Synthesis and Characterization of Nanoporous Carbon from Sugarcane Bagasse 
(Saccharum officinarum) with ZnCl₂ Activator by Ultrasonic Irradiation 
as Electrochemical Energy Storage Material

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Abstract. A study on synthesis and characterization of nanoporous carbon derived from sugarcane bagasse (Saccharum officinarum) by ultrasonic irradiation using ZnCl₂ activator for electrochemical capacitor application has been investigated. Nanoporous carbon is a basic material for the electrode in the electrochemical energy storage. Nanoporous carbon has been synthesized based on three-steps procedures, i.e. carbonization in temperature of 350 °C, silica extraction, and activation using ZnCl₂ with ultrasonic irradiation. Activated carbon with irradiation showed an increasing in intensity of the –OH functional group stretch at wave number of 3419,79. The results of XRF analysis showed the highest content of oxide compound in the activated carbon was ZnO as 97.06%, and result of XRD analysis showed that activated carbon has both amorphous and crystalline. The result of SEM analysis showed that the pores evolvement of irradiated activated carbon was better than un-irradiated activated carbon, with diameter of the pores 1.5 to 2 µm. The surface area of the carbon in optimum temperature of 30 °C for 60 minutes was 171,2802 m²/gram and the energy storage capacity was 0.3284 x 10⁻⁵ F/g.

Keywords: electrochemical energy storage, nanoporous carbon, sugarcane bagasse, silica extraction, ZnCl₂ activator, ultrasonic irradiation

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INTRODUCTION

World energy demand is increasing from time to time. But the problem is the source of fossil fuels as the only reliable source of energy that is now diminishing. This leads to a national energy crisis that required of other renewable energy sources. One of them is electrochemical energy storage.

Electrochemical energy is energy derived from chemical processes. Electrochemical energy storage consists of three types of system as batteries, fuel cells and electrochemical capacitors (Winter and Brodd, 2004). The electrochemical capacitor is a system of energy storage that is much better than batteries and fuel cells. Electrochemical capacitors made from nanoporous carbon (Frackowiak and Beguin, 2011).

Nanoporous carbon is carbon that has a nano-sized pores. Nanoporous carbon has been widely used as an energy storage material due to large surface area, stable, easily polarized, and cheap. Physically porous carbon consists of a solid material that contains carbon (matrix) and empty cavities (pores) (Sembiring and Sinaga, 2003). Nanoporous carbon can be made from a variety of raw materials as long as it contains carbon such as bagasse, rice husks, coconut shell, coal, etc. (Prabowo, 2009). Bagasse is a by product of the milking of sugar cane, which can be used as starting materials in the manufacture of carbon nanopori application of electrochemical capacitors (Wei, X., Et al., 2011).

Activated carbon is made through two stages of carbonization and activation process which is both chemically and physically (Sudibandriyo and Lydia, 2011; Shofa, 2012). Carbonization is the process of burning organic material in the raw materials that cause decomposition of organic material and impurities expenditure and non-carbon compounds. Activation is the process of improvement of the carbonization process. In the carbonization process, carbon adsorption capacity is still low because there is still a residue covering the surface of the pore. In the activation process occurs release of hydrocarbons, tar, and carbon covers inorganic compounds (Aisah, 2010).

One of the methods to increase the value of specific capacitance of activated carbon is to use ultrasonic wave irradiation. On ultrasonic waves irradiation occur acoustic cavitation effects which is bubble formation, bubble growth, and bubble solution so that more pores are formed (Suslick, et al., 1996).

In this study, activated carbon has been made of bagasse through carbonization, silica extraction, and activation with ultrasonic wave irradiation treatment. Furthermore, the irradiated and un-irradiated activated carbons were characterized of pore morphology with SEM (Scanning Electron Microscope), characterization of surface area with methylene blue method, and specific capacitance with LCR-745 Meter.
METHOD

Materials

The materials used in this study was the waste bagasse, the solid ZnCl2, solid NaOH, 300 ppm methylene blue solution, distilled water, PVA powder, natrosol powder, 1 M H2SO4 solution, aluminum foil, pH universal paper, and filter paper.

Tools

The tools used in this study is the furnace (Muffle Furnace type 6000), Oven (type SPNISOSFD), porcelain cup, magnetic stirrer (Fisher Type 115), 100 mesh size sieve, mortar, analytical balance (Shimadzu AW220), pumpkin plastic spray, ultrasonic cleaner (Elmasonic S40H), LCR Meter (LCR-745 type Leader), vacuum pump (Vacuubrand type ME4C), Büchner funnel, desiccator, stative, laboratory glassware, thermometer, FTIR (Shimadzu, IR Prestige21), SEM (Tescan Vega3 Bruker), UV-Vis Spectrometer 20D + Shimadzu.

Procedure

Carbonization

Bagasse samples first washed with distilled water and then dried under the sun and in the oven. Clean and dried bagasse burned with an electric stove to fabricated and burned with a furnace at 350 °C for 1 hour. The resulting carbon is cooled and then sieved to 100 mesh size.

