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Yield and Calorific Value of Bio Oil Pyrolysed from Oil Palm Biomass and its Relation with Solid Residence Time and Process Temperature

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ABSTRACT

The demand of renewable energy had created a foundation for biofuels to grow. Bio oil as secondary biofuels is produced from pyrolysis process using biomass as feedstock. The quality of bio oil mainly calorific value (high heating value) affected by the process temperature and solid residence time during pyrolysis. In this study, the effect of pyrolysis process temperature and solid residence time on the bio oil quality (calorific value) and yield was evaluated on the empty fruit bunch and oil palm trunk pyrolysis process. The huge amount of these biomass creates interesting and potential feedstock to be used in pyrolysis. Pyrolysis process was performed using the home made air tight stainless steel barrel with capacity of 4 L with every batch of process using 300 g of biomass fines. The fines were subjected to 4 different process temperatures; 300, 400 and 500 and 600°C for 30, 60 and 90 min of solid residence time respectively to perform the pyrolysis. Result shows that the highest bio oil yield recorded for the EFB pyrolysis process was 36.49%, while 41.35% for OPT pyrolysis process. Significant interaction among the process variable on calorific value of bio oil was observed. High calorific value of bio oil associated with higher process temperature. Conclusively, yield and calorific value of bio oil is dependent of process temperature and solid residence time.

Key words: Bio oil, oil palm biomass, calorific value, pyrolysis

INTRODUCTION

Exploration of sustainable energy resources has been motivated to substitute the petroleum based-fuel due to fossil fuel crisis. Among the renewable energies that emerged to substitute the conventional fuels, biofuels are one of the most ideal energy sources. Basically, biofuels were classified into 2 categories, which are primary and secondary biofuels. Primary biofuels referred to those unvarying biomass and it can ignite directly, for example firewood, wood chips and pellets. Modified primary fuels belong to secondary bio-fuels. Through the conversion technologies, they were transforms into high value products, which can be used for numerous applications, including substitution of transportation fuel (Nigam and Singh, 2011). Bio oil was classified into secondary biofuels.

Bio oil is a product from condensation of vapors during thermal decomposition of plant based biomass occurring in the vacuum chamber (absence of oxygen). In the shortest term, the process is referred to as pyrolysis. Bio oil pyrolysed from biomass composed of water and complex oxygenated hydrocarbons mixture with a wide range of chemical functionalities (Crocker and Andrews, 2010). The complexity arises from the degradation of cellulose, hemicellulose, lignin and the broad spectrum of phenolic compounds. The degradation process will convert the cellulose and hemicelluloses into low molecular weight organic compounds with high oxygen content and lignin into heavier organic compounds (Brown, 2011). Hence, the quality of bio oil especially calorific value depends on feedstocks as the contents of C, H, O and N vary significantly for different types of biomass (McKendry, 2002).

Pyrolysis can be classified into slow, fast and flash process depending on the operating condition, especially solid residence time and process temperature between the heat and biomass contact. Other operating conditions, such as heating rate and biomass particle size are also used to classify the type of pyrolysis. The type of pyrolysis conditions and effect of operating condition on the yield of bio oil are widely discussed (Jahirul *et al*., 2012; Luo *et al*., 2004; Wright *et al*., 2010). Vice versa, the effect of pyrolysis conditions on calorific value of bio oil is less presented.

The pyrolysis process exhibits both simultaneous and successive reactions, when organic material is heated in a vacuum environment. The reactions of biomass pyrolysis are of great importance in the context of bio oil recovery as well as energy content (Ledakowicz and Stolarek, 2003). Thermal decomposition of organic components in biomass starts as low as 280°C with formation of active cellulose through the exothermic depolymerization process under pyrolysis conditions. The decomposition continues at higher temperature until the secondary cracking of the primary fragments (Shen *et al*., 2013; Chen *et al*., 2006). At temperature between 350-550°C, the long chains of carbon, hydrogen and oxygen compounds in biomass decomposed into smaller molecules in the form of combustible gases that include carbon monoxide, hydrogen and methane together with carbon dioxide gas, condensable vapours methanol that consist of tars and oils and solid charcoal (Lee *et al*., 2010, 2011; Shen and Gu, 2009). The rate and extent of decomposition or degradation of each of these components depend on the process parameters such as temperature, biomass heating rate and feedstock. The effect of pyrolysis conditions on the calorific value and yield of bio oil are of equal importance as the feedstocks.

