Development of Biochar using Non-Direct Firing System from Palm Oil Frond- Physical Characteristics

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Abstract- Oil palm industry is the leading sector for Malaysia's economy and become the largest exporter of palm oil worldwide and the second largest producer after Indonesia. The abundant of waste generated from oil palm industry in the year 2012 about 95.21 million tonnes of oil palm waste with the expectation in 2020 a serious waste management problems occur with approximately 88.74 Mt of biomass can be produced. During pruning period, the average of 4 kg per dry frond that lead to a total production of palm fronds around 5500 kg hectare per year. However, this highest abundance of OPF waste that has the potential to be converted into useful products though the environmental sustainability is still lacking. In this study, it aims to analyze the optimum parameter in preparing bio char from OPF and characterization of bio char based on its physical characteristics. This experiment is a batch experiments using a jacketed pyrolyzer applying non-direct firing system with 500 gram of palm frond biomass feed into the pyrolyzer. The heating rate was used at 20°C/min to rise into target terminal temperature at 400°C, 500°C and 600°C. The terminal pyrolysis temperature used effect the quality of bio char produced. The best temperature parameter for this experiment was found at 400 °C which produced 16.071 m²/g of BET surface area, alkaline pH and porous structure compare to others two temperatures. Thus, it has potential to adsorb heavy metal contaminants with lower pyrolysis temperature, suitable for acidic soil and act as adsorbent. In this study, oil palm frond represents as a source for renewable energy and environment-friendly product.

Keywords— Biomass, Oil Palm Frond (OPF), Bio char, Nondirect Firing System, Physical Characteristics

I. INTRODUCTION

Oil palm industry is the backbone to change Malaysia's economy and plays a major role as the largest exporter of palm oil worldwide and the second largest producer after Indonesia. There are few types of oil palm species available globally but in Malaysia, oil is extracted from mesocarp of oil palm species called Elaeis guineensis. Over the years, oil palm production has shown an increase thus cause the ranking from 10th position to second position (Abdullah, 2011).

The oil palm production in the year 2012 generated 95.21 million tonnes of oil palm waste (Ani, 2016). In 2020, approximately 88.74 Mt of lignocellulosic biomass can be produced, leading to serious waste management problems (Kabir et al, 2017). The average weight of 4 kg per dry frond had entered the pruning period, with a total production of palm fronds around 5500

kg hectare per year (Maulina & Iriansyah, 2018). Oil palm frond (OPF) is the largest amount of biomass abundance after pruning process and contains higher composition of cellulose and lignin.

Bio char known as carbonaceous material is a product from biomass under pyrolysis process with zero or limited supply of oxygen, low temperature and heating rate. The product yields are influenced by the types of feedstock, structural composition, and pyrolysis condition. Thus, these factors should be taken into consideration, means not all bio chars are made equal and for the same end use.

There are two methods to produce bio char either through direct firing method or non-direct firing method wherein non-direct firing method, the heating source not direct contact with the feedstock and heated externally. The combustion of bio char through indirect method produces higher yield of bio char that happens in a separate chamber (air tight container) and heat is transferred by conduction (Odesola & Owoseni, 2010). By using the non-direct method, it produced clean air and no pollution occurred that lead to environmental-friendly. Furthermore, in an indirect firing system, the pyrolysis process produces combustible gases and char from biomass.

Recognizing the highest abundance of OPF waste that has the potential to be converted into useful products in environmental sustainability, this study aims to analyze the optimum parameter in preparing bio char and also to characterize of bio char based on its physical characteristics. Furthermore, this oil palm frond is easily found especially after the pruning process. Non-direct firing method was used in this study because it produced clean and dry air and the heater not release carbon dioxide which can be operated in a tightly sealed space.

II. METHODOLOGY

A. Materials

List of Material

The oil palm frond (OPF) used was coming from palm oil plantation at Tanjung Langsat, Kuala Selangor. For the bio char preparation, the palm frond was obtained after the pruning process and basically still in fresh condition.

Samples Preparation

Initially, at the preparing stage, the oil palm fronds collected from the plantation were cut into small pieces (See Fig.1) and dried in the oven overnight at temperature 70 °C to remove the excessive moisture content from the samples. The OPF was further dried until the moisture content around 5 mf wt%. After that, the dried product was mashed in cutting mill with molecular sieve sizing 1 mm. The mashed product was stored in desiccators to prevent surrounding moisture absorb into the samples due to its hygroscopic nature (Khor & Lim, 2016).



