BIO-OILS AND DIESEL FUEL DERIVED FROM ALKALINE TREATED EMPTY FRUIT BUNCH (EFB)

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Abstract

In this work, EFB was chemically pretreated with different sodium hydroxide (NaOH) concentration. Pyrolysis was conducted in the presence of HZSM-5 after the pretreatment step to assess the effects of pretreatment process on bio-oil production. Conversions of EFB were reported to be 61 wt%, 47 wt% and 42 wt%, after pretreatment with 5 wt%, 15 wt% and 25 wt%, NaOH concentrations, respectively. Furthermore, the pretreatment has effectively improved the bio-oil quality by reducing or even eliminating undesired products. Besides, biomass structure was dissembled and converted to valuable compounds after upgrading the bio-oil with improved quality.

Keywords: Bio-oils; Empty palm fruit bunch (EFB); Pretreatment; Pyrolysis; Upgrading.

1. Introduction

Concerns over environmental problems and diminishing supply of fossil fuels lure increasing attention to look for alternative energy sources [1-3]. In the current situation, oil prices are volatile while supplies are unstable. Besides its vulnerability in energy supply and demand, petroleum still commands as the main source of energy. An alternative and renewable energy source is eminent to solve the current issues of over dependence on fossil fuels for energy [4]. In search of renewable fuels, researchers started to look for potential renewable energy process to convert biomass into petroleum-like liquids such as bio oil. Bio-oil is normally derived from biomass such as empty fruit bunch (EFB) [5]. EFB is the solid wastes from palm oil industries which can be found abundantly in Asian countries like Malaysia, Indonesia, Thailand and tropical African countries [6]. EFB is interesting to study since it is cheap and contained high energy value. Converting palm EFB into valuable fuel resources like bio-oil and biofuel would bring benefit to energy security and increase the economy activity in the countries. For example, Malaysian palm oil industries have utilized EFB as an energy source to generate electricity in a co-generation power plant (CHP) which contributes approximately 2–3 % of the total electricity production [6-8]. However, EFB contained high moisture which led to incomplete combustion and produces emissions. The benefit of energy generation is often offset by the increased emissions, thus restraint its value as fuel for incineration. Therefore, alternative technologies should be invented in order to transform this beneficial renewable biomass into useful products.

Liquefaction of EFB using thermochemical conversion process such as pyrolysis offers an option for conversion of solid biomass into liquid bio-oil. Bio-oil is easier to transport, store, and can be upgraded to improve its quality. Bio-oil is also utilized as specialty chemicals like flavorings, renewable resins and slow release fertilizers [4, 9]. However, bio-oil cannot be used as a direct substitution for petroleum and chemical feedstock since it has high viscosity, high content of unstable oxygenated molecules and high density (≈1.2 kgL^{-1}). Therefore, upgrading of bio-oil into higher quality liquid product with wider applications is necessary. Various upgrading methods have been reported including solvent fractionation, steam reforming, hydrogenation, and catalytic cracking.

The effect of pretreatment steps of EFB plays a crucial role for bio-oil and specialty chemical production. Chemical pretreatment could isolate the lignocellulosic components, disassemble the biomass chains and increase the accessible surface area of EFB to produce important chemicals during pyrolysis. Biomass is also known as lignocellulosic material. There are three main components in lignocellulosic material namely cellulose, hemicellulose and lignin [10]. Lignocellulosic materials, insoluble in most chemical solvents due to crosslinking, can be hardly degraded at pyrolysis temperature (300-500 ^{o}C) [5, 8, 11, 12]. Modification of EFB structure is required in order to alter the biomass structure and to separate the lignocellulosic components [13]. Lignocellulosic components can be altered by various chemical pretreatment approaches. Chemical pretreatment using either acid or alkaline has been found as a potential technique for lignin degradation [5, 13]. The most widely practiced chemical pretreatment method is alkaline pretreatment with sodium hydroxide (NaOH). The use of NaOH was found to enhance the in-vitro digestibility and enzymatic hydrolysis of the lignocellulose [8] and it depends on the lignin content in the biomass. Effect of NaOH and hydrogen peroxide (H_2O_2) in decomposing cotton stalks lignin and pretreatment with

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calcium hydroxide ($Ca(OH)_2$) are some of examples of chemical pretreatment of biomass [14, 15]. Gharpuray et al. [16] has reported that chemical pretreatment was effective in increasing biomass surface area due to lignin removal. Pretreatment with caustic soda and acetic acid has both propelled specific surface area of wheat straw from 0.64 m^2g^{-1} to 1.7 m^2g^{-1}.

