DEVELOPMENT OF BIOCHAR USING NON-DIRECT FIRING SYSTEM FROM GAHARU-CHEMICAL PROPERTIES

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***Abstract*— Biochar production is used as part of modern agenda for agricultural used and to offset some greenhouse gas emissions. This study conducted to find the chemical properties of biochar using different pyrolysis temperature. Characterization of biochar from Gaharu produced at 400, 500 and 600°C were through Elemental analysis, TGA and FTIR analysis. Biochars derived from wood exhibit a high carbon content especially when pyrolysis temperature increased. The observation made through analysis proved that carbon content increased while O/C and H/C decreased because of evaporating volatile matter in the process. TGA results provided that the weight of each sample is indirectly proportional to the pyrolysis temperature. The functional groups for each of the sample will be decided through FTIR analysis. The results demonstrated that production temperature acted as predominant factor which determined the properties of biochar.**

Keywords—Gaharu, Slow pyrolysis, Biochar.

I. INTRODUCTION

The use of biochar extends so far back in time that its origin is impossible to determine exactly. It is widely used as an effective adsorbent in many applications such as solvent recovery, emission control cause by anthropogenic, air separation and purification. All this are commonly made from organic material such as wood and manure. Nowadays, biochar can be produced in an environmentally friendly way which is by pyrolysis where it allows material to be burned at high temperatures and have all the emissions captured. Scientists around the world are researching all aspects of biochar production and chemical compositions based on different feed stocks. In this case, Gaharu or Agarwood is choosen as part of the research. Gaharu is highly regarded as valuable heartwood found in *Aquilaria* and Gyrinops (Pasaribu, K.Waluyo, & Pari, 2016). The infected heartwood is odourless and have light and pale colour but somehow produce a dark aromatic resin (gaharu) after being infected for a long period. Back then, gaharu has been used widely especially in traditional medicine field, aromatic, religious purposes in major markets in Middle East and East Asia (Teck Wyn, 2010). The quality of gaharu can be determined through it chemical, physical and biological properties. This will help to differentiate between the high and low grades.

Properties of biochar are strongly dependent on type of feedstock because its properties affect nature of the original material. On top of that, operating condition for the whole process gives different results that determine the state of product which is biochar. Generally, biochar is a solid-rich carbon product after undergoing pyrolysis of gaharu in the absence of air or oxygen supply. The wood-based biochar is more long-lasting because of lignocellulosic components in the wood. Lignocellulosic which consists of cellulose, hemicellulose and lignin will determine the ratio of volatile matter and fixed carbon after pyrolysis process. Various studies have been done to explore the relationship between biochar properties and pyrolysis conditions. Slow pyrolysis is introduced as thermal conversion of biomass by slow heating at low to medium temperature in the absence of oxygen. Through past study by researchers, temperature gave more impact toward biochar properties plus heating rate (Angin, 2013).The purpose of this study is to analyze the characteristics of biochar using different pyrolysis temperature and determine its chemical properties using proximate and ultimate analysis.

II. METHODOLOGY

i) Biochar feedstock

The type of biomass used in pyrolysis experiment is Gaharu wood or known as Agarwood. It is first grinded into small particles before it is dried in the oven for 24 hrs at 70°C to ensure that the sample free of moisture which is below than 5% M. Then, it will be grinded to less than 2mm and stored the sample in a desiccator before analysis.

ii) Double Jacket Pyrolyzer

The pyrolysis process is performed in a double jacket pyrolyzer lab scale equipment facility with feeding of nitrogen as shown in Figure 2.1. The pyrolyzer is made from metal unit (inner stainless steel; inner diameter 14 cm, height 121 cm) and (outer stainless steel; inner diameter 24 cm, height 121 cm) which can receive heat up to 1200°C. The sample is fed into the pyrolyzer before using indirect heating until it reached the target temperature of 400, 600 and 800°C for 1 hr residence time. Before heating, the pyrolyzer is kept at ambient temperature (25-35°C) and then filled with 500 g of grinded Gaharu. Heat released at the bottom of the pyrolyzer is introduced in between two steels with continuous heating and continue increased in an orderly manner. The firing is controlled by manipulating the amount of liquefied petroleum gas (LPG) and compressor to make sure that it would form into blue fire. Once it reached target temperature, the nitrogen is fed to purge out oxygen gas out of the pyrolyzer. It remains for about an hour before the samples is cooled down below than 50°C to make it easier to handle before taking it out for analysis. The biochar produced is stored in an airtight bag and is placed in a desiccator before analysis. This procedure is necessary to prevent oxidation reactions takes place, changing the number of surface active groups.

