Effect of Pyrolysis Paramater and Catalyst on Oil Production from Empty Fruit Bunch

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***Abstract*—Abundance of empty fruit bunch (EFB) as biomass waste in Malaysia lead to fulfill the requirement of clean carbon emission as a source for renewable energy. Catalytic pyrolysis by using calcium oxide from waste eggshell as a catalyst were conducted to produce bio-oil. The effect of various pyrolysis parameter on bio-oil production were investigated to obtain maximum oil yield in the optimum pyrolysis condition. The objectives of this study are to investigate effect of temperature, heating rate, holding time and catalyst loading on oil yield and to determine optimum condition for high oil yield. Maximum oil yield, which was 36.6% were obtained in the optimum temperature of 400^{o}C, heating rate of 80^{o}C/min, holding time of 4 min, and 10% of catalyst loading.**

Keywords— catalytic pyrolysis; biomass; empty fruit bunch; calcium oxide; bio-oil

I. INTRODUCTION

The Malaysian palm oil industry is leading in technology and production for the global markets. Palm oil and related products represent the second largest export of Malaysia in the first nine months of 2005 [1]. The greatest production of palm oil also generate their residues. Malaysia generate about 80 thousand tones residues from their oil palm plantations include empty fruit bunch (EFB), trunks, fronds, palm fiber, and palm kernel shell [2]. EcoIdeal and Mesilin [3] observes that palm oil mill waste in the form of biomass residue such as EFB can be a potential renewable energy producer in Malaysia. It can help to reduce global warming by displacing the use of fossil fuels [4,5].

Biomass conversion into energy can be achieved in two pathways which are biological and thermochemical process. Biological process consists of fermentation and anaerobic digestion, whereas thermochemical process include gasification, liquefaction and pyrolysis [6]. Among this conversion, pyrolysis is considered to be the one of the most promising technology for liquid oil production. Pyrolysis is thermal decomposition of organic component in the absence of oxygen which produce char, tar, and gaseous fraction.

Several researchers have pyrolyzed palm oil residue to produce bio-oil under certain conditions. Bio-oil is dark brown liquid have high heating value can be used as fuels in boiler, diesel engines for power generation, or upgraded to produce fuels and bulk chemicals. However, direct usage of bio-oil as conventional fuels may present some difficulties due to high viscosity, poor heating value, corrosiveness and instability. The presence of oxygen in the bio-oil has a negative effect such as further increasing the corrosion due to its low pH. The upgrading of bio-oil by catalytic treatment has received increasing consideration. The catalyst is expected to improve the cracking reactions of the heavy molecules in pyrolysis products resulting the production of high yield and high quality of bio-oil.

Calcium oxide (CaO) is usually used as catalyst in bio-diesel production. However, it was reported that using CaO base material such as dolomite and limestone can be more worthwhile in upgrading bio-oil to obtain better liquid yields [7]. Using CaO from dolomite and lime stone may contribute to environmental problem as the source of this commercial CaO is a non-renewable resource. Large usage of non-renewable CaO causes rapid depletion of those resources. This has led to many researches being made in order to find alternative ways to replace commercial CaO. Eggshell waste is expected to be a source of this substance as it is non-corrosive, environmental friendly and economical. Eggshell containing most of CaO composition after the calcination process is a suitable material to be used as a catalyst.

Optimum conditions also important in pyrolysis process to obtain better quantity and quality of bio-oil. Azri et al. [8] investigated that 33% of oil yield was obtained from pyrolysis of EFB at temperature of 500^{o}C. Onay and Kockar [9] also studied that maximum oil yield obtain from pyrolysis of rapeseed with heating rate of 300^{o}C/min, temperature of 550^{o}C and particle size range of 0.6-1.25mm. Meanwhile, the catalytic pyrolysis of Mahua seed with CaO at 2:1 ratio produced higher oil compared to thermal pyrolysis [10]. The objectives of this research are to study the effect of temperature, heating rate, holding time and catalyst loading on production of oil yield by catalytic pyrolysis and to determine the optimum pyrolysis conditions for high oil yield.

