PYROLYSIS LIQUID DERIVED FROM OIL PALM EMPTY FRUIT BUNCHES

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Abstract: *Oil palm waste especially empty fruit bunches (EFB) is a major management and disposal problem in Malaysia. This is an exploratory evaluation of the potential for recovering renewable fuels from the EFB via fast pyrolysis. Preliminary studies were done on the characteristics of the empty fruit bunches, and the thermal behaviours using thermogravimetric analysis (TGA) were included as well. For the fast pyrolysis experimentation, a 150 g/h fluidized bed bench scale unit was used to study the effect of reaction temperature and vapour residence time on the pyrolysis products. Reaction temperatures studied were from 400 to 600ºC. It was found that the maximum organics liquid yield was at a reactor temperature of 450ºC. In all cases the pyrolysis liquid separated into two phases: an aqueous and a tarry phase. The pyrolysis liquid was analyzed by Fourier Transform Infrared (FTIR) spectroscopy. From the FTIR analysis, it was found that the pyrolysis liquid derived from empty EFB consisted mostly of hydrocarbon compounds.*

Keywords: fast pyrolysis, empty fruit bunches, Fourier Transform Infrared spectroscopy

1. INTRODUCTION

The total contribution of biomass to the primary energy supply of Malaysia has been estimated to be at least 2.5 million tonne oil equivalent (MTOE) in 1995, [1,2] which is about 14% of the primary energy supply. However, this is only 26.8% of the total biological waste in Malaysia, and most of the balance of the waste (73.2%) is allowed to decompose naturally or is burned in the open. If these wastes are used to produce energy, it is expected that the biomass contribution for the energy utilization in the country would increase to 53% [3].

Malaysia is the world's largest producer and exporter of palm oil, replacing Nigeria as the chief producer in 1971 [4]. The palm oil mill is self-sufficient in energy, using waste fibres and shell as fuel to generate steam in boilers for processing, and power-generation. The palm oil industry also produces other types of waste in large quantities empty fruit bunches (EFB) and palm oil mill effluent (POME). Figure 1 [5] shows the breakdown of products and wastes from each EFB of the palm oil. Figure 2 [6] shows a proposed plan for the operational process and product of the palm oil industry if EFB are also used as fuel besides palm shells and fibres. If the fibres and shells are sufficient to generate energy in palm oil industry, therefore, the pyrolysis liquids derived from EFB wastes can be used as a fuel in many static applications including furnaces, engines and turbines for electricity generation.

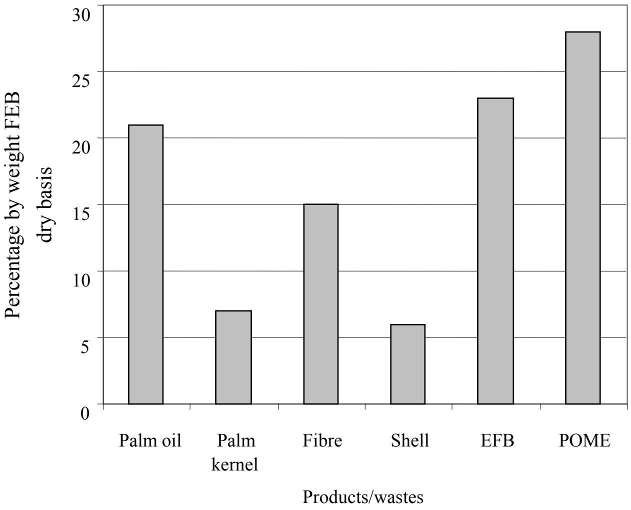

Figure 1: Products/wastes from each bunch of EFB

There is a wide range of processes available for converting biomass and biowastes into more valuable products such as fuel oil, fuel gas or other higher value products for the chemical industry [7]. This can be done by physical, biological (anaerobic digestion and fermentation), chemical or thermal methods produce a solid, liquid or gaseous fuel if fuels are the desired product. From the variety of technologies available, thermochemical processing has received considerable attention for converting biomass into more valuable and usable products. Pyrolysis, one of four main thermochemical methods for converting biomass to provide energy, is the most promising thermochemical conversion technology for the production of pyrolysis liquid oil [8]. This process involves the heating of the biomass in the absence of oxygen or air to produce a mixture of solid char, condensable liquids and gases [9]. The pyrolysis liquid fuel can be used as a substitute for fuel oil in any static heating or electricity generation application [10,11]. This liquid can also be used to produce a range of speciality and commodity chemicals [12]. The key advantage is that the liquid is clean compared to charcoal and can be readily stored and/or transported. In addition, the liquid's density is very high at around 1.2 kg/litre [13].

