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Influence of Chemical and Thermal Pre-Treatment on Pyrolysis Product Constituents of Palm Empty Fruit Bunches

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Bio-oil derived from palm empty fruit bunches (PEFB) mainly consists of oxygenated compounds, which has led to poor quality bio-oil with low energy content. In order to enhance the quality of the bio-oil, PEFB need to undergo a pre-treatment process to eliminate high oxygen content and moisture content from this biomass. In this study, the effect of individual and sequential pre-treatments of demineralization and torrefaction on palm empty fruit bunch (PEFB) samples was investigated and the pyrolysis product yields of untreated and pre-treated PEFB were determined. Pyrolysis of untreated and pre-treated PEFB individually was carried out using a fabricated fixed bed reactor system in nitrogen gas at a flow rate of 150 mL min^{-1}, pyrolysis temperature of 490 °C with heating rate of 85 °C min^{-1} for 210 s. A significant reduction of alkali and alkaline earth metals (AAEMs) and low oxygen content was observed on pre-treated EFB through demineralization and torrefaction pre-treatment. Pyrolysis of demineralized and torrefied EFB (TDPEFB) contributes about 59% of bio-oil, 29% of bio char and 12% of bio gas. Gas chromatography mass spectroscopy (GC-MS) on the bio-oil of pre-treated PEFB samples indicates that the chemical properties were improved. The quality of bio-oil derived from TDPEFB was enriched with ethers, furans, ketone and aldehyde and ester group. Polyaromatic hydrocarbon (PAH) and long chain fatty acid groups were also present with less oxygenated compounds in the group of phenols being detected. There are three factors that contribute to the quality of pyrolysis product yield of pre-treated PEFB i.e., the amount of AAEMs present in the biomass sample, decomposition of lignocellulose, and alteration of chemical structure of the biomass. From the overall results, the sequential pre-treatment of PEFB prior to pyrolysis is found beneficial to produce good quality bio-oil in a high quantity.

Keywords: Demineralization; torrefaction; AAEMs; polyaromatic hydrocarbon (PAH)

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Currently, bio-oil is produced from non-renewable sources such as waste tyres [1], coal [2], lubricant waste [3] and other fossil fuel products. Transforming bio-oil to transportation fuel is an important process to replace gasoline, diesel, and chemical feedstocks. Hence, renewable energy resources such as biomass are excellent sources for replacing chemical feedstocks from non-renewable energy resources by pyrolysis process [4–8].

Oil palm (*Elaeis guineensis*) is an important crop that is used to produce edible oil in Malaysia. There is a huge opportunity to utilize the products of oil palm and its wastes. Oil palm waste is considered the most common biomass waste and the available resources in Malaysia are empty fruit bunches (EFB), palm kernel shells (PKS), mesocarp fibre (MF) and palm oil mill effluent (POME) from mills, as well as oil palm fronds (OPF), and oil palm trunks (OPT) from plantations [9]. Currently, Malaysia is the second largest producer of palm oil in the world and produces a corresponding amount of oil palm wastes [10]. From the approximately 5.81 million hectares of oil palm plantation in Malaysia, almost 61% is owned by private estates, followed by independent smallholders (16.9%), government schemes (16.1%) and government agencies (6.0%) [11]. Palm empty fruit bunches (PEFB) is a by-product of the oil palm industry that has been commercially tested for bio-oil production. Since palm EFB is the major palm oil wastes that contribute about 20% of waste from oil palm mills, it is a more popular choice for investigation by researchers for the production of bio-oil [12].

Generally, PEFB consists of lignocellulosic components with a small amount of moisture content,

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extractives and high amounts of alkali and alkaline earth metals (AAEMs). The composition of lignocellulose was reported to be made up of various percentages of hemicellulose (22.1–48.0%), cellulose (17.1–-59.7%), and lignin (18.1–25%) that correspond to natural variations such as plantation area, soil and climate; these figures change with different EFB samples used [13]. In addition, approximately 5.0% of crude palm oil (CPO) residue is found in PEFB fibre and has high potential to be converted into long chain fatty acid, long chain hydrocarbon and diesel-like product through thermal degradation, hydrocracking and hydrogenation during the pyrolysis process. Charusiri and Vitidsant [14] in their work discovered that palmitic fatty acid and oleic fatty acid are the main components in CPO residue.