II. MATERIALS AND METHODS

A. Raw material

Empty fruit bunches was used as biomass material for pyrolysis process. The samples were collected, dried and separated from physical impurities. The dried empty fruit bunch was ground in a rotary cutting mill and screened into a particle between 212µm-425µm in size. Meanwhile, eggshells were used as catalyst were collected from local industries and rinsed several times with water to remove impurity and interference material. Then, it was dried in the oven at temperature of 100^{o}C for 24 hours. The eggshells were ground with Fritsch Pulverisette 6 Planetary Mono Mill. It was calcined under nitrogen gas at temperature of 900^{o}C for 1 hour in the tube furnace.

B. Characterization of EFB

EFB was characterized for its proximate and ultimate analysis thermal gravimetric analysis (TGA/DSC) 1 Model Mettler Toledo and elemental analyzer, Series II CHNS/O 2400. Heating value was determined based on the proximate and ultimate analysis.

C. Pyrolysis process

The fixed-bed pyrolysis experiments were performed under 100ml/min of nitrogen flow rate. For first series of experiment, the aim was to determine the effect of pyrolysis temperature on oil yield. Experiment were carried out at holding time of 4 min and 10% of catalyst loading. The sample was heated with heating rate of 50^{o}C/min to a temperature of 350^{o}C, 400^{o}C, 450^{o}C, 500^{o}C, and 550^{o}C. Effect of heating rate of 50^{o}C/min, 80^{o}C/min, 100^{o}C/min, 150^{o}C/min, and 200^{o}C/min was conducted in the second series with the optimum temperature of 400^{o}C at holding time 4 min and 10% of catalyst loading. To determine effect of holding time on oil yield, the experiment was conducted with holding time of 0 min, 2 min, 4 min, 6 min, and 8 min. The optimum heating rate, 80^{o}C/min was used in this series with 10% of catalyst loading and temperature of 400^{o}C. For the last series of experiment, effect of catalyst loading was performed with the addition of various amount of catalyst (0, 5, 10, 15, 20wt. % of raw material) at the optimum temperature (400^{o}C), heating rate (80^{o}C/min), and holding time (4 min). The oil product yield was collected and calculated at the end of the pyrolysis process.

III. RESULTS AND DISCUSSION

A. Characterization of EFB

The properties of empty fruit bunch was carried out and presented in Table 1. The proximate analysis showed the maximum volatile matters, which was 48.86% in the EFB. More volatile matter produces more liquid and gaseous fuel during pyrolysis. The high ash content are noteworthy as it lead to reduce liquid yields in pyrolysis [11]. Thus, 7.5% of ash content in this EFB lead to produce high liquid yield. The fixed carbon and moisture content of EFB were 26.45% and 10.39% respectively. From ultimate analysis, it was found that the EFB contained 33.69% of carbon, 3.12% of hydrogen, 3.86% of nitrogen, 0.42% of sulfur, and 58.92% of oxygen. Lower sulfur content in the EFB make them suitable for pyrolysis to produce good quality of oil yield. Heating value of EFB was 13.26 MJ/kg as the measured from ultimate analysis. High heating value produces more heat for pyrolysis process, thus increase the production of oil.

TABLE 1. PROPERTIES OF EFB

Proximate Analysis[a]	**wt. (%)**
Moisture content	10.39
Volatile matter	48.86
Fixed carbon	26.45
Ash content	7.50
Ultimate Analysis[a]	
Carbon (C)	33.69
Hydrogen (H)	3.12
Nitrogen (N)	3.86
Sulfur (S)	0.42
Oxygen[b] (O)	58.92
Heating value = 13.26 MJ/kg	