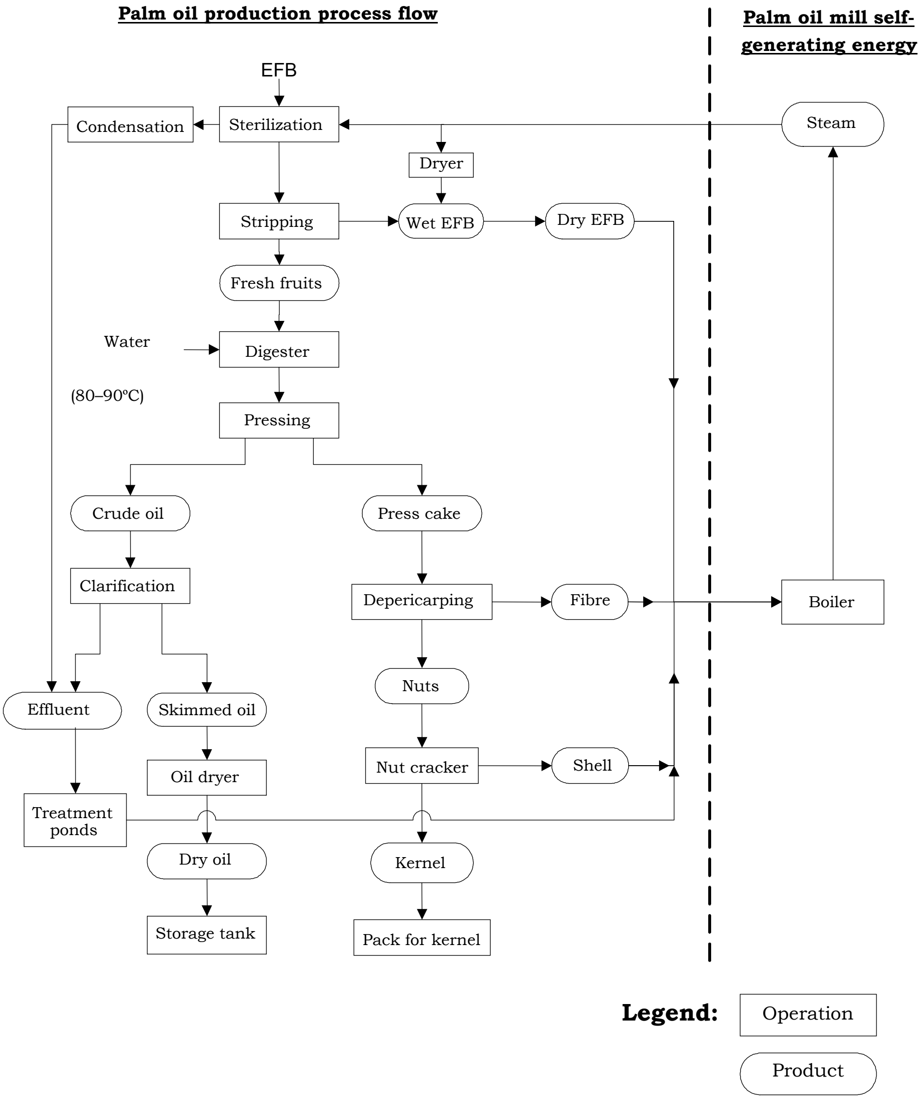

Figure 2: Proposed plan for operation of a palm oil mill
Source: Adapted from Mahlia et al. [6]

The present work has been carried out on fast pyrolysis of EFE in a fluidized bed reactor with a nominal capacity of 150 g/h. The objective is to determine reactor conditions which would maximize liquid yield. The biomass was pyrolyzed in the fluidized bed reactor at temperatures of 400–600ºC and with different vapour residence times.

2. MATERIALS AND METHODS

2.1 Feedstock Preparation

EFB used in the experiments were supplied by Malaysian Palm Oil Board. Samples received in the form of whole bunches, were in a fairly dry condition with less than 10 wt. % mf. Therefore, the bunches were chopped into smaller sizes, and subsequently, a Fritsch grinder with a screen size of 500 µm was used to reduce the size of the feedstock to less than 500 µm. The distribution of feed particle size after the grinding process is given in Figure 3. The particle sizes of interest for our studies are between 250–355 µm as the feedstock of this size range can easily be fed into the feeder.

