Study of Structural and Electrical Conductivity of Sugarcane Bagasse-Carbon with Hydrothermal Carbonization

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Abstract. The important part of fuel cell is the gas diffusion layer who made from carbon based material porous and conductive. The main goal of this research is to obtain carbon material from sugarcane bagasse with hydrothermal carbonization and chemical-physics activation. There were two step methods in this research. The first step was sample preparation which consisted of prepare the materials, hydrothermal carbonization and chemical-physics activation. The second one was analyze character of carbon using EDS, SEM, XRD, and LCR meter. The amount of carbon in sugarcane bagasse-carbon was about 85%-91.47% with pore morphology that already form. The degree of crystallinity of sugarcane bagasse carbon was about 13.06%-20.89%, leaving the remain as the amorphous phase. Electrical conductivity was about 5.36 x 10^{-2} \text{Sm}^{-1} - 1.11 \text{Sm}^{-1}. Sugarcane bagasse-carbon has porous characteristic with electrical conductivity property as semiconductor. Sugarcane bagasse-carbon with hydrothermal carbonization potentially can be used as based material for fuel cell if only time of hydrothermal carbonization hold is increased.

1. Introduction

Fuel cell is a system to converse chemical energy from hydrogen and oxygen directly into electrical energy. It has some advantages compared with another conventional electrical generator, such as high efficiency, does not make air pollution, and having flexible construction that can harness fuel which has been available. One of fuel cell which has been developed is Polymer Electrolyte Membrane Fuel Cell (PEMFC). It has some main components which have important function, one of them is gas diffusion layer. Gas diffusion layer has function to diffuse Hydrogen (anode) and Oxygen (cathode), as catalytic support and as a conductor of electron movement. Gas diffusion layer is commonly made from a porous and conductive carbon based material. This type of carbon is actually similar to that of carbon that commonly used as adsorbent[1].

One of agricultural waste of biomass which nowadays developed for carbon based material is sugarcane bagasse. Sugarcane bagasse is a waste material which has fibrous from rod of cane and been extracted from its roomie. Sugarcane bagasse consist of cellulose 37.65 % with carbon can be up to 24.7%. This high number put forward sugarcane bagasse as potential waste for carbon resource through carbonization.

Carbonization process is a conversion of organics compound into charcoal with no oxygen hence complex compounds inside the organic material separated into charcoal with high content of carbon [2]. One of carbonization method that has been concerned recently is hydrothermal carbonization with
hydro charcoal as result. Hydrothermal carbonization is biomass conversion through thermos chemical process and use water on low temperature. Hydrothermal carbonization has advantage compared with pyrolysis carbonization, such as it is use low temperature hence the energy is low waste and air pollution can be reduced [3]. The purpose of this research is to know the structure of pore and conductivity material carbon from sugarcane bagasse with hydrothermal carbonization process use various temperature over 200 °C, 250 °C and 300 °C.

2. Method

Material used in this research was sugarcane bagasse with no roomie and very dry. Sugarcane bagasse was mashed up until became sugarcane bagasse powder with very soft condition to be moved into a digester tube for hydrothermal carbonization. Sugarcane bagasse and water was placed in tube with 15% from volume of water. Water volume was 1/3 from digester tube. Digester tube is over 20 cm in length and 6.35 cm in diameter completed with electrical heater.

Sugarcane bagasse with good shape (powder) moved into digester tube and mixed until it smooth. The material and aquades was put into digester at room temperature then closed tightly while heater turned on. The temperatures were set at 200 °C, 250 °C, and 300 °C with three times of repetition for getting an appropriate sample weight for being activated and tested in the next step. When the temperature is reached, heating was hold over six hours, afterwards the heating was ended. Charcoal from this hydrothermal carbonization (hydro-charcoal) was cleaned on paper filter to be separated between filtrate and residue. After hydrothermal carbonization, sugarcane bagasse carbon was activated with chemical and physical activation. Chemical activation was conducted using potassium hydroxide (KOH) with ratio of KOH: charcoal was set 3:1. For this, 2 grams of charcoal marinated in 26 ml aquades was reconstituted with 6 gram of KOH in 24 hours of marinated. After chemical activation, the product of charcoal been filtered for filtrate and residue separation. The residue was then heated at 60 °C for 24 hours. The charcoal product of chemical activation was then moved into atmospheric fixed bed reactor and been activated with temperature up to 700 °C. When it was reached, temperature was hold for 30 minutes.

The result of activation was then marinated with HCL 10% for 1 hour and then cleaned up with hot water to remove impurities and neutralizing pH. Next, it was oven dried at 105 °C until reaching constant weight. The dried carbon material was analysed for the content of carbon, structure of atom, and conductivity use SEM-EDS, XRD, and LCR-meter.

