The bio-oil and bio-char produced were characterized via physicochemical and spectrometric analyses. The calorific values of bio-oil ranged from 21 to 22 MJ kg^{-1} while that of bio-char 22-25 MJ kg^{-1}.

Keywords: Pyrolysis, oil palm biomass, bio-oil, bio-char, renewable energy

1. Introduction

The various researches conducted on biomass fuels have indicated that vegetable oil is one of the most promising renewable sources (Song et al., 2014). In fact, it is a simple product of solar energy. When Rudolf Diesel first developed the engine bearing his name in 1895, he intended to use fuels like vegetable oils rather than petroleum to run the engine. Later on, the vegetable oil was chemically modified and thus the born of first generation biofuels. Besides, other forms of biomass such as lignocellulosic materials also have potential as a feedstock to produce alternative fuel. Fuels derived from lignocellulosic materials are referred to as second generation biofuels.

In recent years, second generation biofuel technologies have been gradually developed and become more attractive than first generation biofuels although the latter are better established (Salema and Ani, 2012). The threshold being biofuel production using vegetable oil must not jeopardize and threaten food supplies and biodiversity. Besides, they are not cost competitive compared to fossil fuels and more importantly, some of them have lifecycle emissions exceeding those of conventional fossil fuels. The palm oil industry generates an abundance of oil palm biomass as a potential lignocellulosic feedstock for the production of second generation biofuels. For 100.45 million tonnes of fresh fruit bunches (FFB) processed in 2014, the amount of empty fruit bunches (EFB) was more than 7.73 million tonnes. Second generation biofuels derived from oil palm biomass via pyrolysis might be a better approach compared to the conventional and first generation fuels in terms of sustainability, affordability and environmental-friendliness (Salema and Ani, 2012).

Fast pyrolysis is a thermal decomposition process that occurs at moderate temperature in which the biomass is rapidly heated in the absence of oxygen or air (Jahirul et al., 2012). It is mainly used for optimizing the liquid product at the high heating rate and heat-transfer rate conditions using finely ground biomass feed to minimize moisture content in the bio-oil (Abnisa et al., 2011a). The fast pyrolysis is one of the most recently employed processes which could promise higher liquid yields with a minimum of gas and char under carefully controlled processing environment. For example, when woody feedstock is pyrolysed at around 500 ℃ with short vapour residence time, the bio-oil yield of around 70 wt.% and char and gas yields of around 15 wt.% each are attainable

(Abdullah and Gerhauser, 2008).

Many researchers have studied on fast pyrolysis where the liquid product is of main interest since it offers a flexible and attractive way to produce biofuel and fine chemicals (Abdullah *et al.*, 2010). Abnisa *et al.*, (2013) carried out the fast pyrolysis of oil palm trees residues in a fixed bed reactor. The maximum bio-oil yield was 43.5 wt.% at the pyrolysis temperature of 500 °C using a sweep gas flow rate of 2 L min^{-1} and reaction time of 60 min. The liquid product may be used as a source of low-grade fuel directly, or upgraded as a higher quality liquid fuel. Similarly, a fast pyrolysis on Linseed with particle size of >1.8 mm showed the highest liquid yield of 68.8 wt.% at a final pyrolysis temperature of 550 °C under a nitrogen flow rate of 100 cm^3 min^{-1} (Acikgoz and Kockar, 2007).

Rahman *et al.*, (2014) carried out fast pyrolysis of oil palm fronds in fixed bed reactor. They investigated the effect of pyrolysis temperature on product yields. Based on the results, the maximum bio-oil yield was 47.4 wt.% at 400 °C. Meanwhile, Jeong *et al.*, (2015) studied fast pyrolysis of swine manure at various temperatures using bubbling fluidized bed reactor. The maximum bio-oil yield was 18.5 wt.% at the pyrolysis temperature of 600 °C.

Kim *et al.*, (2013) studied fast pyrolysis of palm kernel shell (PKS), EFB and Jatropha seedshell cake (JSC) using a fluidized bed reactor. The aims of their work were to investigate the yields and properties of pyrolysis products produced from different feedstock and to identify the optimum pyrolysis temperature and gas flow rate for obtaining the highest bio-oil yields. They found that EFB showed the highest bio-oil yield of 36.5 wt.% compared to PKS and JSC of 30.3 and 27.2 wt.%, respectively. This reported bio-oil yield was consistent with that reported by Abdullah *et al.*, (2010) and Sulaiman and Abdullah, (2011).

In this study, oil palm biomass was pyrolysed under different conditions in a fluidized bed reactor to determine the most appropriate operational conditions. The products obtained were characterised for their chemical and physical properties using several established test methods.

2.   Material and Methods

2.1 Materials:

The EFB was collected from a palm oil mill located in Padang Jawa, Klang. It was milled and sieved using a test sieve shaker and then separated into several different fractions consisting of particle size ranging from <90 to 250 µm. The resulting particles were dried at 103 ºC for 24 h until constant weight was achieved. The oil palm trunk, frond and PKS were taken from oil palm plantation and palm oil mill located in Negeri Sembilan, Malaysia. The particle size of trunk, frond and PKS used was 107-125 µm. Hexane, ethanol and concentrated sulfuric acid H_2SO_4 (minimum purity 99.99%) were of analytical grade from Fisher Scientific Sdn. Bhd.

