

Bio-oils from Pyrolysis of Oil Palm Empty Fruit Bunches

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Abstract: Problem Statement: The palm oil industry generates an abundance of oil palm biomass such as the mesocarp fibre, shell, empty fruit bunch (EFB), frond, trunk and palm oil mill effluent (POME). For 80 million tonnes of fresh fruit bunch (FFB) processed last year, the amount of oil palm biomass was more than 25 million tones. The objectives of this study were to: (i) Determine the effect of various pyrolysis parameters on product yields and (ii) Characterise liquid product obtained under different condition. **Approach:** In this study, pyrolysis of oil palm Empty Fruit Bunches (EFB) was investigated using quartz fluidized fixed bed reactor. The effects of pyrolysis temperatures, particle sizes and heating rates on the yield of the products were investigated. The temperature of pyrolysis and heating rate were varied in the range 300-700 °C and 10-100 °C min⁻¹ respectively. The particle size was varied in the range of <90, 91-106, 107-125 and 126-250 µm. The elemental analysis and calorific value of the bio-oil were determined. The chemical composition of the oil was investigated using chromatographic and spectroscopic techniques. **Results:** Under the experimental conditions, the maximum bio-oil yield was 42.28% obtained at 500 °C, with a heating rate of 100 °C min⁻¹ and particle size of 91-106 µm. The calorific values of bio-oil ranged from 20-21 MJ kg⁻¹. A great range of functional groups of phenol, alcohols, ketones, aldehydes and carboxylic acids were indicated in FTIR spectrum. **Conclusion:** The chemical characterisation results showed that the bio-oil obtained from oil palm EFB maybe a potentially valuable source as fuel or chemical feedstocks.

Key words: Empty Fruit Bunches (EFB), palm oil, pyrolysis and bio-oil

INTRODUCTION

Oil palm (*Elaeis guineensis*) was introduced in Peninsular Malaysia in 1870 and was commercially exploited in the 1900s. Today, oil palm is the most economically attractive crop in Malaysia. With a total planted area of 4.2 million hectares, it plays an important role in the socio-economy and well being of the country.

Biomass is mainly derived from the agriculture or forestry sector. Today, various forms of biomass are consumed all over the world for energy generation. Biomass provides a clean, renewable energy source that could dramatically improve the environment, economy and energy security. The use of these materials will depend on safe state of the art, economic and technologies that are used to transform them into manageable products^[17]. One of the indigenous biomass resources in Southeast Asia is derived from the oil palm. The oil palm empty fruit bunches, fiber and shell which are generally considered as 'waste' are generated every year in Malaysian, with an annual increment of 5%^[22]. While much research has been carried out to

utilise them for the manufacture of value added products, its commercial utilization is not widespread. As fossil fuel gets depleted, exploitation of biomass as renewable materials by conversion to a transportable form of green fuel is being fervently researched. These include pyrolysis^[20,23], gasification^[6,24] and liquefaction^[2,21].

Pyrolysis is one of the most promising technologies of biomass utilization^[3,10], which converts the biomass to bio-oil, char and gases depending on the pyrolysis conditions. Pyrolysis may be described as a thermal degradation of materials in the complete absence or inadequate presence of oxygen.

Uzun *et al.*^[19] investigated the effect of temperature, nitrogen flow rates, heating rates and particle sizes, influencing pyrolysis product yields from soybean cake. Ozcimen *et al.*^[14] pyrolysed rapeseed cake for bio-oil and bio-char and identified the various characteristics of bio-oil and bio-char acquired under static atmospheric conditions.

Onay *et al.*^[13] pyrolysed rapeseed in a free fall reactor at atmospheric pressure under nitrogen atmosphere. The effects of final temperature, particle

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size and sweep gas flow rate on the yields of products were investigated. Tsai *et al.*^[18] fast pyrolysed rice straw, sugarcane bagasse and coconut shell in an externally heated fixed-bed reactor. Valuable products were obtained. The effect of process parameters such as pyrolysis temperature, heating rate and holding time on the yields of pyrolysis products and their chemical composition were also investigated.