Typically, hemicellulose is a less thermally stable component that consists of various heteropolysaccharides, and monosaccharide units which mainly include pentoses (xylose and arabinose) and hexoses (mannose, galactose, and glucose) that are high in oxygenated compounds [15]. Poor quality bio-oil is produced through the pyrolysis process due to a high oxygen content in the biomass. The degradation of hemicellulose fraction that occurs around 200 to 300 °C in the absence of oxygen during mild pyrolysis process [16] could reduce the oxygen content and eliminate moisture content. Recently, this process, also known as torrefaction, has been recognized as a promising biomass pre-treatment [17–22] to reduce or eliminate high oxygen and moisture content from biomass. Thus, the quality and quantity of bio-oil from pyrolysis of biomass can be improved. However, cellulose is decomposed quickly at higher temperatures of 315 to 400 °C because it is a linear polymer with uniform units and bonds the size of the chain molecule [23]. This lignocellulosic component is an important material in bio fuel due to its high carbon content that is suitable to produce high quality bio-oil and valuable chemical feedstocks. Another vital lignocellulosic component in biomass is lignin. It is a cross-linked, heteropolyphenol mainly assembled from three monolignols which are sinapyl (S), coniferyl (G), and p-coumaryl (H) alcohols and has a wide temperature decomposition range from 160 to 900 °C [24]. Phenolic compounds possess high value chemicals such as phenol derived from lignin of biomass. Therefore, biomass with concentrated cellulose and lignin components needs to be formed via pre-treatment.

Recently, chemical and thermal pre-treatments of biomass have been applied prior to pyrolysis for the purpose of obtaining bio-oil of high quality and in better quantity in comparison with those derived from untreated biomass [25–30]. High oxygenated compounds, large molecular weight and low hydrocarbon content in poor quality bio-oil are the most important reasons to discover a new effective pre-treatment method. Based on previous studies, poor stability, phase separation propensity, high water and acid content, low heating value, and complicated composition of bio-oil originated from low grade raw biomass materials [25, 29, 31]. Due to these reasons, modification of biomass feedstocks needs to be conducted to reduce AAEM concentration and oxygen content in EFB prior to pyrolysis process.

Several pre-treatments of biomass have been proposed to reduce the AAEM and oxygen content in order to improve the quality and yield of bio-oil [15, 20, 29, 32]. Demineralization and torrefaction pre-treatments were reported to able to alter the biomass properties. Inorganic fraction in biomass was found to promote secondary reaction resulting in reduction of the yield of bio-oil while increasing char yield [33, 34]. Torrefaction pre-treatment however, could reduce the amount of moisture, oxygen and acetyl content of biomass. By combining both pre-treatments an upgraded bio-oil with low inorganic compound, organic acid, water, and aldehyde content was produced [35].

However, the influence of sequential pre-treatment of demineralization and torrefaction of EFB on the quantity and quality of pyrolysis products have not been thoroughly investigated in terms of product distribution and chemical compounds in bio-oil. Therefore, the effects of AAEMs and high oxygen content in EFB on product distribution will be thoroughly discussed according to three different pre-treatment methods: demineralization, torrefaction and sequential demineralization and torrefaction methods.

In this study, the physical characteristics of untreated and pre-treated EFB were determined and compared. The influence of different pre-treatments on EFB including single pre-treatments of demineralization and torrefaction, and sequential pre-treatment of demineralization and torrefaction on qualitative and quantitative pyrolysis product yields were investigated using a fabricated fixed bed reactor and a computer programme to set the operation parameters. The chemical compounds of bio-oil derived from optimal pyrolysis condition for all pre-treated EFB were then identified using gas chromatography mass spectroscopy (GC-MS). The novelty of this study was indicated by enhancing the quality of bio-oil enriched with fewer oxygenated organic compounds through sequential pre-treatment of demineralization and torrefaction on the PEFB.

EXPERIMENTAL PROCEDURE

Biomass Samples Preparation

The palm empty fruit bunches (EFB) were collected from United Oil Palm Industries Sdn Bhd located in Nibong Tebal, Pulau Pinang, Malaysia. The EFB was rinsed with tap water to remove impurities and was dried in an oven at 105 °C for 24 h. It was ground using a FML-0100 hammer mill machine into small particles and sieved to a particle size of 0.5cm^{-1} using a sieve shaker (Retsch, AS 200 basic). The dried pulverized biomass was stored in air-tight containers until further use.

Demineralized empty fruit bunch (DEFB) was obtained through demineralization of EFB using sonication with 1% HNO_3 solution. Demineralized EFB (DEFB) showed positive results with minimum ash content of 0.74% in comparison to 4.21% in untreated EFB. A previous study by Stefanidis et al. [31] reported that a higher yield of bio-oil was produced from demineralized biomass in comparison to bio char and bio gas yield. The reduction of AAEMs in the treated biomass had caused the reduction of undesirable catalytic reaction during pyrolysis [30].

