

Characterisation of Oil Palm Empty Fruit Bunches for Fuel Application

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Abstract: *This study was an attempt to produce bio-oil from empty fruit bunches (EFB) of oil palm waste using fast pyrolysis technology. A 150 g/h fluidised bed bench scale fast pyrolysis unit operating at atmospheric pressure was used to obtain the pyrolysis liquid. A comparison of the elemental composition of unwashed and washed feedstock was made in this study. With the five methods of treatment being considered, elements such as Al, P, Cl, Ti, Fe and Cu were removed during the washing. However, Na, S and K decreased with the reduction of the ash content of the feedstock. The properties of the liquid product were analysed and compared with wood derived bio-oil and petroleum fuels. The liquids produced had high acid content, with a High Heating Value (HHV) of about 50% of conventional petroleum fuel. The char content was in the range of 0.2–2.0%. The composition and particle size distribution of the washed and unwashed feedstock were determined, and the thermal degradation behaviour was analysed by thermogravimetric analysis (TGA). The product yield for washed EFB was similar to that of low ash wood, while the product yield for unwashed EFB was much closer to that of higher ash feedstock. The pyrolysis liquids derived from unwashed EFB were found to be in both an aqueous and an organic phase, which presents challenges for their commercial application as a fuel. Some possibilities of upgrading were also discussed in this work.*

Keywords: Empty fruit bunches, fast pyrolysis, bio-oil, ash, washed feedstock, TGA

1. INTRODUCTION

Palm oil production is on a steeply rising path. The empty fruit bunches (EFB) are waste by-products that are being investigated for further uses. Currently, palm oil mills typically use the shell and the drier part of the fibre product stream, rather than EFB, to fuel their boilers, as the raw EFB contain nearly 60% water.¹

Fast pyrolysis represents a potential route to upgrade the EFB waste to value added fuels and renewable chemicals. For example, the pyrolysis of woody feedstock at temperatures around 500°C, together with short vapour residence times, will produce bio-oil yields of around 70% and char and gas yields of

around 15% each.²⁻⁴ Bio-oil is a high-density oxygenated liquid, which can be burned in diesel engines, turbines or boilers, though further work is still required to evaluate the long-term reliability.⁵ It is also used for the production of speciality chemicals, such as flavourings, which are the main products. Renewable resins and slow release fertilisers are other potential applications, which have been the subject of research.⁶ At this stage, fast pyrolysis is a novel and relatively untested technology. There are several pilot plants in North America and Europe, but there is no consistent track record yet outside of the manufacture of flavourings. Of special significance to the work reported here is that a fast pyrolysis pilot plant processing EFB has recently started production in Malaysia.⁷

Di Blasi *et al.*⁸ investigated the pyrolysis of unwashed and washed straw. A bench scale system was used to investigate the pyrolysis of these samples. They found that the liquid yields increased with the decrease in char yields for washed straw. For example, at a temperature of 500°C, the liquid yield is 43 mf wt% for unwashed feedstock compared to 58 mf wt% for washed feedstock, whereas the char yield is 28 mf wt% for unwashed feedstock compared to 23 mf wt% for washed feedstock. Mullen *et al.*⁹ carried out fast pyrolysis experiments on corn cobs and corn stover (stalks, leaves and husks), using a pilot scale fluidised bed reactor. They found that the bio-oil yield was about 60% from the corn crop residue feedstocks. The specific gravity of these bio-oils was greater than 1.0 and the High Heating Value (HHV) was about 20 MJ/kg, thus, giving these bio-oils 20–32 times the energy density of the biomass feedstocks on a volume basis. They concluded that the transportation of bio-oil was more cost effective than transportation of biomass.

The work on water washing has received only limited attention by researchers. Jenkins *et al.*¹⁰ studied ash reduction in rice straw and wheat straw in order to reduce slagging and fouling in furnaces and other thermal conversion systems. Alkali in the ash of crop biomass fuels, mainly potassium and sodium, creates serious slagging and fouling in conventional boilers. All components, except silica and calcium, were significantly reduced, although only a small proportion of the ash for rice straw was removed. Piyali Das *et al.*¹¹ investigated vacuum pyrolysis of deashed sugarcane bagasse. The objective of their work was to understand the change in the quantity and quality of the oil fraction obtained from the pyrolysis of the deashed biomass. They believed that the presence of alkali metals in ash catalyses the polymerisation reactions in the oils and thereby increases the oil viscosity.^{12,13} In the case of water leaching, it was found that the extractives were washed out, which reduced their levels from 25.8 mf wt% to 13.1 mf wt%.

Scott *et al.*¹⁴ published a preliminary study of the removal rates of alkaline cations present in poplar wood (potassium and calcium mainly) by washing with hot water and mild acid. They found that hot water washing alone is able to remove a major amount of the alkaline cations from wood as the results indicated that over 90% of the potassium and over 65% of the calcium was readily washed out by hot water. A mild acid can readily remove most of the alkaline cations from biomass and it is more significant at a temperature of 60°C.

The palm oil industry is currently expanding rapidly and produces large amounts of poorly utilised waste biomass. Therefore, an investigation of fast pyrolysis technology to convert oil palm waste, such as EFB to liquids, is worthwhile. Results for the production of bio-oil derived from unwashed EFB were presented elsewhere,¹⁵ and it was found that in all cases, the liquid product separated into two phases, which presented difficulties for fuel applications. The aim of this work is to study fast pyrolysis of EFB in a fluidised bed reactor with a nominal capacity of 150 g/h to produce bio-oil as a potential liquid fuel. Another aim of this work is to study the effect of ash reduction on the yield and maximum ash level to produce a homogenous bio-oil. The results are compared to those from pyrolysis of various feedstocks with different ash contents.

2. MATERIALS AND METHODS

2.1 Feedstock Preparation

The EFB used in the experiments were supplied by the Malaysian Palm Oil Board (MPOB). Samples received were relatively dry, having less than 10 mf wt% moisture, and were in the form of whole bunches. Particle size reduction was required to allow fast pyrolysis of the EFB on the available 150 g/h system. The bunches were first manually chopped into smaller pieces that could be fed into a shredder. Then, a Fritsch grinder with a screen size of 500 µm was used to reduce the feedstock size to less than 500 µm. After extensive feeding trials, it was found that only particles between 250–355 µm were easily fed. Both the size fractions below and above this range frequently led to blockage of the available feeder.