Utilizing the oil palm biomass in pyrolysis to produce bio oil is one of the great advancement in the high value addition process for oil palm biomass. Oil palm widely planted in all tropical areas of the world especially in South East Asia countries. Oil palm is indigenous from West Africa and currently ranks as the most important industrial crops for the edible oils production. The success of oil palm plantation and industries come with a huge cost, the amount of biomass produced by an oil palm tree, inclusive of the oil and lignocellulosic materials, is on the average of 231.5 kg dry weight/year (Abdul-Khalil *et al*., 2007). Thus, 23% of Empty Fruit Bunch (EFB) were generated from successful extraction of single weight of fresh fruit bunches (H'ng *et al*., 2011; Fan *et al*., 2011). In addition, Goh *et al*. (2010) also reported that 66 tons of Oil Palm Trunks (OPT) were produced from replanting activity of every hectare of oil palm trees. The huge amount of these biomass creates interesting and potential feedstock to be used in pyrolysis. Therefore, the bio oil pyrolysed from oil palm biomass as pyrolysis feedstock was chosen in this study. Comparison was made between the energy content (yield and calorific value) of bio oil pyrolysed from EFB and oil palm trunk.

Thus, this study evaluates the energy content of bio oil produced from oil palm biomass pyrolysed at different process variables; solid residence time and process temperature. In addition, this study also aims to determine the effectiveness of process temperature and solid residence time on the yield of other products from oil palm biomass pyrolysis process.

MATERIALS AND METHOD

Oil Palm Trunk (OPT) and Empty Fruit Bunches (EFB) located in the Malaysia were used in this study. The experiment was carried out between June, 2012 and May, 2014. The empty fruit bunch was collected from commercial palm oil mill located in Dengkil, Selangor and oil palm trunk was felled from Taman Pertanian Universiti (TPU), Universiti Putra Malaysia (UPM). The collected EFB was dried in kiln dryer at 60°C to reduce the moisture content before proceed to grinding process. In the same time, the oil palm stem was cut into 8 feet length and further saw into disc like block with thickness 20 cm. Both OPT and EFB were further grinded into fine of 20 mesh size. Finally the fines were oven dried to 5% moisture content and stored in the conditioning room. The chemical composition of the EFB and OPT were determined according to the TAPPI. (1978): T222-74 for lignin content, TS os-73 for extractive content and T203 os-61 for α-cellulose. The procedure of Wise and Addieco (1946) was used for holocellulose content determination.

Pyrolysis process was performed using the home made air tight stainless steel barrel with capacity of 4 L. Three hundred gram of biomass fines were placed in the stainless steel barrel before the barrel being sealed by connecting to the condenser to limit the oxygen content during pyrolysis process. The fines were subjected to four different process temperatures; 300, 400, 500 and 600°C for 30, 60 and 90 min of solid residence time, respectively to perform the pyrolysis. Table 1 shows the experimental design for this study.

The bio oil was formed by condensing the vapors gases and it was collected in a measuring cylinder. Then the weight of bio oil was measured using electronic balance. The weight of other products after pyrolysis was measured. All the single treatments were carried out for triplicate.

The calorific value of pyrolysis oil was determined by using AC-350 Automatic Bomb Calorimeter. The calorific value used in the study is presented as higher heating value (mg kg^{-1}). The products yield of char and bio oil were calculated based on percentage as a fraction of 100 for final weight of products to the original biomass weight prior to the pyrolysis process. The calculated gas yield was based on subtraction of 100% over total products yield.

All data were statistically analyzed using Analysis of Variance (ANOVA) technique and Tukey Kramer test was used to separate means that are statistically significant at 0.05 level of significance.

RESULTS AND DISCUSSION

Chemical composition of oil palm trunk and empty fruit bunch: Table 2 shows the chemical composition of empty fruit bunch and oil palm trunk. As mentioned, type of biomass was one of the factors that will affect the pyrolysis yields. EFB exhibits higher amount of cellulose and lignin

Table 1: Experiment variables used in this study

Feedstocks	Process temperature (°C)	Solid residence time (min)
EFB	300	30
OPT	400	60
	500	90
	600	

compare to OPT. Overall, the chemical composition for EFB and OPT reported here found to fall into the same range that published by Chin *et al*. (2011) and Chin and H'ng (2013).

Calorific value of bio oil and yield of products from pyrolysis process: Generally, 3 products were produced from the pyrolysis process, which are liquid, char and gas. Figure 1 shows the mean yield of the products obtained from the pyrolysis process, while Fig. 2 exhibits weight loss of the feedstock as a result of the pyrolysis process. The percentage of these three products were highly dependence on the solid residence time and process temperature. Furthermore, the yield of these products was interrelated with each other, the higher liquid yield resulted in lower char and calculated gas yield.

