Pyrolisis Temperature Effect to the Biochar Product from Chocolate's Fruit Skin (*Theobroma cacao*L.)

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Abstract
This research's aim is to find out the effect of pyrolisis temperature to the biochar product from chocolate's rind. The sample of rind of 20 kg is come from Indrapuri, Great Aceh. The water level of the sample is determined and then it was pyrolised with pyrolisator at the temperatures of 300, 400, and 500°C. The biochar gotten is then measured its rendemen and characterized which comprised of flying substance level, ash, bonded carbon, nitrogen, phosphor, potassium, and then the chemical substances were identified by using Gas Chromatography-Mass Spectroscopy (GCMS). Pyrolisis product of biochars at the temperatures of 300, 400, and 500°C were gained rendemen of 8.98; 8.45, and 8.35% (w/w) in a row. These biochars have physical appearance of black with brittle texture. It were gained biochars's characteristic product of water level at 3.93% (300°C), 2.43% (400°C), and 1.50% (500°C) respectively; flying substance level at 47.13% (300°C), 29.58% (400°C) and 25.48% (500°C); ash level at15.70% (300°C), 17.14% (400°C), and 18.02% (500°C), bonded carbon at 37.16% (300°C), 53.37% (400°C), and 56.32% (500°C). The highest level of nitrogen (3.51%) is gained with biochar's pyrolisis product at the temperature 300°C, meanwhile for the 500 dan 400°C, their nitrogen level are 1.29 and 0.86%. Phosphor level at biochar's pyrolisis product at the temperature of 300, 400 and 500°C in a row are 0.90; 0.43; 1.39% and potassium level at this biochar are 3.34,4.73, and 4.41% consecutively. GCMS analysis result to the biochar's pyrolisis product at the temperature of 300°C was identified 40 compounds with their main contents is 4-beta-5-dihydroneronin (22.02%), whereas at the temperatures of 400 dan 500°C respective are identified of 11 and 23 compounds, however their main contents is oleat acid with the level of 62.47 dan 49.84% in a row. It can be concluded that biochar's characteristics of chocolate's rind is determined by pyrolisis temperature.

Keywords: pyrolisis temperature, pyrolisator, chocolate's rind, biochar

Introduction

Indonesia is a country that produces many agricultural crops; one of those is cocoa plant that is commonly known as chocolate. The growth of cocoa plants in the various provinces in Indonesia is very rapidly every year. According to the data from the Indonesian Cocoa Association (2009), the cocoa plantations in Central Sulawesi produced 160-170 thousand tons, while community plantations in Palu produced 56.000 tons. The production of cocoa plants reachs seed-pulp with a ratio of 25:75%, so that the production of leather waste of cacao fruit in Central Sulawesi province is estimated at 120 to 127.5 thousand tons (Indonesian Cocoa Association, 2009). Furthermore, according to the Central Bureau of Statistics of North Sumatra (2010), the production of cocoa beans in the North Sumatra province in 2009 reached 68.828 tons, which means they produced cocoa rind waste as much as 193.874 tons that were discarded as waste of the plantation.

This day, the utilization of the cocoa plants is still limited to the seeds which are ranged from 16-53 seeds per fruit, while the other remaining parts, like fruit skin and pulp, are not widely used yet. Leather cacao fruit can be fermented to be used as animal feed and compost fertilizer (Bentil, et al., 2015). According to Pratama, et al. (2015), the cocoa peel can be used as the raw material for sangkuriang catfish feed. Biomass of cocoa fruit skin contains similar nutrients to lawns, especially protein and energy, so it can be used for feeding animals (goats) (Bentil, et al., 2015). Meanwhile, according to Daud, et al. (2013), skin and flesh (fruit meat) of a cocoa contains lignin and tannin ranged from 14.70 to 23.65%. In addition, Mensah, et al. (2012) reported that cocoa fruit meat contains 0.84%-5.10% tannin compounds. Furthermore, Nurida et al. (2010), declared that the skin and flesh of cocoa contains chemical compounds, such as pectin, protein and phosphorus, potassium, and nitrogen.

Currently, the waste management technique of cocoa rind that is commonly used by public is by composting to produce compost manure. However, this technique is still less eco-friendly because its opened process causes the formation of methane gas and odors. Methane gas is one of the contributors to geothermal effect (GHG). Environmentally friendly technique that can be used in the management of solid waste agricultural products is by pyrolysis technique. Pyrolysis is a technique of organic waste management through a heating process with no or little oxygen that chemically decomposes the waste into charcoal, tar, and gas (Jassal, et al., 2015; Gronwald, et al., 2015; Haji, et al., 2010). The advantage of this pyrolysis technique compared to the other techniques is that it can quickly degrade material to produce biochar that can be used in agriculture field and as adsorbent in sewage water treatment. The success of pyrolysis technique relies heavily on the type of raw material and the temperatures of pyrolysis process. Pastor, et al. (2006) stated that, in order to obtain biochar, it can be performed pyrolysis process of materials which contains hemicellulose compounds that will be decomposed at temperatures of 200-260°C, cellulose compounds at temperatures of 240-350°C, and lignin compounds at temperatures of 280-500°C.