Silica Extraction

Bagasse carbon from the carbonization process then silica-extracted to obtain carbon-free silica. Carbon sample was added with NaOH with a concentration variation 2.5 and 5M and without extraction of silica as a comparison. The three samples were then stirred for 60 minutes accompanied by heating at a temperature of 95 °C. Then, samples were filtered and the resulting carbon is washed with distilled water until neutral pH then dried in oven at 110 °C. The oxide compounds of three types of carbon were analyzed by XRF to determine levels of silica in the carbon.

Activation

Free silica-carbon then activated using 10% ZnCl2 activators. Carbon mixed with a solution of 10% ZnCl2 then homogenized. Mixed container then sealed and allowed to stand for 24 hours. The mixture is then treated with and without irradiation of ultrasonic waves. Previously, the specified time and temperature of the irradiation optimum temperature of 15, 30, 45, and 60 °C and a time of 10, 30, 60, 90, and 120 minutes. After that the two types of samples were filtered and washed with distilled water until neutral pH. Then carbon was dried in oven at 110 °C and then burned in a kiln at a temperature of 350 °C for 1 hour.

Characterization

Bagasse activated carbon characterized of surface area by using methylene blue method, pore morphology
characterization by Scanning Electron Microscope (SEM), and characterization of specific capacitance with LCR-Meter.

**Determination of Surface Area by Methylene Blue Method**

Determination of the surface area with methylene blue method is based on the ability of activated carbon to absorb substances methylene blue. A total of 0,3 grams of activated carbon is added to the erlenmeyer containing 50 mL of 300 ppm methylene blue solution, then closed. The mixture is stirred with a magnetic stirrer for 30 minutes, then filtered. The absorbance of the filtrate then measured with UV-Vis spectrometer at a wavelength of 658 nm. Absorbance data obtained is used to calculate the concentration after adsorption of the calibration curve. Final concentration value is then used to calculate the surface area of the carbon by the following equation.

\[
S = \frac{Xm \cdot N \cdot A}{Mr}
\]

- **S**: Adsorben surface area (m²/g)
- **N**: Avogadro number (6,022 .10\(^{23}\) mol\(^{-1}\))
- **Xm**: Adsorbed adsorbate weight (mg/g)
- **A**: Wide closure by one molecule methylene blue (197 .10\(^{-20}\) m²)
- **Mr**: Relative molecular mass of methylene blue (320,5 g/mol)

**Determination of Spesific Capacitance of Bagasse Activated Carbon**

Bagasse activated carbon have been synthesized then made into electrodes and molded to measure their storage capacity. Capacitors are made by making two pieces of electrodes separated by an electrolyte hydrogels using a simple mold. In this study, the mold is made from a 1,5” PVC pipe with a length of 3 cm which one side in the cover with aluminum foil. Molding was done by mixing 2 mL 1M H\(_2\)SO\(_4\), 2 mL of 5% Polyvinyl Alcohol (PVA), and 0,25 grams of carbon, then stirred. Once added to natrosol, the mixture immediately poured into a mold. After the first carbon electrode layer is formed, then a hydrogel layer of electrolyte made in the same way that a mixture of 2 mL H\(_2\)SO\(_4\), 2 mL of 5% PVA, and 0,5 grams natrosol and immediately poured over the electrode layer in the mold. Once the hydrogel layer of electrolyte, then made another one like carbon electrode layer on the first layer, thus resulting electrochemical capacitor consists of two layers of carbon electrodes flanking bagasse hydrogel layer electrolyte. Capacitors which have been printed then dried at room temperature for 3 days. Electrochemical capacitors that have been made then was storage capacity measured using LCR-meters.

**RESULTS AND DISCUSSION**

**Sugarcane Bagasse Preparation**

Preparation of materials made with bagasse washed with water and distilled water to be cleaned from impurities. After that, the material is dried under direct sunlight for 5 hours in 5
days, and in the oven at 110 °C for 2 hours to remove the water content in the carbon. Furthermore, bagasse materials chopped into small pieces.

![Figure 1. Cleaned and dried bagasse samples](image)

**Carbonization**

Carbonization is the process of burning organic material in the raw material that would cause decomposition of the organic material and impurities expenditures where most non-carbon elements will be lost at this stage. Carbonization process bagasse is done through two stages. The first stage, carried out by burning bagasse by using an electric stove for 20 minutes to be charcoal (C). At the time of combustion, the container used must be sealed to avoid direct contact with O\(_2\) in the atmosphere to prevent oxidation which can cause carbon continues to ashes. This combustion would form a lot of smoke which indicated evaporation of volatile compounds and water vapor contained in the material bagasse. Combustion was stopped when it was not formed smoke anymore. The second phase, the combustion was done by using a furnace at 350 °C for 1 hour. The optimum temperature carbonization bagasse is 350 °C. Too high temperature would cause the formation of ash. At this stage, there would be breaking of C-C bonds in lignin and cellulose in materials and non-carbon compounds will be lost.