The main objective of this paper is to investigate the potential of chemically pretreated EFB as a promising feedstock for chemicals and biofuel production. The usage of alkaline chemical in the pretreatment of EFB to degrade lignocelluloses biomass is expected to alter the original biomass structure. The physical and chemical properties of the biofuel was analyzed and evaluated by comparing with that of typical bio-oil and petroleum diesel.

2. Experimental

2.1. Materials

EFB was supplied by an oil palm mill in Felda Bukit Besar, Johor, Malaysia. The feed biomass was shredded and crushed to give particle size ranging from 0.1-0.5 cm in a high-speed rotary cutting mill. EFB fibrous strands were washed with water and dried at 105 ^oC for 24 h prior to chemical pretreatment. The compositions, physical properties and elemental analysis of EFB were recorded in Table 1.

Table 1 : Main characteristics of EFB

Characteristics	Method/Standard	Measured	Literature values	Ref.
Component/property (wt%)				
Cellulose		59.7	38.1–42.0	[9, 17]
Hemicellulose		22.1	16.8–18.9	[9, 17]
Lignin		18.1	10.5–11.7	[9, 17]
Physical properties analysis				
Ash	TGA	5.36	3.02, 4.60, 5.36, 7.30	[9, 18-21]
Moistures	ASTM E871	7.48-8.96	8.75,7.95	[9, 18]
High heating value, HHV (MJ/kg)	Bomb calorimeter	16.74	19.30, 19.35	[9, 20]
Elemental analysis	CHNS/O Analyzer			
Carbon	-	47.89	40.70, 46.30, 48.80, 48.90, 49.07	[18-22]
Hydrogen	-	6.05	5.40, 5.90, 6.30, 6.48, 7.33	[18-22]
Nitrogen	-	0.65	0.0, 0.2, 0.3, 0.5, 0.7	[18-22]
Oxygen[1]	-	45.41	36.70, 38.29,40.20, 44.60, 47.80	[18-22]

[1] The oxygen content was determined by difference.

HZSM-5 zeolite (Zeolyst International, USA) was used as catalyst for EFB pyrolysis. Its characteristics are displayed in Table 2. The particle size was determined from scanning electron microscopy (SEM). Meanwhile physico-chemical properties of HZSM-5 were measured using isotherm nitrogen adsorption (NA) at 77 K. Prior to analysis the catalyst was outgassed for 20 h at 100 ^oC. In addition, ammonia temperature programmed desorption (NH3-TPD) was employed to determine the acidity of the catalyst.

Table 2 : Physical properties of HZSM-5 zeolite

Characteristics	Value
SiO_2/ Al_2O_3 (w/w)	30.00
Particle size (nm)	14.30
BET surface area, S_{BET} (m^2g^{-1})	444.80
Total pore volume, V_{Total} (cm^3g^{-1})	0.16
Micropore volume, V_{micro} (cm^3g^{-1})	0.17
Micropore width, W_{micro}(Å)	8.20
Average pore diameter, W_d (Å)	1.55
Total weight loss at 50-150°C (%)	9.45
Acidity (mmol NH_3/g)	1.20, 0.90
T_{max}[2](°C)	165.00, 415.00

[2]From ammonia TPD analysis. Two peaks were detected at two different temperatures for HZSM-5 corresponding to two types of acid centres.

2.2. Pretreatment of EFB

50 g EFB fiber was pretreated with three different cooking liquor concentrations containing 5 %, 15 % and 25 % (w/v) NaOH at a maximum cooking temperature of 100 ^oC until the lignocellulosic material was completely concentrated. The ratio of EFB to cooking liquor was 5:1. After pretreatment, the concentrated sample was dried in the oven for 24 h prior to pyrolysis. Duration of pretreatment and drying process for treated EFB was observed.

2.3. Pyrolysis of EFB

The pyrolysis experimental rig consists of a semi-batch stainless steel reactor with jacketed electrical heating monitored by a K-type thermocouple equipped with water-cooled product recovery system. Fig. 1 illustrates the schematic diagram of the experimental rig. Inert nitrogen was initially purged into the reactor approximately 30 min after the treated EFB with 5 wt% HZSM-5 catalyst were mixed. The pyrolysis process was operated under optimum temperature (300 ^oC) for 20 min at atmospheric pressure. During the reaction, nitrogen gas was purged in the reactor to control pressure and avoid vapor loss. Vapors released from the reactor were cooled at -5 ^oC and the liquid products, namely bio-oil was collected in round bottom flask while non-condensable gaseous components were collected into a gas sampling bag.

