# Development of Biochar Using Non-Direct Firing System from Gaharu-Physical Characteristic

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*Abstract*— **Biochar has an ability to increase crop yield, reduce soil emission of greenhouse gases, decrease nutrient leaching, improve soil quality, reduce irrigation and fertilizer requirement, and store large amount of carbon. Gaharu that pyrolyzed at different temperatures results in different physical characteristic. Gaharu was firstly place manually in the reactor and pyrolyzed at temperature of 400,500, and 600°C. Produced biochar were further analyzed in observing its pH, surface area, adsorption uptake of dye, and surface morphology. pH, Brunaeuer, Emmett, and Teller (BET) Test, Methylene Blue (MB) Absorption Using UV-Vis Spectroscopy, and Microscope Scanning Images analysis provide physical data information of the produced biochar. pH increases from 6.34 to 9.25 with the increase of temperature. BET surface area, micropore surface area, and specific pore volume shows identical pattern as temperature increases which slightly increased between 400 and 500°C and drastically increased as it reached 600°C. The maximum BET surface area and micropore surface area were 131.5542 and 108.0602m²/g. The maximum specific pore volume observed was 0.042179 cm³/g. At 400°C, the amount of MB dye solution absorbed increased from 2495.63mg/g to 12489.30mg/g as the initial concentration of MB dye solution increases. Microscope scanning images represents the surface morphology of the biochar. Some pores are impeded by volatile and ash contents can reduce the pore volume. The physical data obtained shows biochar produced under different pyrolysis condition influences the physical characteristic of the produced biochar. Higher temperature result in higher surface area. Increase in surface area improve the adsorption characteristic of the biochar produced.**

***Keywords— Gaharu, Biochar, Pyrolysis, Adsorption, Pore volume***

## I. INTRODUCTION

According to a research done by The Wildlife Trade Monitoring Network of WWF and IUCN (TRAFFIC), Malaysia is considered as important country that produce and trade any kind and forms of agarwood (Gaharu) which includes oil, chips, and processed derivatives like incense sticks and medicine [1]. In 2005, Convention on International Trade in Endangered Species of Wild Flora and Fauna (CITES) declared out of half percent from entire gaharu products originated from Malaysia are being traded internationally. This in returned, make Malaysia a place that is as the main manufacture of gaharu according to recorded trade published by CITES. The invention of the forest species that are producing agarwood gaining more attention from time to time from the notional to the local levels. As sources of natural forest species is decreasing from time to time, planters see the advantages of agarwood species development as green gold mine for the future sources of natural forest. Agarwood can also be known as gaharu, aloes wood, eagle wood, oud, chen-xiang, kalambak among other common names, can be considered as the most valuable non-timber forest product worldwide. Agarwood is produced from the resinous fragrant and highly prized heartwood of species of Aquilaria, Aetoxylon (A.symeatalum) and Gonystylus of the family Thymelaeaceae [2]. Agarwood species producer can be mainly found in Southeast Asian countries includes Malaysia, Thailand, Vietnam, and also Indonesia. It is also can be found in New Guinea Island [3]. The agarwood production is irregular that it is estimated that the Aquilaria tress in forest that contain agarwood only present around 10% [4]. Based on the historical record, agarwood in Peninsular Malaysia has undergo harvesting and trading activities before 684 centuries [5]. As the agarwood have such a pleasant smell, the application of the agarwood has increases widely with various uses. The oil from the extraction of the agarwood and the wood itself has an expensive priced [2].

Biochar has highly-porous structure which contain various functional group such as carboxyl, hydroxyl, and phenolic groups that causes the biochar to has great relation for heavy metals [6]. The properties of biochar depend on the technology and type of feedstock used in the production [7].

By product results from pyrolysis of various biomass material, produces biochar that has carbon enriched, higher specific surface area, porous aromatic structure, the diverse chemistry of surface functional groups, higher adsorption affinity for cations and anions than the biomass feedstock [8]. Various uses and application of Biochar depends on the physical and chemical characteristic of the biochar itself. These characteristics are influence that result from the pyrolysis of biomass operating condition such as duration of the process and the temperature [9].

The objective of this paper is to analyze physical characteristics of biochar produced from indirect firing system which run at temperatures of 400,500, and 600°C.