Biomass Pre-treatment of Demineralization and Torrefaction of Empty Fruit Bunch

Initially, demineralization of EFB was carried out to eliminate alkali and alkaline earth metals (AAEMs) and this reaction simultaneously reduced the ash content in the sample. Demineralization pre-treatment was carried out according to our previous work [36]. Meanwhile, untreated EFB and DEFB samples were put through torrefaction process at 240 °C for 30 min, denoted as TEFB and TDEFB, respectively. Torrefaction experiments were performed in a fabricated vertical tube fixed bed reactor system. Each experiment was conducted by loading 10.0 g of DEFB sample in a vertical tube reactor with a nitrogen flow rate of 100 mL min^{-1}. Nitrogen gas flow was purged before and after 5 mins of experiment and the sample was removed from the reactor after cooling.

ICP-OES Analysis

The inorganic metals content of the EFB and DEFB was determined using the inductive couple plasma optical emission spectrometer (Perkin Elmer Optima 8000 ICP-OES). About 300 ±10 mg of samples were digested with 2.5 mL of 65% nitric acid and 2.5 mL of 30% hydrogen peroxide (H_2O_2) in high performance microwave digestion system, Ethos One. The temperature was ramped to 90 °C over 15 minutes, held for 5 minutes, then ramped again to 180 °C over 10 minutes and held for 15 minutes [30].

Pyrolysis Process

Pyrolysis experiment was conducted in a fixed bed reactor system that was attached with a bio-oil trap cooling unit. The fixed and manipulated process parameters such as pyrolysis temperature, heating rate, nitrogen flow rate and holding time were controlled by the computer programme during the pyrolysis. The optimum operation parameters were at pyrolysis temperature of 490 °C, heating rate of 85 °C min^{-1}, nitrogen flow rate of 150 mL min^{-1} and holding time of 250 s. About 5.0 g of the biomass sample was loaded in a stainless steel reactor tubing and placed in the fabricated fixed-bed reactor for pyrolysis in the inert nitrogen environment. For all experiments, the bio-oil was collected after completion of the holding time. The bio-oil collected was weighed and stored in a sample bottle for further analysis. The bio-oil yield, bio char yield and bio gas yield were calculated according to Mohamed et al. [7] and the calculations are shown in equations (1), (2) and (3), respectively.

GC-MS Analysis

The bio-oils produced under optimum conditions of pyrolysis were analysed using gas chromatography-mass spectrometry (GC-MS) model Agilent 6890N equipped with a HP-5MS capillary column (30 m x 250 µm x 0.25 µm). A 1 µL quantity of bio-oil sample diluted in dichloromethane (DCM) was injected into the injector using auto sampler in splitless mode. The flow rate of helium as carrier was set at 1 mL min^{-1}. The GC oven temperature was controlled with the programme as follows: (i) 50 °C held for 3 min, (ii) 50 °C to 180 °C at a rate of 6 °C min^{-1} and (iii) 180 °C to 240 °C at a rate of 8 °C min^{-1} and held for 30 min. Identification of the GC–MS peaks were based on the NIST MS Search 2.0 library.

$$\% \, Bio\,oil\ yield = \frac{mass\,of\ bio\,oil\,(g)}{mass\,of\ EFB\,(g)} \times 100 \tag{1}$$

$$\% \, Bio\,char\ yield = \frac{mass\,of\ bio\,char\,(g)}{mass\,of\ EFB\,(g)} \times 100 \tag{2}$$

$$\% \ Bio\,gas\,yield = 100 - (\% bio\,oil\ yield + \% bio\,char\ yield) \tag{3}$$

Table 1. Proximate and ultimate analyses of untreated EFB and treated EFB.

Characteristic analyses	EFB	DEFB	TEFB	TDEFB
Proximate analysis (wt. %)				
Moisture content	6.57	2.27	1.49	0.65
Volatile matter (VM)	53.85	73.60	45.95	63.04
Fixed carbon (FC)	41.94	25.65	49.12	35.08
Ash content	4.21	0.74	4.91	1.87
Ultimate analysis				
O/C	0.79	0.78	0.69	0.68
H/C	1.66	1.52	1.27	1.39
N/C	0.03	0.01	0.00	0.00
S/C	-	-	-	-
Calorific value (MJ kg^{-1})	17.80	17.30	20.60	19.70

RESULTS AND DISCUSSION

The Effect of Demineralization on the Characteristics of Pre-treated EFB

Table 1 summarizes the proximate, ultimate and thermal analyses of untreated and pre-treated EFB. With reference to Table 1, the moisture content of torrefied biomass samples i.e., TEFB and TDEFB were lower than that of untreated EFB at 1.49% and 0.65%, respectively. Likewise, the volatile matter for DEFB and TDEFB samples increased to 73.60% and 63.04%, respectively in comparison to the untreated EFB at 53.85%. The volatile matter for TEFB however, decreased to 45.95% with increasing ash and fixed carbon content. These observations are due to decomposition of a large amount of hemicellulose and partial depolymerization of cellulose and lignin during the torrefaction pre-treatment [32].