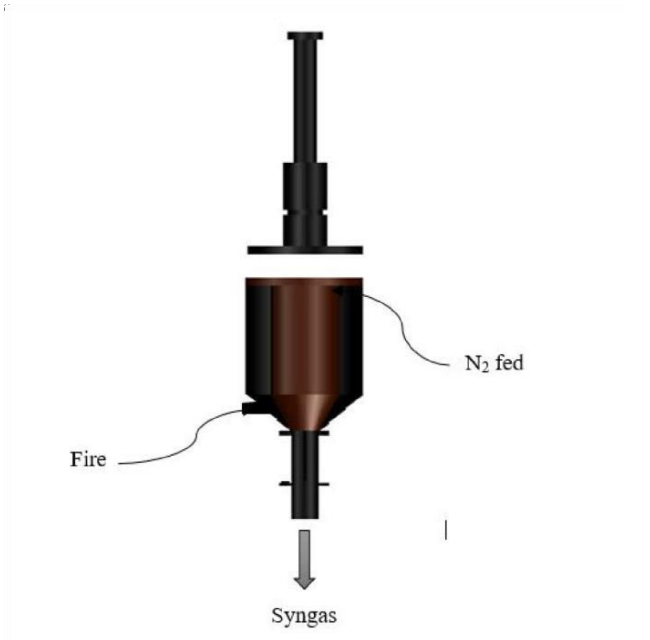

Figure 2.1: Double-Jacket Pyrolyzer

iii) Biochar Chemical Analysis

Elemental Analysis

In case of ultimate (elemental) analysis which can act as stability indicator, it analyse C, H, and N by using elemental analyser-Thermo Finnigan Flash EA1112. About 40 mg of biochar is dried at 105°C for 24 hr, and cooled to room temperature. The dried biochar is compacted in tin box paper, and place on the automatic sampler. With high purity-nitrogen gas as the carrier gas, the element content analysis is carried out using this analyzer.

Fourier-transform Infrared (FTIR) Spectroscopy

Perkin Elmer Spectrum One FTIR spectrometer will analyse the surface functional groups and structural changes in material. Then, rinse the biochar in a beaker using 1 mol/L HCl, and then filtered. This step is repeated until the removal of ash and non-water soluble substances of the samples is maximized. Then, after the sample was dried at 70°C for 6 hr, 1 mg of the biochar was mixed with 300 mg of KBr powder in agate mortar, fully lapping to uniform, and then was pressed in the press machine at 150 kPa for 5 min. Lastly, the surface functional groups were determined via FTIR with a wave range of 400-4000 cm^{-1} and resolution ratio of 8 cm^{-1}.

Thermogravimetric Analysis

Thermal analysis of biochars was performed by using thermal analyzer. Due to small amount of biochar needed for TGA analysis, moisture can be rapidly absorbed by the sample during transport and handling prior to analysis. Samples are first heated for 10 min at 105°C under N_2 to determine moisture content. Then, the temperature is then raised at 25°C min^{-1} to 900°C where it remained for a further 10 min to eliminate volatile matter. After that, air is introduced to the system and the samples is combusted at 900°C for 15 min to determine ash content. Another one is fixed carbon where it is calculated on a weight percent basis by subtracting moisture, volatile and ash values from the original mass.

$$\% C = (100 - C - VM - Ash) \%$$

III. RESULTS AND DISCUSSION

i) Elemental Analysis

Pyrolysis temperature during biochar production show large effects on the biochar elemental compositions. An increase in temperature resulted in a larger loss of H and O composition compared to that of C because of the high temperature of the charring which resulted from dehydration and decarboxylation reactions. These trends are common which indicated that aromaticity of biochars enhanced while polarity decreased. In general, biochar yield decreased with rising temperature as observed throughout the experiment. These declines were mainly due to the released of moisture and volatile organic compounds in the biochars, as well as the decomposition of hemicelluloses, celluloses and lignin.