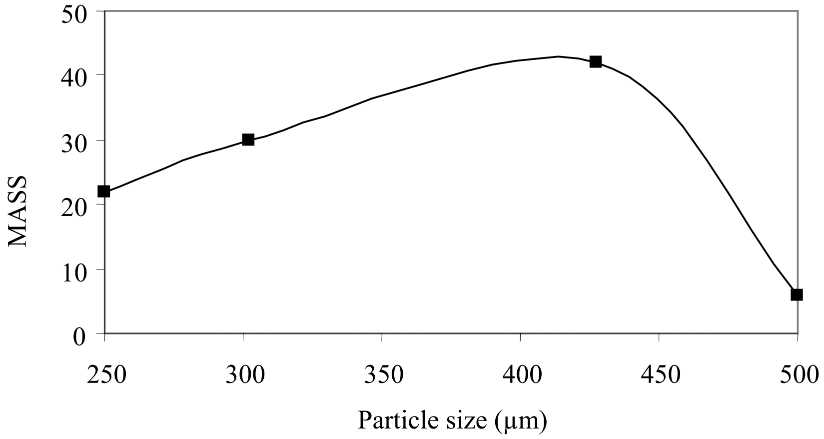

Figure 3: Particle size distribution of EFB powder

2.2 Properties of Feedstock

The properties of the ground EFB are given in Table 1. The ash content of the feedstock was determined using the National Renewable Energy Laboratory (NREL) Standard Analytical Method LAP005. The samples were tested using the hydrolysis method for cellulose, hemicellulose and lignin (supplied by Professor Farid Nasir Ani of University Teknologi Malaysia). The samples were sent to Medac Ltd. for testing using the combustion analysis method for carbon, hydrogen, nitrogen and sulphur content, but oxygen content was determined by difference as shown in Table 1. The volatile matter was analyzed in accordance to ASTM E872-82. The elemental analysis indicates that EFB is environmental friendly, with trace quantities of nitrogen and sulphur.

Table 1: Properties of EFB (wt. % mf)

Component		Standard method
Cellulose	59.7	hydrolysis analysis, as received
Hemicellulose	22.1	hydrolysis analysis, as received
Lignin	18.1	hydrolysis analysis, as received
Elemental Analysis		combustion analysis, as received
Carbon	49.07	combustion analysis, as received
Hydrogen	6.48	combustion analysis, as received
Nitrogen	0.70	combustion analysis, as received
Sulphur	< 0.10	combustion analysis, as received
Oxygen (by difference)	38.29	estimated
Proximate analysis		
Moisture	7.95	ASTM E871
Volatiles	83.86	ASTM E872-82
Ash	5.36	NREL LAP005
Fixed carbon	10.78	Estimated
High heating value (MJ/kg)	19.04	Dulong's formula [14]

2.3 Thermogravimetric Analysis of EFB

The thermal characteristics of the ground EFB were analyzed with a computerized Perkin-Elmer Pyris 1 TGA thermogravimetric analyzer. TGA was performed under 100 ml/min nitrogen with a heating rate of 10ºC/min. Representative TGA and differential DTG for the EFB are presented in Figure 4. In this figure, the DTG curves show the change in weight loss of feedstock represented by fraction as a function of temperature. From 100 to 270ºC, the weight loss was insignificant. It was found that the weight loss was highest from 270 to 400ºC. This may be due to the thermal degradation of the polymer blocks of biomass (such as hemicellulose, cellulose and lignin). The weight loss above 400°C is attributed to the present of compounds that are more difficult to degrade thermally. Figure 4 also shows the DTC represented by the derivative weight loss as a function of temperature. Yang et al. [15] had previously reported that decomposition of hemicellulose, cellulose and lignin occurred at 220–300ºC, 300–340ºC and 750–800ºC respectively. Based on this, the DTG peak observed in Figure 4 for the range of temperatures 250–400ºC represents hemicellulose and cellulose degradation of the EFB.