2.2 Fast Pyrolysis Experiment:

The fast pyrolysis of oil palm biomass was carried out using a fluidised bed reactor. An electric furnace heated the reactor with a heated length of 135 mm and an inner diameter of 40 mm. The temperature of the reactor was determined by inserting a thermocouple to the upper fritz as near as possible. The whole experimental rig consisting of the volatiles and gas collection system is illustrated in Fig. 1. Argon gas was used as an inert gas to purge air from inside the reactor. Moreover, Argon was also employed to sweep the vapor products from the reactor into the bio-oil collectors. The sand bed was fluidised using argon at rate of 0.5 L min^{-1}. 100 g zircon sand of 180 – 250 µm was used as the sand bed. For each experiment, 5 g of EFB feedstock was placed in the glass tube and fed into the reactor using argon at rate of 2.5 L min^{-1}. The feeding system consists of two screw feeders. The first screw feeder runs at lower speed for quantitatively feeding, meanwhile the second screw feeder runs at higher speed for un-plugging feeding.

The whole experiment must be held for either a minimum of 20 min or until no further significant release of smoke was observed. The connection tubes between the reactor and the cooling system were heated using heating tape 100 ±2 ^{0}C to avoid condensation of vapors during pyrolysis.
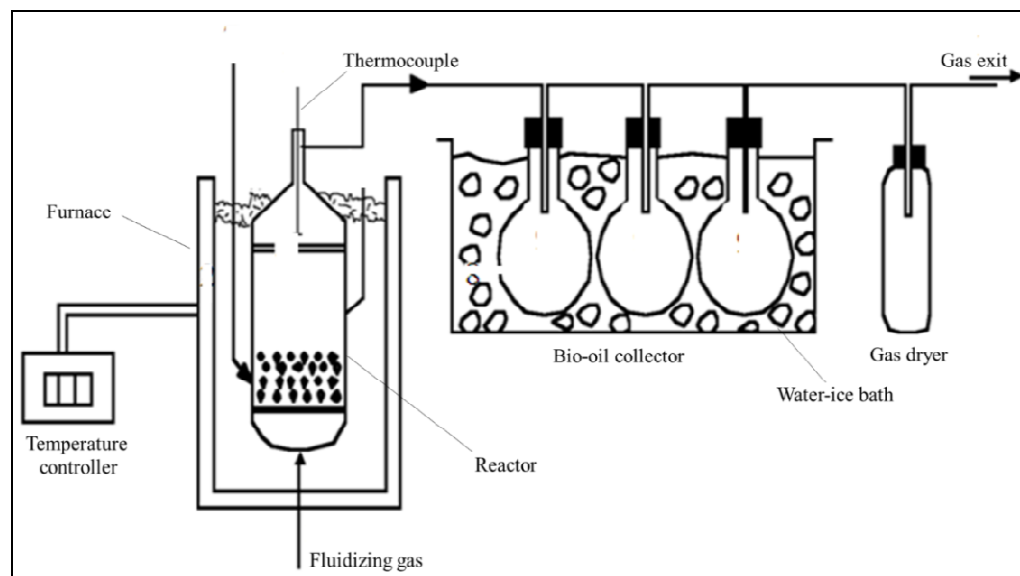
Figure 1.   Schematic Diagram of the Pyrolysis System

The reactor was weighed before the experiment started. After a run, the cooled reactor was weighed again to determine the char yield from the difference in the weight of reactor before and after used. The char remaining in the reactor was elutriated by introducing Argon to the sand bed at rate of 5 – 10 L min^{-1}. The bio-oil was collected in a series of flask placed in a cold trap containing ice. The bio-oil accumulated in the flask was transferred to a small bottle and the remaining liquid product retained in the flask and in all the connection tubes were dissolved with ethanol. The solvent from the bio-oil was removed in a rotary evaporator and the quantity of the bio-oil was then established. The bio-oil comprised a dark liquid was weighed. The yields of bio-oil and bio-char were calculated using Equation 1.

Product yield (bio-oil/bio-char) (wt.%) = X_1 / X_0 x 100%   (1)

where, X_1 is the mass of desired product (bio-oil/bio-char) (g) and X_0 is the initial mass of the raw material (g).

The gas released from the pyrolysis process was intermittently trapped in a gas bottle as the temperature of the pyrolysis was increased. Finally, the yield of the gas was calculated by the difference between the percentage of bio-oil and bio-char and the total of 100%. Each experiment was repeated three times and the average value of each parameter was calculated.

The first series of experiment was performed to study the effect of different type of oil palm biomass on the pyrolysis products. The oil palm biomass used were EFB, trunk, frond and PKS. For each experiment, 5 g of oil palm biomass was introduced into the sand bed at 500 °C and the particle size of oil palm biomass was 107-125 µm.

