Extremely high surface area of activated carbon originated from sugarcane bagasse

Murie Dwiyaniti1, Elang Barruna A.G1, Muhamad Naufal R1, Iyan Subiyanto1, Rudy Setiabudy1, Chairul Hudaya1

1Department of Electrical Engineering Faculty of Engineering, Universitas Indonesia, Depok 16424, Indonesia

Email: murie.dwiyaniti82@ui.ac.id

Abstract. In this study, the extremely high specific surface area of activated carbon originated from sugarcane bagasse was produced by dry chemical activation. In this process, KOH was used as a chemical agent and directly mixed sugarcane bagasse carbon with KOH powder, which has been treated in a solid form. In particular, the influences of the impregnation ratio and activation temperature were investigated. The as-prepared activated carbons were characterized by Brunauer-Emmet-Teller (BET), which aims to determine the surface area of activated carbon and Raman Spectra analysis to examine the vibration modes of material characteristics. The maximum specific surface area of the activated carbon reached 3554 m²/g at 800 °C and an impregnation ratio of 1:4. Furthermore, the Raman spectra of activated carbon exhibited graphite structure for sample in impregnation ratio 1:2 and 1:3 due to having of G and G' band. This material is essential for make battery.

1. Introduction
Sugarcane bagasse (SB) is waste generated from the process of extracting sugar water from sugarcane stems. Sugarcane is the primary raw material of the sugar industry, which is one of the plantation commodities that has a strategic role in the economy in Indonesia. With an area of around 420.15 thousand hectares in 2017, thousands of sugar cane farmers and workers are very dependent on the sugar industry for their survival [1]. However, to produce sugar at 8% will produce as much as 30% bagasse waste [2]. Therefore, this is an opportunity for researchers to be able to change their inconvenience in nature into a very useful product.

In general, sugarcane bagasse has been used as raw material for a pulp and paper [3, 4], particleboard [5], animal feed, and fertilizer. However, this utilization is very limited and has low economic value. New technology is needed to diversify the utilization of sugarcane bagasse into high economic value products. One of the alternatives is to be processed into activated carbon. The carbon content in sugarcane bagasse is quite high, which is 24.7% [6]. Also, sugarcane bagasse has a chemical composition of 25% hemicellulose, 50% cellulose, and 25% lignin [7]. Cellulose has a high degree of crystallinity, while hemicellulose and lignin are amorphous. High cellulose and low lignin content are indicated to produce micropore structure on activated carbon [8, 9]. So that sugarcane bagasse is very potential to be an excellent active carbon material.

Activated carbon, which has a porous structure and a large surface area > 3000 m²/g, is needed in the manufacture of lithium-ion capacitor batteries [10] to accommodate more lithium-ion during charge and discharge. Until now, the activated carbon material that produces the largest surface area is
graphene, about 3355 m$^2$/g [11]. However, graphene is very expensive, and the manufacturing process is complicated and dangerous for health. Active carbon originated from SB is an alternative, environmentally friendly material that is expected to reach a large surface area.

The process of making SB into activated carbon consists of three stages, namely dehydration, carbonation, and activation. The activation process can be carried out through two methods, namely physical activation with different oxidizing gases, such as air, O2, CO2, or steam, and ii) chemical activation with chemical compounds [12]. Chemical activation results in better pore structure and surface area. Many researchers have been activated carbon from SB using an activator agent H3PO4 [13, 14], ZnCl2 [6, 15, 16], NaOH [17], and KOH [18-20]. The high surface area of activated carbon is produced by NaOH in temperature 700°C, result around 2400 m$^2$/g [17]. However, NaOH is only effective for the activation of irregular materials and irregular intercalation processes [21]. While the activated carbon desired in this study must have high porosity.

One aspect that influences the process of forming a porosity is intercalation. KOH activator has an advantage over NaOH; namely, potassium is more easily intercalated between graphene layers [21], because potassium has a lower boiling point [22]. KOH can react effectively to a variety of polymer and carbon materials, including the high arrangement of hexagonal carbon structure and the formation of nano-sized pores.