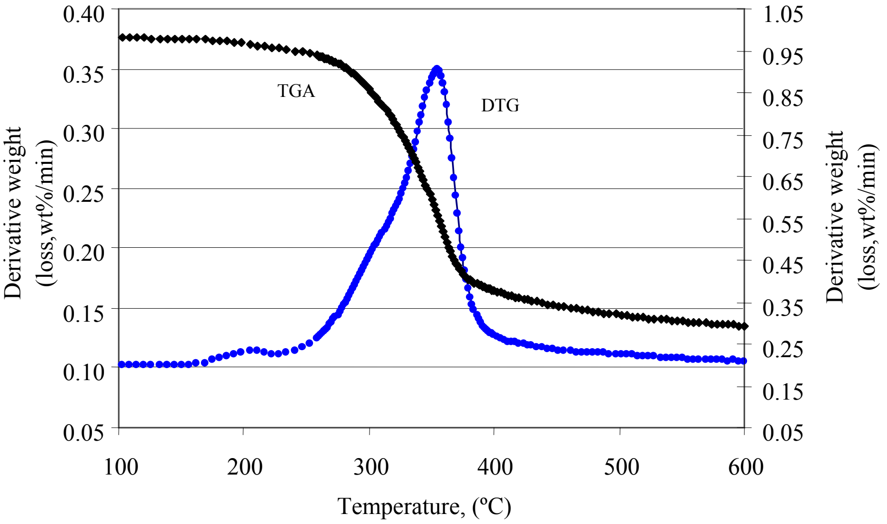

Figure 4: TGA and DTG of EFB

3. EXPERIMENTAL PROCEDURE

3.1 Pyrolysis Experiment

Fast pyrolysis experiments were performed with a fluidized bed bench scale unit operating at atmospheric pressure.

Figure 5 shows the schematic diagram of the fluidized bed pyrolysis system consists of three main parts, which are feeder, reactor and product collection. The reactor consists of a 316 stainless steel cylinder with a length of 260 mm and an internal diameter of 40 mm. The heating medium in the reactor is inert sand of size between 355–500 µm. The sand fills the reactor to a depth of approximately 8 cm and expands during fluidization to 12 cm. The fluidizing gas was nitrogen, which was preheated in its flow line by the tube furnace prior to entering the base of the reactor.

Pyrolysis experiments were carried out at a vapour residence time of 1.02–1.05 s over the temperature range of 400–600°C, increasing in steps of 25°C, on feedstocks size 250–355 µm.

The ranges of vapour residence times of 0.79–1.32 s were used at the fluidized bed temperature of 500ºC. The char and vapours were carried out of the reactor body by the fluidizing gas flow, and known as "blow-through" mode [16]. They then enter the first stage of the product collection system, which consists of the cyclone and the char pot. Due to density differences and centrifugal forces, the vapours then leave the cyclones at the top, while the char falls into the char pot. The vapours were condensed and collected in the liquid products collection component, which consists of two cooled condensers, an electrostatic precipitator and a cotton wool filter.