The second series of experiment was performed to determine the effect of the pyrolysis temperature on pyrolysis yields. For each experiment, 5 g of feedstock were sieved to the range of particle size of 107-125 µm and placed in the reactor. The experiments were conducted at different temperatures i.e 400 ºC, 450 ºC, 500 ºC, 550 ºC and 600 ºC. The experiment was conducted using the optimized conditions obtained from the first series of experiment.

The third series of experiment was performed to investigate the effect of particle size on pyrolysis products. These experiments were conducted using four different ranges of particle size, namely < 90, 91-106, 107-125 and 126-150 µm at 500 °C. The experiment was conducted using the optimized conditions obtained in this study.

2.3 Characterisation of EFB:

The proximate analysis of EFB was conducted to determine the moisture content, volatile matter, fixed carbon and ash content. The moisture content was determined according to ASTM E871-82. The fixed carbon and ash contents were determined according to ASTM D3174-89 and ASTM D1102-84, respectively. The volatile matter was estimated by difference between the percentage of fixed carbon, moisture and ash content and the total of 100%. The gross calorific value (CV) of EFB was determined using a bomb calorimeter, Leco AC-600 according to ASTM D5865-07. The carbon, hydrogen and nitrogen contents of EFB were determined using a CHN Analyzer (Leco, CHN 268) according to ASTM D5373.

2.4 Characterisation of Bio-oils:

The water content of the bio-oils was obtained by Karl Fischer titration method. The carbon, hydrogen and nitrogen contents of bio-oils were determined using a CHN Analyzer (Leco, CHN 268) according to ASTM D-5373. The CV of the bio-oils was determined using a bomb calorimeter, Leco AC-600 according to ASTM D-240. The pH of the bio-oils was measured by a pH meter (Eutech Instruments, pH Tutor).
The density of bio-oils was determined using Digital Density Meter, type DE 40 according to ASTM D-4052. The total acid value was determined by using Pontentiometric Titration, 702 SM according to ASTM D-664. 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 an ash by heating in a furnace at 775 °C for 20 min, followed by cooling and weighing. The functional groups of the bio-oils were detected using Fourier Transform Infra-Red (FTIR) Spectroscopy, Magna-IR550 (Nicolet, Madison). A small amount of the bio-oils was mounted on a potassium bromide (KBr) disc that was previously scanned as a background.
The GC/MS analysis of the bio-oil was performed with Agilent Technology 6890-N equipped with a SGE BPX5 column and MSD detector, using 30x250x0.25 mm capillary column to separate various organic compounds that were formed during the pyrolysis process. The starting temperature of the oven was 35 °C. It was held for 2 min before the temperature was increased to 250 °C at a rate of 20 °C min^{-1} and held at this temperature for 20 min. The injector port temperature and the detector temperature were set at 280 °C. The spectra obtained was identified and characterised via the MS search libraries (Wiley7n.L and NIST98.L).

2.5 Characterisation of Bio-char:
The CV of the bio-char was determined using a bomb calorimeter, Leco AC-600 according to ASTM D5865-07. The carbon, hydrogen and nitrogen contents of bio-oils were determined following the ASTM D5373 using a CHN Analyzer (Leco, CHN 268). The physical properties of the char relating to specific surface area and total pore volume were measured based on their nitrogen adsorption-desorption isotherms at –196 °C using an Accelerated and Porosimetry System (ASAP 2010, Micromeritics USA). Brunauer-Emmet-Teller (BET) surface area, S_{BET} was calculated using the adsorption data in relative pressure ranging from 0.05 to 0.20. The total pore volume, V_T was assessed by converting the amount of nitrogen gas adsorbed (expressed in cm^3 g^{-1} at standard temperature and pressure) at relative pressure of 0.97 to the volume of liquid adsorbate. The analytical method consisting of three steps i.e. dehydration of samples, degassing of sample under low vacuum pressure and nitrogen gas adsorption at –196 °C.

3. Results and Discussion

3.1 Fast Pyrolysis Experiment:

In Fig. 2, EFB pyrolysed at 500 ºC gave the highest bio-oil yield (47 wt.%) while the lowest from PKS (18.9 wt.%). The yields of bio-oil for trunk and frond were 29.4 wt.% and 25.7 wt.%, respectively. The highest bio-char yield was obtained from PKS (55.3 wt.%) and the lowest from trunk (16.8%). The highest and lowest yield for the gas were 53.9 wt.% and 25.9 wt.% from trunk and PKS, respectively. The differences among the bio-oil yields (Fig.2) from the four types of oil palm biomass used might be attributed to their different chemical compositions (Table 1) in the forms of cellulose, hemicellulose and lignin. The lignocellulose of oil palm biomass is polymer consisting of a large amount of monomers with O-bearing functional groups such as glucose and xylose, which generally have low thermal stability (Yang *et al*., 2006) resulting in decomposition at elevated temperature. Hence, in pyrolysis of oil palm biomass, an increase in cellulose and hemicellulose content such as in the case of EFB caused an increase in the release of volatiles (Uzun *et al*., 2007) that condensed back as liquid. On the other hand, lignin is more thermally stable, thus an increase in the lignin content such as in the case of PKS caused an increase in the char yield. As a result, the pyrolysed PKS had the highest char yield owing to its highest lignin content, while bio- oil was the lowest compared to other oil palm biomass due to its lower cellulose contents.
The various yield of the pyrolyzed products at different temperature was shown in Fig. 3. At the lowest pyrolysis temperature of 400 ºC, decomposition of oil palm biomass was relatively slow and bio-char was the major product (44.6 wt.%). As the temperature increased from 400 ºC to 500 ºC, the amount of condensable liquid product increased to a maximum of 47.4 wt.%. Similar trend was reported in pyrolyzing sugarcane bagasse (Montoya *et al*., 2014). The bio-char yield significantly decreased from 44.6 wt.% to 18.7 wt.% as the final pyrolysis temperature reached 600 ºC. The bio-char yield significantly decreased when the temperature increased most probably due to a greater primary decomposition of EFB at higher temperatures or a secondary decomposition of the bio-char residues. The gas yields increased when the temperature increased from 400 to

