Slow Pyrolysis of Empty Fruit Bunches to Produce Biochar

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***Abstract*—The objective of this study were to convert the unwanted empty fruit bunches into biochar via slow pyrolysis. Then the characteristic of the biochar produced were studied. BET surface area, proximate analysis, Methylene blue adsorption, and XRD were perform to characterize the biochar produced. 50 gram of EFB were pyrolyzed under specific temperature with fix heating rate of 10°C/min. After reaching the desired temperature, the pyrolyzer were left to heat for an hour. Proximately, biochar of 700°C contain the least volatile matter with 7.58% while biochar of 500°C produced the biggest fixed carbon content at 56.02%. For surface area, the biochar that came from 700°C yield the biggest area with 10.354 m^2/g. XRD shows that all of the samples is amorphous. For removal of methylene blue from aqueous solution, biochar that is produced at 500°C has the best adsorption capacity due to the facts that it able to remove up to 91% of the methylene blue.**

***Keywords*: Biochar, Empty Fruit Bunches, Adsorption, XRD, Methylene blue.**

I. Introduction

With about 15.4 million tons of palm oil produced annually in Malaysia, the oil palm industry is much related to the environment because it is land based industry. Oil palm is one of the most important products of Malaysia that trigger its economic and agricultural growth. Raw materials from palm tree consist of about 10% oil while the rest is biomass that account of 90% of the total. For each fresh fruit bunch, 23% of it is made up of empty fruit bunch. Therefore, it is crucial to do more research involving the utilization of the empty fruit bunches(EFB). Most of the biomass produced in palm oil mill is underutilized and this might cause environmental impact as these waste will left disposed naturally without being fully utilized.[1] Thus, pyrolysis is one of the methods that can be apply to utilize the usage of biomass.

As the second biggest producer of palm oil, about 80 million tonnes of wastes from palm oil is produced annually.[2] Utilization of EFB is crucial as it will help to reduce problems due to solid waste management and reduce release of methane and nitrous oxide has that release due to degradation of dumped EFBs .[3] EFB is very high in volume and exist as bulky brown bunch that left at mills of palm oil factory after extraction of sterilized fruit. It has irregular shape and normally weighs about 3.5 kg with 130 mm thickness. Thickness of EFB usually ranging from 170 to 300 mm long with 250 to 350 mm wide. From analysis it has been found out that during thermochemical conversion. EFB is easily decompose due to high moisture content.

Pyrolysis is a process whereby biomass is convert into liquid bio oil, solid biochar and gas mixture with direct thermal decomposition of biomass without the presence of oxygen. The temperature for pyrolysis ranging from 350 to 550°C. There were two type of pyrolysis that is always under development which is fast pyrolysis and slow pyrolysis. The different between this two methods is in terms of yielding, chemistry and quality of the resulting products. Endothermic reaction for pyrolysis is as shown below:[4]

$$\text{Biomass} + \text{Heat} \rightarrow \text{Bio-oil} + \text{Gas} + \text{Biochar}$$

The properties of the product of pyrolysis will greatly depend on the pyrolysis parameter such as temperature of heating, rate of heating and residence hour [3]. Pyrolysis temperature plays a significant role on the properties of the product produced. The temperature will cause the char fraction to contain inorganic materials ashes but at different degrees.[5]

In slow pyrolysis, biomass usually be heated up to 500°C and will be left at fixed residence time. In slow pyrolysis, the heating rate used is much lower than that used in fast pyrolysis. The feedstock able to be held at fixed temperature as they are or gradually heated. Residence time for slow pyrolysis usually ranging from 5 to 30 minutes. (Mohan et al., 2006). In experiment conducted, the temperature heating rate of the pyrolyzer is at 10°C/minutes with a residence time of one hour.