In this study, pulverised empty fruit bunches was pyrolysed under different conditions in a fluidised fixed-bed reactor and the products obtained were characterised.

MATERIALS AND METHODS

Raw material: An empty fruit bunch of about 5 kg was collected from a palm oil mill located in Padang Jawa, Klang. The bunch was dried at 100 ± 5 °C and cut into smaller pieces. It was then milled, sieved and separated in fractions using the test sieve shaker, Endecotts EFL 2000. The separated portion level particle size was <90 μm , 91-106 μm , 107-125 μm and 126-250 μm .

Characterisation of the EFB includes proximate analysis, calorific value and elemental analysis. The proximate analysis was used to determine the moisture content, volatile matter, fixed carbon and ash content in EFB. The calorific value of the EFB was determined using a bomb calorimeter, Leco AC-350. The test procedure consists of EFB weighing (0.5-1.0 g), installing a fuse and charging the bomb with oxygen to approximately 200 psi. The carbon, hydrogen and nitrogen contents of EFB were determined using a Euro EA3000 series, Elemental Analyzer.

Pyrolysis experiments: Pyrolysis of the oil palm empty fruit bunches was carried out using a quartz fluidised fixed bed reactor. A weighed sample of pulverised biomass was introduced into the reactor. The reactor with a length 135 mM and an inner diameter of 40 mM was introduced into the electric furnace. The temperature of the reactor was determined by inserting a thermocouple as near the upper fritz as possible.

The whole experimental rig that consists of the volatiles and gas collection system is as illustrated in Fig. 1.

Fluidised bed was generated using Argon at rate 1.5 litre per min, on 160 g zircon sand of 180-250 μm . For every experiment, 2 g of EFB feedstock was introduced into the bed of zircon sand.

Three series of experiments were carried out. The first was to determine the effect of the final pyrolysis temperature of 300, 400, 500, 600 or 700 °C on pyrolysis products. The heating rate was maintained at 30 °C

min^{-1} and particle size of empty fruit bunches used was 91-106 μm .

The second series of experiments was to determine the effect of particle size on the pyrolysis products. Four different particle size ranges of <90 μm , 91-106 μm , 107-125 μm and 126-250 μm were pyrolysed at heating rate of 30 °C min^{-1} . Final temperature was maintained at 500 °C.

The third series of experiments was to determine the effect of heating rate on the pyrolysis products. Heating rates of 10, 30, 50 and 100 °C min^{-1} were studied. The final pyrolysis temperature was maintained at 500 °C and particle size of empty fruit bunches was 91-106 μm .

Bio-oils characterisation: The water content of the bio-oils product was measured using Karl Fischer Titration, 784 KFP (Titrimo, Metrohm). The bio-oils to be analysed was titrated with standard Karl Fischer reagent to an electrometric end point.

The carbon, hydrogen and nitrogen contents of bio-oils were determined using a Euro EA3000 series, Elemental Analyzer. Identified by reference to standard calibration and percent element of samples were determined by peak areas.

The calorific value of the bio-oils was determined by using a bomb calorimeter, Leco AC-350. The pH of the bio-oils measured by a pH meter from Eutech Instruments, type of pH Tutor.

The density of bio-oils was determined using Digital Density Meter, type DE 40 (Mettler, Toledo). The total acid value determined by using Potentiometric Titration, 702 SM (Titrimo, Metrohm). The acid value is expressed as the amount (in miligramms) potassium hydroxide required to neutralize one gram of the bio-oils (mgKOHg^{-1}).

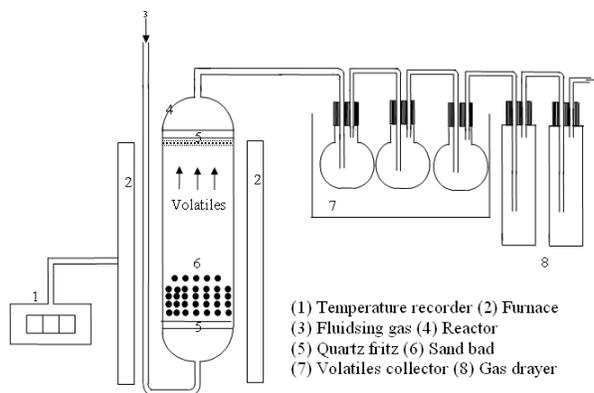


Fig. 1: Schematic diagram of the pyrolysis system

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 is reduced to an ash by heating in a furnace at 775 °C with a heating time of 20 min, followed by cooling and weighing.