600 ℃ (Fig. 3). This trend was similar to the findings reported previously (Jeong *et al.*, 2015;Tsai *et al.*, 2007; Sembiring *et al.*, 2015). The gas yields increased from 32.8 wt.% to 50.1 wt.% when the temperature increased from 400 to 600 ℃, respectively (Fig. 3). Predominantly, the secondary cracking of the pyrolysis vapours at higher temperatures had taken place. In addition, the secondary decompositions of the bio-char at higher temperatures might also contribute to increased gas yield in the form of other non-condensable gas products (Sukiran *et al.*, 2014; Auta *et al.*, 2014).
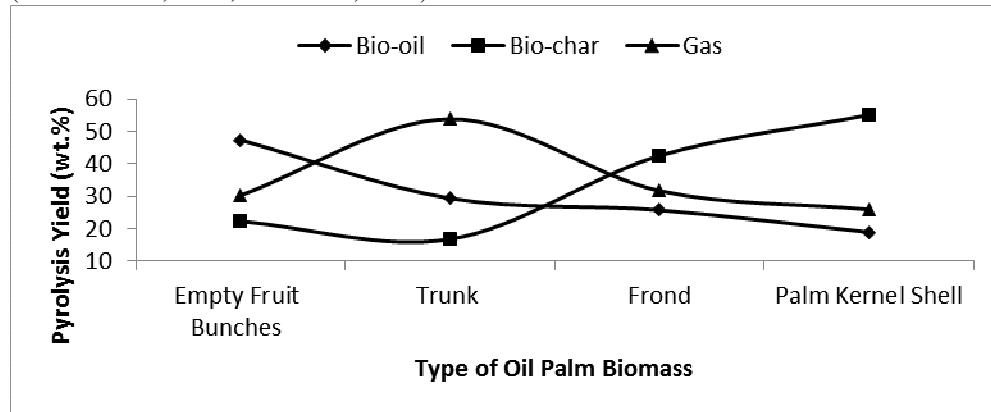

Figure 2. Yields of pyrolysis products using different type of oil palm biomass
(Remark: Temperature: 500 ℃, particle size: 107-125 µm, Argon flow rate: 2.5 L min^{-1})

Figure 4 shows the effect of particle size on pyrolysis products. When the EFB's particle size increased from < 90 to 150 µm, the pyrolysed bio-oil (49.5 wt.%) and bio-char yields (31.5 wt.%) increased to a maximum, while the gas yield decreased. The trend was similar to that reported previously (Abnisa *et al.*, 2011b). The smallest particle size of < 90 µm produced the most gas (49.1 wt.%) and the least bio-oil (32.2 wt.%) and bio-char (18.7 wt.%). These results indicated that particle size could affect the yields of the pyrolysis products. If the particle size of a biomass is sufficiently small, it can be heated uniformly; hence less char will be produced (Encinar *et al.*, 2000; Seebauer *et al.*, 1997). A particle size range of 126-150 µm seems the most suitable for a high bio-oil production in fast pyrolysis of EFB.
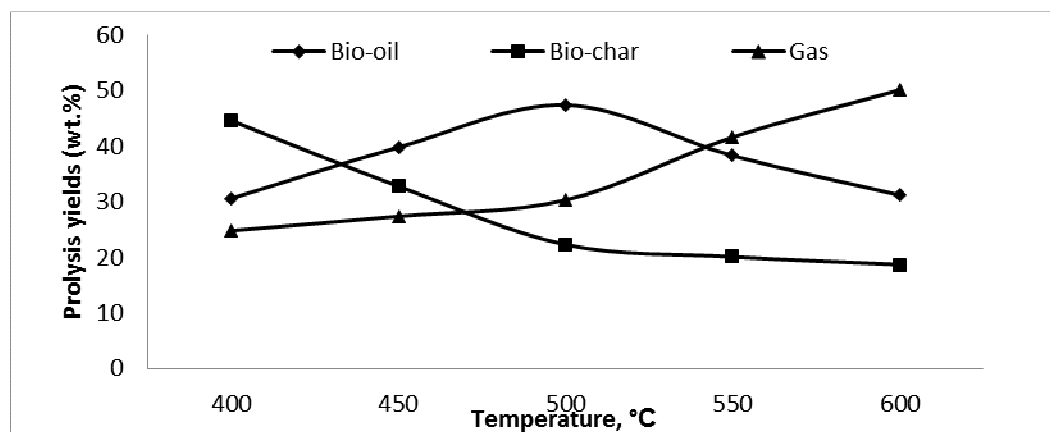