The percentage of volatile matter is inversely related to ash content for all conditions of samples. Nevertheless, the presence of AAEMs is directly related to ash content. The concentration of AAEMs for all samples is tabulated in Table 2. In general, AAEMs consist of K, Ca, Mg and Fe and are lower in DEFB and TDEFB samples. On the one hand, the ash content of DEFB dramatically decreased to 0.74 wt.% in comparison to EFB at 4.21 wt.% and this is due to the removal of AAEMs from the biomass during the demineralization pre-treatment [32]. On the other hand, the ash content for both TEFB and TDEFB were higher in comparison to untreated EFB samples. The fact that volatile matter was released from TEFB and TDEFB after the torrefaction process caused the AAEMs to concentrate and consequently increase the ash content [17, 20].

In contrast, the fixed carbon content of DEFB and TDEFB samples were significantly reduced in comparison to untreated EFB going down to 25.65% and 35.08%, respectively. Apparently, the TEFB sample exhibits the highest value of fixed carbon content at 49.12%. These results are due to total degradation of hemicellulose and partial decomposition of cellulose and lignin during torrefaction in the presence of AAEMs [20]. A similar trend of ash content reduction can also be observed for DEFB and TDEFB samples. Raveendran et al. [37] and Asadieraghi et al. [38] pointed out that the decrease in ash or AAEM content is conducive to suppressing the problems of slagging, agglomeration, heating surface and corrosion. This implies that sequential pre-treatment of demineralization and torrefaction on EFB reduces the ash content and offsets the negative impact of the increased ash due to torrefaction.

Table 2. Concentration of alkali and alkaline earth metals (AAEMs) in untreated and treated EFB using ICP-OES.

Samples	Concentration of AAEMs (ppm)			
	K	Ca	Mg	Fe
Untreated EFB	842.34	76.34	89.69	19.53
DEFB	61.87	35.53	38.75	16.95
TEFB	997.34	82.12	130.24	20.43
TDEFB	61.62	29.70	34.52	16.82

All untreated and pre-treated EFB samples present a ratio of elemental composition over carbon typically from lignocellulose components. Lignocellulose present in biomass can be classified into three major components, which are hemicellulose, cellulose and lignin. The ultimate analysis revealed that alteration of the chemical composition of EFB has occurred after demineralization and torrefaction pre-treatments. Table 1 shows the H/C and O/C ratios and calorific values for EFB, DEFB, TEFB and TDEFB. With reference to Table 1, the O/C and H/C ratios decreased for all the pre-treated samples. This observation is due to the decarboxylation and dehydration reactions that occurred during demineralization and torrefaction pre-treatments. Further, it appears that the calorific value for TDEFB is between the DEFB and TEFB values and these values are higher than the untreated EFB.

The Effect of Demineralization and Torrefaction on EFB Pyrolysis Product Yields

The percent of pyrolysis product yields (%) for EFB, DEFB, TEFB and TDEFB at optimal condition of 490 °C pyrolysis temperature, 85 °C min^{-1} heating rate, 150 mL min^{-1} nitrogen flow rate and 250 s holding time are shown in Figure 1. In comparison to pyrolysis of untreated EFB, the bio-oil yield of DEFB greatly increased to about 67% with slightly decreased bio char yield at 19% and about 12% bio gas yield.