Bio-char is a carbon rich materials that is derived by thermo-chemical reaction decomposition of organic compound with the absence of oxygen. During pyrolysis, biomass able to retain 50% of its fixed carbon content. Biochar is produced for mitigate climate change, generation of energy, soil amendment and solid waste management. There is still a little search conducted about the long term effect of biochar to soil.[6]

Biochar added to soil to decrease the amount of N_2O release from soil, raise the capacity of soil to hold water and due to its stability, high carbon content and potential to stay in soil for a long time thus it has a potential to become a long-term carbon sink. Usually, pyrolysis is conducted at temperature that is less than 700°C. Type of feedstock, pre-treatment process and parameter of pyrolysis are the factors that affect the properties, yield and composition of the biochar.[3] In raw EFB feedstock, it will have calorific value of 17.08 MJ/kg while biochar produced has highest calorific value at 25.98 MJ/kg which is pyrolyzed at 400°C with heating rate of 30°C/min.[4]

The surface area of biochar produced ranging from 3.3 to 5.76 m^2/g depending on the temperature. Biochar produced from pyrolysis at 400°C yield product with highest surface area which at 5.76 m^2/g and are said to be link with completion of solidification stage that occur within the biochar. Biochar that have high fixed carbon content and low oxygen content is good as solid fuel. The calorific value of elemental composition of fuel is primarily important for modeling performance and thermal system calculations. To increase the rate of chemical reaction, surface area play a crucial part.[3]

Biochar has high energy content, however it is better to be applied into soil as soil amendment as in long term basis it is able to increase the carbon in soil storage and reduce greenhouse gases. Biochar can accommodate pyrolysis system with additional heat through combustion. It is reported that averagely 25% larger mitigation impact of biochar is recorded compare to results obtained with same biomass that fully utilized combusted for energy. If to increase the plant growth and N_2O emission is concern, than biochar production is favor than bio oil. It is also suggested that biochar able to retain the nutrients in soil, increasing soil pH, neutralize toxin, increase water retention capacity, decrease soil strength and increase efficiency of Nitrogen fertilizer used. Biochar also act as binding agent in soil that retain and adsorb cations such as Ca^{2+}, K^{+}, NH^{4+} and Mg^{2+}[6].

(a)

(b)

Fig 1: (a) The shredded fiburous raw empty fruit bunches, (b) biochar produced

For this research project, EFB were thermally deposited at certain temperature without the presence of oxygen to produce bio char. The bio char produced is then to be characterized. The end product yield and composition of the process were depending on the biomass type, structural and chemical composition of the feed biomass. Temperature, type of reactors, rates of heating, size of the particle is among the physical condition that also affect the yield and composition of the end product.[7]

The objective of this research is to convert the empty fruit bunches from production of palm oil to biochar via slow pyrolysis. The characterizations of biochar were also study.

II. METHODOLOGY

A. Materials

Empty fruit bunch sample is the main materials used in this study. The samples was obtained from Felda Palm Industries SDN BHD, Sungai Tengi and in a form of shredded dried EFB. The sample were already in a dry for when receive.

B. Biochar conversion experimental set-up and analysis.

Experiment was conducted using dry shredded empty fruit bunch as per Fig 1(a). The sample was already in shredded form when received. Some of the raw samples were grind using blender for thermogravimetric Analysis (TGA) test. Biochar is produced by pyrolyzer or pyrolysis unit as per Fig 2, which consist of fixed bed reactor that has external electrical heater. The heating temperature of the pyrolysis unit is controlled by control panel. The heating rate is fixed at 10°C.

The perforated tray with aluminium foil that is used to hold the EFB was weigh before the weighing balance is re-zeroed. Then, 50 gram of sample of EFB was weighed and wrap in the aluminium foil before located on perforated tray. Then the perforated tray with sample was put inside a reactor. The reactor was sealed tightly by tighten all the screw and nut on top of the reactor lid. After that, the pyrolyzer switch was turned on and the temperature desired was keyed in on the control panel. Nitrogen valve was also opened and adjusted. Nitrogen supply is crucial to prevent any other reaction happen between the sample and surrounding air. After reaching the desired temperature, the sample was left for an hour before left to cool. When one hour is reached, the switch of pyrolyzer was turned off and valve supplying nitrogen gas is closed. After the reactor is cooled enough, the sample was taken out and the sample of biochar was measured. In this research, sample of biochar prepared is at 400^{o}C, 500^{o}C, 600^{o}C and 700^{o}C.

Fig 2 : Pyrolysis Unit for the conversion of EFB to biochar.