Functional groups analysis of the bio-oils was 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 had been previously scanned as a background.

The Gas Chromatography/Mass Spectroscopy (GC/MS) analysis of the bio-oils was performed with a Agilent Technology 6890-N equipped with a SGE. BPX5 column and MSD detector, using 30x250x0.25 mM capillary column. The starting temperature of the oven was 35 °C. It was held for 2 min before the temperature was increased to 250 °C at the rate of 20 °C min⁻¹ and held at its temperature for 20 min. The injector port temperature and the detector temperature was set at 280 °C.

RESULTS

Raw material: Empty fruit bunches a by-product of a palm oil mill were used in the work. The results of proximate analysis, elemental analysis and calorific value of palm oil empty fruit bunches are listed in Table 1. The calorific value of empty fruit bunches was 17.08 MJ kg⁻¹ generally which is typical for biomass is higher than the energy content of olive-oil residue 16.40 MJ kg⁻¹[20].

The volatiles, fixed carbon and ash content of empty fruit bunches are 81.9 wt%, 12.6 wt% and 3.1 wt%, respectively. The elemental analysis provides the chemical composition of the EFB in elemental terms and is used to determine the combustion air requirements, flue losses and likely emission levels. From this analysis, it was found that the EFB contained 53.78 wt% of Carbon, 4.37 wt% of Hydrogen, 41.50 wt% of Oxygen and 0.35 wt% of Nitrogen. The H/C and O/C ratios of EFB were 0.98 and 0.58, respectively. If considering only the main elements (C, H, O, N), the molecular formula of the studied samples based on one C atom can be written as CH_{0.98}O_{0.58}N_{0.02}.

Pyrolysis experiments:

Effect of temperature: The effect of final pyrolysis temperature on product yields is shown in Fig. 2. At the lowest pyrolysis temperature of 300 °C, decomposition was insignificant as char was the major product. At 500 °C, the amount of condensed liquid product (bio-oil) increased to a maximum value in the range of 33-35 wt% of feedstock. At higher pyrolysis temperatures of 600 °C and 700 °C, the bio-oil decreased to 30-32 wt%

of feedstock. Yorgun *et al.*[23] and Acikgoz *et al.*[11] studies on pyrolysis of sunflower oil cake and linseed respectively, indicated the same trend. Gas yield was obtained at the range 31-46 wt% of feedstock over the temperature range of 300 °C to 700 °C. The maximum liquid product yield obtained was 35wt% of feedstock at the pyrolysis temperature of 500 °C.

Effect of particle size: The effect of particle size on the product yields is given in Fig. 3 at a pyrolysis temperature of 500 °C at heating rate of 30 °C min⁻¹. Biomass of particle size of <91 µm produced a bio-oil yield of 33 wt% of feedstock was only about 2 wt% higher than that of the highest particle size with a char yield of 28 wt% of feedstock and gas yield of 39 % wt% of feedstock. Larger particle size of 126-250 µm produced a bio-oil yield of 31 wt% of feedstock with a char yield of 28 wt% of feedstock and gas yield of 41 wt% of feedstock. A maximum bio-oil yield was obtained with particle size of 91-106 µm about a 35 wt% of feedstock with a char yield 25 wt% of feedstock.