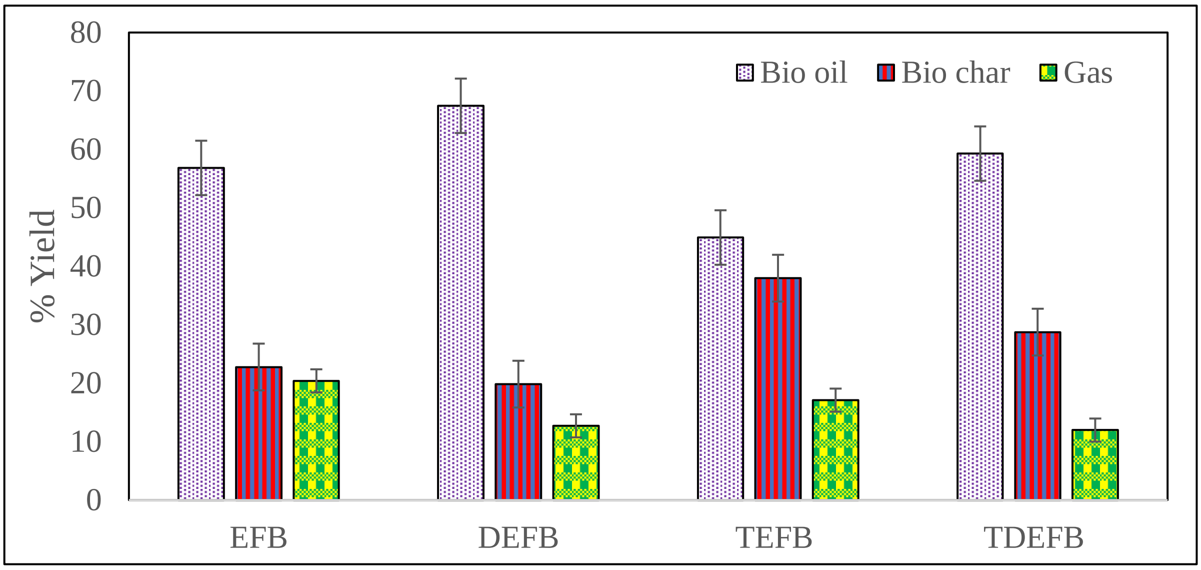

Figure 1. Pyrolysis products yield of demineralization, torrefaction and torrefied demineralized EFB.

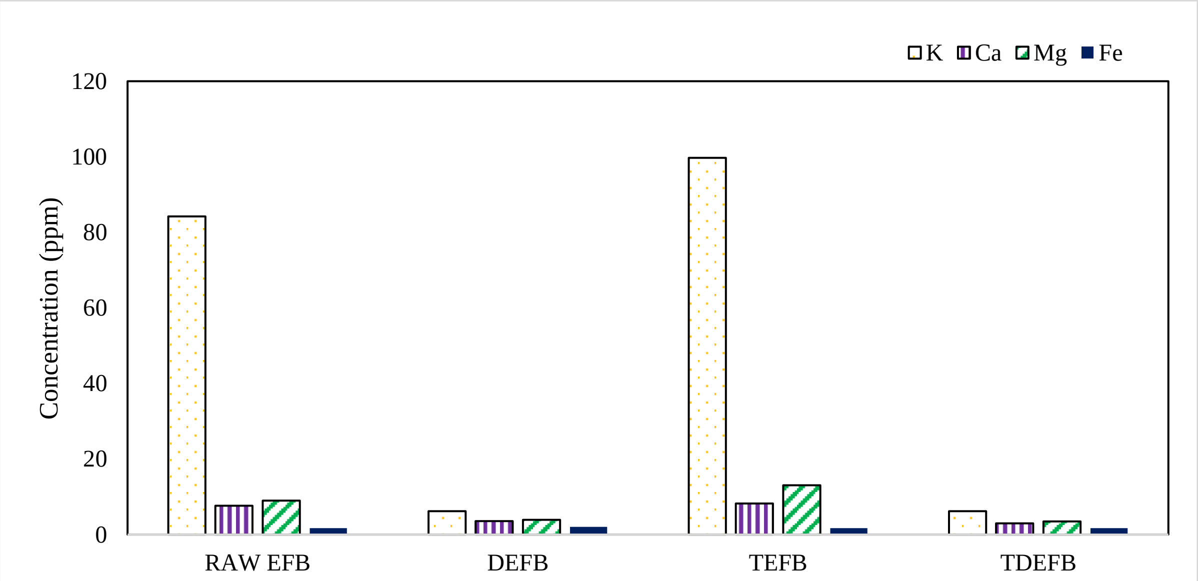

Figure 2. Concentration of AAEMs in untreated and pre-treated EFB using ICP-OES.

This phenomenon is mainly due to lesser effect of autocatalytic reaction during pyrolysis since a large amount of AAEMs has been removed during demineralization pre-treatment as shown in Figure 2. A previous work by Tan and Wang [39] reported that a decrease in the secondary reaction of volatiles resulted in an increase in bio-oil yield. The high percentage of volatile content in DEFB as shown in Table 1 indicates that the degradation pathway of pyrolysis was altered to yield a high percentage of bio-oil.

The torrefaction pre-treatment appears to have had an adverse effect on the distribution of bio-oil and bio char yields. The bio-oil yield of TEFB decreased to about 45%, while bio char yield increased to 38% in comparison to untreated EFB and DEFB. These observations can be explained by the contribution of three factors which are AAEMs content, decomposition of lignocellulose, and alteration of the chemical structure of TEFB. Firstly, the presence of AAEMs in the TEFB sample after torrefaction pre-treatment enhanced the autocatalytic reaction and suppressed the bio-oil production. The presence of AAEMs such as potassium (K), calcium (Ca), magnesium (Mg) and ferum (Fe) in untreated and pre-treated EFB promotes the secondary reaction during pyrolysis of biomass as shown in Figure 2. Wigley et al. [29] reported that lowering the amount of inorganic metals in the biomass reduced the secondary reaction during pyrolysis reaction.