TGA Analysis (Proximate adaptation)

In proximate adaptation analysis the biochar's moisture content, fixed carbon content and organic matter was evaluated by using thermogravimetric (TGA) analyzer. 20 mg of the sample was heated at 20^{o}C min^{-1} from initial room temperature to temperature of 1050^{o}C. The weight of the sample was recorded until a constant value was achieved. The ash content was determined by measuring the remained samples after the process. The samples that undergoes this method was raw EFB, and all the biochar of 400^{o}C, 500^{o}C, 600^{o}C and 700^{o}C.

Brunauer–Emmett–Teller (BET) Analyzer

In BET method, specific area of the biochar was determined by using Micromeritics Gemini Analyzer at -196^{o}C which is boiling point of nitrogen with adsorption of N_2. Then the equation of BET will be keyed in to experimental adsorption isotherm. Adsorption and desorption capacity of the biochar samples was also determined.[3]

XRD diffraction analysis

In this test, about 0.5 grams grinded of biochar samples were placed in the sample holder. Then the software was opened and the XRD was running under 40 kV of tube voltage and 30 mA of tube current. Then analysis using the XRD machine will be conducted. XRD pattern will be recorded in range of 3 to 80 degree along with 10 degree per minute or 0.167 as step size, with every step size last for 1 second. [8]

Methylene blue number

The capacity of the adsorption for each biochar can be test via methylene blue adsorption. Prior to analysis, a calibration curve of methylene blue was plotted by the analysis of 0.1 ppm, 0.5 ppm, 1 ppm and 10 ppm of methylene blue solutions. The wavelength that is used for methylene blue is at 645 nm. The plotted calibration curve was then used for the next analysis of determining adsorption of the biochar samples. In biochar analysis, measurement of adsorption is done with fixed 2 gram of each of the biochar samples mixed with 20 mL of 10 ppm methylene blue solution in a beaker that is covered with aluminium foil as methylene blue will change color when exposed to sunlight. The beaker was left for approximately one hour before the solution is filtered. The filtrate was then analyzed by using uv/vis spectrophotometer. The efficiencies and the capacity if adsorption were calculated by using the following equation:[9]

$$\text{Qt} = \left(\frac{C_0 - C_t}{m}\right)(V) \qquad \text{Equation 3.2}$$

$$\%\ \text{Adsorption} = \left(\frac{C_0 - C_t}{C_0}\right)\times 100\% \qquad \text{Equation 3.3}$$

Where,
Q_t : Removal efficiencies
Co : initial dye concentration (mg/L)
Ct : Concentration of dye at any time, t
V : volume of dye solution
M : mass adsorbent (g)

III. RESULTS AND DISCUSSION

A. Characterization of adaptation proximate analysis

Table 1-The results from proximate adapted analysis of the samples by using TGA-analyzer.

Properties (%)	Raw EFB	Temperatures(°C)			
		400	500	600	700
Volatile Matter	44.65	17.93	12.68	13.36	7.58
Carbon content	10.08	49.90	56.02	50.85	53.02
Moisture content	7.09	5.34	10.00	5.82	7.67

Based on the results from table 1, the proximate analysis conducted on the raw EFB gives 44.65% of volatile matter to as low as 7.58% at the highest pyrolysis temperature of 700°C. The increase in temperature also causes the increase in the carbon content. Biochar of 500°C have the highest fixed carbon content. This indicates that at this temperature, there were many carbon that can be converted into bichar. Char with low ash content and low volatile matter, will become a good activated carbon. [10]. Biochar that is at 700°C has the least volatile matter due to the facts that most of the organic matter in the biochar had been decomposed due to the high temperature.