Table 1: Main characteristics of the treated oil palm EFB

Characteristics	EFB
Proximate analysis (wt%)	
Volatiles	81.90
Fixed Carbon	12.60
Ash	3.10
Moisture	2.40
Ultimate analysis (wt%)	
Carbon	53.78
Hydrogen	4.37
Nitrogen	0.35
Oxygen ^a	41.50
H/C	0.98
O/C	0.58
Empirical formula	CH _{0.98} O _{0.58} N _{0.01}
Calorific value (MJ kg ⁻¹)	17.08

^a By difference

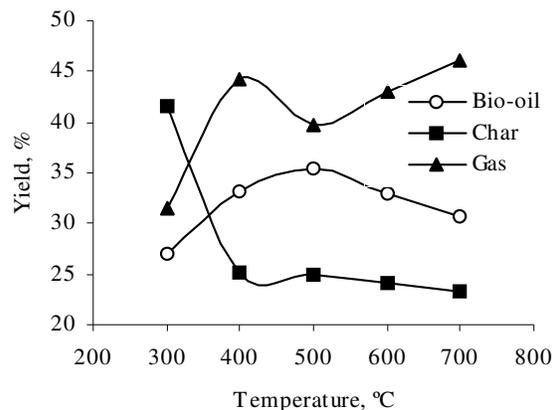


Fig. 2: Yield of pyrolysis products at various final pyrolysis temperatures with a heating rate of 30 °C min⁻¹ and particle size of 91-106 µm

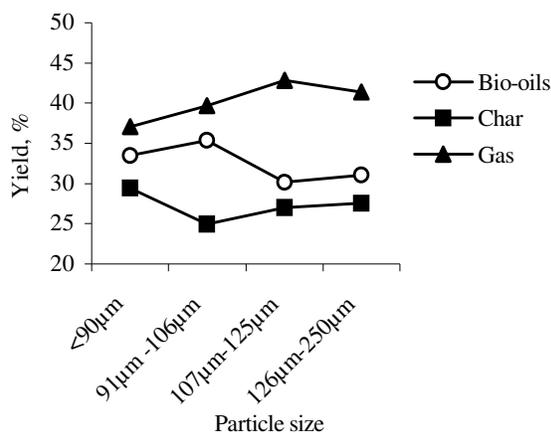


Fig. 3: Yield of pyrolysis products at various particle size with a final temperature of 500°C and heating rate of 30 °C min⁻¹

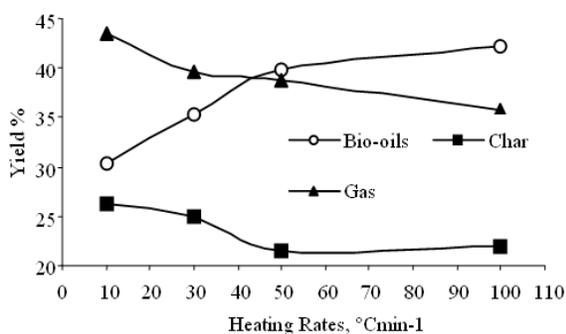


Fig. 4: Yield of pyrolysis products at various heating rate with a final temperature of 500 °C and particle size of 91-106 µm

Effect of heating rate: The effect of heating rate on product yields is as shown in Fig. 4. The bio-oil yield reached a maximum value of 42 wt% of feedstock with a highest heating rate of 100 °C min⁻¹. The lowest bio-oil yields were obtained at the heating rate 10 °C min⁻¹ (30 wt% of feedstock). In this study, the highest char yield was obtained at the heating rate of 10 °C min⁻¹ (26 wt% of feedstock). The lowest char yield was obtained at the heating rate of 50 °C min⁻¹. (21 wt% of feedstock). Gas yield was obtained at the range 35-43 wt% of feedstock over the temperature range of 10-100 °C min⁻¹.

Bio-oils characterisation: The bio-oils obtained at temperature of 400, 500 and 600 °C with heating rate of 30 °C min⁻¹ and particle size of 91-106 µm was characterised with respect to liquid fuel

Table 2: Characteristics of bio-oil obtained at heating rate of 30 °C min⁻¹ and particle size of 91-106 µm