Fig.1. Picture of a few cut pieces of fresh OPF

Pyrolysis Experiment and Analysis

This experiment conduct was a batch experiment. A jacketed pyrolyzer sizing 118 cm in height, 14 cm in internal diameter and 24 cm in external diameter (See Fig.2 and Fig.3) used with 500 gram of palm frond biomass was fed into a char combustion chamber with indirect method has been applied. The heating rate was used at 20° C/min to rise into target terminal temperature. The target pyrolysis temperatures were at 400° C, 500° C and 600° C. Once, the terminal temperature was achieved, carbonization was allowed to proceed at the temperature for one hour. Nitrogen gas was purged into the double jacket pyrolyzer when the target temperature attained, to ensure no or low oxygen in the process. With the presence of oxygen, the biomass will be converted into ash. After each of the experiments completed, the sample was left inside the chamber for 24 hours to let the bio char to cool down before collecting it.

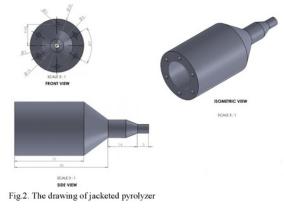




Fig.3. The drawing of the cap for jacketed pyrolyzer

Brunaeuer, Emmett, and Teller (BET)

BET surface area of the biochar was measured using Autosorb-1 Surface Area Analyzer (Quantachrome Instruments) which samples 0.2 g were degassed at 120 °C for 30 minutes under continuous nitrogen flow.

pН

Samples were immersed in deionised water with ratio 1:10 (wt/wt). After one hour of stirring at rate 600 rpm, the pH was measured using Model 420 Thermo Orion (Thermo Fisher Scientific pH meter) (Ronsse et al, 2013).

UV-Vis Spectroscopy

A stock solution of methylene blue was prepared by dissolving 0.1 g of methylene blue solid in 1000 mL of distilled water in 1 L volumetric flask. In order to prepare the methylene blue (MB) with desired concentration, 10, 20 and 50 ppm concentration of MB stock solution were diluted in 1000 mL distilled water separately. The solution was shaken vigorously to ensure the mixture was dissolved well. The adsorption of methylene blue by bio char sample was conducted using 0.25 g sample (Nurul 'Uyun Ahmad et al, 2016) into 25 mL of 10 ppm, 20 ppm and 500 ppm concentration in 200 ml of Erlenmeyer flasks. Then, the flasks were shaken using orbital shaker for one hour at 120 rpm and room temperature (Nurul 'Uyun Ahmad et al, 2016). The sample was determined by UV-Vis Spectroscopy at wavelength 660 nm (Nahrul Hayawin Zainal et al, 2018) with R^2 = 0.9994.

Scanning Electron Microscopy (SEM)

Surface morphology of bio char samples were analyzed which the pores have been carbonized and activated after the carbonization process at scanning electron microscopy mag 100x.

III. RESULTS AND DISCUSSION

A. Characterization of palm frond biochar

BET

Table 1: Surface area of the bio char derived from OPF for different temperatures

Temperature (⁰ C)	Surface Area (m ² /g)
400	16.071
500	14.674
600	14.381

Table 1 indicates that bio chars even from same feedstock are not possessing similar surface area due to its differences in production conditions; especially in its final temperature (Mukherjee & Lal, 2013). As a result, the highest BET surface area was at temperature 400 °C which is 16.071 m²/g compare to the other two temperatures of bio chars derived from oil palm frond (OPF). Based on the previous study, the BET surface area for palm frond analysed from that experiment was 9 m²/g after carbonization process at temperature 320°C (Som et al, 2013), that means considerably comparable with the surface area gained from this experiments. Surface area of bio char was decreasing with the increasing of the process temperature. Generally, surface area will be increased with the increasing of temperature however there is no actual correlation between this two because certain surface area will increasing until it reached its peak temperature to a certain threshold that cause the evaporation of volatile components and then decreases (Mukherjee & Lal, 2013). Furthermore, the decreasing accessible BET surface area is probably causing by the inorganics (ash content) due to ash melting at higher temperatures and filling up the pores (Ronsse et al. 2013). High surface area indicates that it have more reactive sites for the adsorption process to occur (Liew, et al., 2018).