Figure 3. Effect of Temperature on Pyrolysis Yields.
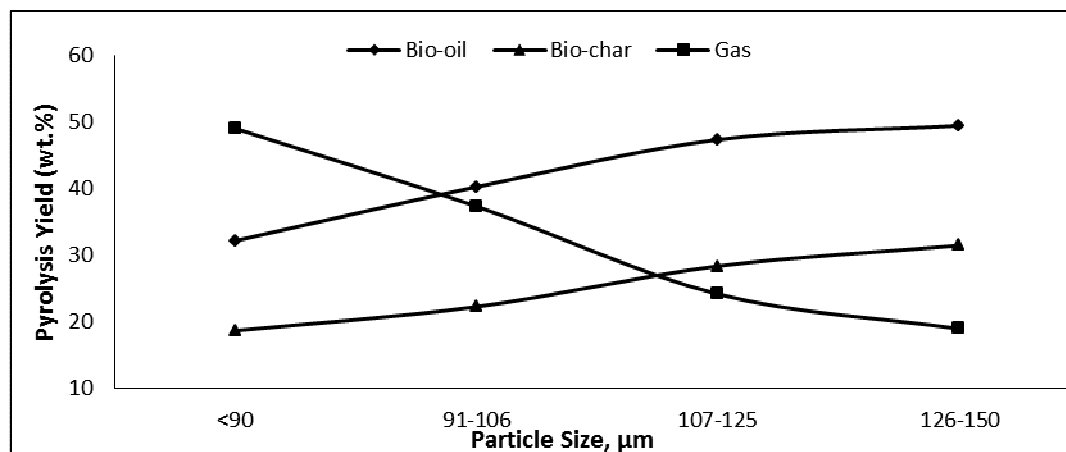(Remark: Feedstock: empty fruit bunches, particle size: 107-125 µm, Argon flow rate: 2.5 L min^{-1}).

Figure 4. Yields of pyrolysis products at various particle size
(Remark: Feedstock: empty fruit bunches, temperature: 500 ℃, Argon flow rate: 2.5 L min^{-1})

Table 1. Typical chemical compositions of different oil palm biomass

	Cellulose (% of dry matter)	Hemicellulose (% of dry matter)	Cellulose + Hemicellulose (% of dry matter)	Lignin (% of dry matter)
Empty Fruit Bunches	39.0	22.0	61.0	29.0
Trunk	59.0	10.0	69.0	11.0
Frond	42.0	21.0	63.0	23.0
Palm Kernel Shell	20.8	22.7	43.5	50.7

3.2 Characterisation of EFB:
EFB is one of the by-products from the palm oil milling process which is characterized by high carbon, oxygen and volatile contents (Table 2). The typical CV of EFB i.e 17.56 MJ kg^{-1} was generally comparable with other biomass such as olive oil residue of 15.18 MJ kg^{-1} (Uzun *et al*., 2007), birch wood of 17.02 MJ kg^{-1} (Zanzi *et al*., 2002) and rice husk of 16.79 MJ kg^{-1} (Tsai *et al*., 2007). The difference in CV is explained by the biomass's chemical composition, moisture and ash content. The volatiles, fixed carbon and ash content of EFB were 73.62 wt.%, 16.38 wt.% and 4.47 wt.%, respectively. The high volatiles in EFB indicated its vulnerability towards thermal degradation. EFB contained 48.72 wt.% of carbon, 6.69 wt.% of hydrogen, 44.22 wt.% of oxygen and 0.37 wt.% of nitrogen. A higher carbon content leads to a higher CV while high oxygen content tends to lower the CV.

Table 2. Main characteristics of EFB

Characteristic	Value
Proximate analysis (wt.%)	
Volatiles	73.62
Fixed Carbon	16.38
Ash	4.47
Moisture	5.53
Ultimate analysis (wt.%)	
Carbon	48.72
Hydrogen	6.69
Nitrogen	0.37
Oxygen[a]	44.22
Calorific value (MJ kg^{-1})	17.56

[a] By difference

3.3 Characterisation of Bio-oil:

The bio-oils obtained from EFB pyrolysed at temperature of 450, 500 and 550 ℃ with particle size of 107-125 µm were evaluated for liquid fuel properties as shown in Table 3. The moisture content of bio-oils from EFB ranged between 27% and 34% depending on the production condition. The moisture in bio-oils is originated from the trace water retained in the biomass feedstock used and also via condensation during the pyrolysis reaction. As the raw EFB used contained only 5.5% moisture (Table 2), most probably the high moisture in the derived bio-oil was due to water generation during biomass decomposition, pyrolysis vapour condensation during process cooling and water adsorption during product storage as bio-oil is highly polar and can readily absorb water up to 35 wt.% (Demirbas, 2007). The amount of water present is also dependent on the process parameters such as the extent of secondary reaction or cracking and the temperature of the gases leaving the liquid collection system. The presence of water in bio-oils is important in many ways; the higher content of water usually reduces viscosity and improves stability but at the same time reduces the CV of the bio-oils produced (Zhang *et al.*, 2007), and this will lower the energy density thus causing ignition difficulties.