As for the moisture content, there were oscillatory pattern that were observed. This might be cause by the biochar itself. The samples should be put into desiccator to prevent it from absorbing the surrounding moisture. [3]

B. Surface area and adsorption capacity

Table 2-BET-Surface area and pore volume of the biochar

	Temperatures(°C)			
	400	500	600	700
BET Surface(m^2g^{-1})	1.162	5.698	0.983	10.354
Pore Volume($cm^3\ g^{-1}$)	0.0025	0.0080	0.0034	0.0100
Pores size (nm)	8.6	5.6	13.9	3.9

Based on BET-surface results in Table 2. It shows that the surface area will significantly increase with the pyrolysis temperature. It is observed that surface area of biochar will increase with increase in temperature at which deforation will occur. However, as what is observed at biochar of 600°C is out specs. This result might cause by the process condition on preparing the samples. One of the possible cause might due to collapse of the sample at the earlier stage.[11] The sample of biochar produced at 700°C produce a biochar with highest surface area which is at 10.35 m^2/g. High surface area will have a more exposure for the adsorption to occur. High surface also will indicate a high pore volume. From the pore sizing, all the sample has a pore sizing that fall on mesopores range and therefore has a potential as adsorption capacity at liquid-solid interface which is ranging from 2-50 nm.[12] Adsorption capacity will hugely depend on the surface area of the biochar.[13]

C. XRD diffraction

XRD diffraction data will determine wether the biochar samples that we have is amorphous or crystalline. These structure is crucial Amorphous will have a great sorption ability. The presence of amorphous shows that the structure has a good pore surface area.[14]

Figure 3(a), Figure 3(b), Figure 3(c) and Figure 3(d) represents X-ray diffraction results for the 400°C, 500°C, 600°C and 700°C respectively. Based on the peaks obtained and compare it to the standard of raw amorphous biochar. It shows that these biochar is amorphous and therefore have good sorption ability and also has a good pore surface area. Amorphous structure intensity will have intensity that is less than 150. All the XRD results show that all the biochar produce is amorphous. This structure is also fragile and therefore it has a potential as a fuel.[14]