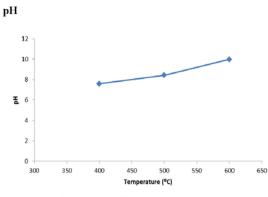
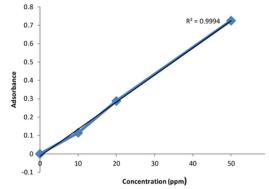


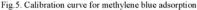
Fig.4. pH value for bio char at different temperatures

The data of the graph in Fig.4 show that an increasing in process temperature will increase in the pH value of bio char solution. At temperature 600 °C, the solution was alkaline with the highest pH value which approximately pH 10 rather than temperature 400 °C and 500 °C. According to previous study, the palm frond bio char has a high pH of 9.5 (Som et al, 2013), means the pH value is slightly equivalent to this experiments. In theory, the value of solution pH is affecting due to the value of ash content in the bio

char and also pyrolysis conditions (Ronsse et al, 2013). With the increasing of pyrolysis time, the amount of carboxyl group in bio char reduce and acid is conjugate to base affecting the alkalinity of bio char.

UV-Vis Spectroscopy





The measured absorbance of different methylene blue concentration was estimated at wavelength 660 nm, as shown in Fig.5. The calibration curve of absorbance against MB concentration was obtained by using standard MB solutions was obeying the Beer's Law in concentration range (0-50 mg/L).

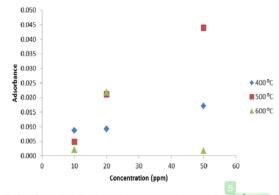
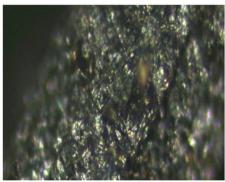


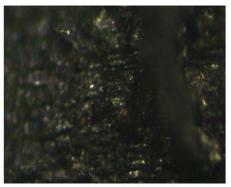
Fig.6. Effect on MB absorbance with concentration (ppm) for $\overline{400}$ °C, 500 °C and 600 °C pyrolysis temperature

The effect of initial concentration of MB plays main role in determining the absorbance value. The analysis of MB absorbance was conducted using 10 ppm, 20 ppm and 50 ppm concentration. The higher the initial concentration of MB, the higher the absorption process to occur. This is because the surface of absorbents molecules tends to compete with ions in MB solution that creates more numbers of collisions between them (Nurul 'Uyun Ahmad et al, 2016). From Fig. 6 the highest concentration of MB for absorbance is at 50 ppm, which the absorbance value was 0.0048 compare to other concentrations. For temperature 400 $^{\circ}$ C, the adsorption value is increasing with the increasing of initial MB concentration. Furthermore, absorption is also depending on the surface area (Nahrul Hayawin Zainal et al, 2018). For concentration of MB at 10 ppm, the absorbance value is decreasing with the decreasing of temperature.

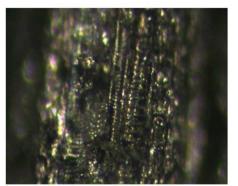
Scanning Electron Microscopy (SEM)







b) At 500 °C



c) At 600 °C

Fig.7. Scanning Electron Microscope Mag (100x) of Bio char

From Fig. 7, the visualization of surface morphology and pore size distribution of bio char at temperature 400 $^{\circ}$ C, 500 $^{\circ}$ C and 600 $^{\circ}$ C using Scanning Electron Microscope (SEM) analysis were shown. The pores were formed due to the evaporation of volatile matter and breakdown of non-carbon compound into bio char (Maulina & Iriansyah, 2018). SEM analysis shows that the suitability of bio char in adsorption study; the more porous the structures of bio char, the more suitable it can be used as adsorbent (Yakub, et al., 2015). High temperature caused the outer surface to be overheated; creating cracks compare to lower temperature similar to the previous study (Sulaiman et al, 2013).

IV. CONCLUSION

Various temperature 400 °C, 500 °C and 600°C have been used for OPF pyrolysis that been carried out in a jacketed pyrolyzer at heating rate 20°C/min. The optimum temperature parameter for this experiment was found at 400 °C which produced 16.071 m²/g of BET surface area which means has potential to adsorb heavy metal contaminants with lower pyrolysis temperature. Also, it has quite high value of pH that is suitable for acidic soil and it has porous structure that suitable to act as adsorbent. In this study, oil palm frond has potential to become a source for utilization of abundant waste into renewable energy and environment-friendly product.

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