## II. METHODOLOGY

### A. *Pyrolysis feedstock preparation*

Feedstock material agarwood or gaharu which was obtained from the oil extraction was dried at 120°C in an oven overnight to remove moisture content [10]. The dried gaharu was packed in the air tight plastic bags to prevent air moist contact.

Fig 1: Extracted Gaharu

## B. *Slow pyrolysis process*

Biochar was produced from feedstock using double jacket pyrolyzer, pyrolyzing the feedstock at 400,500 and 600°C. Approximately 500 g of feedstock was manually placed in the main chamber of the reactor. The dried feedstock was heated from the ambient temperature (25-35°C) to the targeted temperature with 1 hour residence time [9]. The residual air was purged by using constant supply of nitrogen, $N_2$ gas to the feedstock via nitrogen gas inlet at the top of the main chamber to provide the inert reaction medium [10].

Fig 2: Gaharu sample is placed in the reeactor

Fig 3: Full set up of double jacket pyrolyzer

After the pyrolysis process was complete, the reactor was left cooled before the biochar stored in sealed plastic bags until used.

## C. *Gaharu Biochar Physical Analysis*

### 1) *pH*

A mixture of biochar and distilled water with ratio of 1:10 (weight/volume) was shaken on a mechanical shaker at 180 rpm for 24 hours [11]. The pH of the mixture was then analyzed by pH meter.

### 2) *Brunaeuer, Emmett, and Teller (BET) Test*

The measurement of $N_2$ gas adsorption for BET surface area determination of biochars were undertaken with Autosorb-1 Surface Area Analyzer (Quantachrome Instruments) measurement system [12].

### 3) *Methylene Blue (MB) Absorption Using Uv-Vis Spectroscopy*

MB or methylthioninium chloride having a molecular weight of 319.85 g/mol was selected as adsorbate. A stock solution of 1,000 mg/L was prepared by dissolving 1000mg powder of MB in 1,000 ml volumetric flask and filled distilled water. Different experimental dye concentrations of 10, 20, and 50ppm were prepared by diluting the stock solution with distilled water which labelled as solution A, B, and C respectively. 0.1g of biochar was added to Erlenmeyer flask containing 25ml of MB dye solution and the suspension was shaken by mechanical shaker at 120rpm for 1 hour. The Uv-Vis spectrophotometer was used to measure the concentration MB dye in solution where the maximum adsorption for the dye solution was measured at $\lambda max$ = 660 nm [13]. The calibration curve was plotted between the absorbance and concentration of the dye solution to obtain the linear calibration equation [14].

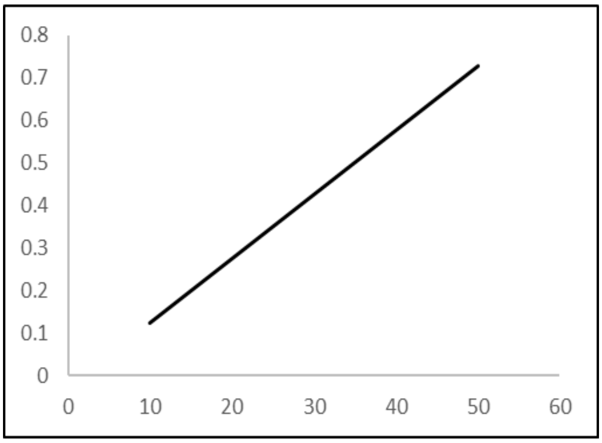


Fig 4: Graph of Absorbance vs Concentration

This calibration curved was plotted from the prepared different experimental dye concentration solution (without biochar sample). The concentration of the unknown solution was measured from the calibration plot. The value of $r^2$ observed was 0.9994. The amount of adsorbed MB at time t (mg/g) was calculated using Eq (1)

$$qt = V(C_0-C_t)/w \quad (1)$$

where $C_0$ and $C_t$ (mg/L) are the liquid-phase initial and final concentrations of MB respectively. V (L) is the volume of the MB solution, and w (g) is the mass of dry biochar used [13].

### 4) *Microscope Scanning Images*

The surface physical morphology of the biochar was examined by microscope scanning images. [12].