To reduce the ash content of the EFB by varying amounts, a range of simple water washing techniques was employed. The treatments used for this work are briefly described in Table 1. Notably, freshly sterilised empty fruit bunches typically have a water content of 60% on a wet basis. Water washing, as described in Abdullah,¹⁵ therefore does not have to bear a large additional cost burden from drying, as drying is required in any case.

Table 1: Ash content of washed EFB according to washing method.

Ash content, mf wt%	Water washing method
1.03	Soak 100 g of feedstock of size 250–355 μm for 24 hours at ambient temperature in 7 litres of distilled water.
2.14	Soak 100 g of feedstock of size 2–3 cm for 20 minutes at ambient temperature in 5 litres of distilled water (mentioned as method 3 in Section 3.1.1 and shown in Table 3)
3.05	Soak 100 g of feedstock of size 2–3 cm for 10 minutes at ambient temperature in 5 litres of distilled water (mentioned as method 2 in Section 3.1.1 and shown in Table 3)
3.68	By manual agitation of 100 g of feedstock of size 2–3 cm for 1 minute at ambient temperature in 5 litres of distilled water (mentioned as method 1 in Section 3.1.1 and shown in Table 3)
5.43	Unwashed feedstock that was not subjected to any washing.

2.1.1 Surface structure and EDX analysis

Scanning Electron Microscope (SEM) analysis and Electron Dispersive X-ray Spectroscopy (EDX) analysis were carried out on unwashed and washed feedstock for a range of ash content in order to study their surface structure and elemental composition. These analyses were performed at Aston Microscopy of Engineering with the assistance of the expert operator, who used a Cambridge S-90 Scanning Electron Microscope with digital computer imaging.

2.1.2 Thermogravimetric analysis of unwashed EFB and washed EFB

The thermal characteristics of washed and unwashed EFB were analysed with a computerised Perkin-Elmer Pyris 1 thermogravimetric analyser. Thermogravimetric analysis (TGA) was performed under 100 ml/min nitrogen with a heating rate of 10°C/min.

2.2 Experimental Setup

A fluidised bed bench scale fast pyrolysis unit with a nominal capacity of 150 g/h available at University of Aston was employed for nearly all runs. This reactor was operating at atmospheric pressure. Figure 1 shows a flow chart of the fluidised bed pyrolysis process. The reactor was a stainless steel cylinder and the heating medium in the reactor was inert sand. The fluidising gas was nitrogen, which was preheated prior to entering the base of the reactor.

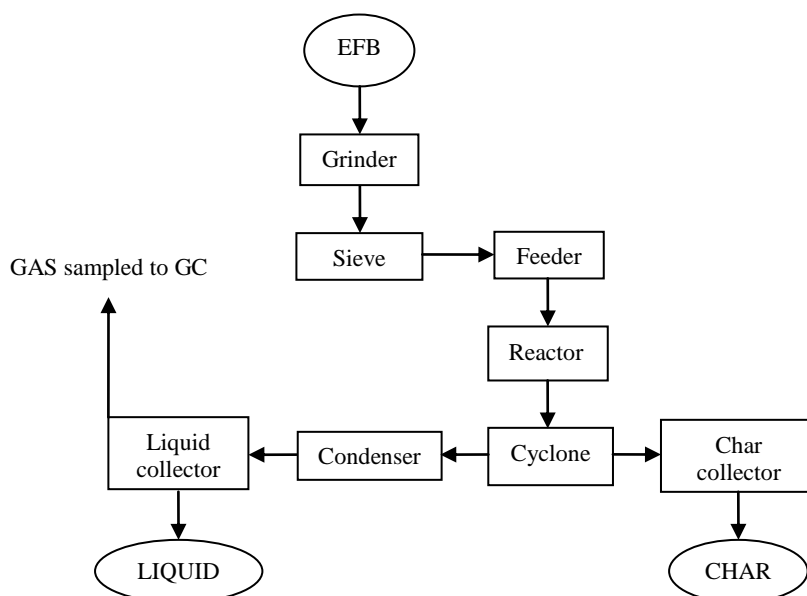


Figure 1: Flow chart of a fluidised bed pyrolysis process.

The char was carried out of the reactor body by the fluidising gas flow, which is known as ‘blow-through’ mode.¹⁶ The char was then separated from the product stream in a cyclone. The condensable vapours were collected in the liquid products collection system, which consisted of two cooled condensers, an electrostatic precipitator (EP) and a cotton wool filter. The incondensable gases left the system through a gas meter and were then sampled by gas chromatography (GC) to assess the quantity and type of gas produced.

To investigate the quality and characteristics of pyrolysis liquid of this work, the pyrolysis experiment was carried out at a temperature of about 500°C and at a residence time of 1.1 s on the washed feedstock with a size range of 355–600 μm and ash content of 1.06 mf wt% using a 1 kg/h rig. Even though most of the pyrolysis liquids from washed feedstock were homogenous, the liquids collected were not sufficient for other analyses.

The operation of the 1 kg/h system is similar to the 150 g/h system, which also employed nitrogen as the fluidising gas and sand as the bed material. However, the reaction products were passed through two cyclones where the char was removed. The remaining vapours were quenched with cooled recycle isopar, a proprietary isoparaffin supplied by Exxon Mobil Corporation. To remove aerosols not captured by the quench column, the gas was then passed through an EP, which was very effective at capturing aerosols. The liquids collected by the

quench column and EP drain into a common storage tank, which also contained the isopar that is lighter than bio-oil. Bio-oil sank to the bottom of the tank, whereas isopar accumulated at the top, where the pump inlet for the quench column recycle pump was located.