Biochar is a porous charcoal that is produced by using high temperature with wastes of agricultural products as its raw materials; one of these is cocoa rind waste. According to Gani (2009), biochar serves as soil repairing material because it is rich of nutrients and minerals that are essential for plants. In addition, biochar can increase the growth and productivity of plants because by applicating biochar into soil, it can add the moisture and fertility of the soil. Biochar can also absorb carbon in the atmosphere. Nurida et al. (2010) stated that in Indonesia the potential use of charcoal or biochar is quite large considering the availability of raw materials like cocoa rind waste. The quality of biochar greatly depends on the type of its raw materials and the pyrolysis process temperatures. According to Zain (2009), a cocoa rind contains cellulose (38.65%), lignin (20.15%), crude protein (9.07%), and other organic materials (32.13%). Therefore, this study was conducted to determine the effect of varied pyrolysis temperature of 300, 400, and 500°C towards the quality of biochar that is made from cacoa rind (Theobroma Cacao L.) as its raw material.

Materials and Methods

Procedure

Chocolate rind that is used as samples were came from the harvest of farmers fields in the Indrapuri district of Great Aceh. Samples were cleaned with water and cut to size of approximately 1-2 cm. Subsequently, the samples were dried at room temperature. The samples were weighed to 150 grams, and then were pyrolyzed at the temperature o 300°C for 5 hours by using thermoline. The resulting biochar products were weighed, determined their rendemen, and characterized which includes analysis of the levels of flying substance, ash, bonded carbon by using the procedure developed by Association of Official Agricultural Chemistry (AOAC), nitrogen content with Kjehdahl method, phosphorus and potassium with SSA (Haji, 2007), as well as the identification of chemical components by using GCMS. The same procedures are repeated for pyrolysis process at temperatures of 400 and 500°C. At each pyrolysis temperature, the steps are repeated as many as three times.

Results and Discussion

Generally, resulting biochar have a physical appearance in the form of black, light, and fragile of small chunks. The side products produced is liquid smoke that is generally brown and watery. Then the obtained biochar was crushed into powder and was sieved by using a 100 mesh sieve in order to get a uniform size for analyzing its basic properties that are compatible with charcoal quality standard of SNI-01-1682-1996 for knowing its quality.

Rendemen

Biochar rendemens produced were ranged from 8.35 to 8.98%. The biochar rendemen continued to fall with the increasing of pyrolysis temperature. At a temperature of 300°C, the average of biochar rendemen that was produced was 8.98%, which was different from the results of pyrolysis at temperature of 500°C that was 8.35% which indicates that the higher the temperature, the lower the rendemen. This is due to the higher the temperature the more decomposed an organic material into ashes and volatile gases such as CO_2, H_2, and so forth. The above results similar to the results of Tarwiyah's (2001) research that proved when pyrolysis happened, the thermal energy encourages the oxidation to happen so that the majority complex of carbon molecules deomposed into biochar. Likewise, the weight of produced biochar will be more decrease with the increasing of pyrolysis temperature (Pastor, et al., 2006). This is due to the reduction of organic components in the material. In addition, Suyitno et al. (2008) concluded that, the high and low of biochar rendemen produced is depend on the water content of the sample because the high composition of water causes the decomposition of the material slightly, so the rendemen of biochar obtained is low.

The Flying Substance Levels

The biochar volatile matter content of pyrolysis results at temperatures of 400 and 500°C were 29.58 and 25.48% which meet SNI-01-1682-1996 standards that specified maximum amount of volatile matter is 30%, except the result of biochar pyrolysis that was proceed at temperature of 300°C did not meet this standards. This is due to the incomplete carbonization process done. Flying substance level of biochar tends to decline continuously as the rise of pyrolysis temperature so that the better its biochar quality. This is in accordance with the study results of Gronwald, et al. (2015) and Haji et al. (2010) that the evaporate substance level tends to worsen with the increase of carbonization temperature. The higher the carbonization temperature of a material, the lower the flying substance level so that the biochar quality produced is better. The low of this level in cocoa rind wastes because of the residue of clinging hydrocarbons were oxidized again when they are heated at high temperature. This result is consistent with Lempeng (2009) research that high levels of volatile matter are happened because of the incompleteness of carbonization process occured. Therefore, there are many compounds such as CO, CO_2, H_2, and CH_4 that have not yet evaporated during the carbonization process, so that these compound are still attached to the biochar

Ash Contents

The analysis results of ash contents produced were ranged from 15.70 to 18.02%. According to SNI-01-1682-1996, the maximum amount of charcoal ash content is 4%. This indicates that the ash content produced do not meet the standard. High ash content due to in the cocoa rind waste there are a number of minerals such as potassium, magnesium, and calcium that are estimated come from soil and fertilizer used (Fauzi, 2002). Likewise, the research result of Tanaike and Inagaki (1999) that the mineral contents in the ash, such as calcium oxide, sodium oxide, magnesium oxide, and potassium oxide will diffuse into the biochar's lattice, which influence absorptive capacity of both gas and solution molecules.