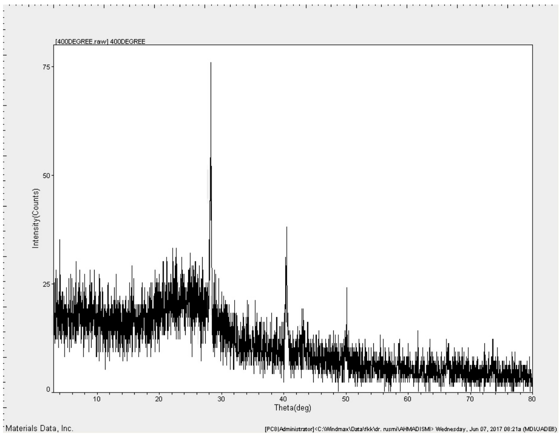

Figure 3(a)-XRD diffraction results for 400^{o}C biochar sample

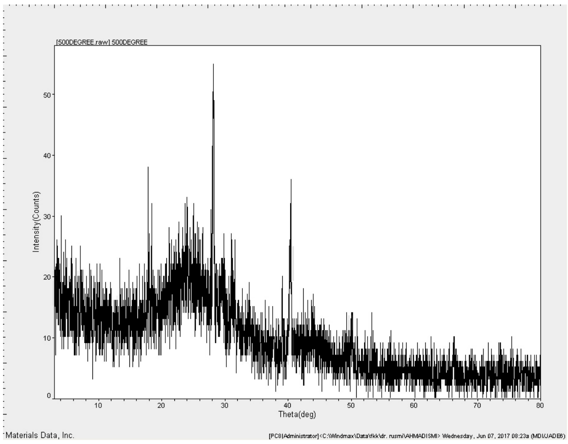

Figure 3(b)-XRD diffraction results for 500^{o}C biochar sample

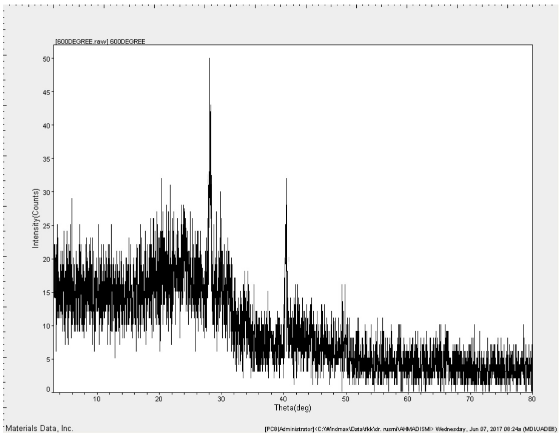

Figure 3(c) -XRD diffraction results for 600^{o}C biochar sample

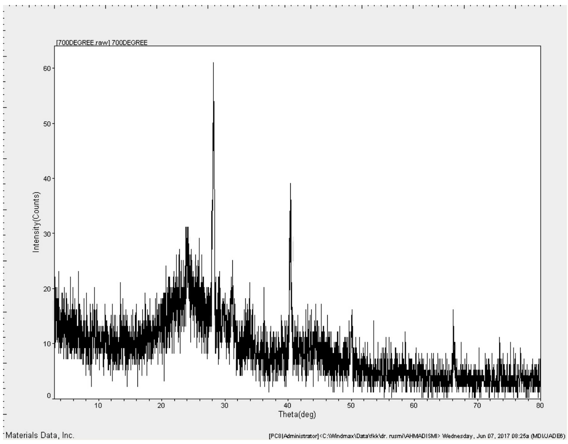

Figure 3(d)-XRD diffraction results for 700^{o}C biochar sample

Methylene blue data analysis

Table 3-Percentage of removal of methylene blue from the solution.

	Temperatures(oC)			
	400	500	600	700
Adsorption(%)	69.8	91.1	81.4	81.4

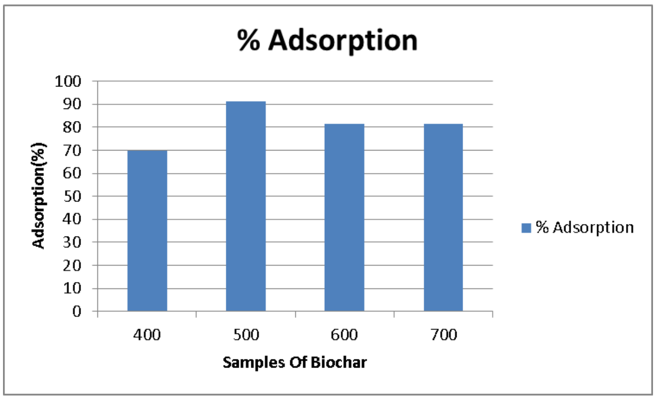

Figure 4-Percentage of adsorption of Methylene blue

Methylene blue analysis is whereby the sorption of the organic contaminants is studied. Based on the data obtained from Table 1, it shows that at 500^{o}C pyrolysis temperature, the biochar produced still have very high fixed carbon content. If more fixed carbon can be converted into biochar, then the methylene blue might have a higher adsorption capacity up to 98%.able to remove or adsorb the methylene blue effectively. The biochar produced at 500^{o}C have adsorption capacity of 91.1% which is the best among all the samples. By considering that the biochar able to adsorb more than 60 percent of the methylene blue, it can be said that it is suitable to be used as a adsorbent for industry that used dye as it's by product. [15]

IV. CONCLUSION

Based on the studies that had been conducted, we can conclude that empty fruit bunches is a suitable feedstock to produce biochar. Therefore, this will help to decrease the wastage produce from the palm oil mill. Production of biochar can be advantageous to the palm oil company themselves as it act as a soil amendment. For biochar that able to retain a very high carbon content, the pyrolysis temperature that is suggested is at 500^{o}C as in this temperature, the carbon yield is at 56%. The biochar produce at this temperature has a high adsorption capacity as it able to 91.1% of the methylene blue solution and it is the highest among the samples. The biochar produced from EFB also has an amorphous characteristic as its intensity reading is below 150 and therefore indicates good sorption ability an. For surface area, biochar that is produce at pyrolysis temperature of 700^{o}C yield the biggest surface area per gram which is at 10.354 m^2g^{-1}.

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References

[1] Nurhayati, A., & Fauziah, S. (2013). The Oil Palm Wastes in Malaysia. *Biomass Now - Sustainable Growth and Use*. doi:10.5772/55302.