Table 2: Chemical composition of empty fruit bunch and oil palm trunk

	Feedstock	
Components	EFB (%)	OPT (%)
Holocellulose-(Extractive free)	74.85	73.15
Cellulose	44.24	33.44
Acid-insoluble lignin	12.69	10.84
Extractives	6.37	6.78
Ash	5.96	1.33

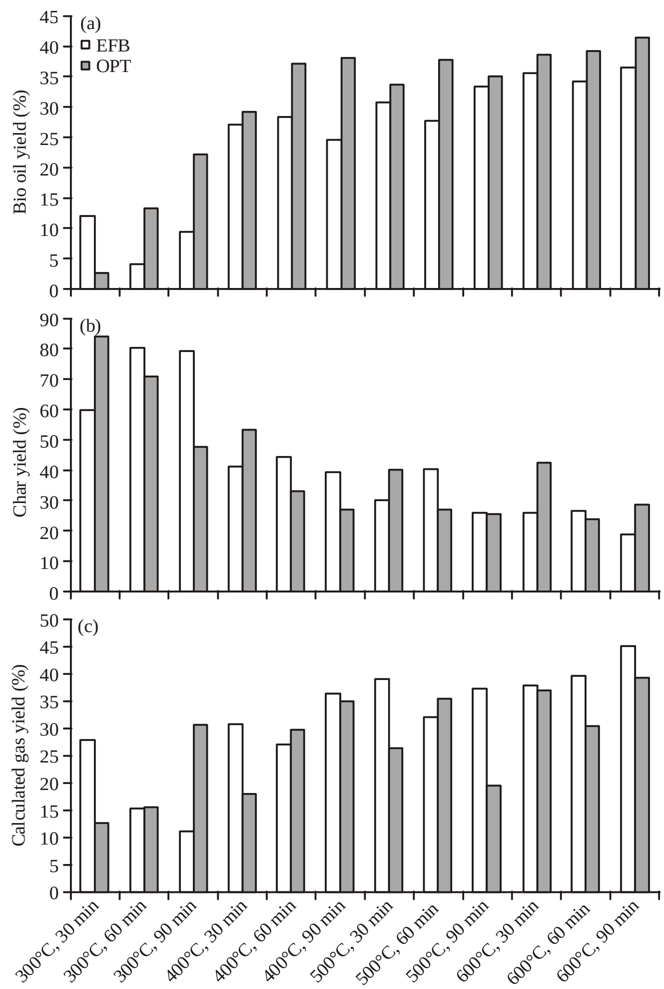

Fig. 1(a-c): Mean calculated (a) Bio-oil yield, (b) Char yield and (c) Gas yeild from pyrolysis process

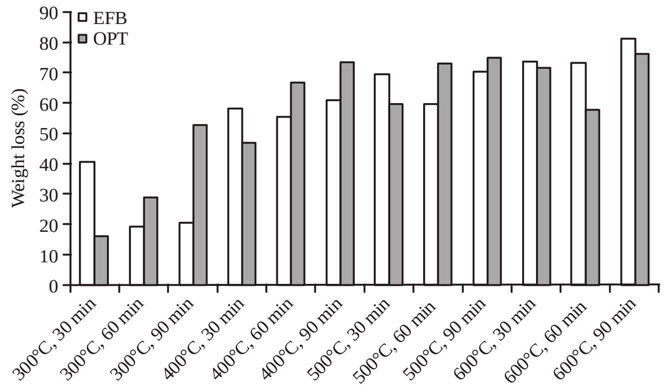

Fig. 2: Mean weight loss as a result of pyrolysis process

Table 3: Summary of ANOVA for mean value of calorific value of EFB and OPT bio oil

		p-value	
Source	DF	EFB	OPT
Temp×time	3	<0.0001	<0.0001
Temp×time	2	<0.0001	0.0035
Temp×time	6	0.0006	<0.0001

Significant difference at $p \le 0.05$

Table 4: Mean comparison of the calorific value of bio oil from pyrolysis process on EFB and OPT

		Calorific value (MJ kg^{-1})	
Temperature (°C)	Time (min)	EFB	OPT
300	30	29.61^{bc}	27.00^{bc}
300	60	28.27^{cd}	24.90^{c}
300	90	27.34^{d}	25.28^{c}
400	30	30.90^{a}	27.20^{bc}
400	60	28.86^{bcd}	24.96^{c}
400	90	29.36^{bcd}	26.57^{bc}
500	30	31.16^{a}	27.74^{abc}
500	60	28.68^{cd}	27.06^{bc}
500	90	29.94^{bc}	26.46^{bc}
600	30	30.44^{abc}	27.39^{bc}
600	60	29.59^{bc}	29.61^{a}
600	90	29.37^{bcd}	26.94^{bc}

Means followed by the same letters in the same column are not significantly different at $p \le 0.05$

As shown in Fig. 3, the calorific value of bio oil obtained from different pyrolysis treatments range from 25 to nearly 32 MJ kg^{-1}. The highest calorific value of 31.15 MJ kg^{-1} for EFB pyrolysis at process temperature 500°C and solid residence time of 30 min. The effects of process temperature and solid residence time on the bio oil were presented using the ANOVA and presented in Table 3-4.