So in this study proposes KOH in a solid form as an activator agent to directly mixed with carbon originate from SB. This method called dry activation. The dry activation method on carbon originated from sugarcane bagasse is estimated to be able to produce a large surface area. The carbon activation process becomes simple and easy.

2. Research Method

The experimental works were conducted to synthesize the activated carbon starting from preparation, carbonation, and activation process. As the samples, SB was obtained from the sugar factory of PT Gendhis Multi Manis (GMM), which is located at Tinapapan, Tadonan, Blora, Central Java, Indonesia - 58256.

2.1. Activated carbon synthesis

The synthesis of activated carbon material from SB will be carried out using the thermal carbonization method. First, SB is drained for 24 hours in the oven at 150°C to ensure that there is no H2O compound left. After drying, the SB is mashed so that the material particles become very small by blending it. Then, the material is carbonized using a furnace at 500 °C for one hour with an increase in temperature of 10 °C/minute under the Ar atmosphere at 200 cc/min. After carbonized, the carbon is rinsed with distilled water. Then the final product is put into an oven at 80 °C for 24 hours. The carbonation yield of SB after this referred to as sugarcane bagasse carbon (SBC). The stages of carbonization can be seen in Figure 1.

The carbon activating process is conducted through the dry chemical activation method using KOH as an activator agent. Carbon and KOH are mixed with a ratio of 1:2, 1:3, 1:4, and 1:5. After the stirring process, the carbon is heated using a furnace to a temperature of 800 °C for one hour, with a 10 °C temperature increase per minute. The carbon is neutralized using HCl solution and rinsed with distilled water. Then the final product is put into an oven at 80 °C for 24 hours. Activated carbon resulting from KOH activation of 1: 2, 1:3, 1:4, and 1:5 hereinafter referred to as SBAC12, SBAC13, SBAC14, and SBAC15, respectively. The stages of activating carbon can be seen in Figure 2.
2.2. Characterization

Two methods characterized the samples. First, Brunauer-Emmet-Teller (BET) using a Quantachrome NovaWin instrument, with degassing nitrogen for four hours, which aims to determine the surface area of activated carbon. Second, Raman Spectroscopy using a micro-RAMAN spectrometer with 532 nm of laser source wavelength to identifying the structure crystal of material.

3. Results and Discussion

3.1. The process of making carbon from sugarcane bagasse

The first stage to make SB activated carbon is to dry and grind sugarcane bagasse to form a powder. Then the powder is filtered using 100 mesh. In Figure 3, we can see changes in SB.

In this study, the carbonization temperature used was 500°C. This temperature was chosen based on the process of degradation of the chemical composition of sugarcane bagasse consisting of hemicellulose, cellulose, and lignin. Hemicellulose is degraded by heat at temperatures of 220–315°C with the fastest decomposition at temperatures around 270°C. Cellulose is degraded at temperatures of 315–400°C with the fastest decomposition at temperatures around 350°C. Lignin is slowly degraded with a temperature range of 160 - 900°C [23]. The result of SBC is shown in Table 1.
In the carbonization process, mass loss occurs when the temperature is increasing. Most lost mass occurs in the cellulose content and the least lost in lignin [23]. It has happened in our experiment, as shown in Table 1. Lost SBC mass is an average of 75.14%. While the yield of SBC is an average of 24.86%. It is similar to the result of the carbonization process of SB from several studies where yield is around 20-30% and lost mass is around 70-80% [6], [7], [24], [25], [26].

3.2. The process of activating the carbon

The next process is activating SBC. The activation method used is chemical activation (pyrolysis), with KOH as an activation agent. The method is by directly mixing SBC with KOH powder, which has been processed from a solid form. The purpose of this activation is to produce higher activated carbon yields and form more pores so that a higher surface area of carbon is produced. In this research used four samples, SBAC12, SBAC13, SBAC14, and SBAC15. SBC activation results are in Table 2.

| Activation Variable | SBC + KOH (gram) | after activated (gram) | % lost | % Yield |
|---------------------|------------------|------------------------|--------|---------|
| SBAC12 800 1:2      | 6.379            | 4.974                  | 21.96  | 78.04   |
| SBAC13 800 1:3      | 6.353            | 4.912                  | 22.69  | 77.31   |
| SBAC14 800 1:4      | 6.323            | 4.808                  | 23.97  | 76.03   |
| SBAC15 800 1:5      | 6.046            | 4.489                  | 25.76  | 74.24   |

From table 2, it can be seen that the activating process decreases the mass. The percentage of mass loss tends to increase with increasing ratio KOH. The most significant percentage of mass loss occurs in SBAC15, with a percent loss of 25.76%. This is caused by the process formation of new pores of carbon [27].