Secondary reaction during pyrolysis has been reported to promote an increase in bio char and bio gas yield while reducing bio-oil yield. Secondly, the effect of torrefaction processes on EFB caused the decomposition of hemicellulose. This caused the composition of lignin to enrich and thus increased the amount of bio char while decreasing the formation of bio-oil. Thirdly, during the torrefaction process, the chemical structure of EFB was altered through carbonization and distracted cross-linking of cellulose. This trend of results concurs with the observations by others researchers [29, 40, 41] whereby torrefaction pre-treatment has an influence on the distribution of pyrolysis product yields.

The sequential pre-treatment of TDEFB sample also affected the distribution of pyrolysis products. The bio-oil yield of pyrolyzed TDEFB was about 59% and is slightly lower than that of DEFB at 67%. Though the TDEFB sample had a lower amount of AAEMs that could control the secondary reaction, the consecutive torrefaction pre-treatment as mentioned earlier caused the hemicellulose to degrade and this resulted in the reduction of bio-oil yield. Hence, the influence of individual pre-treatments of demineralization and torrefaction seems to play an important role in the sequential pre-treatment through reduction of AAEMs and oxygen content, respectively.

GC-MS Analysis

The composition of bio-oil derived from pyrolysis of untreated EFB and treated EFB (DEFB, TEFB and TDEFB) was identified in all bio-oil samples and it was found that the chemical components were mostly due to decomposition of hemicellulose, cellulose and lignin. Bio-oil components of EFB, DEFB, TEFB and TDEFB which were obtained from optimal pyrolysis condition were analysed using semi-qualitative gas chromatography mass spectroscopy (GC-MS) analysis as shown in Table 3. Apparently, the chemical compounds of bio-oil derived from untreated EFB when compared against the bio-oil derived from pre-treated EFB samples were found substantially different in functional groups as observed in Table 3. The complex organic compounds were identified and categorised according to their functional groups of ether (ETH), furans (FUR), ketone (KET), aldehyde (ALD), phenolic compounds (PH), organic acid (AC), hydrocarbon (HC, including cycloalkane, polyaromatic and aliphatic hydrocarbon), long chain fatty acid (FA), sugar (SUG), ester (EST) and nitrogen containing group (N) based on their total ion chromatograms. The peaks of mass spectra that did not match criteria (≤ 70 % similarity) were grouped as unidentified (UN).

Table 3. List of chemical compounds detected in the pyrolysis bio-oil of EFB, DEFB, TEFB and TDEFB at 490 °C.

RT (min)	Compound	Chemical functional group	Identified			
			EFB	DEFB	TEFB	TDEFB
Phenolic compounds						
10.07	Phenol	Phenol	*	*	*	*
12.51	Phenol, 2-methoxy	Guaiacol	*	*	*	*
13.43	Phenol,2-methyl	Phenol	*	*		*
16.33	Phenol, 2-methoxy-4-methyl	Guaiacol	*	*	*	*
19.03	Phenol, 4-Ethyl-2-methoxy	Guaiacol	*	*		*
26.93	5-Tert-butylpyrogallol	Pyrogallol	*		*	
20.10	1,2-Benzenediol, 3-methoxy	Catechol	*		*	*
20.41	Phenol, 2-methoxy-4-vinyl	Guaiacol	*	*	*	*
21.62	Phenol, 2,6-dimethoxy/	Syringol	*	*	*	*