The pH of the bio-oils ranged between 2.2 and 3.0. The result obtained corresponded well with the published data (Czernik and Bridgwater, 2004), indicating that bio-oil contained substantial amount of organic acids, mostly acetic acid and formic acids that lower the pH (2 – 3) of the bio-oil. The presence of acids in the bio-oil is the main reason to account for its corrosiveness to materials during the storage and application process. The low pH of bio-oils makes bio-oil extremely unstable.

The total acid number of the bio-oils was high, 69-84 mg KOH g^{-1}. The presence of acids in bio-oils was probably due to the degradation of hemicellulose in biomass. Fast pyrolysis-based bio-oils typically contains 3-6 wt.% volatile acids, with the main compounds being acetic and formic acids. Other groups of compounds in bio-oil that influence acidity include phenolics and fatty, resin and hydroxy acids (Oasmaa *et al.*, 2010).

The CV of bio-oils ranged from 21 to 22 MJ kg^{-1} which was much lower than that for conventional fuel oil such as gasoline (47 MJ kg^{-1}), diesel fuel (43 MJ kg^{-1}) and petroleum (42 MJ kg^{-1}), but higher than bio-oil from corn stover, 17.51 MJ kg^{-1} (Table 3) (Sensoz et al., 2000). The lower CV of bio-oil was mainly due to the presence of oxygenated compounds in bio-oil as evidenced by the FTIR (Fig. 5). The high water content in combination with a high O/C atomic ratio gave poor CV of the bio-oils. Interestingly, there was no significant effect of temperature on the CV of bio-oil (Table 3).

The ash content in the bio-oils ranged from 0.38 to 0.55% which was lower compared to ash content in bio-oil from slow pyrolysis (0.65%) (Sukiran *et al.*, 2009). The density of bio-oils ranged between 0.88 and 0.95 g cm^{-3}. Ash content represents the residue after combustion of a fuel. 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 (Oasmaa & Peacock, 2001). Density is a fundamental physical property that can be used in conjunction with other properties to characterise the mass and volumetric energy density of the bio-oil products relative to petroleum liquids.

Table 3. Characteristics of bio-oils obtained at different pyrolysis temperature

Property	Temperature (℃)		
	450	500	550
1. Calorific Value (MJ kg^{-1})	20.54	21.50	21.64
2. Total Ash (%)	0.41	0.55	0.38
3. pH	3.0	2.4	2.2
4. Moisture (%)	30.12	27.45	34.15
5. Total Acid (mg KOH g^{-1})	84.11	72.58	68.96
6. Density (g cm^{-3})	0.88	0.95	0.90
7. Ultimate analysis (wt.%)			
Carbon	35.28	47.77	56.29
Hydrogen	5.67	6.69	6.77
Oxygen[a]	57.64	43.86	35.38
Nitrogen	1.41	1.68	1.56
H/C molar ratio	1.93	1.68	1.44
O/C molar ratio	1.23	0.69	0.47
Empirical formula	$CH_{1.93}O_{1.23}N_{0.03}$	$CH_{1.68}O_{0.69}N_{0.03}$	$CH_{1.44}O_{0.47}N_{0.02}$

[a] By difference

The carbon content in the bio-oil increased as the reaction temperature was increased up to 550 ^{0}C (Table 3). This trend was similar to that reported previously (Jeong *et al.*, 2015). The average carbon content for bio-oils produced at temperature ranged from 450 - 550 ^{0}C was 46 wt.%. The oxygen content of the bio-oil varied in the range of 35-58 wt.%. The significant decrease in the oxygen content (35 wt.%) of the bio-oil derived from pyrolysis at 550 ^{0}C (Table 3) compared to the original feedstock (raw EFB) was favourable, since high oxygen content would lower the CV and was immiscible with hydrocarbons, hence was not desirable as a transport fuel (Sensoz *et al.*, 2006). The high oxygen content also showed that lots of oxygenated compounds were present in the bio-oil as shown in the FTIR spectra (Fig. 5). The presence of reactive oxygen-containing compounds has a major contribution to the inherent instability of the bio-oils. The instability of bio-oil will cause an increase in viscosity over time or "ageing" especially when heated. Ageing reactions produce water which might lead to the separation of an aqueous phase when the total water content of bio-oil exceeds 30 wt.% (Lehto *et al.*, 2013).