Table 3.1: Elemental analysis of biochar produced at different temperature with retention time.

Temperature (°C)	Elemental analysis quantity			
	C (%)	H (%)	N (%)	S (%)
Gaharu (raw)	83	13	4	0
400	90	7	3	0
500	90	6	4	0
600	89	8	3	0

The result consistently increased as temperature become higher from previous result. As gaharu is pyrolyzed at 400°C, the composition of C increased from 83 to 90 wt%. This finding shows that carbonization is promoted with increasing pyrolysis temperature. Other than that, hydrogen contents of the feedstock after pyrolysis ranged between 6 to 8 wt%. Pyrolysis led to significant H content losses that continued with increasing pyrolysis temperature (Table 3.1). This lost caused by high pyrolysis temperature which is due to cleavage and breakage of weak bonds within biochar structure. It is also due to decomposition of oxygenated bonds and the released of low molecular weight by-product containing H and O. The complex structure was attributed to this outcome as it was not resistant to lower temperature and was not easily volatilized rather than at high temperature. Lower H/C ratios demonstrate an increased aromaticity caused by pyrolysis and therefore indicate higher stability of the material compared with the initial feedstock. High fixed carbon content shows that it has a very low H content and also that volatile matter released during pyrolysis is composed of compounds with higher H/C ratios than the remaining biochar (fixed carbon). Thus, devolatilization removes most of the H from the biomass as the pyrolysis reaction takes place.

Nitrogen concentration decreased as temperature increased to 600°C. This is due to cracking of nitrile-N and heterocylic-N compounds from the dehydrogenation and polymerization of amine-N during pyrolysis (Tian et al., 2013). However, at 600°C, the carbon content decreases to 89%. This might happen because of exposure of the sample to the surrounding before it being pyrolyzed. To make it worst, the process was affected by the limited flow rates of nitrogen because of some error in the piping system. Thus, the air in the pyrolyzer was not being fully purged out. This explain why the carbon composition of biochar at 600°C was smaller than other pyrolysis temperature.

ii) Thermogravimetric Analysis

The TGA analysis was carried out under air atmosphere to evaluate the thermal stability of the biochar samples. Recent research suggested that higher pyrolysis temperature give better thermal stabilities. The end-products of the decomposition were pyrolysis products rather than products of oxidative degradation since nitrogen was used as the carrier gas. Undergoing pyrolysis process caused gaharu lose it volatile matter where most of it turned into gas phase and minerals (Yan et al., 2013). Heating rate and residence time are the main factors for biochar distribution. In Figure 3.1, the weight pattern for each pyrolysis temperature is presented. When volatile matter was expelled out from biochar particles, the weight of product became lower. Not only that, this will determine the fixed carbon content left in final product.