## III. RESULTS AND DISCUSSION

**Table 1**
Surface area and pH of Biochar at different temperatures.

| Temperature (°C) | BET surface area (m²/g) | Micropore surface area (m²/g) | Specific pore volume (cm³/g) | pH |
|---|---|---|---|---|
| 400 | 1.4004 | 0.4111 | 0.000164 | 6.34 |
| 500 | 1.4885 | 1.077 | 0.000418 | 7.28 |
| 600 | 131.5542 | 108.0602 | 0.042179 | 9.25 |

### *A. pH*

Physical properties such as pH which is depend solely on the composition and concentration of inorganic mineral constituents. The pH value observed at temperature 400°C, 500°C, 600°C, are 6.34, 7.28, 9.25 respectively.

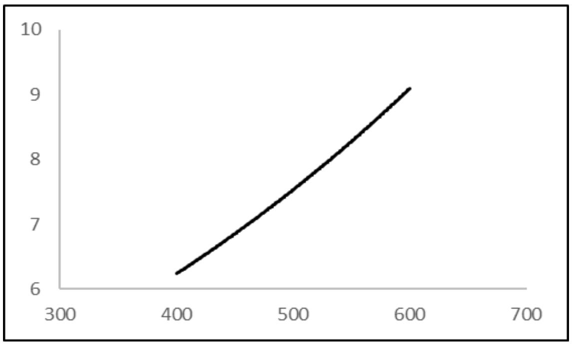


Fig 5: Graph of pH vs Temperature

The increased of pH value of biochars with the increase of temperature probably results from the relative concentration of non-pyrolyzed inorganic elements, which already present in the original feedstock [15].

### *B. Brunaeuer, Emmett, and Teller (BET) Surface Area*

Biochar BET surface area is a fundamental feature that regulates its pollutants and nutrients adsorption and retention capacity [16]. Pore structure parameters (BET surface area, micropore surface area, specific pore volume and pore size) of biochar is presented in Table 1. BET surface area, micropore surface area, and specific pore volume shows identical pattern as temperature increases which slightly increased between 400 and 500°C and increased drastically as it reached 600°C. The maximum BET surface area and micropore surface area were 131.5542 and 108.0602m²/g with increase of temperature. These results are quite similar to literature reported studies of biochar produced from different biomass materials under diverse pyrolysis conditions [17, 18]. The behavior of the BET surface area in various temperatures can be observed in figure 6.

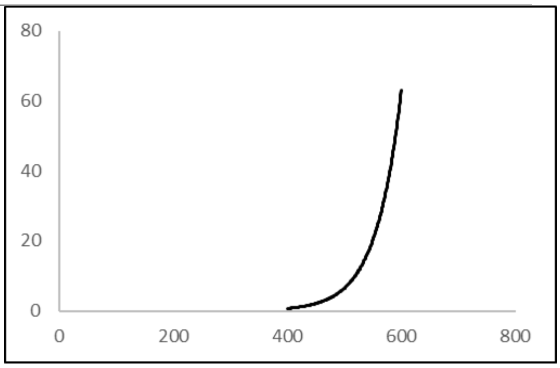


Fig 6: Graph of BET Surface Area vs Temperature

The maximum specific pore volume observed was 0.042179 cm³/g. The increase in the volume probably influences by biomass particle size as reported by [10] which more reduction size contributes to more specific pore volume. More pores are generated as the temperature increases, and consequently their size reduces. From this result observed, as temperature increases, the BET surface area, micropore surface area, specific pore volume increases. The pores in C-skeleton of biochar developed due to the thermal degradation and release of volatiles from feedstock material. Comparatively less surface area of biochar at a lower temperature could be interrelated to the tar formation during pyrolysis, that can either impede pores continuity or prevent the pores creation, but at elevated temperature, these biochar tars volatilize, thus these pores developed which contributed greater surface area [17].

### *C. Methylene Blue Absorption Using Uv-Vis Spectroscopy*

The initial dye concentration gives significant effects to the percent of its removal. It was observed that, at 400°C, the amount of MB dye solution absorbed increased from 2495.63mg/g to 12489.30mg/g as the initial concentration of MB dye solution increases from A, B and to C respectively. Similar trend was found for 500 and 600°C as seen on Table 3 and Fig 7.