3. Result and Discussion

Table 1 indicates the weight of the dregs of mashed sugarcane bagasse before hydrothermal carbonization and the formed charcoal following hydrothermal carbonization. The mass charcoal decreases with increase in temperature. This is because the volatile compounds contained in sugarcane bagasse evaporate. Increasing temperatures cause the more evaporated compounds so that the remaining charcoal mass decreases.

| Hydrothermal Carbonization Temperature (°C) | Sugarcane Bagasse Mass (grams) | Charcoal Mass (grams) | Missing Mass (grams) | Missing Mass Percentage (%) | Charcoal Mass Percentage (%) |
|---------------------------------------------|-----------------------------|-----------------------|---------------------|---------------------|---------------------|
| 200                                         | 4.02                        | 7.38                  | 64.74               | 35.26               |
| 250                                         | 11.4                        | 3.53                  | 7.87                | 69.04               | 30.96               |
| 300                                         | 2.56                        | 8.84                  | 77.54               | 22.46               |
After hydrothermal carbonization, the charcoal is activated in either physics or chemical activation. The data of comparison of charcoal mass before and after activation can be seen on Table 2. The average of charcoal mass is approximately 21.67 % from prior to the activation process. Based on these data, the mass loss indicates that carbon materials and volatile materials as well as ash materials degrade during the process.

Table 2. Comparison of charcoal mass before and after activation.

| Hydrothermal Carbonization Temperature (°C) | Charcoal Mass (grams) | Missing Mass (gram) | Missing Mass Percentage (%) | Charcoal Mass Percentage (%) |
|-------------------------------------------|-----------------------|---------------------|-----------------------------|-----------------------------|
|                                           | Before Activation     | After Activation    |                             |                             |
| 200                                       | 2                     | 0.25                | 1.75                        | 87.5                        | 12.5                        |
| 250                                       | 2                     | 0.33                | 1.67                        | 83.5                        | 16.5                        |
| 300                                       | 2                     | 0.72                | 1.28                        | 64                          | 36                          |

Based on the table, the smallest charcoal mass is 0.25 grams which was obtained from the charcoal of hydrothermal carbonization process at 200 °C (charcoal HC 200 °C). The next smallest one is charcoal HC 250 °C with 0.33 grams and the largest one charcoal HC 300 °C with 0.72 grams. The differences of obtained results show that there are still a volatile and ash material specifically inside charcoal HC 200 °C so that the loss mass is approximately 1.75 grams. It also works for charcoal HC 250 °C and HC 300 °C. After activation, along with the increase in temperature of carbonization thermal, the loss mass decreases. It is due to the slight remaining of volatile and ash material on charcoal HC 300 °C before activation.

3.1. Analysis of Carbon Content
The active carbon is a porous material with activated carbon content of 87 % - 97 %. Table 3 showed that the carbon content in sugarcane bagasse charcoal which is produced by hydrothermal carbonization has reached the value of 85.02 % - 91.47 %. The highest result is 91.47 % which is obtained from carbon charcoal hydrothermal carbonization results with temperature 200 °C (charcoal HC 200 °C). The next one are charcoal HC 250 °C with 88.39 % carbon content and charcoal HC 300 °C with 85.02% carbon content.

Table 3. The content of carbon in charcoal.

| Temperature charcoal HC (°C) | Carbon content (%) |
|------------------------------|--------------------|
| 200                          | 91.47 ± 9.74       |
| 250                          | 88.39 ± 9.32       |
| 300                          | 85.02 ± 8.99       |

Carbon content inside sugarcane bagasse charcoal seems decreasing along with the increase in hydrothermal carbonization temperature. As for the carbon content of charcoal HC 250 °C and 300 °C HC, the measured content carbon is only for the part that got shot X ray. Each part of charcoal has the different carbon content so we can assume that it could be the area with the less optimum content of carbons. This is also supported by data electrical conductivity which gets bigger as the increasing of hydrothermal carbonization temperature. One of the factors that affects the increased electrical conductivity is the carbon content, as the more carbon content will increase the electrical conductivity.
of the charcoal itself [4]. Therefore it cannot be concluded that the decreasing carbon content is along with the increasing temperature.

3.2. Analysis of the Structure of Charcoal

In this research, Scanning Electron Microscope (SEM) is used to observe the structure of the charcoal characters. It was used to know the morphology appearance of the sugar cane husks charcoal as the result of hydrothermal carbonization process. The character structure of the desired sugarcane bagasse charcoal is a porous structure with a diameter of 1-30 μm, because one of the carbon properties which is used in gas diffusion layers is porous carbon with a diameter of 1-30 μm.

Figure 1a, 1b, and 1c showed the results of morphology observations of the sugar cane husks charcoal with 1000 times magnification. Based on the results, the pore morphology on sugar cane husks charcoal has been formed with a diameter range 4-11 μm. Morphology of porous charcoal looks broken and irregular. Porous structure of coals HC 200 °C (Figure 1a) is more evident than charcoal HC 250 °C (Figure 1b) and charcoal HC 300 °C (Figure 1c).