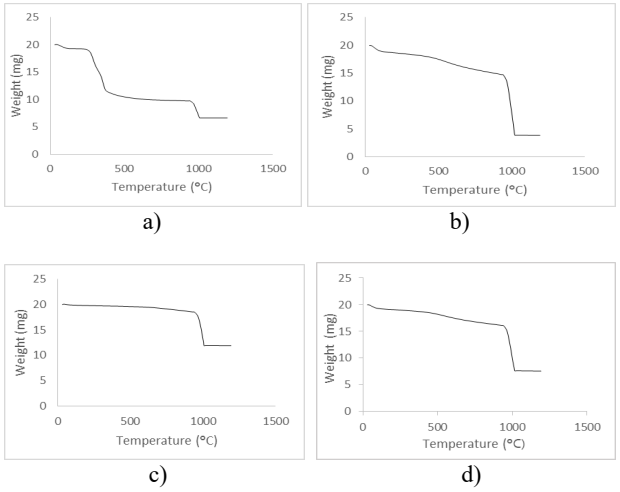

Figure 3.1: TGA results a) Feedstock b) 400°C c) 500°C d) 600°C

The data from TG and DTG curves of biomass and biochar at different pyrolysis temperature were collected and was shown in the Table 3.2. Between 31°C to 112°C, the mass lost happened due to moisture and some extractives compounds evaporation. After 59°C, the process was mainly attributed to hemicelluloses and cellulose thermal degradation until 112°C. At maximum curve, the cellulose was in complete degradation. However, lignin was stable from 112°C to 931°C and started to degrade after 1021°C.

Most of the graph show a significance trends where the moisture will start to loss at the starting temperature and it continued when it reach around 150°C. The process proceed to cast out the volatile matter which showed the evaporate component released from biochar. At the end, the biochar will be left with fixed carbon and ash residue. The percentage of each component was different for each of the pyrolysis temperature since it has different heating rate. As shown in Table 3.2, at 600°C, the percentage of moisture, volatile matter, fixed carbon and ash residue are 5, 40, 17 and 38%. The fixed carbon left was much lower at high temperature rather than at lower temperature. Based on Table 3.2, the biochars' ash contents increased with pyrolysis temperature due to volatilization. The highest content of ash was found at 500°C which is due some error during the process. Furthermore, there was an accumulation of inorganic components which caused the ash content to be higher than at 600°C. Not only that, there was some clogging happened during the process that caused the flow of nitrogen gas and syngas failed. The air inside the pyrolyzer was not fully purged out and caused some of the products oxidized.

Table 3.2: Thermal analysis of biomass and Biochars

Sample (T°C)	Moisture (%)	Volatile (%)	Fixed Carbon (%)	Ash (%)
Gaharu (raw)	3	18	46	33
400	7	52	22	19
500	1	33	7	59
600	5	40	17	38

iii) FTIR analysis

Table 3.3: Classification of FTIR analysis for each sample at different pyrolysis temperature

Sample	Frequency (cm^{-1})	Bond
Raw material	3324	O-H stretch, H-bonded
		-C=C-H:C-H stretch
		C-O stretch
	1028	C-N stretch
400°C	1203	C-O stretch
		C-N stretch
500°C	1143	C-O stretch
		C-N stretch
600°C	1218	C-O stretch
		C-N stretch

Under FTIR analysis conducted on the feedstock, the spectra showed a strong band at 3324 cm^{-1}, which attributed to –OH ion from H_2O or phenolic groups. This showed that, it contained a number of moisture which will then be evaporated under pyrolysis process. Increasing pyrolysis temperature assigned the O-H stretching vibration and the aliphatic C-H stretching vibration decreased significantly and almost disappeared. This indicates that labile aliphatic compounds become lower when pyrolysis temperature increased. Other than that, the demethoxylation, dehydration of lignin and demethylation occurred (Kloss et al., 2012). The FTIR spectra for biomass detect a C-O stretching vibration at 1028 cm^{-1}. These absorption bands indicated the presence of a mixture of carboxylic acid, esters, aldehyde, acid halides and (Mante & Agblevor, 2010). When it was being pyrolyzed at 400°C, there was strong C-O stretch in between 1320-1000 cm^{-1} and it was associated with oxygenated functional groups of cellulose, hemicellulose, and methoxyl groups of lignin (Domingues et al., 2017). This intensify dehydroxylation where the loss of OH and aliphatic groups will actually escalate pore formation due to a concurrent development of fused-ring structures (Kloss et al., 2012). The changes in structure continued when it was pyrolyzed at 500°C. The intensities of bands of C-O stretch at 1143 cm^{-1} plunged sharply due to degradation and dehydration of cellulosic and ligneous components. The decreased of the bands between 1200 and 1000 cm^{-1} marks the loss of polysaccharides during pyrolysis (Kloss et al., 2012). At 600°C, the intensity for C-O bonds increased to 1218 cm^{-1} meant there was increased in carboxylic acid and its derivatives.