Tied Carbon Levels

Produced biochars at all pyrolysis temperatures did not meet the standard because obtained carbon contents were less than 60% . This is in accordance with SNI-01-1682-1996 that stated the carbon content of biochar should minimally reach 60%. The quantity of tied carbon in biochar is influenced by the ash content, flying substances, and hydrocarbons compounds that are still attached to the surface of biochar. The levels of bounded carbon in biochar is always inversely proportional to the ash and flying substances levels, in which the higher ash and flying substances contents, the lower bounded carbon content. This corresponds to the Rumidatul (2006) statement that the low level of bounded carbon content indicates many carbon atoms react with water vapor to produce CO and CO_2 gases so that the rearranged carbon atoms form a few of hexagonal structures. The big or small (the size) of bounded carbon content is affected by the ash and flying substances levels.

Nitrogen Level

Biochars that are intended to be applied to land as fertilizer substitutes do not have their own quality standards yet, therefore they were synchronized their standard based on compost quality standard (SNI-01-1683-2004). Based on SNI-01-1683-2004, nitrogen has a minimum standard of 0.40%. The levels of nitrogen in the biochar product obtained did not meet the standard. This result is supported by Nurida et al. (2010) research that stated biochar nitrogen levels decreased with the increase of pyrolysis temperature. This is due to instability of the temperature when pyrolysis process is run.

Phosphorus Level

Based on the analysis result, all biochar products produced known that they contain phosphorus levels that meet the standard of SNI 01-1683-2004 which sets the minimum levels of phosphorus is 0.10% for every product that is applied to the soil. This is consistent with the studies that have been reported by Nurida et al. (2010) that biochar's phosphorus levels continue to increase with the increase of pyrolysis temperatures.

Potassium Level

The analysis result of biochar's potassium levels obtained from the pyrolysis result of cocoa rind at temperatures of 300, 400, 500°C were 3.34, 4.73, and 4.41% respectively. Based on SNI-01-1683-2004, the minimum amount of potassium is 0.20%, so that based on the data above; all biochar products meet the standard. Biochar's potassium levels from pyrolysis result at temperature of 400°C did not meet the standard. Based on Nurida et al. (2010) research, the potassium levels of biochar increases with the increase of pyrolysis temperatures. This error was occured because of the temperature instability when pyrolysis process was performed.

Biochar Identification Results with GCMS

Biochars that were produced in the pyrolysis process were identified their chemical contents by using GCMS. Determination of compounds contents in the biochars were performed by using the HP Ultra 2 column with injector temperature of 250°C, oven temperature of 280°C/10 minutes, helium carrier gas, flow rate of 0,6 L/min, and injection volume of 1 µL. Line spectrum chromatogram for MS shows a pattern of mass spectra of fragments result from sample molecules and the illustration of GC chromatogram pattern in curve shaped as a function of time. Biochar's GCMS chromatogram produced in this study are shown in Figure 1, 2, and 3.

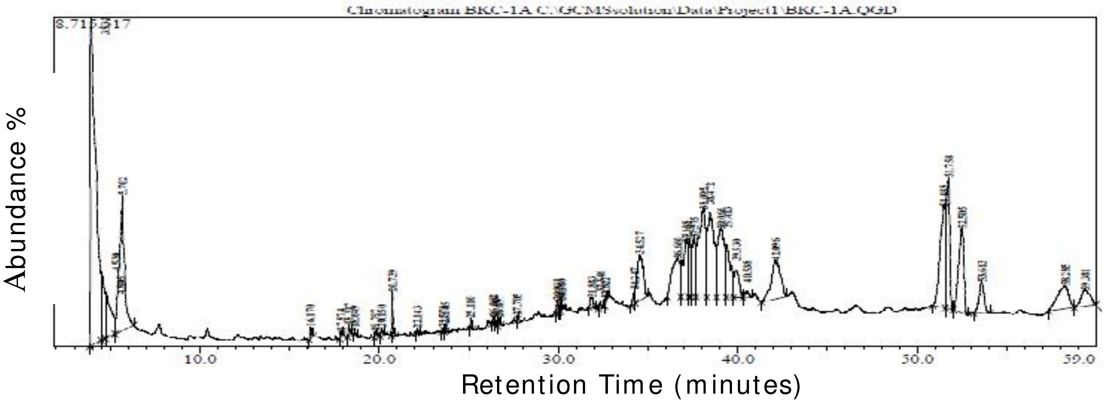

Figure 1. Biochar Chromatogram of Cocoa Rind Pyrolysis Results at temperature of 300°C