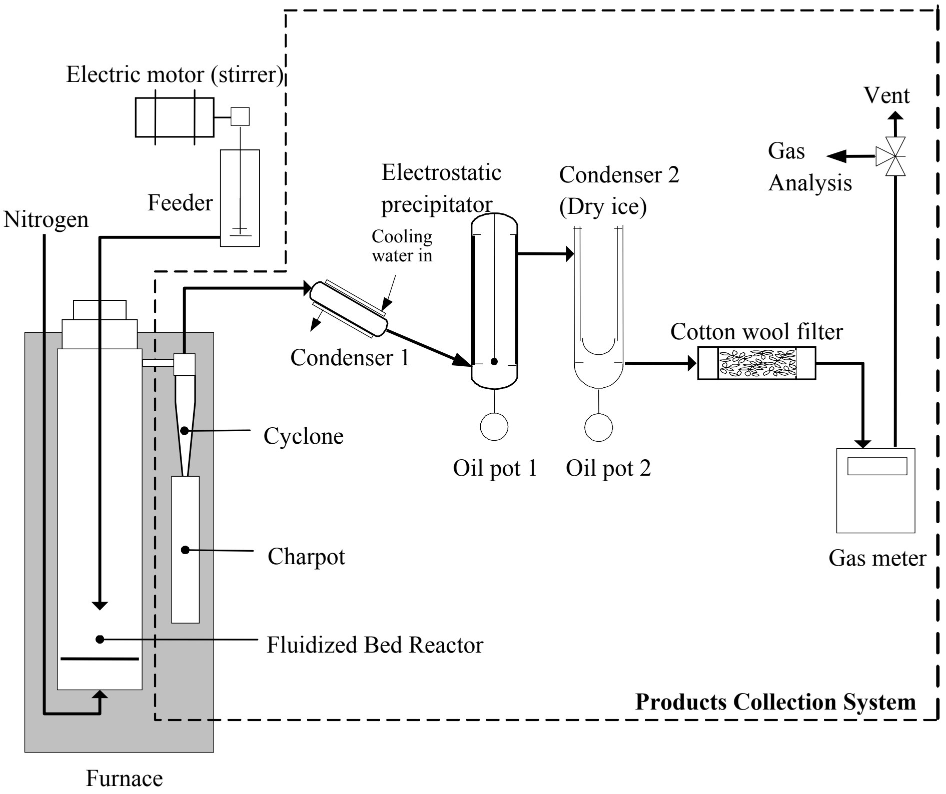

Figure 5: Fluidized bed pyrolysis system

3.2 Fourier Transform Infrared Spectroscopy

The basic functional groups of the pyrolysis liquids were analyzed by Fourier Transform Infrared (FTIR) spectroscopy.

4. RESULTS AND DISCUSSION

4.1 Effect of Reactor Bed Temperature on Product Yield

Table 2 shows the percentage yield of total liquid, solid char and gas at various bed reactor temperatures from 400 to 600ºC. It shows that the product yields are influenced by the process temperature. The results showed that maximum liquid yield recovered at about 450ºC and this was 52.5 wt.% mf with the char product yield and gaseous product yield were 25.7 and 19.8 wt. % mf respectively. It was found that char yield decreases as temperature is raised, while gas yield increases as temperature increases. At a higher temperature of 600ºC, the liquid product yield was only 44.7 wt. % mf, the char yield was only 20.8 mf wt % and the gaseous product yield was 29.8 wt. % mf. At a lower temperature of 400ºC, the liquid product yield was only 49.6 mf wt.%, the char yield and the gaseous product yield were only 27.8 and 18.4 wt. % mf respectively.

Table 2: Product yields with variation of reactor bed temperature at vapour residence time 1.02–1.05s

Run no.	Reactor bed temperature (°C)	Product yields (wt. % mf) liquid	char	gases
1	400	49.6	27.8	18.4
2	425	50.3	26.8	19.3
3	450	52.5	25.7	19.8
4	475	50.5	25.1	20.8
5	500	49.9	24.5	22.3
6	525	49.3	23.8	24.9
7	550	47.3	23.3	27.6
8	575	45.9	21.8	28.0
9	600	44.7	20.8	29.8

Actually the 150g/h rig has been used for many feedstocks establishing good repeatability. Furthermore, biomass feedstocks all have similar curves, with the main difference being the peak yield temperature. With runs requiring a lot of time to do properly, it makes sense to choose to look at many temperatures, rather than to do repeat runs and only do runs at a few temperatures. The smooth curve (yield as a function of temperature) obtained is also a good indication of the repeatability and accuracy of the work, further obviating the need to establish repeatability and accuracy through repeated runs at the same temperature. However, several analytical techniques on pyrolysis products have been applied in order to quantify the major pyrolysis products and produce good quality reproducible mass balances.

4.2 Effect of Vapour Residence Time on Product Yield

Table 3 shows the results obtained over a range of vapour residence times for feed particle size of 300–355 µm at a reactor bed temperature of 500ºC. The maximum liquid yield was 55.1 wt. %, mf with the solid char yields at 23.9 wt. % mf while the gaseous yield was 18.57 wt. % mf at the vapour residence time of 1.03 s. The liquid yield decreased to a value of 50.6 wt. % mf with the decrease of vapour residence time up to 0.79 s, but with the increase of vapour residence time of up to 1.32 s, the liquid yield decreased to a value of 45.3 mf wt%. This could be caused by the fact that at shortest vapour residence times the fluidisation was not achieved completely as the biomass was too quickly blown from the reactor thus producing more char. On the other hand, longer vapour residence times resulted in slightly lower liquid yields as there may be more secondary reactions occuring.