**Table 2**
Final concentration of MB dye solution

| Temperatures (°C) | $C_t$ (ppm) | | |
|---|---|---|---|
| | A | B | C |
| 400 | 0.0175 | 0.0134 | 0.0070 |
| 500 | 0.0131 | 0.0088 | 0.0592 |

| | | | |
|---|---|---|---|
| 600 | 0.0061 | 0.0151 | 0.0428 |

**Table 3**
Adsorbed amount of MB dye solution

| Temperatures (°C) | qt (mg/g) | | |
|---|---|---|---|
| | A | B | C |
| 400 | 2495.63 | 4996.65 | 12498.30 |
| 500 | 2496.73 | 4997.80 | 12485.20 |
| 600 | 2498.48 | 4996.23 | 12489.30 |

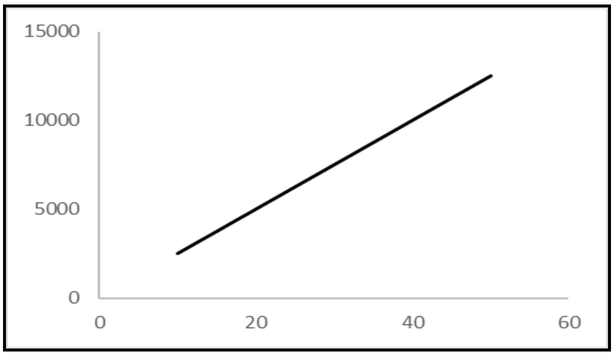

Fig 7: Graph of adsorption capacity vs initial concentration of MB solution.

The result exhibit similar behavior as reported by [14]. The initial dye concentration provides a high driving force to overcome the resistance to the mass transfer of dye between the aqueous solution and the solid phase of a fixed adsorbent dose [14].

### *D. Microscope Scanning Images*

The visual structure of biochar for temperature 400, 500, and 600°C was inspected by taking the Microscope Scanning Images as shown in fig 7,8, and 9 respectively. These images demonstrate that porous structure of synthesized biochar. Some pores are impeded by volatile and ash contents can reduce the pore volume.

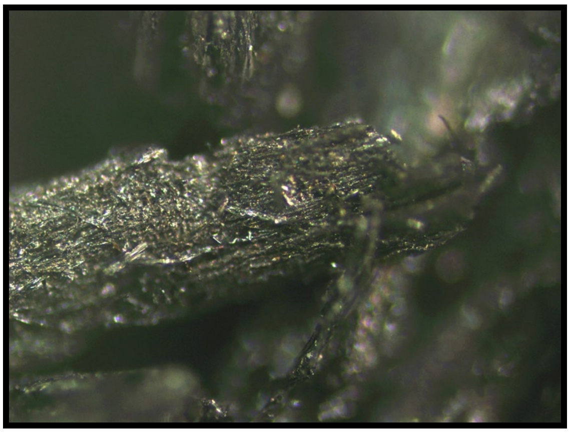
Fig 8: Biochar sample at 400°C


Fig 9: Biochar sample at 500°C

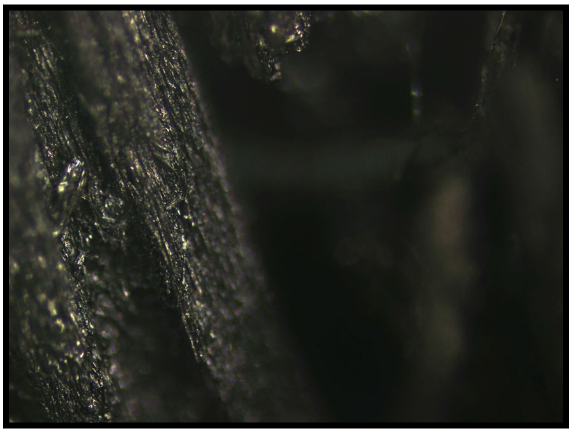
Fig 10: Biochar sample at 600°C

## IV. Conclusion

Results from pyrolysis of various biomass material, produces biochar that has different physical characteristic which stimulated under different temperature condition. The increased of pH value of biochars with the increase of temperature probably results from the relative concentration of non-pyrolyzed inorganic elements, which already present in the original feedstock. More pores are generated as the temperature increases, and consequently their size reduces. As temperature increases, the BET surface area, micropore surface area, specific pore volume increases. The increase in the volume probably influences by biomass particle size. The pores in C-skeleton of biochar developed due to the thermal degradation and release of volatiles from feedstock material. Comparatively less surface area of biochar at a lower temperature could be interrelated to the tar formation during pyrolysis, that can either impede pores continuity or prevent the pores creation, but at elevated temperature, these biochar tars volatilize, thus these pores developed which contributed greater surface area. It was observed that, the amount of MB dye solution absorbed increased from as the initial concentration of MB dye solution increases from A, B and to C respectively. The initial dye concentration provides a high driving force to overcome the resistance to the mass transfer of dye between the aqueous solution and the solid phase of a fixed adsorbent dose. Microscope scanning images shows that some pores of biochar are impeded by volatile and ash contents can reduce the pore volume result from different temperature conditions of pyrolysis process. All the data observed in this analysis shows that the temperature influences the physical characteristic of the biochar. The increases in temperature improved the adsorption property of the biochar.