In Fig. 5, the O-H stretching vibrations between 3200 and 3400 cm^{-1} indicated the presence of phenol and alcohols. The C-H stretching vibrations between 2800 and 3000 cm^{-1} and C-H deformation vibrations between 1200 and 1400 cm^{-1} indicated the presence of alkanes. The C=O stretching vibrations between 1650 cm^{-1} and 1750 cm^{-1} showed the presence of ketones, aldehydes, carboxylic acids and their derivatives. The absorbance peaks between 1500 cm^{-1} and 1600 cm^{-1} represented C=C stretching vibrations indicative of alkenes and aromatics. Absorption possibly due to C-O vibrations from carbonyl components (i.e alcohols, esters, carboxylic acids or ether) of the bio-oil occurred between 1000 cm^{-1} and 1200 cm^{-1}. Absorbance peaks between 700 and 750 cm^{-1} indicated the possible presence of single, polycyclic and substituted aromatic groups. The FTIR spectra (Fig. 5) showed that bio-oil can be upgraded by extracting some of these valuable oxygenated compounds as bio-chemicals.
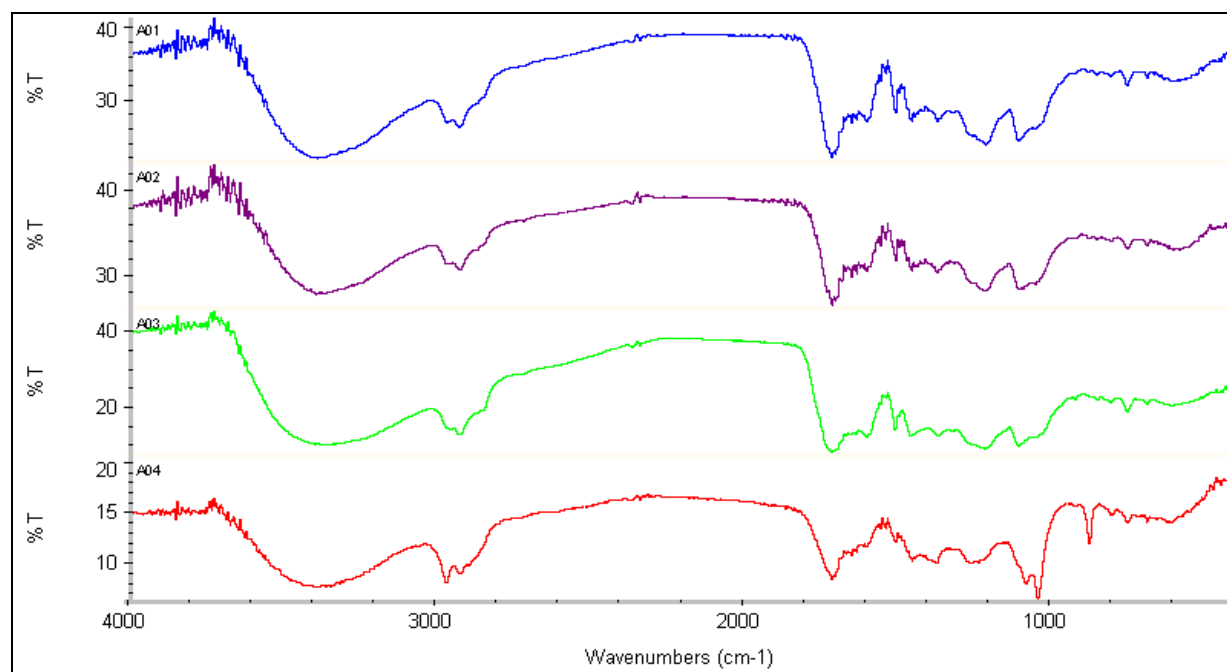

Figure 5. FTIR Spectra of Bio-oil at Different Temperature (A01 = 400 ºC, A02 = 450 ºC, A03 = 500 ºC and A04 = 550 ºC)

The GC-MS showed that phenol was dominated in the bio-oil (area percent, 15.91%) followed by furfural (10.68%) and butanoic acid (8.56%) (Table 4). This finding showed that the chemical compositions of the EFB-derived bio-oil in this study were consistent with that of other reported bio-oils using similar feedstock (Khor *et al.*, 2009). The presence of aromatic and oxygenated compounds in EFB-derived bio-oil was attributed to its biopolymer textures - cellulose and hemicellulose - containing xylan and glucose that underwent cleavage and structural transformation during thermal decomposition and degradation (Tsai et *al.*, 2007).

Table 4. Chemical compounds of bio-oil* derived from empty fruit bunches according to the GC/MS analysis.