a – as received
b – by different

B. Effect of temperature on oil yield

In the first series of experiment, pyrolysis was performed at temperatures of 350^{o}C, 400^{o}C, 450^{o}C, 500^{o}C, and 550^{o}C under constant heating rate of 50^{o}C/min, holding time of 4 minutes, and 10% of catalyst loading. As can be seen from Fig. 1, the oil yield increase from 6.1% to 35.6% as temperature raised from 350^{o}C to 400^{o}C. However, oil yield starting to decreased from 32.8%, 7.8%, and 4.9% at temperature of 450^{o}C, 500^{o}C, and 550^{o}C due to the formation of more non-condensable gases [12]. Further increased of temperature enhanced gas products only. Secondary cracking reactions of the liquid fraction of volatiles at higher temperature reduced oil yield [13,14]. Chang et al.[15] revealed that pyrolysis at high temperature produces higher amount of H2 and CO gas which does not condense, hence resulting in less oil yield.

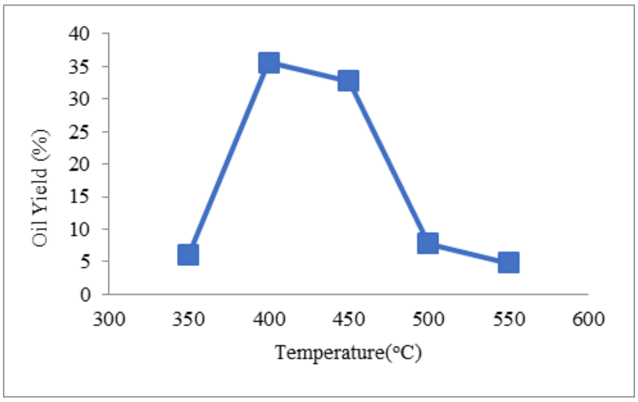

Fig. 1. Effect of temperature on oil yield

C. Effect of heating rate on oil yield

In the second series of experiment, pyrolysis were conducted at heating rates of 50°C/min, 80°C/min, 100°C/min, 150°C/min, and 200°C/min, with a constant gas flow rate of 100ml/min, at temperature of 400°C. Fig. 2 showed the percentage of oil yield increase from 21.2% to 36.6% at heating rate of 50°C/min to 80°C/min. However, it decreased from 11.5% to 7.5% as the heating rate increased from 100°C/min to 200°C/min.

Maximum oil yield obtained at heating rate of 80°C/min showed that the optimum heating rate exceeded the heat and mass transfer limitations in the pyrolysis condition, preventing secondary reaction and resulting in maximum oil yield [16]. The decreasing of oil yield as the heating rate increase was due to the high heating rate could not exceeded the heat and mass transfer limitations as it had short period of time to achieve the temperature of 400°C.

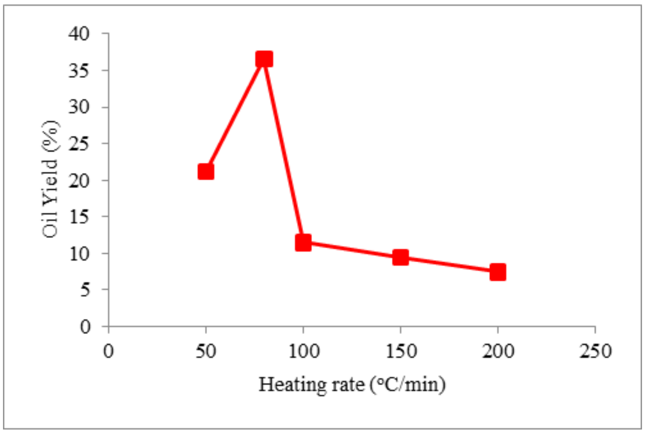

Fig. 2. Effect of heating rate on oil yield.

D. Effect of holding time on oil yield

Effect of holding time on oil yield can be seen in Fig.3. The experiment was conducted at holding time of 0 min, 2 min, 4 min, 6 min, and 8 min, with constant gas flow rate of 100 ml/min, temperature of 400°C, heating rate of 80°C/min, and 10% of catalyst loading. Oil yield increased from 6.9% at holding time of 0 min to 23.3% at holding time of 2 min. Maximum oil yield obtained at holding time 4 min were 30.9%. It was seen that, increasing holding time from 1 min to 2 min would increase the oil yield as reported by Tsai et al. [17].