Table 3: Product yields with variation of vapour residence time at reactor bed temperature of 500ºC

Run no.	Vapour residence time (s)	Fluidization gas flow rate (l/min)	Product yields (wt. % mf)		
			liquid	char	gases
1	0.79	7.0	50.6	27.2	17.9
2	0.96	6.0	51.5	26.5	17.7
3	1.03	5.0	55.1	23.9	18.6
4	1.16	4.5	50.2	25.9	19.1
5	1.23	4.0	47.8	27.5	22.4
6	1.32	3.5	45.3	27.6	25.1

4.3 Functional of Group Composition in the Liquid Product

The absorption frequency spectra representing the functional group composition of the pyrolysis liquid is shown in Table 4. The strong absorbance peaks of C-H vibrations of between 3000–2800 cm^{-1} and the C-H deformation vibrations of between 1500 and 1450 cm^{-1} indicate the presence of alkanes. The absorption peak between 1750 and 1625 cm^{-1} representing the C=O stretching vibration is suggestive of the presence of carboxylic acids, ketones and aldehydes. The absorbance peaks between 1675 and 1600cm^{-1} representing C=C stretching vibrations is suggestive of the presence of alkanes while the peaks between 1300 and 1000 cm^{-1} are due to the presence of phenols and alcohols. Finally the absorption peaks between 900 and 650 cm^{-1} indicate the presence of single, polycyclic or substituted aromatic groups.

Table 4: 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 O-H bending	alcohol phenol
900–650		aromatic compounds

4.4 Properties of the Liquid Product

The pyrolysis liquids produced separated into two phases, a phase predominated by tarry organic compounds and an aqueous phase. The tarry organic phase is a sticky brown tar containing high molecular weight compounds derived from lignin [17]. Table 5 shows a comparison of key properties for the two phases with those of wood derived bio-oil, light fuel oil and heavy fuel oil. It is expected that the value of sulphur in the EFB pyrolysis liquid would be much less than 0.1% because the value of sulphur in the raw EFB is already less than 0.1%, therefore the presence of this element may safely be ignored in the pyrolysis liquid. The elemental analysis of the aqueous phase of the pyrolysis liquid shows that it is highly oxygenated while its carbon and hydrogen contents are not high, hence, it is expected that the calorific value of the aqueous phase is low. This pyrolysis liquid is unlikely to be suitable as a fuel in diesel engines turbines or standard furnaces for home heating as the viscosity of this kind of liquid is very low (too viscous). Therefore it, is unlikely to be suitable as a liquid fuel. Both physical and chemical methods may be used to improve this liquid quality. Water washing pre-treatment of the biomass is one option that will be considered in the further work.

Table 5: Characteristics of pyrolysis oil compared to petroleum fuel [18]

	EFB			Wood derived bio-oil	Light fuel oil	Heavy fuel oil
	organics phase	aqueous phase	char			
Elemental analysis (wt. % mf)						
C	69.35	13.83	71.43	32–48	86.0	85.6
H	9.61	11.47	1.8	7–8.5	13.6	10.3
N	0.74	0.14	0.63	< 0.4	0.2	0.6
O (by difference)	20.02	74.56	8.72	44–60	0	0.6
S	ND	ND	ND	< 0.05	<0.18	2.5
Moisture content (wt. % mf)	7.90	64.01	ND	20–30	0.025	0.1
HHV (MJ/kg)	36.06	ND	ND	–	–	–
LHV (MJ/kg)				13–18	40.3	40.7

Note: ND – not determined

5. CONCLUSIONS

Oil palm EFB were pyrolyzed in a bench scale fluidized bed reactor at temperatures of between 400–600ºC. Organic liquid yields of up to 55.15 wt. % mf are obtainable at a fluidized bed temperature of 450ºC with residence time of 1.03 s. The pyrolysis liquids produced separated into two phases a phase predominated by tarry organic compounds and an aqueous phase. This liquid also known as the non-homogenous liquid, which contains of two liquids that exist in different form. One was in sticky form and very viscous and another one was very watery, thus, presenting challenges for their commercial application as a fuel. Possible solutions include upgrading of the liquids, or water washing pre-treatment of the EFB before pyrolysis. The process of pyrolysis is complex, but the most accepted theory is that primary vapours are first produced. These primary vapours then further degrade to secondary tars, char and gases, and this degradation can be enhanced by catalysis, high temperature and longer residence time. High ash in biomass generally promotes secondary reactions of primary pyrolysis products since some ash components, primarily potassium and sodium, are known to be catalytically active. Therefore, secondary reactions should be avoided for the production of liquid. Biomass pre-treatment by water washing in order to remove some ash might be required to modify the pyrolysis reaction sufficiently to produce homogenous bio-oil.

6. ACKNOWLEDGEMENT

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