As shown in Fig. 3 the highest bio oil yield recorded for the EFB pyrolysis process was 36.49%, while it was 41.35% for OPT pyrolysis process, both were achieved using process temperature of 600°C for 90 min. In respond to that, the lowest char yield was observed for the mentioned process temperature and solid residence time. The fact behind this observation may be explained by the high process temperature would produce high portion of bio oil, while lower temperature was encouraged for the formation of char as found in many literatures (Bridgwater, 1999; Crocker and Andrews, 2010; Brown, 2011). The maximum char yield obtained at shortest process

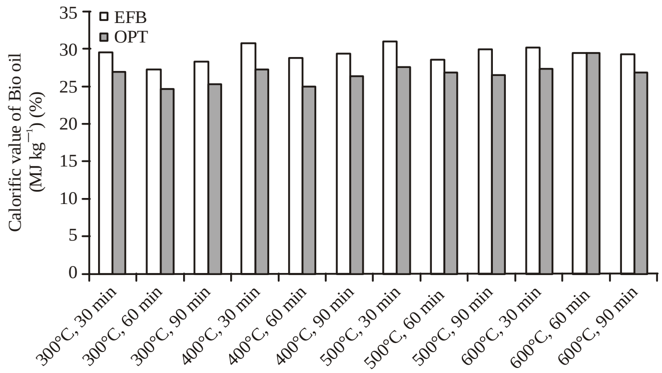

Fig. 3: Mean calorific value of bio oil

temperature of 30 min was probably due to incomplete decomposition of the oil palm biomass structure. On other observation, the calculated gas products of pyrolysis are directly proportional to bio oil yield. The highest gas yield was achieved at process temperature of 600°C and solid residence time 90 min. The weight loss of biomass was inversely proportional to the char yield. In pyrolysis process, it transformed the biomass into pyrolysis products, this led to the lose of original biomass weight, which is referred to as weight loss. The highest weight loss for EFB pyrolysis process was 81.36 and 75.95% for OPT pyrolysis, both achieved at process temperature of 600°C and solid residence time of 90 min.

Effect of process parameter and solid residence time on calorific value of bio oil: The ANOVA revealed statistically significant difference in calorific value of bio oil pyrolyse from EFB and OPT at different process temperature and solid residence time. Significant interaction at $p \leq 0.05$ of all multiple independent variables of process temperature (Temp) and solid residence time (time) were observed for the EFB and OPT pyrolysis, respectively. Table 3 shows the result of statistical analysis of p-value from ANOVA.

As shown in Table 3, highly significant interaction ($p \leq 0.05$) among the independence variables (solid residence time and process temperature) in calorific value of bio oil was observed for both feedstock (EFB and OPT) in pyrolysis process. The Tukey-Kramer multiple comparison test was employed in this study to separate the means that are significantly different. Table 4 shows the mean comparison of EFB and OPT bio oil calorific value using Tukey-Kramer multiple comparison test for different process temperature and solid residence time.

Generally, the summary of ANOVA in Table 3 suggested that both process temperature and solid residence time significantly affected the calorific value of pyrolysis oil yield. As mentioned, the calorific value for oil palm biomass pyrolysis ranged from 24.90-31.16 MJ kg^{-1}. The calorific value recorded in this study similar with those found from previous work done by Abdullah *et al.* (2011), which were ranged from 20-26 MJ kg^{-1}. Regardless of solid residence time, it is noteworthy that higher calorific value of bio oil was observed using higher process temperature as found in EFB and OPT pyrolysis. Bridgwater (2004) and Nanda *et al.* (2014), stated that higher heating value of bio oil is produced from higher temperature at shortest time. The fact is that the functional groups of C-H, C-O, O-H, N-H and C-N linkages were intense in bio oil from pyrolysis due to the higher degree of cross-linking. This reaction will resulted in high molecular weight components in bio oil such as phenolics, aromatics, carboxylic acids and aliphatic in the bio oil.

CONCLUSION

Conclusively, the bio oil successfully produced from pyrolysis employed different process temperature and solid residence time. The yield of bio oil significantly affected by the process temperature as lower process temperature produced higher char yield and higher temperature produced higher bio oil yield. Besides, solid residence time also was found significantly affected the yield of bio oil as the longer the residence time, the higher the bio oil yield. The calorific value of bio oil although exhibit significant interaction among the process parameters, nonetheless the effect is relatively small. The higher heating value of bio oil produced in this study increase with increasing of the process temperature and solid residence time.

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