2.2.1 Char content

A filtration method was used to determine the char content in pyrolysis liquids.¹⁷ To enable the pyrolysis liquids to pass through the filter, the pyrolysis liquids need to be diluted with a suitable solvent. Approximately 1 g of pyrolysis liquids was weighed and then diluted in about 10 g of methanol before it was filtered. The filter was then placed in an oven at 105°C for a minimum of 6 hours and then cooled in a desiccator for 1 hour before weighing. The char content was then calculated, and an average of three samples was taken. All measurements of weight were taken up to four decimal places with an accuracy of ± 0.001 g.

2.2.2 Viscosity

Viscosity describes a fluid's internal resistance to flow and can be thought of as a measure of fluid friction. For fuel, the viscosity is important because of its effect on pumping and injecting.¹⁸ Viscosity measurements were carried out using capillary viscometers at a fixed temperature of 25°C. Only about 4 ml of sample was required for the test using this type of viscometer. The viscosity was measured by determining the time taken for a fixed volume of pyrolysis liquids to flow between two marked points, and the viscosity was calculated using the following equation:

$$V = Ct \quad (1)$$

where,

V is the viscosity in centipoises, C is the viscometer constant and is not affected by the temperature, and t is the time in seconds it takes for the liquid to fall from the first timing mark to the second mark.

2.2.3 Stability

The Viscosity Index (VI) measures the relative change in viscosity with time and is used to provide a measure of stability. VI was calculated using the following equation:

$$VI = (\mu_f - \mu_i) / \mu_i \quad (2)$$

where,

μ_i is the initial viscosity, the viscosity of the fresh pyrolysis liquid tested at 25°C after 24 hours from which it was produced, and μ_f is the final viscosity, the viscosity of the pyrolysis liquid stored for 24 hours at 80°C, which is now referred to as an aged pyrolysis liquid, as recommended by the Aston Viscosity Index.

The viscosity of two pyrolysis liquids were re-tested at 25°C as well. A lower VI number indicates greater stability of the pyrolysis liquid. A VI of zero would be a completely stable liquid.

2.2.4 Fourier transform infra-red spectroscopy

Fourier transform infra-red (FTIR) is a fast scanning, high resolution, high signal-to-noise ratio, and non-destructive analytical technique that is used to ascertain the presence of specific functional groups in pyrolysis liquids. The PerkinElmer Spectrum 100 Series FT-IR spectrometers were used in this work. Analysis of FTIR spectra at wave numbers 4000 to 200 cm^{-1} of pyrolysis liquids provides a quick and simple qualitative technique that uses the standard IR spectra to identify the functional group(s) of the components of the derived pyrolysis liquids.

2.2.5 Lignin content

The pyrolytic lignins were obtained from pyrolysis liquids by dropwise addition of the pyrolysis liquids to distilled water¹⁹ under vigorous stirring (> 5000 rpm) using an ultra turrax. The ratio of pyrolysis liquids to water used in this study was 1:50. After slowly adding the pyrolysis liquids to distilled water, pyrolytic lignin precipitated. After precipitation, the liquid smoke (water soluble part of pyrolysis liquids) was dissolved in a large amount of distilled water. Subsequently, the solid was filtered and thoroughly washed until the filtrate reached a neutral pH. Finally, the wet solids (pyrolytic lignins) were dried in a vacuum at ambient temperature for 24 hours.

2.2.6 Gel permeation chromatography

The molar mass and molecular weight of pyrolytic lignins were determined using a gel permeation chromatography (GPC) assay. The Waters 717 Plus Autosampler GPC system was used in this study. The chromatography was set to 40°C and equipped with columns which have pore sizes of 50 and 100 Å and lengths of 300 and 600 mm. The pyrolytic lignin sample was diluted in THF (tetrahydrofuran, Aldrich 99.5% / HPLC grade) to make a 5 mg/ml solution. This

sample solution was filtered through filter paper with a 0.2 μm pore size to remove insoluble impurities, and toluene was added into the sample solution to act as a flow marker. About 100 μl of sample solution was injected into a mobile phase to allow the sample to elute through the columns.

A series of polystyrene samples with molar masses ranging from 161 g/mol to 72200 g/mol were used as calibration standards. The Cirrus GPC software was used to determine the experimental data process with regards to molar mass and analysis. The number average molar mass (M_n), weight average molar mass (M_w), molecular weight at highest peak (M_p) and polydispersity index ($PD = M_w/M_n$) were calculated from refractive index (RI) signals using the software. Detectors consist of a differential refractive index and a photometer in the UV range of 280 nm.

3. RESULTS AND DISCUSSION

A dark brown, sticky mass stuck to the walls of the EP, although the pyrolysis experiment was carried out using a 1 kg/h rig. The amount of dark brown, sticky mass on the walls of the EP and liquids collected in the tank were about 22.8% and 74%, respectively, of total pyrolysis liquids produced from the pyrolysis experiment. Therefore, in the future, a system that is capable of collecting the liquid in one single collecting point is recommended, by implementing a flushing system in the EP for the purpose of analysing the liquid quality as shown in Figure 2. The liquid product collected in the tank was analysed for its properties as a potential fuel in comparison to petroleum fuel or other applications. However, only a few analyses were carried out for the organic mass that stuck to the walls of the EP, as it was very viscous.

3.1 Properties of Feedstock

The key properties of EFB, both measured for this research and from the literature, are given in Table 2. The high ash and potassium values are noteworthy because ash, and potassium in particular, leads to reduced liquid yields in fast pyrolysis.⁵ The carbon and hydrogen content are comparable to woody biomass, as is the measured heating value. The lowest HHV in the literature²⁰ could be due to confusion between values quoted on a dry basis as opposed to a wet basis, a problem apparent elsewhere in the literature. For example, a value of 10 MJ/kg is quoted for dry oil palm matter,²¹ which is clearly too low for a ligno-cellulosic biomass on a dry basis, or values for wet FFB were used for dry FFB.²²