Peak No.	Possible Chemical Compound	Area % (Retention Time)
1	2H-Pyran, 3,4-dihydro-	4.97 (3.81)
2	Phenol	15.91 (4.23)
3	2- Cyclopenten-1-one, 2-hydroxy-	3.16 (4.67)
4	Phenol, 2-methoxy	4.30 (5.17)
5	1,2 Benzenediol	5.27 (5.96)
6	Phenol, 2,6-dimethoxy-	5.50 (7.13)
7	Phenol, 2, 6-dimethoxy-4- (2-propenyl)-	1.37 (9.31)
8	Butanoic acid, 3-methyl	8.56 (1.46)
9	Butanal, 2-methyl	2.33 (2.65)
10	Furfural	10.68 (3.13)
11	Furan, tetrahydro-2, 5-dimethoxy	2.06 (3.36)
12	2,5-Dimethoxytetrahyrdofuran	2.01 (3.51)
13	2 (3H)-Furanone, 5-methyl	6.36 (3.85)
14	Phenol, 2-methyl	2.72 (4.85)
15	Phenol, 4-methyl	3.38 (5.02)
16	1,2-Benzenediol, 3-methoxy	1.34 (6.50)
17	Dehydroacetic acid	1.65 (7.74)

Remark: *Obtained at temperature of 500°C and particle size of 107-125 μm (optimum condition).

3.4 Characterisation of Bio-char:

The CV of bio-char produced from different temperature ranged from 22 to 25 MJ kg^{-1} (Table 5). Unlike bio-oil, the CV of bio-char at 450 ^{0}C was significantly different compared with the other two bio-char products at higher temperatures. The bio-char at pyrolysis temperature of 450 ºC showed the highest CV (24.85 MJ kg^{-1}) probably due to a complete charring process to reach solidification stage within the bio-char. The other two bio-char products underwent carbonization at higher temperature which might affect the development of a porous structure in the bio-char (Guo and Chong Lua, 1998). This was supported by the resulting highest surface area (5.21 m^2 g^{-1}) and total pore volume (0.02 cm^3 g^{-1}) in bio-char at 450 ºC. The surface area decreased to 4.74 and 3.52 m^2 g^{-1} with increased pyrolysis temperature to 500 and 550 ^{0}C, respectively. This trend was similar to that reported previously (Paethanom and Yoshikawa, 2012). The percentage of carbon in bio-char ranged from 70 – 72 wt.% with the highest (72 wt.%) attainable at pyrolysis temperature of 550 ºC. The oxygen content of bio-char ranged from 21 –23 wt.% with the highest (23 wt.%) at pyrolysis temperature of 500 ºC (Table 5). The elemental compositions i.e. H/C molar ratio, O/C molar ratio and empirical formula of the bio-char according to different temperatures (450 ºC, 500 ºC and 550 ºC) were shown in Table 5. The H/C ratios of bio-char ranged 0.66 to 0.71, whereas the O/C ratios in the range between 0.22 and 0.25. It is well established that high carbon but low oxygen contents of bio-char is desirable for it to be used as a solid fuel. This study showed that 550 ºC was the optimum temperature to produce bio-char with the highest C/O ratio as a suitable solid biofuel.

Table 5. Characteristics of biochar product according to different temperature

Property	Temperature (°C)		
	450	**500**	**550**
1. Calorific Value (MJ kg^{-1})	24.85	22.75	22.43
2. Ultimate analysis (wt.%)			
Carbon	70.52	69.69	72.33
Hydrogen	3.89	4.11	4.06
Oxygen[a]	22.18	23.25	21.22
Nitrogen	3.41	2.95	2.39
H/C molar ratio	0.66	0.71	0.67
O/C molar ratio	0.24	0.25	0.22
Empirical formula	$CH_{0.06}$ $O_{0.24}N_{0.04}$	$CH_{0.71}$ $O_{0.25}N_{0.04}$	$CH_{0.67}$ $O_{0.22}N_{0.03}$
3. Surface Area ($m^2 g^{-1}$)	5.21	4.74	3.52
4. Total pore volume ($cm^3 g^{-1}$)	0.02	0.01	0.01

[a] By difference

4. Conclusions

In pyrolysing oil palm biomass at optimum conditions i.e. 500 ℃ and particle size of 107-125 µm, EFB gave the maximum bio-oil yield whereas that of PKS and trunk produced the most char and gas. As a result, 1 tonne of EFB could produce about 474 kg of bio-oil, 223 kg of bio-char and 303 kg of gas at optimum conditions. The produced bio-oil had moderate CV ranged from 21 to 22 MJ kg^{-1} and contained a lot of chemical constituents which were valuable as specialty chemicals. The produced bio-char was higher in carbon content (68-70 wt.%) and CV (22 to 25 MJ kg^{-1}) compared to the bio-oil, thus was a better fuel.

At the evaluation and the employment of the bio-oil as a fuel, the following options should be recommended. Crude bio-oil derived from empty fruit bunches maybe combusted in existing fuel burning systems or as a mixture with other fuel-oils as it has good fuel characteristics. Its low nitrogen content is quite promising for its evaluation as fuel from the view point of environmental pollution. Besides that, bio-oil may be used as a raw material in fractioning processes for obtaining specific fuels. By its distillation, gasoline, diesel oil or alternative fractional products to fuel oils may be obtained. These fractions may either be used directly or by mixing with other conventional fuels. By the application of various processes such as cracking, hydrogenation, etc. fuel characteristics may be improved and under this circumstance oil may either be used directly or its fractions may be evaluated as an alternative to gasoline, diesel fuel and fuel-oil.

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