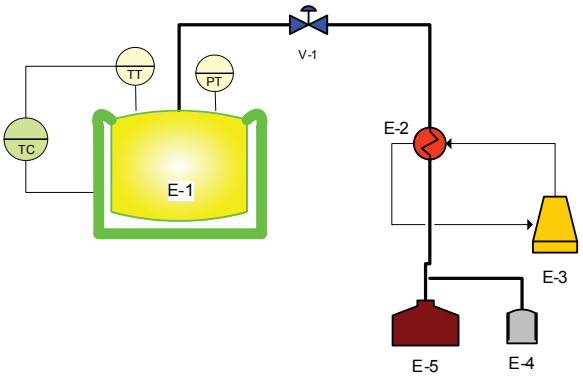

Figure 1 : Schematic diagram of pyrolysis system. (E-1: Stainless steel semi-batch reactor; E-2: Condenser; E-3: Chilled water bath; E-4: Gas sampling port; E-5: liquid collector.)

2.4. Upgrading of Bio-Oil

The reactive distillation technique proposed by Mahfud et al. [23] was employed in this study. Reactive-distillation experimental rigs consisted of a round bottom flask (250 mL) equipped with a magnetic stirrer and a glass condenser. Bio-oil (50 mL) and n-butanol (50 mL) were mixed into the flask. Subsequently, 1.6 wt% of H_2SO_4 catalyst was added and the mixture was heated to 60 ^oC. The rig was connected to a vacuum pump to allow the distillation reaction to occur under reduced pressure.

2.5. Analysis

2.5.1. Lignin degradation

Lignin degradation was calculated based on direct spectroscopic kappa number since the kappa number is generally comparative to the lignin content. The detail procedure was reported by Mission et al. [5]

2.5.2. FTIR

The functional groups of untreated, concentrated EFB and bio-oil samples were analyzed using FTIR spectrophotometer (Perkin–Elmer, USA). KBr pellet technique was employed in this analysis. For untreated and concentrated EFB, the small amount of each sample was grounded with laboratory grade KBr powder and pelletized in a hydraulic press. Meanwhile, the KBr pellet was used for bio-oil sample. Then, the pellet was tested through infrared spectrum in a range of 4000–370 $cm^{-1}$with 4 cm^{-1} resolution. The compounds were identified by comparing the results with standard IR-spectra of organic compounds.

2.5.3. GC-MS

The compositions of bio-oil and upgraded oil were analyzed using Agilent Technology 6890N gas chromatography-mass spectroscopy (GC-MS, Agilent, USA). The GC-MS was equipped with HP-5MS nominal column (30 mm x 250 μm x 0.25 μm) and mass selectivity (MS) detector. Helium was used as a carrier gas at a constant flow rate of 1 mL min^{-1}. The oven was operated at 80 ^oC for 0.5 min and then ramped at 10 ^oC min^{-1} up to 250^oC, and held for 5 min at 250 ^oC. Finally, the temperature was ramped to 300 ^oC at the same rate and kept isothermal for 15 min. Eqs. (1) – (3) were used to calculate the EFB conversion and product yield of gaseous and liquid oils based on weight basis.

$$EFB\ conversion\ (\%) = \frac{EFB\ \ feed\,(\mathrm{g}) - solid\ residue\ (\mathrm{g})}{EFB\ \ feed\ (\mathrm{g})} \times 100\% \quad (1)$$

$$Liquid\ \ oil\ \ yield\ (\mathrm{wt.\%}) = \frac{Desired\ \ liquid\ \ product\ (\mathrm{g})}{EFB\ \ feed\ (\mathrm{g})} \times 100\% \quad (2)$$

$$Gaseous\ \ yield\ (\mathrm{wt.\%}) = \frac{Desired\ \ gases\ product\ (\mathrm{g})}{EFB\ \ feed\ (\mathrm{g})} \times 100\% \quad (3)$$

2.5.4. Physical properties of bio-oil and upgrading oil.

The basic fuel properties were described by density, kinematic viscosity, and pH. The density of bio-oil and upgrading oil was determined using ASTM 4052 method. Meanwhile, ASTM D445-94 was employed to determine the kinematic viscosity and pH probe with digital meter (Lab 850 Schott) was used to measure pH value.