ACKNOWLEDGMENT

Thank you to my supervisor and Universiti Teknologi Mara.

## References

[1] WYN, L.T., *Wood for Trees: A review of the agarwood (gaharu) trade*. 2010, Petaling Jaya, Selangor, Malaysia: TRAFFIC Southeast Asia.

[2] Mamat, M.F., et al., *Costs and Benefits Analysis of Aquilaria Species on Plantation for Agarwood Production in Malaysia.* International Journal of Business and Social Science, 2010. **1**.

[3] Compton, J. and F. Zich, *Gyrinops ledermannii (Thymelaeaceae), being an agarwood producing species prompts call for further examination of taxonomic implications in the generic delimitation between Aquilaria and Gyrinops*. Vol. 13. 2002.

[4] Puri, D.G.D.a.R.K., *Learning from Traditional Knowledge of Non-timber Forest Products: Penan Benalui and the Autecology of Aquilaria in Indonesian Borneo.* Ecology and Society, 2004.

[5] Shuhaimi, N.H., *Encyclopedia of Malaysia, Volume 4: Early History*. 1998: Archipelago Press.

[6] Alagammal, M., G. Sakthidevi, and V. Mohan, *Mohan et al., Anti-fertility activity of whole plant extracts of Polygala rosmarinifolia Wight & Arn against male albino rats*. Vol. 3. 2013. 385-393.

[7] Keiluweit, M., et al., *Dynamic Molecular Structure of Plant Biomass-Derived Black Carbon (Biochar).* Environmental Science & Technology, 2010. **44**(4): p. 1247-1253.

[8] Yuan, H., et al., *Influence of pyrolysis temperature on physical and chemical properties of biochar made from sewage sludge.* Journal of Analytical and Applied Pyrolysis, 2015. **112**: p. 284-289.

[9] Enders, A., et al., *Characterization of biochars to evaluate recalcitrance and agronomic performance.* Bioresour Technol, 2012. **114**: p. 644-53.

[10] Qumber Abbasa, b., Guijian Liua,b,⁎, Balal Yousafa,b, Muhammad Ubaid Alia, Habib Ullaha, Mehr Ahmed Mujtaba Munira, Ruijia Liua, *Contrasting effects of operating conditions and biomass particle size on bulk characteristics and surface chemistry of rice husk derived-biochars.* Journal of Analytical and Applied Pyrolysis.

[11] K. Jindo1, H. Mizumoto3, Y. Sawada2, M. A. Sanchez-Monedero1, and T. Sonoki3, *Physical and chemical characterization of biochars derived from different agricultural residues.* Biogeosciences, 2014.

[12] Herath, H.M.S.K., M. Camps-Arbestain, and M. Hedley, *Effect of biochar on soil physical properties in two contrasting soils: An Alfisol and an Andisol.* Geoderma, 2013. **209-210**: p. 188-197.

[13] Lonappan, L., et al., *Adsorption of methylene blue on biochar microparticles derived from different waste materials.* Waste Manag, 2016. **49**: p. 537-544.

[14] Dawood, S., T.K. Sen, and C. Phan, *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, 2016. **57**(59): p. 28964-28980.

[15] Novak, J., et al., *Impact of Biochar Amendment on Fertility of a Southeastern Coastal Plain Soil*. Vol. 174. 2009.

[16] Yue, Y., et al., *Characteristics and potential values of bio-oil, syngas and biochar derived from Salsola collina Pall. in a fixed bed slow pyrolysis system.* Bioresour Technol, 2016. **220**: p. 378-383.

[17] Brown, R.A., et al., *Production and characterization of synthetic wood chars for use as surrogates for natural sorbents.* Organic Geochemistry, 2006. **37**(3): p. 321-333.

[18] Tsai, W.-T., et al., *Textural and chemical properties of swine-manure-derived biochar pertinent to its potential use as a soil amendment.* Chemosphere, 2012. **89**(2): p. 198-203.