3.3. BET and Raman Spectra

3.3.1 BET analysis

Having a high surface area is one indication of a good quality of activated carbon. The amount of adsorption power depends on the surface area of activated carbon. The surface area can be determined by the BET method. The surface area test results are in Table 3.
Table 3. The surface area test results of sugarcane bagasse active carbon (SBAC)

|          | Temperature (°C) | ratio SBC: KOH | Specific surface area |          |
|----------|------------------|----------------|-----------------------|----------|
| SBAC12   | 800              | 1:2            | 2136.828 m²/g         |          |
| SBAC13   | 800              | 1:3            | 2236.926 m²/g         |          |
| SBAC14   | 800              | 1:4            | 3554.820 m²/g         |          |
| SBAC15   | 800              | 1:5            | 2747.290 m²/g         |          |

A comparison of the largest specific surface area (SSA) due to the influence of KOH activation can be seen in Table 3. Activation using KOH on carbon material is used to increase surface area and improve its electrochemical performance [28]. The results show that SSA increases with the addition of KOH because the amount of KOH can affect pore development. The smallest SSA is in SBC12, about 2136 m²/g, and the largest is given by SBC14, which is 3554 m²/g. Kalderis and Shofa also reported the same study of using KOH as an activator on carbon from sugarcane bagasse where the presence of KOH activator will reduce pore diameter and expand pore volume and surface area with an SSA value of 864 m²/g by Kalderis [29] and Shofa with a value of 1135 m²/g [18]. However, the SSA value obtained in our study is extremely high, even surpassing activated carbon from graphene material, which has an SSA of 3523 m²/g [30]. Graphene is a superior material for numerous applications.

3.3.2 Raman analysis

All samples are characterizing by Raman spectroscopy to know vibration modes of material characteristics, which is plotted as a Raman shift. The result of Raman spectroscopy can be seen in fig 4. From figure 4, we can see that all samples have the sharpness band in value of 1575-1583 cm⁻¹, it is known as G band that is composed of sp² bonded carbon and graphene material. The sharpness of the band also tells us that the bonds are, for the most part, very uniform [31]. Furthermore, in fig 4, we also see a prominent band around 1346 – 1362 cm⁻¹. This band is called the D band. The D band shows some disorder in the graphene structure originating from the hybridization vibrational mode associated with the graphene edge [31]. The results of the Raman show that the addition of KOH did not cause a significant change in the shifts in the G and D bands. However, the small KOH ratio (1:2 and 1:3) caused an additional band, in around 2600-2700 cm⁻¹. It is known as the G' band, referred to as a 2D band, which indicates the number of graphene layers [32]. It is also indicated that SBAC12 and SBAC13 have graphite structure [33].

The quality of the sample is determined by the intensity ratio of the ID / IG band. For high-quality samples, the ID / IG ratio is generally less than 2%. In this study the ID / IG results for SBAC12, SBAC13, SBAC14, and SBAC15 were 0.70, 0.83, 1.06, and 0.92 respectively. It shows that the ID / IG ratio for all samples is less than 2%, which indicated the sample has a good quality.
4. Conclusion
Activated carbon originates from SB has been produced using a dry chemical activation method with KOH as an activator agent. This method provides an extremely surface area of about 3554 m$^2$/g and graphene carbon structure for sample SBAC14. While another sample SBAC12 and SBAC13 have graphite structure even though the surface area is less than SBAC14. Thus, sugarcane bagasse can be an alternative material for activated carbon because it has a large surface area and contains graphite material.

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