Properties	Temperature (°C)			Bio-oil from rapeseed ^a
	400	500	600	
1. Calorific Value (MJ/kg)	20.23	21.41	21.17	38.40
2. Total Ash, %	0.49	0.65	0.37	-
3. pH	3.40	3.00	3.00	-
4. Moisture (%)	17.89	18.74	18.21	None
5. Total Acid (mg, KOH.g ⁻¹)	81.81	75.62	67.75	-
6. Density (g/cm ³)	1.00	0.90	0.99	0.92
7. Ultimate analysis (w/w%)				
Carbon	35.29	49.80	53.75	74.04
Hydrogen	6.67	7.98	8.81	10.29
Oxygen	57.02	40.29	36.04	11.70
Nitrogen	1.02	1.93	1.40	3.97
H/C molar ratio	2.27	1.92	1.97	1.67
O/C molar ratio	1.21	0.61	0.50	0.12
Empirical formula	CH _{2.27} O _{1.21} N _{0.02}	CH _{1.92} O _{0.61} N _{0.03}	CH _{1.97} O _{0.50} N _{0.02}	CH _{1.67} O _{0.12} N _{0.05}

^a Data taken from Sensoz,

characteristics as shown in Table 2. The moisture content of bio-oils varied between 18 and 19 % depending on the production condition. The pH value of the bio-oils varied between 3.0 and 3.4. The finding is in agreement with the same published data^[3] that is, bio-oil generally contained substantial amount of organic acids, mostly acetic acid and formic acids, which give the bio-oil its low pH (2-3). The acid values of the bio-oils vary between 68 and 82 mg, KOH g⁻¹.

The calorific values of bio-oils ranged from 20-21 MJ kg⁻¹, which is much lower than that of gasoline 47 MJ kg⁻¹, diesel fuel 43 MJ kg⁻¹ or petroleum 42 MJ kg⁻¹^[16]. The ash content in the bio-oils varied from 0.37 to 0.65%. Ash can result from oil or water-soluble metallic compounds or from extraneous solids such as dirt and rust. The density of bio-oils ranged between 0.90 and 1.00 g cm⁻³. Density is a fundamental physical property that can be used in conjunction with other properties to characterize of bio-oil products.

The elemental compositions analysis, H/C molar ratio, O/C molar ratio and empirical formula of the bio-oils are also shown in Table 2. The IR absorbances of the bio-oil are given in Fig. 5. A great range of functional groups of phenol, alcohols, ketones, aldehydes and carboxylic acids were indicated.

GC-MS analysis was carried out in order to get an idea of the nature and type of organic compounds in the pyrolysis liquid products. Table 3 lists the possible compounds identified by the MS search libraries (Wiley7n.L and NIST98.L) of the bio-oil. The highest percentage of area was phenol at 18.10%.

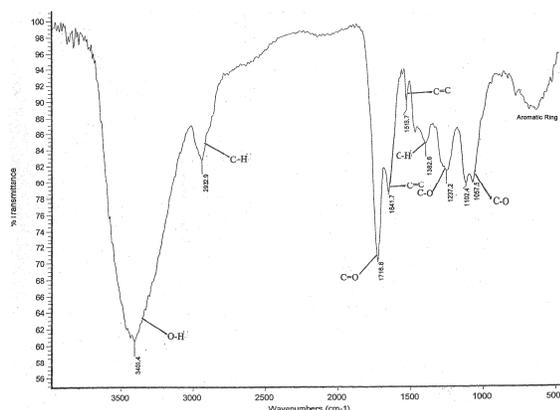


Fig. 5: Infrared spectra of the bio-oil obtained at temperature of 500°C heating rate of 30 °C min⁻¹ and particle size of 91-106 μm

Table 3: Chemical compounds of bio-oil* according to the GC/MS analysis

Peak no.	Chemical compound identification	Area %
1	Furan, 2,5-dimethyl	7.38
2	2-Cyclopentene-1-one, 2-methyl	2.20
3	2H-Pyran, 3,4-dihydro	2.99
4	Cyclopentanone, 2-methyl	7.15
5	Phenol	18.10
6	Furantetracarboxylic acid	3.52
7	Phenol, 3-methyl	1.98
8	Phenol, 4-methyl	2.69
9	Phenol, 2-methoxy	4.46
10	Phenol, 2,6-dimethoxy	6.14
11	2-Pentyn-1-ol	4.08

*Obtained at temperature of 500°C heating rate of 30 °C min⁻¹ and particle size of 91-106 μm

DISCUSSION

The higher treatment temperature has led to more bio-oil cracking resulting in higher gas yield and lower bio-oil yield^[6,8, 24]. Generally, the pyrolysis of the solid biomass conversion increased from a lower temperature to higher temperature^[12,18]. The decrease in char yield with increasing temperature could either be due to greater primary decomposition of the EFB at higher temperatures or through secondary decomposition of the char residue. The secondary decomposition of the char at higher temperatures may also give non-condensable gaseous products, which would also contribute to the increase in gas yield with increasing pyrolysis temperatures^[16].