3. Results and Discussion

3.1. Pretreatment of EFB

The saponification reaction of intermolecular ester bonds crosslinking xylan hemicellulose and other polymeric materials such as lignin or other hemicellulose is proposed to be a mechanism of pretreatment process in presence of NaOH [5, 24]. According to Damisa et al. [25], removal of lignocellulose crosslinks led to increase porosity and internal surface area of the lignocellulose, but decrease the crystallinity and degree of polymerization. As a consequence, pretreatment using NaOH had facilitated the breakdown of lignin in order to increase the surface area prior to pyrolysis. In the present study, the EFB was treated with three different concentrations of NaOH (i.e. 5 wt%, 15 wt% and 25 wt %) at 100 ^oC. Dilute NaOH pretreatment lead to the swelling of lignocellulosic compound, increasing a surface area and decreasing the polymerization degree of EFB, then resulting to lignin and

hemicellulose removal [26-28]. The degradation of lignin after treated at 5 wt%, 15 wt% and 25 wt% of NaOH was observed to be 61 wt%, 47 wt% and 42 wt%, respectively (Table 3).

Table 3 : The effect of NaOH concentrations on lignin degradation

NaOH concentration/ wt.%	Duration/ hrs		Lignin degradation[3]/ %
	Drying process	Pretreatment process	
5	6	1.5	61
15	12	3.5	47
25	48	5	42

[3] 50g EFB, EFB: cooking liquor = 5:1, 5 wt.% HZSM-5 catalyst, pyrolyzed at 300°C for 20 min.

Pretreatment of EFB at higher NaOH concentration theoretically will lead to easier degradation of lignin. However, an opposite trend was observed in the present study where pretreatment at lower NaOH concentration yields higher lignin degradation. It was believed that the lower conversion at high NaOH concentrations is possibly because of the loss of some important lignocellulose component during the pretreatment process [5]. During pretreatment step, NaOH will play a role as a nucleophiles pulping chemical. The nucleophiles will react with lignin, and then fragmented, modified and dissolute the lignin structure in the reaction medium. The lignin structure modification occurred in two steps as to improve its dissolution. First step involved the cleavage of inter-unit linkages of lignin into smaller units. Then, the hydrophilic groups were introduced into the polymer and the cleaved fragments; as a result, lignin will be more soluble [5].

Duration for both drying and pretreatment process of EFB for each NaOH concentration is also shown in Table 3. Duration for both drying and pretreatment was proportional with the NaOH concentration: the lower the concentration, the shorter the time taken to dry and pretreat the EFB. The longer time taken for pretreatment using 25 wt % of NaOH was explained in the reference [29] where, the researchers have reported that the use of more than 20 wt% NaOH led to the extensive swelling, separation of the structural elements and the transformations of cellulose I (native cellulose) to cellulose II. This is because of dissolution of cellulose in NaOH and reorganization [30]; however, different cellulose substrate would give different response towards pretreatment process.

3.2. Performance evaluation on bio-oil production

Pyrolysis of treated EFB was conducted after the pretreatment with the untreated EFB as the control. The pyrolysis reaction converted EFB to several products including vapors that further condensed to form liquid oil, white non-condensable fume gas and char. The effect of the treated samples on the char, liquid and gas product yields in pyrolysis reaction are depicted in Fig. 2. Results demonstrated that both liquid and gas yields were recorded circa 25 wt% and 30 wt% from treated and untreated samples, respectively. Similar product trends were obtained from pyrolysis for all the treated EFB with char as the highest product followed by liquid oil and gas except for the EFB treated with 5 wt% of NaOH. At 5 wt% NaOH concentration pretreatment, the gas yield is higher than the liquid product. This indicates that, the lignin degradation leads the gases formation and decreased the char formation. However, the pretreatment of EFB increases the liquid product compares to untreated EFB. In theory, pretreated EFB sample can be degraded easily to give higher conversion and high liquid yield during pyrolysis and char formation is decreased with degrading the lignin structure in biomass. However, higher char yield was reported for the treated sample with 15 wt% and 25 wt% of NaOH. Higher yield of char produced in the 25 wt% of NaOH concentration may be explained by the lower conversion of EFB due to the loss of some important compounds during pretreatment process [5]. Besides, the bio-char have a potential as solid bio-fuel and have been widely used as a soil amendment agent [31].

Next, further discussion focused on characterization of bio-oil and upgrading of the bio-oil for 25 wt% of NaOH pretreatment. The difference in liquid yield between 5 wt% and 25 wt% of NaOH was small and 25 wt% of NaOH produced more biochar. The biogases have not been considered in this study since our scope focused on solid and liquid products only.