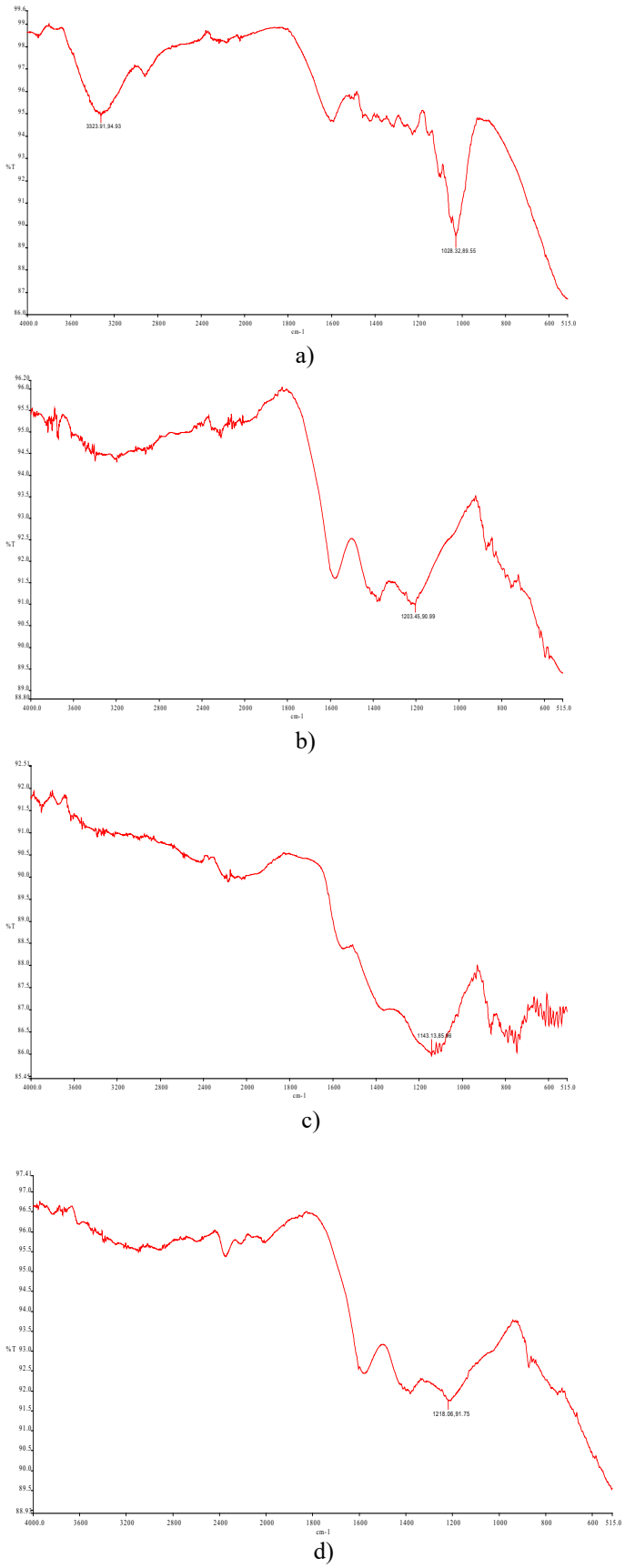

Figure 3.3: FTIR analysis: a) Feedstock b) 400°C c) 500°C d) 600°C

In general, the maximum loss was obtained in –OH, -CH_2, and C-O functional groups in biochars as a function of pyrolysis temperature which was shown from their elemental composition in Table 3.1. Moreover, lower values of O, H and H/C at high temperature revealed the significant elimination of polar functional groups (-OH and C-O). Since the temperature increased, most of the organic functional groups present in the biochar structure were lost. Compared to original sample, the C-H bonds gradually weakened as pyrolysis temperature increased. The intensity for each graph at the end remained unchanged even after the biomasses were subjected to the charring process for three temperatures. Addition to that, organic materials were converted to water and carbonaceous gas which increased the quantity of volatile compounds and lowering the content of acidic groups (Zhao, Ta, & Wang, 2017). The strong direct correlation after 500 cm^{-1} was for basic functional groups that are mainly associated with the ash fraction especially for biochar at 500°C. If this biochar was to be applied in agricultural used, a lower temperature may be suitable for the application to improve the soil fertility. Last but not least, a higher pyrolysis temperature was very selective and it predominantly produces more aromatic compounds which resulting in recalcitrant structure (Jindo et al., 2014).