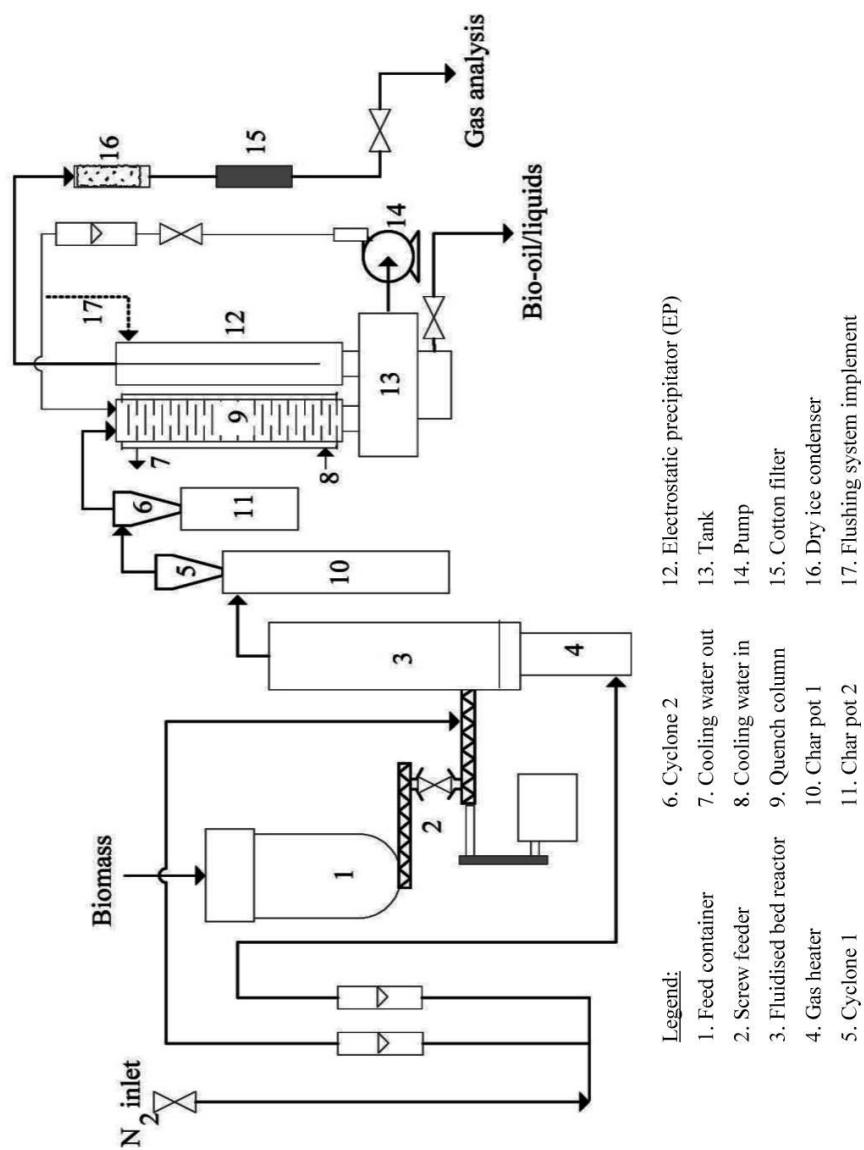


Figure 2: A 1 kg/h fluidised bed system with implementation of flushing system in EP.

Table 2: Properties of EFB (mf wt%).

Component / Property	Literature values	References	Measured	Method
Cellulose	59.7	[24]	na	na
Hemicellulose	22.1	[24]	na	na
Lignin	18.1	[24]	na	na
<i>Elemental analysis</i>				
Carbon	48.9	[25]	49.07	Combustion analysis
Hydrogen	6.3	[26]	6.48	
Nitrogen	0.7	[26]	0.7	
Sulphur	0.2	[26]	<0.10	By difference
Oxygen	36.7	[26]	38.29	
K	2.24	[27]	2.00	Spectrometry
K ₂ O	3.08–3.65	[28]	na	na
<i>Proximate analysis</i>				
Moisture	na	na	7.95	ASTM E871
Volatiles	75.7	[25]	83.86	ASTM E872
Ash	4.3	[20]	5.36	NREL LAP005
Fixed carbon	17	[26]	10.78	By difference
HHV (MJ/kg)	19.0	[25]	19.35	Bomb calorimeter
LHV (MJ/kg)	17.2	[27]	na	na

Notes: na - not available

The distribution of feed particle size after grinding is shown in Figure 3. The ash content of each size fraction was determined using National Renewable Energy Laboratory (NREL) Standard Analytical Method LAP005,²³ and the mass average of the size fractions of 5.39% compares well, within the accuracy of the measurements, with the original sample sent by MPOB, which had an ash content of 5.36%.

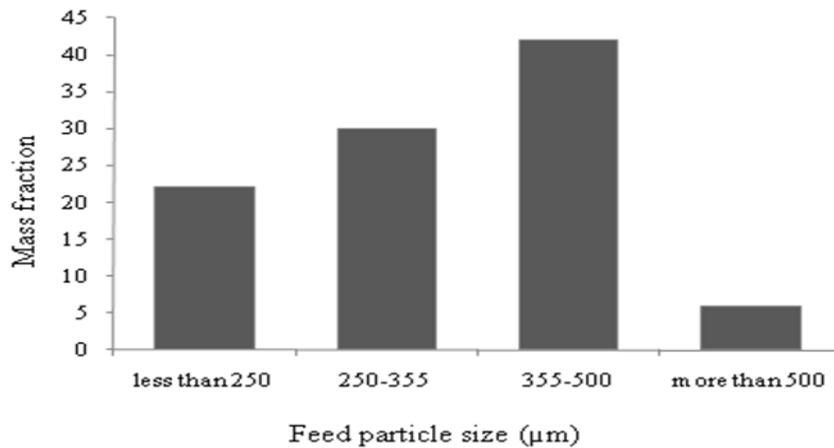


Figure 3: Particle size distribution of EFB.

3.1.1 Surface structure and EDX analysis

We found that the surface of the washed feedstock was clean, and there was no dirt or particular matter on the surface. However, the unwashed feedstock of sizes ranging from 355–500 μm could not be easily fed into the feeder because the particles tended to stick to each other easily, thus, making the feeding process for the 150 g/h reactor difficult.