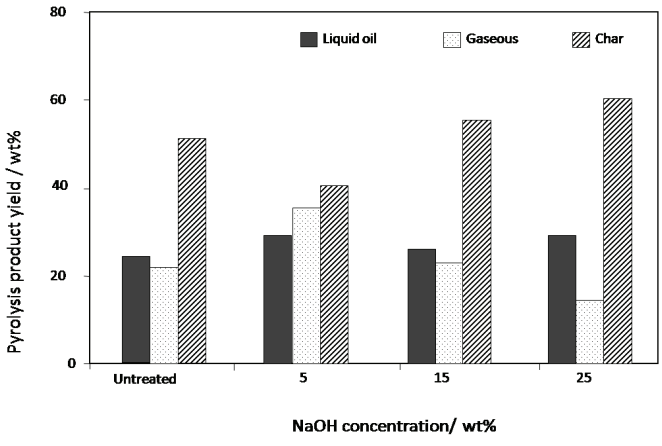

Figure 2 : The yield (wt.%) of char, liquid and gas products in pyrolysis oil of treated EFB in various NaOH concentrations. 50g EFB, EFB: cooking liquor = 5:1, 5 wt.% HZSM-5 catalyst, pyrolyzed at 300 °C for 20 min.

3.3. Product characterization

3.3.1. Characterization of treated EFB

The resulting pretreatment products appeared as concentrated lignocellulose and black liquor residue. The black liquor contained predominantly lignin as the FTIR analysis of the precipitated black liquor was in accordance to standard IR for lignin as presented in Ibrahim et al. [32]. The FTIR spectra of both treated (concentrated) and untreated EFB are shown in Fig. 3. The broad band in both spectra at 3000-4000 cm^{-1} was due to absorption of hydroxyl group as characterized by phenolic group. Meanwhile, C-H stretching showed reduction in the absorption of spectra after pretreatment at 2900 cm^{-1}. Some alterations were observed in concentrated lignocellulose in the range of 1200-1500 cm^{-1}. Obvious shoulder at 1407 cm^{-1} due to C-H bending of alkanes was detected on the sample. The untreated sample however, demonstrated broad shoulder at 1034 cm^{-1} characterizing primary alcohol [33]. According to Putun et al. [34], the band at 900-650 cm^{-1} was assigned to C-H bending of aromatics group. Sharp bands at 514 cm^{-1} of the concentrated lignocellulose proved that lignin has precipitated as a consequence of the pretreatment step in accordance with the previous finding [35].

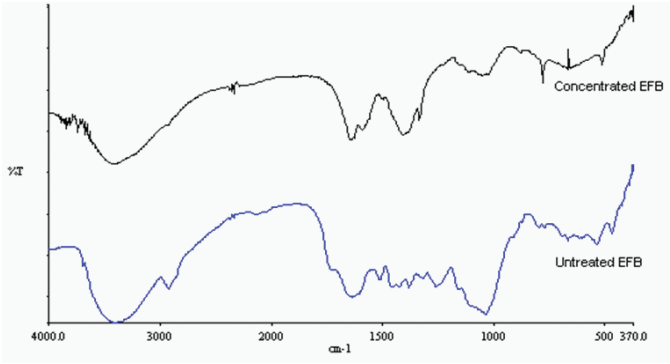

Figure 3 : FTIR spectra of (a) Untreated EFB and (b) Concentrated EFB. 50g EFB, pretreated in 25 wt% NaOH at 100 ^{o}C, EFB: cooking liquor = 5:1, and 100 ^{o}C

3.3.2. Characteristics and composition of bio-oil

The compound distributions of pyrolysis oil were analyzed using GC-MS based on chemical functional groups, and summarized in Fig. 4. Pyrolysis of cellulose at temperatures between 430 ^{o}C and 730 ^{o}C produced bio-oil with mixed compounds namely hydrocarbons, esters, acids, ketones and aldehydes [36]. The distribution of compounds was semi-quantitatively determined via the percentage area of the chromatography peaks. Surprising outcomes were revealed by the treated EFB where fatty acid methyl esters (FAME) appeared as the dominant compound in the bio-oil. Obviously, 58 wt% of FAME was detected compared to barely 18 wt% from the untreated sample. The encouraging performance could be attributed to the pretreatment employed where the biomass structure was dissembled and converted to valuable compounds. Interestingly, the pretreatment also has increased the hydrocarbon yield to approximately 20 %. Hydrocarbons are highly valuable for the production of biofuel as an alternative energy source to petroleum-derived fuel [7, 37, 38].