IV. Conclusion

In this study, the biomass which is Gaharu itself undergoes several pyrolysis temperatures where it is a primary factor condition in determining biochar characteristics. The experiment used temperature as the main parameter which will act as modify, changing the chemical nature and increasing the aromatic character of the organic compounds of biochar. The study was done to find the approximate and proximate analysis. A lot of finding obtained show the differences before and after the biomass went through charring process. Biomass before charring was not compact with carbon as much as after it being pyrolyzed at higher temperature. Higher temperature increased the amount of carbon component while increasing the aromatic character that makes the feature more consistent and compact. There were also phase transition occurred for material. Finally, the higher-heat production (above 600°C) causes the decomposition of the functional groups through heat degradation.

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References

1. Angin, D. (2013). Effect of pyrolysis temperature and heating rate on biochar obtained from pyrolysis of safflower seed press cake. *Bioresource Technology*, *128*, 593–597. https://doi.org/10.1016/j.biortech.2012.10.150

2. Domingues, R. R., Trugilho, P. F., Silva, C. A., De Melo, I. C. N. A., Melo, L. C. A., Magriotis, Z. M., & Sánchez-Monedero, M. A. (2017). Properties of biochar derived from wood and high-nutrient biomasses with the aim of agronomic and environmental benefits. *PLoS ONE*, *12*(5), 1–19. https://doi.org/10.1371/journal.pone.0176884

3. Jindo, K., Mizumoto, H., Sawada, Y., Sanchez-Monedero, M. A., & Sonoki, T. (2014). Physical and chemical characterization of biochars derived from different agricultural residues. *Biogeosciences*, *11*(23), 6613–6621. https://doi.org/10.5194/bg-11-6613-2014

4. Kloss, S., Zehetner, F., Dellantonio, A., Hamid, R., Ottner, F., Liedtke, V., … Soja, G. (2012). Characterization of Slow Pyrolysis Biochars: Effects of Feedstocks and Pyrolysis Temperature on Biochar Properties. *Journal of Environment Quality*, *41*(4), 990. https://doi.org/10.2134/jeq2011.0070

5. Mante, O. D., & Agblevor, F. A. (2010). Influence of pine wood shavings on the pyrolysis of poultry litter. *Waste Management*. https://doi.org/10.1016/j.wasman.2010.07.007

6. Pasaribu, G., K.Waluyo, T., & Pari, G. (2016). Analysis of Chemical Compounds Distinguisher for Agarwood Qualities. *Indonesian Journal of Forestry Research*, *2*(1), 1–7. https://doi.org/10.20886/ijfr.2015.2.1.644.1-7

7. Teck Wyn, L. (2010). Wood for the Trees: A review of the agarwood (gaharu) trade in Malaysia. In *TRAFFIC Southeast Asia, Petaling Jaya, Malaysia*.

8. Tian, Y., Zhang, J., Zuo, W., Chen, L., Cui, Y., & Tan, T. (2013). Nitrogen conversion in relation to NH3 and HCN during microwave pyrolysis of sewage sludge. *Environmental Science and Technology*, *47*(7), 3498–3505. https://doi.org/10.1021/es304248j

9. Yan, Q., Toghiani, H., Yu, F., Cai, Z., & Zhang, J. (2013). Effects of Pyrolysis Conditions on Yield of Bio-Chars from Pine Chips. *Forest Products Journal*, *61*(5), 367–371. https://doi.org/10.13073/0015-7473-61.5.367

10. Zhao, S. X., Ta, N., & Wang, X. D. (2017). Effect of temperature on the structural and physicochemical properties of biochar with apple tree branches as feedstock material. *Energies*, *10*(9). https://doi.org/10.3390/en10091293