Table 3 shows the results of the elemental analysis of unwashed feedstock and washed feedstock over a range of ash content and leachate, using Electron Dispersive X-ray Spectroscopy (EDX). It shows that hydrogen cannot be detected by this method. Elements such as Al, P, Cl, Ti, Fe and Cu were removed during the washing. However, only Na, S and K were decreased with the reduction of the ash content of the feedstock. The treatment of manual agitation on large feedstock at ambient temperature for 1 minute and soaking the large feedstock at ambient temperature for 10 minutes are referred to as method 1 and method 2, respectively. We found that method 2 was more effective than method 1 in removing potassium, sodium and sulphur. The treatment of stirring the large feedstock at 90°C for 2 hours, referred to as method 4, was more effective in removing potassium, sodium and sulphur by 70.4%, 100% and 87.9%, respectively. However, soaking the large feedstock at ambient temperature for 20 minutes, referred as method 3, was also effective at removing potassium, sodium and sulphur by 67.2%, 100% and 37.9%, respectively. The treatment of soaking the large feedstock at ambient temperature for 1 minute refers to method 5. The leachate is the washed water that was collected after the washing treatment. An EDX analysis on the leachate of method 5 showed that it has a high potassium content of about 82.53 wt%, which was expected because the ash content of the leachate was even higher. It was expected that the leachate contain insoluble inorganics, such as soil and insoluble organics.

Table 3: Elemental composition of unwashed and washed feedstock.

Element	Unwashed EFB	Method 1	Method 2	Method 3	Method 4	Method 5 (leachate)
(wt%)						
C	64.3	65.8	69	73.4	72.4	0.03
O	19.8	20.2	18.9	17.8	19.0	3.79
Na	0.33	0.41	0	0	0	0.63
Mg	0.19	0.25	0.29	0.35	0	1.68
Al	0.16	0.1	0.51	0.03	0	0
Si	1.95	1.87	1.34	2	1.72	0.1
P	1.06	0.43	0.8	1.39	1.71	5.39
S	0.48	0.55	0.39	0.36	0.07	1.54
Cl	1.37	0.37	0.5	0.19	0.36	3.48

(continued)

Table 3: (continued)

Element	Unwashed EFB	Method 1	Method 2	Method 3	Method 4	Method 5 (leachate)
			(wt%)			
K	8.61	9.1	7.68	2.82	2.55	82.5
Ca	1.43	1.47	1.76	1.56	1.53	1.06
Ti	0.13	0	0.06	0	0.29	0.03
Cr	0.15	0.25	0	0.55	0	0
Mn	0	0	0.06	0	0.05	0.02
Fe	0.29	0	0.48	0.08	0	0
Ni	0	0.26	0	0	0.59	0
Cu	0.31	0	0.28	0	0.23	0.04
Zn	0.12	0	0	0	0.66	0.06
Ash content (mf wt%)	5.43	3.68	3.05	2.14	1.15	34.1

3.1.2 Thermogravimetric analysis of unwashed EFB and washed EFB

The thermal degradation characteristics of unwashed and washed feedstock are displayed in Figure 4 and Figure 5 by thermogravimetry (TG) and differential thermogravimetry curves (DTG), respectively. The washing procedure employed for the washed sample gave an ash content of 1.15 mf wt% after two hours of stirring 100 g of EFB in 7 litres of distilled water at 90°C. The ash content of the unwashed sample was 5.43 mf wt%. The thermal behaviour of the two samples substantially differed. The unwashed sample showed a small DTG peak around 200°C, which might be indicative of extractives.²⁹ No such peak was apparent for the washed sample. A possible explanation is that the high washing temperature could have led to the loss of extractives during washing.

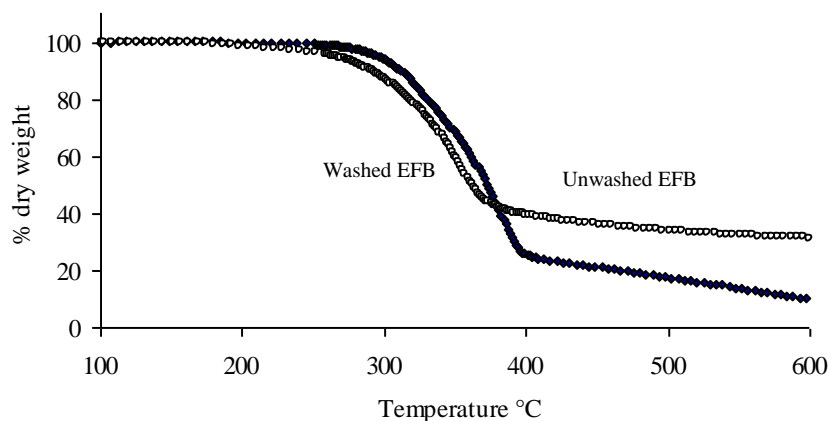


Figure 4: Thermogravimetric analysis of washed and unwashed EFB.

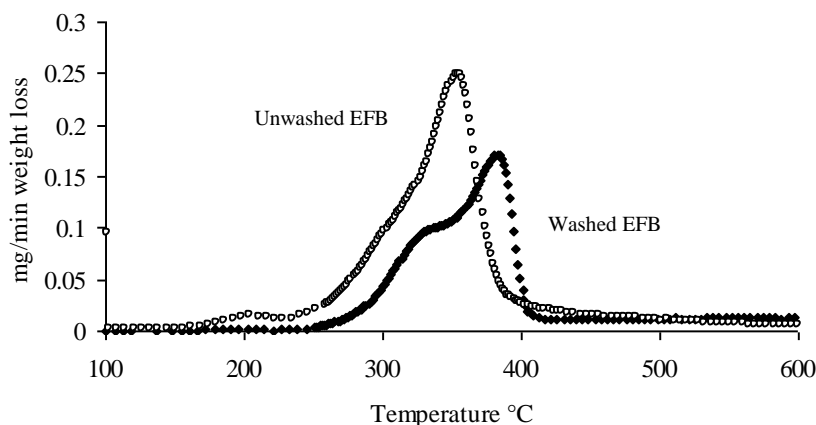


Figure 5: Differential thermogravimetric analysis of washed and unwashed EFB.