24.67	Phenol, 2-methoxy-4-(1-propenyl)	Guaiacol	*			
32.03	Phenol, 2,6-dimethoxy-4-(2-propenyl)	Syringol	*	*	*	*
45.21	Phenol, 4,4-methylenebis [2,6-dimethoxy]	Syringol	*	*		*
Furan						
4.47	Furfural	Furans	*	*	*	*
5.32	3-Furanmethanol	Furans	*			*
5.7	2-Furanmethanol	Furans		*	*	*
Hydrocarbon compounds						
26.76	2,2-Dimethylbiphenyl	Aromatic hydrocarbon		*		
27.01	Benzene, 1,1-ethylidenebis	Aromatic hydrocarbon		*		*
28.34	Ethylene, 1,1-diphenyl	Aromatic hydrocarbon				*
33.10	Benzene, 1,2-dimethyl-4-(phenylmethyl)	Aromatic hydrocarbon		*		
41.42	Cycloeicosane	Cycloalkane		*		
39.45	1-Hexacosene	Long chain alkene	*			
40.38	9-Tricosene	Long chain alkene	*			
43.25	Tricosane	Long chain alkane				*
Carbonyl compounds (Aldehyde and ketone)						
8.52	2-Furancarboxaldehyde, 5-methyl	Aldehyde		*	*	*
19.32	2-Furancarboxaldehyde, 5-(hydroxymethyl)	Aldehyde			*	*
31.36	Benzaldehyde, 4-hydroxy-3,5-dimethyoxy	Aldehyde	*	*	*	*
33.32	Ethanone,1-(4-hydroxy-3,5-dimethoxyphenyl)	Ketone		*	*	*
33.80	Desaspidinol	Ketone		*	*	*
34.01	1-Butanone, 1-(2,4,6-trihydroxy-3-methylphenyl)	Ketone	*	*	*	*
39.07	9-Tetradecenal, (Z)	Aldehyde		*		*
41.66	Cyclopropaneundecanal, 2-nonyl	Aldehyde	*			*
45.91	2,5-Dipiperonylidene-1-cyclopentanone	Ketone				*
Sugar						
17.90	1,4:3,6-dianhydro-alpha-d-glucopyranose	Sugar		*		
Ester						
36.87	Hexadecanoic acid, methyl ester	Ester	*	*		*
40.51	Elaidic acid, isopropyl ester	Ester	*			*
43.16	2,3-Dihydoxypropyl elaidate	Ester		*		
43.45	1,2-Benzenedicarboxylic acid, mono (2-ethylhexyl) ester	Ester		*	*	*
43.85	Di-n-octyl phthalate	Ester	*			*
45.23	9-Octadecenoic acid (Z)-,2-hydroxyethyl ester	Ester			*	*
Long chain fatty acid						
38.04	n-Hexadecanoic acid	Long chain fatty acid	*	*	*	*
40.64	Oleic acid	Long chain fatty acid	*	*		*
40.67	14-Pentadecenoic acid	Long chain fatty acid				*
40.72	Octadecanoic acid	Long chain fatty acid		*		
44.95	6-Octadecenoic acid, (Z)-	Long chain fatty acid		*		*
N-containing group						
9.18	5-Methoxypyrimidine	N-containing group			*	*

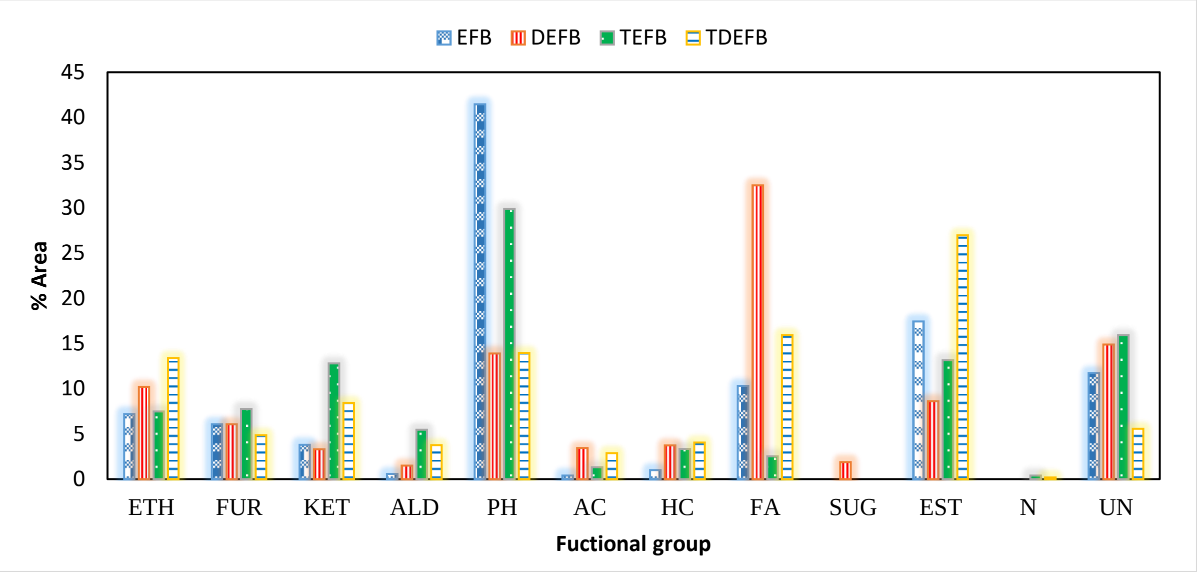

Figure 3. Qualitative analysis of bio-oils derived from treated and untreated EFB pyrolysis based on percentage of peak area.