The porous of charcoal HC 250 °C and charcoal HC 300 °C appears more broken and irregular which is caused by the rising temperature of hydrothermal carbonization. It is also caused by stirring charcoal when leached with aquades to neutralize the pH. Charcoal HC 200 °C is the first charcoal leached by using aquades. At first, the process stirring is only done in the late minute when approaching a neutral pH. But for the charcoal HC 250 °C and 300 °C, stirring starts from beginning to end of the leaching. Charcoal HC 300 °C is the last leached charcoal by using aquades after previously soaked with HCl Solution. Because of that matter, neutralizing pH charcoal takes a longer time. The neutralization time charcoal affects stirring. The more frequent stirring will damage porous structure of coals.

The next structure observation is done by using X-ray Diffraction. This observation is aimed to inform the change of the charcoal structure after passing stages of hydrothermal carbonization and activation as well as knowing the degree of crystallinity of coals. After the match with no. 22 Graphite JCPDS- 1069, X-ray diffraction pattern of sugar cane husks charcoal approached the X-ray diffraction patterns of graphite (Figure 2).
Figure 2 shows the X-ray diffraction pattern of charcoal cane dregs for the entire hydrothermal carbonization temperature variations. X-ray diffraction pattern of charcoal HC 200 °C, 250 °C and 300 °C indicates that carbon peak specific respectively appears at an angle 2θ; 23.61°, 23.61° and 23.93°. The overall x-ray diffraction pattern shows the hill with a large area and the blunt end. It indicates that the crystal structure of charcoal tends to be amorphous. The present of amorphous phase causes the low degree of crystallinity. The degree of crystallinity is ratio comparison of crystal phase against amorphous phase and phase crystal. It represents the regularity of crystal structures on a material. The degree of crystallinity of commercial carbon which can be used for the base material of gas diffusion layer components is 27.79%. Table 4 shows that the highest degree of crystallinity is obtained from charcoal HC 200 °C with 20.89% and the lowest one is on charcoal HC 300 °C with 13%. The degree of crystallinity successively decreases along with the rising of hydrothermal carbonization temperature. It is influenced by stirring factor when leaching charcoal after activation. Leaching charcoal aims to rid the pollutant which sticks to the charcoal after soaked in acid neutralizer and activator. It is performed by using charcoal until it reaches a pH close to neutral pH. The needed time is various so because of that, it can affect speed of neutralization. The more frequent stirring will damage porous structure of coals so that the crystal structure of charcoal becomes more amorphous.

| The temperature of the charcoal HC (°C) | Crystallinity index (%) |
|----------------------------------------|-------------------------|
| 200                                    | 20.89                   |
| 250                                    | 18.31                   |
| 300                                    | 13.06                   |

3.3. Analysis of Electrical Conductivity
Electrical conductivity is a measure of a material ability in the conduct an electric current. Beside porous carbon structure condition, electrical conductivity of charcoal is also one of the important terms in the use of carbon for gas diffusion layer [5]. Electrical conductivity of charcoal is measured using LCR meter. Electrical conductivity data can be seen in Table 3. The data is measured at 136 Hz frequency because with this frequency the pattern of electrical conductivity of charcoal is clearly
visible. The electrical conductivity of sugar cane husks charcoal increases along with the rising of hydrothermal carbonization temperature. The electrical conductivity of the activated charcoal was from the lowest to highest HC 200 °C, HC 250 °C and 300 °C with values as shown in Table 5.

Table 5. Electrical conductivity of charcoal.

| Temperature of the charcoal HC (°C) | Electrical conductivity (Sm⁻¹) |
|-------------------------------------|-------------------------------|
| 200                                 | 5.36 x 10⁻²                   |
| 250                                 | 1.18 x 10⁻¹                   |
| 300                                 | 1.11                          |

From Table 5, we can conclude that electrical conductivity of charcoal cane dregs is categorized into semiconductors. It is because the range of electrical conductivity of semiconductor material is 10⁻⁸ Sm⁻¹ - 10⁻³ Sm⁻¹, while the electrical conductivity of a conductor material is more than 10³ Sm⁻¹. This value is very low in comparison with the graphite which has 3.4 x 10³ Sm⁻¹ in value of the electrical conductivity.

References
[1] Han M, Xu JH, Chan SH, Jiang SP 2008 *Electrochimica Acta* **53** 5361-5367
[2] Kalderis D, Bethanis S, Paraskeva P, Diamadopoulos 2008 *Biorec technol* **99** 6809-6816
[3] Kannan AM, Kanagala P, Veedu V 2009 *Journal of Power Sources* **192** 297-303
[4] Nishimiya K, Hata Ishihara S 1995 *Wood Research* **82** 34-36
[5] Mochidzuki K, Soutric F, Tadokoro, Antal MJ 2003 *Industrial & Engineering Chemistry Research* **42(21)** 5140-5151