The unwashed sample showed a single peak at 355°C, and the washed sample had its greatest weight loss at 383°C. Furthermore, there was a hump at around 320°C for the washed sample, which was not visible in the DTG curve of the unwashed sample. Similar trends have been reported by other authors for low ash and high ash biomass feedstock.^{30–32} It is generally assumed that the temperature shift is due to the catalytic effect of the ash and that this shift leads to a single DTG peak for both cellulose and hemicellulose for high ash biomass. However, the hump apparent in the DTG curve for low ash biomass is indicative of hemicellulose and the actual peak is due to the decomposition of cellulose.

The total weight loss between 100–450°C is 77.4% for the washed sample and only 65.8% for the unwashed sample. There are two explanations. Firstly, the ash itself will largely not volatilise and therefore contribute to the char yield. Secondly, the ash is also believed to contribute to greater char production through its catalytic activity.

A number of other washed samples with intermediate ash contents have been subjected to TGA analysis. The resulting curves vary smoothly between the two extremes as presented in Figure 4 and Figure 5. The total weight loss between 100–450°C and temperature of maximal weight loss are listed in Figure 6.

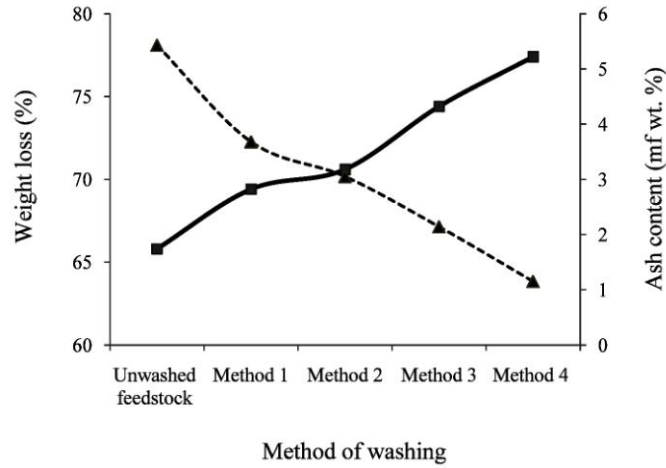


Figure 6: Weight loss in TGA between the temperatures of 100–450°C.

3.2 Properties of Liquid Product

Table 4 shows the characteristics of pyrolysis liquid from this work in comparison with pyrolysis liquid derived from olive bagasse³³ and petroleum fuel.³⁴ The HHV was calculated from the data of the elemental analysis using Channiwala and Parikh’s formula³⁵ as shown below:

$$HHV = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.0211A \quad (3)$$

where HHV stands for high heating value on a dry basis and the unit is MJ/kg.

Most of the characteristics of the pyrolysis liquid are in Table 4, and the results of liquid product analysis discussed in following subtopics.

Table 4: Comparison of characteristics of pyrolysis liquid and petroleum fuel.

Type of liquids	Pyrolysis liquid collected in EP’s wall	Pyrolysis liquid collected in tank	Pyrolysis liquid of olive bagasse	Petroleum fuel
Reference	this work	this work	[33]	[34]
Water content, mf wt%	6.66	21.68	–	0.1
<i>Elemental analysis (mf wt%)</i>				
C	56.47	41.86	66.9	85.2
H	7.85	7.82	9.2	11.1
O	35.46	33.94	21.9	1.0
N	0.22	0.1	2.0	0.3

(continued)

Table 4: (continued)

Type of liquids	Pyrolysis liquid collected in EP's wall	Pyrolysis liquid collected in tank	Pyrolysis liquid of olive bagasse	Petroleum fuel
Reference	this work	this work	[33]	[34]
S	0	0	0	2.3
HHV, MJ/kg (Channiwala and Parikh's formula)	25.29	20.32	31.9	42.94
Density, kg/m ³	1548	1206	1070	940
Viscosity, cP@25°C	not determined	46.31	51	180
pH	2.33	2.7	–	–
GPC analysis (g/mol)				
M _p	447	222	–	–
M _n	382	357	–	–
M _w	562	564	–	–
Polydispersity	1.47	1.57	–	–

3.2.1 pH value

All the liquids produced from unwashed feedstock and washed feedstock gave a pH of between 2 and 3, which indicated higher acid contents that arose from organic acids, such as acetic and formic acids. It showed that treating the feedstock by water washing did not increase the pH value of liquids. Furthermore, mild steel is not suitable for handling or storage as it could have a reaction with the pyrolysis liquid. Polypropylene piping, for example, has been used to overcome this problem.

3.2.2 Density

As expected, the density of liquids stuck on the walls of the EP are more viscous and have much higher density than the density of liquids collected in the tank. The densities of liquids collected in the tank and on the walls of the EP are 1206.1 kg/m³ and 1548 kg/m³, respectively. The densities of petroleum and a typical pyrolysis liquid are 940 kg/m³ and 1230 kg/m³, respectively.³⁴ Pyrolysis liquid density is higher compared to the density of petroleum, which means that the liquid has about 42% of the energy content of fuel oil on a weight basis, but 61% on a volumetric basis.

3.2.3 Heating value

Typically, pyrolysis liquid has a heating value of about 40–50% of conventional petroleum fuel. The HHV of the liquid collected in the tank and on

the walls of the EP had an average value of 21.49 MJ/kg, which is about 50% of conventional petroleum fuel.

3.2.4 Char content

Char is a coarse powder with particle sizes ranging from less than a micron to several millimetres, which have similar size and shape characteristics as the feedstock. Overall, the char content of all liquids from unwashed and washed feedstock is in the range of 0.2–2.0%. According to Peiyan,³⁶ very small particle size char was more easily blown into the collection system. Therefore, higher temperatures gave high oil char contents.