More importantly, the pretreatment has successfully improved the bio-oil quality by reducing or even eliminating the undesired products. For example, the treated oil has clearly reduced acids and ketones by approximately 12 % and 10 % compared to untreated sample, respectively, while nitrogenated compounds were completely eliminated. The acid presence in pyrolysis oil is a major drawback for the oil from being used in the transportation sector. The product distributions of the untreated sample on the other hand were in good agreement with the normal pyrolysis oil [7, 37].

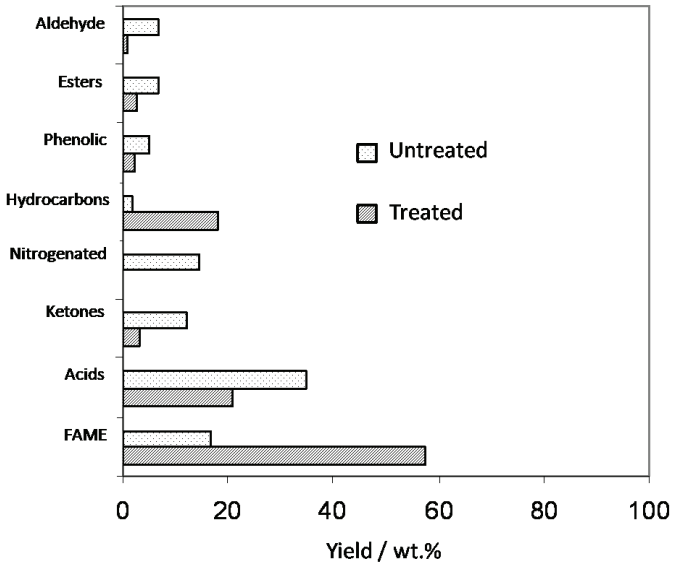

Figure 4 : Classification of bio-oil chemical compounds based on functional groups. 50g EFB, pretreated in 25 wt% NaOH at 100 ^{o}C, EFB: cooking liquor = 5:1, 5 wt% HZSM-5 catalyst, pyrolyzed at 300 ^{o}C for 20 min.

The bio-oil products were further analyzed with FTIR to supplement the chemical compounds analysis detected via GC-MS. FTIR absorption bands of the functional groups and its corresponding compounds present in bio-oil are listed in Table 4. Meanwhile, Fig. 5 displays the IR spectra of bio-oil. Bio-oil derived from treated EFB contained a greater diversity of organic compounds with an indication of higher number of functional groups present than that

of untreated EFB. These results were in good agreement with results from GC-MS analysis where a remarkable yield of hydrocarbon was present in the bio-oil derived from treated-EFB. The presence of phenol was verified by the existence of O-H stretching vibrations at 3390 and 3418 cm^{-1} for both treated and untreated EFB samples. The vibration at 2961, 2928, 2871 cm^{-1}(C-H stretching) and at 1595, 1648 cm^{-1}(C=C stretching) of the bio-oil derived from treated EFB indicated the appearance of alkanes and alkenes, respectively while no vibration was detected for the chemicals in the untreated oil. Furthermore, the presence of C=O stretching vibration at 1683 cm^{-1} and 1714 cm^{-1} are compatible with the presence of ketone, aldehyde, carboxylic and ester group. Meanwhile, the peak between 1300 and 950 cm^{-1} due to the presence of primary, secondary, tertiary alcohols and esters indicated the C-O stretching and O-H bending, respectively [33, 34]. Other weak absorbance observed at nearly 650-900 (cm^{-1}) shows the existence of some substituted aromatic groups.

Table 4 : FTIR absorption bands of treated and untreated EFB-derived bio-oils

Functional group	Wavenumber/ cm^{-1}		Compounds
	UntreatedEFB[4]	TreatedEFB[5]	
O-H stretching	3418	3390	Phenols, alcohols
C-H stretching (CH_2, CH_3)	-	2961, 2928 and 2871	Alkanes
C=O stretching	1683	1714	Ketones, aldehydes, acids, esters
C=C stretching	1647	1595, 1648	Alkenes
C-H stretching	1394	1389	Alkanes
C-O stretching	1277	1016, 1268	Primary, secondary and tertiary alcohols, phenols, esters
C-H bending	-	755, 890	Aromatic compounds

[4] Bio-oil derived from pyrolysis of untreated EFB.