The qualitative GCMS analysis of the bio-oils derived from the untreated EFB, DEFB, TEFB and TDEFB as shown in Figure 3 is based on percentage peak area of identified functional groups. Most of the group compounds were monitored in the untreated and pre-treated EFB bio-oil samples with the exception of sugar (only in DEFB bio-oils) and nitrogen containing groups (only in TEFB and TDEFB bio-oils).

Noticeably, 1,4:3,6-dianhydro-alpha-d-glucopyranose which represents the sugar group was detected in DEFB bio-oil. This compound forms from the depolymerization of glycoside fragments as a result of the primary reaction of pure cellulose during pyrolysis [42]. In addition, Stefanidis et al. [31] also reported that the demineralized biomass increased the organic fraction yield which is mainly from the sugar group and decreased CO_2 production. This observation can be further explained from a previous work by Yang et al. [42] who studied the influence of minerals on the pyrolysis of biomass with the aid of a proposed conceptual mechanism for biomass pyrolysis. In the absence or low amount of AAEMs, levoglucosan or sugar was produced from the depolymerization of *o*-glucosydic scission from transglycosidation reaction.

Likewise, the presence of AAEMs in the biomass causes the homolysis cleavage of pyranose rings to produce low molecular weight product, carbonyl compounds, acid and CO during the pyrolysis. Furfural, ketone and aldehyde are the products from secondary decomposition of anhydrosugars (especially levoglucosan). These chemical compounds were found most favourable in TEFB bio-oil that contains high AAEMs where secondary reaction occurred during the pyrolysis process. Moreover, the absence of levoglucosan in untreated EFB and TDEFB bio-oils suggests that the levoglucosan compound was decomposed into furfural and 5-hydroxymethyl-furfural via secondary cracking [23].

The results in Figure 3 also indicate that phenolic compounds derived from the degradation of lignin which consists of phenol, guaiacol, pyrogallol, catechol, and syringol were the major compounds obtained in untreated EFB and TEFB bio-oils. However, the intensities of phenolic compounds in DEFB and TDEFB bio-oils were comparable but slightly lower than the untreated EFB and TEFB bio-oils. A similar observation has been reported by Chen et al. [20] who obtained a higher amount of phenol in bio-oil produced from torrefied cotton stalk and torrefied demineralized cotton stalk biomass due to the concentrated lignin content in biomass after the torrefaction pre-treatment was applied. These findings indicate that torrefaction pre-treatment could alter the chemicals' structure by decomposition of hemicellulose and partial decomposition of cellulose which results in an increase in the lignin component in torrefied biomass. Furthermore, the presence of AAEMs in torrefied biomass has escalated the secondary reaction since they are not being removed during the pre-treatment. In fact, AAEMs present in EFB and TEFB play an important role during pyrolysis under optimal conditions as a natural catalysis [20, 31, 42]. The cracking of lignin structure and oligomers by metal cations such as K^+ and Ca^{2+} from AAEMs resulted in increasing formation of phenolic compounds in bio-oil.

Further, more of various long chain fatty acids were identified in bio-oil from untreated and pre-treated EFB as listed in Table 3. This observation is due to the presence of 5.0% of crude palm oil (CPO) residue in the EFB fibre [14]. What happened is during the pyrolysis reaction these fatty acids were extracted and degraded to produce carboxylic acid compounds. From GC-MS analysis, n-hexadecanoic acid was observed in all bio-oils of untreated and pre-treated EFB samples. However, the amount of n-hexadecanoic acid was lower in TEFB bio-oil that contains high AAEMs. These results are supported by the formation of 1,2-Benzenedicarboxylic acid, mono (2-ethylhexyl) ester and 9-Octadecenoic acid (Z)-,2-hydroxyethyl ester in the bio-oil of TEFB through complex chemical reactions to generate ester compounds.

CONCLUSION

The sequential pre-treatment of demineralization and torrefaction of EFB has been carried out in this study. The effect of this pre-treatment was investigated with the aid of EFB individual pre-treatments of demineralization and torrefaction based on pyrolysis product distribution. The results indicated that both pre-treatments of demineralization and torrefaction contribute to the significant production of bio-oil with lower bio char and bio gas yields. The sequential pre-treatment of demineralization and torrefaction on EFB seems beneficial since it can reduce the amount of AAEMs content and decrease the oxygen content, respectively. Hence, the occurrence of secondary reaction during pyrolysis that results in the alteration of lignocellulose composition and chemical structure in TDEFB could be minimized. As a result, bio-oil in high quantity and quality was observed as the most dominant pyrolysis product. The quality of bio-oil derived from TDEFB was enriched with ethers, furans, ketone and aldehyde and ester group which are products of the degradation of cellulose and lignin. Further, polyaromatic hydrocarbons (PAH) and long chain fatty acid groups were also present with less oxygenated compounds in the group of phenols being detected.

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