3.2.5 Viscosity

Because the liquid stuck on the walls of the EP was too viscous, the viscosity was measured on the liquid collected in the tank only. The viscosities of the fresh liquid and old liquid at 25°C were 46.31 cp and 67.58 cp, respectively. The fresh liquid is the liquid tested after 24 hours from which it was produced and old liquid is the liquid that is stored for 24 hours at 80°C. We expected that the viscosity on the whole liquid of this run would be higher than 46.31 cp if the viscosity of the liquid stuck on the walls of the EP was taken into account. As shown in Table 4, the viscosities of petroleum and pyrolysis liquid of olive bagasse at 25°C is 180 cP and 51 cP, respectively. Therefore, this result shows that the density of petroleum is much higher compared to the viscosity of pyrolysis liquid derived from olive bagasse or pyrolysis liquid from this study.

3.2.6 Stability

The stability of the pyrolysis liquid was examined by monitoring the changes in viscosity, density and pH. The density and pH of the pyrolysis liquid remained constant but the viscosity changed with time. The oil's stability was measured by calculating the viscosity index using Equation 2. The Aston Viscosity Index (AVI) number for pyrolysis liquid produced from the pyrolysis process on woody biomass at 500°C is about 2.2.³⁷ The AVI for the liquid in this study is 0.46. Thus, this liquid is quite stable as the AVI number is low. According to Salter,³⁶ the lignin content of the pyrolysis liquid greatly influenced the stability of the liquid because the more lignin in the pyrolysis liquid, the more stable the liquid is, hence, the lower AVI.

3.2.7 Functional group

The pyrolysis liquid was analysed using FTIR spectroscopy to obtain a qualitative impression of the basic functional groups present in the oil. The

measured absorption frequency spectrum is shown in Table 5. The C-H bend vibration between 1500 and 1450 cm^{-1} indicates the presence of alkanes. The absorption peak between 1750 and 1625 cm^{-1} represents the C=O stretching vibration and is suggestive of the presence of carboxylic acids, ketones and aldehydes. The absorbance peaks between 1675 and 1600 cm^{-1} represent C=C stretching vibrations. The peaks between 1300 and 1000 cm^{-1} are due to the presence of phenols and alcohols, and absorption peaks between 900 and 650 cm^{-1} indicate the presence of single, polycyclic or substituted aromatic groups.

Table 5: FTIR functional group composition of pyrolysis liquid.

Frequency range (cm^{-1})	Group	Class of compound
3000 – 2800	C-H stretching	alkanes
1750 – 1625	C=O stretching	aldehydes, carboxylic acids, ketones
1675 – 1600	C=C stretching	alkenes
1500 – 1450	C-H bending	alkanes
1300 – 1000	C-O stretching	alcohol
900 – 650	O-H bending	phenol aromatic compounds

3.2.8 Pyrolytic lignin content

Lignin is one of the major wood components, and pyrolytic lignin represents the water insoluble part of the pyrolysis liquids. Pyrolytic lignin can be obtained by precipitating pyrolysis liquid in an excess of water. In this work, pyrolysis liquid collected in the tank derived from washed EFB was precipitated. The content of pyrolytic lignin in the pyrolysis liquid collected in the tank is 12.42% w/w, similar to the pyrolytic lignin yield from bio-oil derived from hard wood.³⁷ The pyrolytic lignin has a relatively high calorific value and has been proposed as a phenol formaldehyde resin replacement.³⁹ For this application, it would have to be separated from the remainder of the bio-oil by differential condensation and collection and presents an energy efficient option.

3.2.9 Molecular weight

The pyrolytic lignin of liquid collected in the tank was prepared by precipitating this liquid in water, and the molar masses of the lignin were determined using GPC. We found that the average molar mass (M_w), the average molar number (M_n) and the molar mass at maximum peak (M_p) of the pyrolytic lignin were 886 g/mol, 588 g/mol and 660 g/mol, respectively. The results of molar masses for both liquid fractions (EP fraction and tank fraction) are mentioned in Table 4. The molecular weight is an important indicator of the degree of polymerisation and that the peak molecular weight of the liquid collected in the tank is much lower than that of the pyrolytic lignin fraction.

3.2.10 Feedstock comparison

A comparison of EFB with results from the literature for other biomass feedstock is presented in Figure 7 and Table 6. The product yield for washed EFB is similar to that of a low ash wood, such as poplar, whereas the product yield for unwashed EFB is much closer to that obtained for higher ash feedstock, such as wheat straw.^{40,41}

Table 6: Comparison of EFB with other biomass feedstock.

Feedstock	Unwashed EFB	Washed EFB	Poplar aspen	Corn stover	Wheat straw
Reference	this work	this work	[36]	[37]	[37]
Cellulose [mf wt%]	59.7	–	42.3	31.0	32.4
Hemicellulose [mf wt%]	22.1	–	31.0	43.0	41.8
Lignin [mf wt%]	18.1	–	16.2	13.0	16.7
Moisture [mf wt%]	7.48–8.96	6.04–6.54	5.0	6.5	9.0
Ash [mf wt%]	5.29	1.03	0.39	11.0	4.6
Yields [mf wt%]					
Char	24.52	10.76	11	42.2	22
Gas	22.31	14.70	14	13.7	19
Organics	34.71	61.34	58.9	27.3	37
Total Liquids	49.8	72.36	74.1	43.1	54

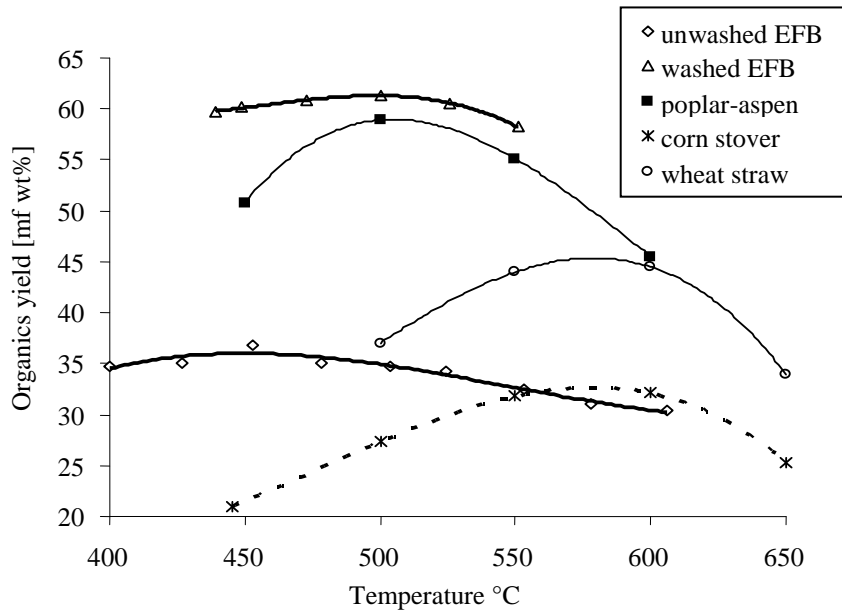


Figure 7: Organics yield as a function of temperature for a number of feedstock.