[5] Bio-oil derived from pyrolysis of NaOH (25 wt.%) treated EFB.

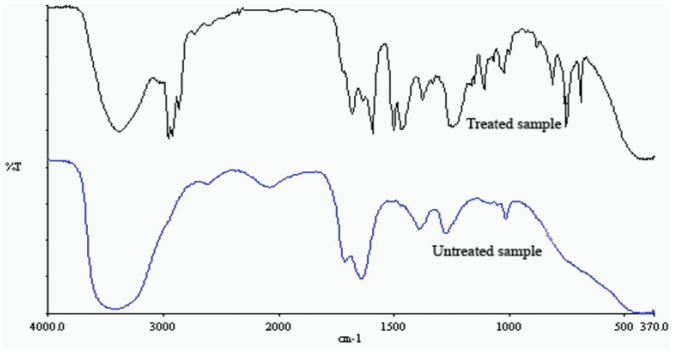

Figure 5 : IR spectra of bio oil from treated and untreated EPFB

The properties of the bio-oils are tabulated in Table 5. The pyrolysis oil product was dark brown in colour. The pretreatment with NaOH was the most probable reason attributed to the alkalinity of the oil product. The bio-oil of the untreated sample, however, was highly acidic due to the production of high acid contents. Meanwhile, the density of the bio-oil derived from the treated sample (0.87 kg/L) was slightly lower than the original untreated EFB (0.93 kg/L) but was about similar to that of petroleum diesel (0.85 kg/L). The pretreated EFB produced oil with lower viscosity (1.3 cSt) compared to 1.6 cSt for the untreated sample. Fortunately, the viscosity of the both bio-oils was found within the tolerable range of the available diesel viscosity.

Table 5 : Comparison of physical properties of EFB derived bio-oils with petroleum diesel

Properties	Crude Bio-oil		Upgraded Bio-oil		Petroleum Diesel [23]	Test method
	Untreated EFB[6]	Treated EFB[7]	Top layer	Bottom layer		
Appearance (colour)	Dark brown	Dark brown	Black	Brown		-
pH	2	10.3	3.8	3.3	7	pH meter
Water content (wt%)	-	30	10	17	0.5	-
Ash (wt%)	-	-	1.03	0	0.10	-
Density (kg/L)	0.93	0.87	0.73	0.85	0.85	ASTM 4052
Kinematic Viscosity, 40 °C(cSt)[8]	1.6	1.3	3.63	1.34	1.2-4.1	ASTM 455-94
High heating value (MJ/kg)	-	-	27	15.3	-	Bomb calorimeter

[6] Bio-oil derived from direct pyrolysis of EFB without pretreatment with NaOH.

[7] Bio-oil derived from pyrolysis of NaOH (25 wt. %) pretreated EFB.

[8] 1 cSt (centiStokes) = 10^{-6} m^2/s

3.4 Upgrading of Bio-Oil

Upgrading of bio-oil was conducted by the reaction between crude bio oil and alcohol using reactive distillation under reduced pressure. The properties of upgraded oil are summarized in Table 5. The upgrading process has resulted in the production of two layers of oil. The upper layer was found to be black in colour while a dark brown fraction remained in the bottom layer. Both layers were burned to evaluate the capability as fuel. Interestingly, the heavier bottom layer (dark brown colour) has a higher burning rate at room temperature compared to the lighter upper fraction (black colour). Oil with sweet banana-like odour was obtained due to the formation of butyl ester. Removal of water throughout reaction offered merit on the oil combustion properties [23] . It was observed that the upgrading process gave significant effect on the oil properties. The acidic property was contributed by H_2SO_4 used

as catalyst during upgrading process. The upper layer of the upgraded oil demonstrated much lower density as compared to the bottom layer and the crude oil. Most importantly, the upgrading process has contributed to a remarkable effect in increasing HHV value of bio-oil. Before upgrading, the HHV value was too low to be determined by bomb calorimeter. The upper layer possessed higher HHV value at 27 MJ/kg compared to 15.3 MJ/kg in the bottom layer, respectively. According to Vitolo et al. [39], increase of HHV can be considered as an index of the deoxygenation of the oils. The decrease of oxygen content is responsible for the increase of HHV in biomass [40]. Significant aromatization and reduced oxygenated functional groups were observed as the HHV of the oil in the upper layer increased. The oxygen in the oxygenated compounds of biomass pyrolysis oils was mainly converted to CO, CO_2, and H_2O [41]. The pH value of the upgraded bio-oil changed from 10.3 (crude bio-oil) to 3.8 and 3.3 for the upper and bottom layers, respectively.