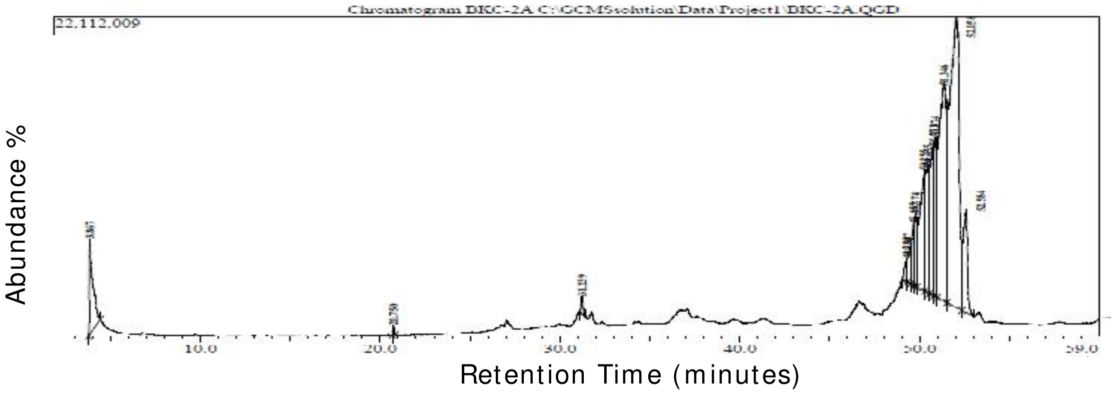

Figure 2. Biochar Chromatogram of Cocoa Rind Pyrolysis Results at temperature of 400°C

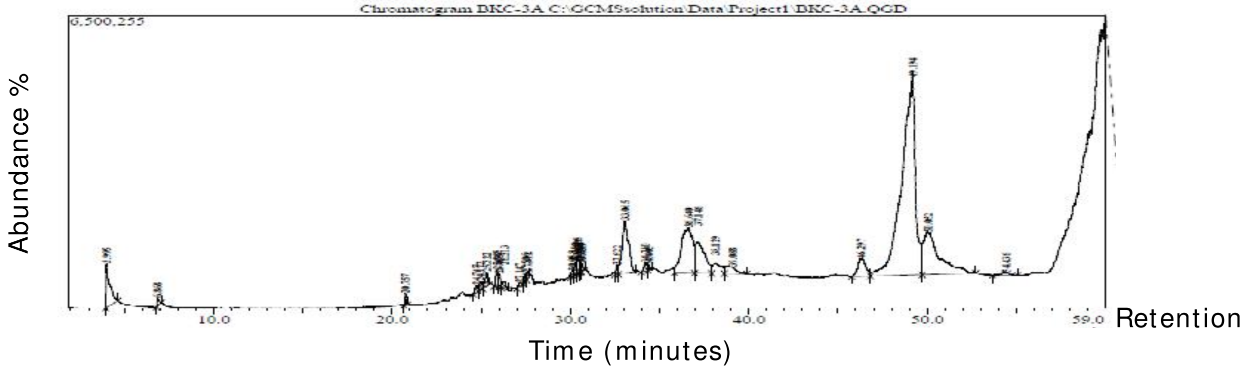

Figure 3.Biochar Chromatogram of Pyrolysis Results of CoRind at temperature of 500°C

The above chromatograms generally exhibit biochar produced in the pyrolysis process of cocoa rind with a certain temperature variations that show the separation of their chemical components through peaks that appear on the GC. Peaks at a temperature of 300°C (Figure 1) begin appearing at a retention time of 3.995 to 59.381 minutes. Based on chemstation data system in GCMS, there were 40 compounds identified in biochar products with the main content was 4-beta-5-dihidroneronin (22.02%), whereas the pyrolysis results of biochar at temperature of 400°C (Figure 2), and 500°C (Figure 3), 11 compounds and 23 compounds were dentified respectively, but the same main contents produced by them were oleic acid with the level of 62.47 and 49.84% consequtively.

Conclusion

The higher the pyrolysis temperature of chocolate rind, the lower the obtained rendemen and generally the lower the quality, especially in terms of the ash levels, bonded carbon, and nitrogen levels. The analysis results of the biochar's chemical components from pyrolysis results at temperature of 300ºC with GCMS 40 compounds were identified, while in biochars of the pyrolysis results at higher temperatures, it tends to decrease.

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