3.2.11 Physical and chemical properties of products

The pyrolysis liquids produced separated into two phases; a phase predominated by tarry organic compounds and an aqueous phase. The relative shares of the total liquid product yield of the two phases are approximately 60% for the former and 40% for the latter. A comparison of key properties for the two phases with those of wood derived bio-oil, light fuel oil and heavy fuel oil is given in Table 7, which also contains the ultimate analysis of the char product. The value for sulphur was not determined, as there is very little sulphur in the EFB itself. Because of its high water content, the higher heating value of the aqueous phase was not measured.

The viscosity of the aqueous phase is close to that of water, whereas the organic phase hardly flows at all. At room temperature, the organic phase clearly has a viscosity above 10,000 cP, the limit for the measuring equipment available to the authors of this work.

The empirical formula of the organics in the organic phase is $\text{CH}_{1.51}\text{O}_{0.14}$. By comparison, the empirical formula for carbohydrates is CH_2O , that of phenol is $\text{CHO}_{0.17}$ and longer chain straight alkanes approach an empirical formula of CH_2 . It is possible that the organic phase contains a small amount of palm oil, as the organics in the organic phase have a significantly higher hydrogen to carbon ratio than is the case for wood-derived slow pyrolysis tars.⁴²

Table 7: Characteristics of pyrolysis oil compared to petroleum fuel.

	EFB			Wood derived bio-oil	Light fuel oil	Heavy fuel oil
	Organics phase	Aqueous phase	Char			
C	69.35	13.83	71.43	32–48	86.0	85.6
H	9.61	11.47	1.80	7–8.5	13.6	10.3
N	0.74	0.14	0.63	<0.4	0.2	0.6
O	20.02	74.56	8.72	44–60	0	0.6
S	–	–	–	<0.05	<0.18	2.5
Moisture content	7.9	64.01	–	20–30	0.025	0.1
HHV (MJ/kg)	36.06	–	–	–	–	–
LHV (MJ/kg)	–	–	–	13–18	40.3	40.7

The phase separated liquid product would represent a challenging fuel for boilers and engines, because of the high viscosity of the organic phase and the high water content of the aqueous phase. These could be overcome by upgrading. The addition of polar solvents such as methanol or ethanol represents one of the easiest routes,⁵ and it was established by the authors of this study that the two phases both readily dissolve in methanol to give a homogeneous single-phase

product with a low viscosity. Several researchers⁴³⁻⁴⁵ have studied the addition of solvent to reduce viscosity and aging rates because the bio-oil composition changes during aging and mutual solubility of the components changes to make phase separation more likely. Further research would be required to establish how much methanol would have to be added at a minimum to obtain a single-phase liquid. The addition of ethanol could also reduce corrosivity and allow the removal of the water through low temperature vacuum distillation,⁴⁶ which is otherwise difficult because of the thermal instability of pyrolysis liquids.

Thermochemical upgrading is another possibility, either via gasification and Fischer-Tropsch, where it may be advantageous to gasify a bio-oil char slurry rather than the biomass itself,⁴⁷ or via catalytic steam reforming of the aqueous phase to obtain the hydrogen for hydrogenation of the organic phase.⁴⁸

The organic phase might also be directly used in engines, turbines and boilers, if it is first pre-heated to reduce its viscosity, though its thermal instability might limit the temperature it can be brought up to. The aqueous phase could potentially be co-fired to reduce thermal NO_x and enable efficient burning of its dissolved dry matter. As mentioned in the introduction, it might also be possible to obtain useful chemicals, such as phenolic compounds for resin making, as a commercial by-product.

Due to the low liquid yield, not all of the char and gas would be required for internal process heat. Some could be used to dry the very wet fresh EFB. Burning the char, which contains nearly all the minerals, would allow the recovery of the ash, which is useful as a fertiliser.²¹ The gas is high in carbon dioxide and has a higher heating value of only approximately 4 MJ/kg. It may potentially be utilised for carbon sequestration enhanced oil recovery schemes.⁴⁹

Because the fresh EFB is very wet, washing of the EFB prior to fast pyrolysis represents another interesting avenue to enhance the value of the fuel products obtained, as drying is required already and would therefore add a little extra expense. Simple soaking in water at room temperature can remove most of the ash, with small biomass losses, giving a feedstock with similar yield characteristics as low ash woody biomass.¹⁵

4. CONCLUSION

A study of fast pyrolysis on unwashed and washed Empty Fruit Bunches (EFB) was performed using a 150 g/h fluidised bed reactor. The liquids produced from both the unwashed and washed EFB had high acid content and a density of a typical pyrolysis liquid, with a High Heating Value (HHV) of about 50% of the

conventional petroleum fuel. The char content of all liquids from unwashed and washed feedstock was in the range of 0.2–2.0%. The viscosity of the liquid had an overall value higher than 46.31 cp. The liquid had low Aston Viscosity Index (AVI) and therefore was considered stable. The measured absorption frequency spectrum was shown in Table 5. The content of pyrolytic lignin in the pyrolysis liquid collected was similar to pyrolytic lignin yielded from bio-oil derived from hard wood. The results of molar masses for both liquids were presented in Table 4. By feedstock comparison, the product yield for washed EFB was similar to that of a low ash wood, whereas the product yield for unwashed EFB was much closer to that of higher ash feedstock. However, the pyrolysis liquids that were produced separated into two phases; a phase predominated by tarry organic compounds (60%) and an aqueous phase (40%).

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