[2] Hossain, M. A., Jewaratnam, J., & Ganesan, P. (2016) Prospect of hydrogen production from oil palm biomass by thermochemical process – A review. *International Journal of Hydrogen Energy, 41*(38), 16637-16655. doi:http://dx.doi.org/10.1016/j.ijhydene.2016.07.104

[3] Adilah, S., Nur, S. M. A., & Nurhayati, A. (2014). Slow Pyrolysis of Palm oil empty fruit bunches for biochar production and characterization. *Journal of Physical Science, Vol. 25*(2), 97-112.

[4] Mohammed, M. A. A., Salmiaton, A., Wan Azlina, W. A. K. G., Mohammad Amran, M. S., Fakhru'l-Razi, A., & Taufiq Yap,Y. H. (2011). Hydrogen rich gas from oil palm biomass As potential source of renewable energy in Malaysia. *Renewable andSustainable Energy Reviews, 15*(2), 1258 1270.doi:http://dx.doi.org/10.1016/j.rser.2010.10.003

[5] Yaman, S. (2004). Pyrolysis of biomass to produce fuels and chemical feedstocks. *Energy Conversion and Management, 45*(5),651-671.doi:http://dx.doi.org/10.1016/S0196 8904(03)00177-8

[6] Kyle, C. (2014). *Biochar – synergies between carbon storage, environmental functions and renewable energy production.* (Doctor of Philosophy), The University of Edinburgh, Scotland.

[7] Rozhan, A. N., Ani, M. H., Salleh, H. M., Akiyama, T., & Purwanto, H. (2015). Development of Carbon-infiltrated Bio char from Oil Palm Empty Fruit Bunch. *ISIJ International, 55*(No. 2),436-440. doi: 10.2355/isijinternational.55.436

[8] Diogenes, R. L. V. (2012). *Development of Methodologies for Improving Thermal Stability of Plant Fibers for Application inThermoplastic Composites.* (Doctor of Philosophy In Chemical Engineering), University of Waterloo, Canada.

[9] Lonappan, L., Rouissi, T., Das, R. K., Brar, S. K., Ramirez, A. A., Verma, M., . . . Valero, J. R. (2016). Adsorption of methyleneblue on biochar microparticles derived from different waste materials. *Waste Management, 49*, 537-544. doi:http://dx.doi.org/10.1016/j.wasman.2016.01.015

[10] GUO, A. C. L. J. (1997). PREPARATION AND CHARACTERIZATION OF CHARS FROM OIL PALM WASTE. *Elsevier Science Ltd*. doi:PII: S0006223(98)001614

[11] Al-Muhtasebg., W. A. W. A. K. G. A. M. G. d. S. R. T. B.Y. H. T.-Y. U. R. A. a. H. (2013). Biochar production from wasterubber-wood-sawdust and its potential use in sequestration: Chemical and physical characterization. *Elsevier Science Ltd*.

[12] RaphySari, N. A., Ishak, C. F., & Bakar, R. A. (2014) *CHARACTERIZATION OF OIL PALM EMPTY FRUIT BUNCH AND RICE HUSK BIOCHARS AND THEIR POTENTIAL TO ADSORB ARSENIC AND CADMIUM.* Merlimau: American Journal of Agricultural and BiologicalSciences.

[13] W. M. F. W. MAHMOOD, M. A. A., Z. HARUN, N. A. I. MD. ISHAK, J. A. GHANI, M. N. AB. RAHMAN1. (2015). CHARACTERISATION AND POTENTIAL USE OF BIOCHAR FROM GASIFIED OIL PALM WASTES.*Journal of Engineering Science and Technology*.

[14] Stephen Joseph, Olivier Husson, Ellen Ruth Graber, Lukasvan Zwieten, Sara Taherymoosavi, Torsten Thomas, Donne., S. (2015). The Electrochemical Properties of Biochars and How TheyAffect Soil Redox Properties and Processes *Agronomy*.

[15] Dawood, S., Sen, T. K., & Phan, C. (2016). Adsorption removal of Methylene Blue (MB) dye from aqueous solution by bio-char prepared from Eucalyptus sheathiana bark: kinetic, equilibrium, mechanism, thermodynamic and process design. *Desalination and Water Treatment, 57*(59), 28964-28980. doi:10.1080/19443994.2016.1188732