However, oil yield decreased from 26.5% to 8.2% as holding time increased from 6 min to 8 min. The value slightly decreased was possibly attributed to the thermal cracking and/or gasification of pyrolysis products [18].

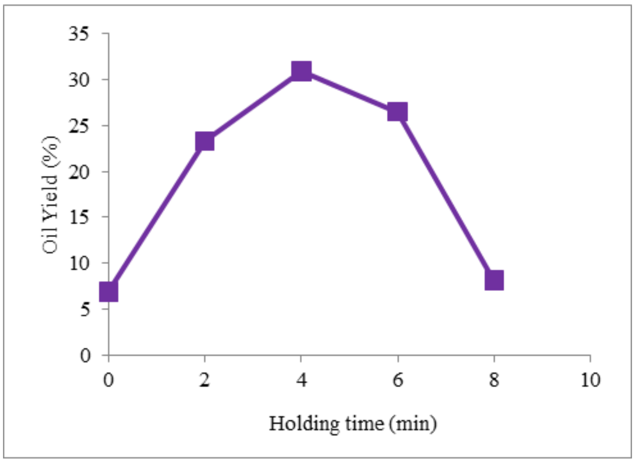

Fig. 3. Effect of holding time on oil yield.

E. Effect of catalyst loading on oil yield

In the last series of the pyrolysis experiment, it was conducted at catalyst loading of 0%, 5%, 10%, 15%, and 20% wt. of biomass, with constant gas flow rate of 100 ml/min, temperature of 400°C, heating rate of 80°C/min and holding time of 4 min. Effect of catalyst loading on oil yield can be seen in Fig. 4. Oil yield percentage for non-catalyst, which was 0% catalyst loading were 21.9%, then increased to 22.3% of oil yield at 5% of catalyst loading. Besides, the maximum oil yield, 36.6% obtained at 10% of catalyst loading. Lin et al.[19] observed that increasing the CaO to biomass ratio led to an increase in oil yield. However, oil yield slightly decreased from 14.4% to 3.2% with catalyst loading of 15% to 20%. It could be due to the agglomeration of active CaO phase and the cover of basic sites by exceeded CaO [20], hence resulting in less oil yield.

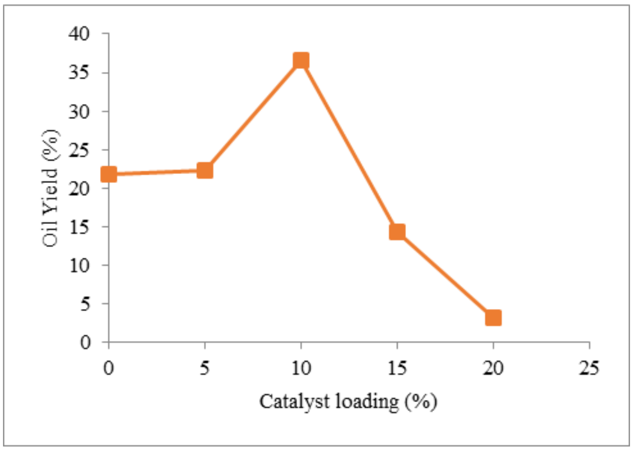

Fig. 4. Effect of catalyst loading on oil yield.

IV. CONCLUSION

Based on the proximate analysis, the volatiles, fixed carbon, moisture and ash content of EFB were found to be 48.86%, 26.45%, 10.39%, and 7.5% respectively. It was also found that the EFB contained 33.69% of carbon, 3.12% of hydrogen, 3.86% of nitrogen, 0.42% of sulfur, and 58.92% of oxygen. Meanwhile, heating value of EFB was 13.26 MJ/kg. Optimum conditions for pyrolysis process to obtain maximum oil yield, which was about 36.6% of oil yield were temperature of 400^{o}C, heating rate of 80^{o}C/min, with holding time for 4 min, and 10% of catalyst loading.

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