The product distributions of the upgraded oil are presented in Fig.6. The compounds were referred to previous report by Adisak et al. [42]. Most of the compounds like aromatics and oxygenated were likely to have originated from cellulose, a smaller part of the carbohydrate polymer structures. There were also small amount of lignin-originated compounds. The results confirm that lignin degradation occurred during the pretreatment as mentioned in a previous study that stated softwood with lignin content below than 26 % was easier to be degraded [29, 39]. In the original feed oil, the major components observed were acidic compounds and esters. After the upgrading process, it was observed that the yields of both acidic and ester contents have been reduced. Interestingly, a total of 50 wt% of hydrocarbon compound (alkanes, alkenes and aromatic) were detected in the upper layer. Both upper and bottom layers contained formate esters (FE) as per previous report [23], but the bottom layer gave approximately higher percentage.

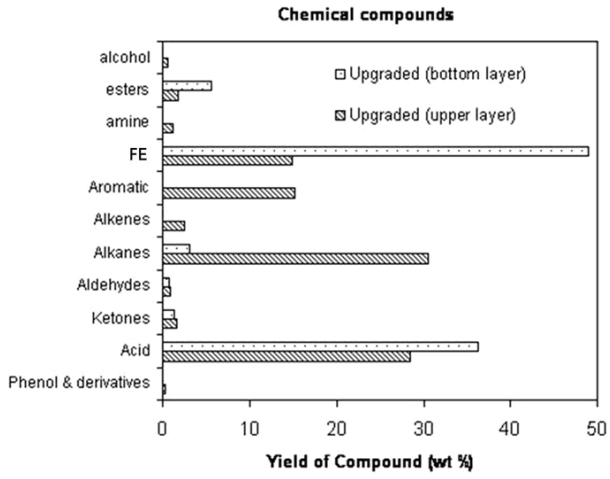

Figure 6 : Product distribution in upper and bottom layers of upgraded bio oil

Further evidence on the upgrading product characterization is presented by the FTIR spectra as revealed in Fig.7. Large intensity band of the intermolecular O–H stretching vibrations between 3200 and 3500 cm^{-1} for the upgraded bio-oil indicated the presence of phenols and alcohols. The presence of oxygenated functional groups also is made evident by the large intensity band of the intermolecular hydrogen bonds O–H stretching vibration at the same band. The absorption band at 1060 cm^{-1}, is due to the C–O stretching vibration.

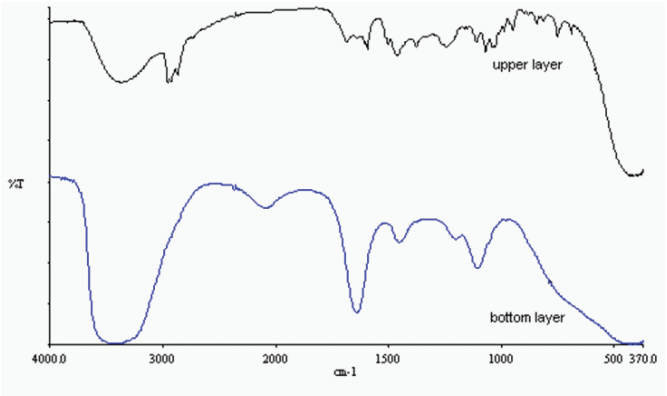

Figure 7 : FTIR results for bottom and upper layer of upgraded bio oil

4. Conclusions

Chemical pretreatment using NaOH was found to be an effective method for degrading lignin in EFB. The EFB conversion was lower at higher NaOH concentrations (25 wt%), but the liquid yield (~30 wt%) and bio-char (~60 wt%) was higher compared to lower NaOH concentrations. The study provided a sustainable method and a viable solution for waste management. In addition, the pretreatment of the biomass and upgrading of the bio-oil have improved its quality by reducing or even eliminating undesired products. The encouraging performance could be attributed to the pretreatment employed where the biomass structure was dissembled and converted to valuable compounds.

Acknowledgement

The authors would like to acknowledge the Ministry of Science, Technology and Innovation of Malaysia (MOSTI) and the Ministry of Higher Education of Malaysia (MOHE) for the financial supports received for this work through Vot 79049 under e-Science Fund and Vot 78232 under Fundamental Research Grant Scheme (FRGS).

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