Encinar *et al.*^[7] pyrolysed cardoon (*Cynara cardunculus* L.) with size ranged 0.43-2.00 mm hypothesized that an increase in particle size causes greater temperature gradients inside the particle so that at a given time the core temperature is lower than that

of the surface, which possibly gives rise to an increase in the char yields and a decrease in liquids and gases. Particle size is known to influence pyrolysis products yield. If the particle size is sufficiently small it can be heated uniformly, as is consistent with earlier studies^[15]. However, in this work it was observed that particle size had no significant influence on the bio-oil.

The increase of the heating rate leads to increase yield of bio-oil. It was noted that, the higher heating rate, the lower effect of mass transport limitations^[17]. The increase of the heating rate leads to decrease the char yield. This may be related to the rapid heating leads to a fast depolymerization of the solid material to primary volatiles, while at the lower heating rate dehydration to more stable anhydrocellulose is too slow and limited to occur^[5].

The moisture content (water) that is produced in the pyrolysis reaction together with any water contained from the biomass feedstock. The amount of water in the product also depends on the process parameters including the extent of secondary reaction or cracking and the temperature of the product gases leaving the liquid collection system. Water is important in many ways as; higher water content usually reduces viscosity, improves stability but reduces calorific value of bio-oils^[4].

Hemicellulose from EFB contain glucuronic acids. This might be the reason for the higher amount of free acids in bio-oil which can cause polycondensation reactions of aldehydes and phenol. As pH measures the concentration of H₃O⁺ ions, KOH addition may lead to some saponification of esters and hence an unproportional consumption of alkali^[4]. Obviously, there is no strong relationship between acid number and pH.

For the bio-oils, high water content in combination with a high O/C atomic ratio gives poor calorific values. On the other hand, at similar water content the calorific value of bio-oil is higher due to its lower O/C atomic ratio^[11]. The significant decrease in the oxygen content of the bio-oil compared to the original feedstock (CHON) is favourable, since the high oxygen content is not attractive for the production of transport fuel^[16].

The FTIR analysis showed that the bio-oil composition was dominated by oxygenated species. The high oxygen content is reflected by the presence of mostly oxygenated fractions such as carboxyl and carbonyl groups produced by pyrolysis of the cellulose and phenolic and methoxy produced by pyrolysis of the lignin. The GC-MS results showed that the chemical compositions of the bio-oil which are very similar to the inclusion of a lot of aromatics and oxygenated

compounds such as carboxylic acids, phenols, ketones and aldehydes. The presence of these aromatic and oxygenated compounds was attributed to its biopolymer textures such as cellulose and hemicellulose^[18].

CONCLUSION

In this study, pyrolysis experiments of oil palm empty fruit bunches were performed in a fluidised fixed-bed reactor. The highest bio-oil yield of 42% was obtained at an optimum pyrolysis temperature of 500 °C with particle size of 91-106 µm and the heating rate of 100°C min⁻¹. The higher treatment temperature has led to lower bio-oil yields and higher quality liquid fuels. The highest calorific value of the bio-oil obtained was 21.41 MJ kg⁻¹.

ACKNOWLEDGEMENT

The financial support for research and equipment from the Malaysian Palm Oil Board (MPOB) and University of Malaya is acknowledged. We also grateful to all staff Energy and Environment Unit, MPOB for their valuable assistance with the experiments. The permission and technical assistance of Dr. Chun-Zhu Li of Monash University, Chemical Engineering Department to set-up the experimental pyrolysis rig is much appreciated without which this study would not have been possible.

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