After carbonization, carbon sifted with a 100 mesh size sieve to reduce its size. Due to the small size of the carbon particles provide a large surface area. Moreover, this was done to have same size of carbon particles. Carbon bagasse was sieved with a 100 mesh size is shown in the following figure.

![Figure 2. Bagasse carbon after carbonization](image)

**Silica Extraction**

The content of silica in the carbon bagasse according to Kristianingrum et al. (2011) amounted to 73.5%. According to Wei, et al (2011), extraction of silica on carbon will provide the initial structure thus generated pure carbon. In addition, if the silica in the carbon extracted, it will form more space in the carbon. In this research, the extraction of silica done by using a solution of NaOH with variation concentration of 2.5 M and 5 M, and without extraction silica as a comparison. Variations of concentration intended to determine the optimum concentration of NaOH are used to extract all of the silica. Silica extraction is done by mixing 5 grams of carbon bagasse with 100 mL of NaOH solution. The mixture is then
stirred with a magnetic stirrer for 1 hour at a temperature of 95 °C. Stirring aims to optimize the extraction of silica on carbon. Beside that, the heating is done to accelerate the pace of extraction and rising temperatures will increase the amount of silica dissolved into the extractant. The reaction is here below.

\[
\text{SiO}_2(s) + 2\text{NaOH}(l) \rightarrow \text{Na}_2\text{SiO}_3(s) + \text{H}_2\text{O}(aq)
\]

On silica (SiO\(_2\)), O atom has high electronegativity so Si becomes more electropositive and formed intermediates [SiO\(_2\)OH\(^-\)] which is not stable. In this process, there will be dehydrogenation and second hydroxyl ions will bind with hydrogen to form water molecules. Two Na\(^+\) ions will balance the negative charge formed and interact with SiO\(_3^{2-}\) ions to form sodium silicate (Mujiyanti, et al 2010).

After that, the mixture was filtered to separate the filtrate and residue. The residue is then washed with distilled water until neutral pH. This washing is done to remove the sodium silicate which is still contained in the residue. Then carbon was dried in oven at 110 °C for 4 hours. In the silica extraction process, three types of carbons were namely bagasse without silica extraction (Kat-Eks0), silica extracted bagasse carbon using 2.5 M NaOH (Kat-Eks2,5), and silica extracted bagasse carbon using 5 M NaOH (Kat-Eks5). This three types of carbon and oxide compounds characterized by XRF obtain the data in Table 1.

**Table 1. Oxide compound in carbon after silica extraction**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Kat-Eks0 (% w/w)</th>
<th>Kat-Eks2,5 (% w/w)</th>
<th>Kat-Eks5 (% w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2)</td>
<td>53,15</td>
<td>10,93</td>
<td>-</td>
</tr>
<tr>
<td>Fe(_2)O(_3)</td>
<td>29,16</td>
<td>64,08</td>
<td>72,53</td>
</tr>
<tr>
<td>K(_2)O</td>
<td>5,01</td>
<td>3,58</td>
<td>3,59</td>
</tr>
<tr>
<td>CaO</td>
<td>4,90</td>
<td>0,94</td>
<td>10,81</td>
</tr>
<tr>
<td>P(_2)O(_5)</td>
<td>3,11</td>
<td>-</td>
<td>0,83</td>
</tr>
<tr>
<td>MnO</td>
<td>2,52</td>
<td>6,17</td>
<td>6,94</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>1,45</td>
<td>3,75</td>
<td>4,33</td>
</tr>
<tr>
<td>Cr(_2)O(_3)</td>
<td>0,194</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ZnO</td>
<td>0,169</td>
<td>0,232</td>
<td>0,185</td>
</tr>
<tr>
<td>SrO</td>
<td>1,132</td>
<td>0,389</td>
<td>0,397</td>
</tr>
<tr>
<td>NiO</td>
<td>0,092</td>
<td>-</td>
<td>0,198</td>
</tr>
</tbody>
</table>

Dominant oxide compounds in the carbon bagasse were SiO\(_2\), FeO\(_3\), K\(_2\)O, CaO, P\(_2\)O\(_5\), MnO, TiO\(_2\), and SrO. While other oxide compounds only at concentrations of less than 1% of the weight of the samples analyzed. Kat-Eks0 sample containing 53.16% silica. In the sample Kat-Eks2,5 silica content is reduced to 10.93%, and finally run out on samples Kat-Eks5. It is proved that the silica in the carbon successfully extracted by using 5M NaOH. Silica-free carbon would then be activated.

**Activation**

Activation aims to activate carbon by lifting residues on the surface of the pore so that it can be produced carbon with a large surface area (Aisah, 2010). In this research, the activation done by using ZnCl\(_2\) 10%.

Activation of carbon bagasse done by mixing 5 grams of carbon bagasse with 60 mL of 10% ZnCl\(_2\) activator then soaked for 24 hours. Soaking done to maximize the contact between the carbon
with activator so residues that cover the carbon pores will be lifted so that the pores of the carbon would be open. Thus, the active side of the carbon would be formed. The more pores are formed, the more space available for storage of electrical charge in the form of ions in the electrolyte in nanoporous carbon (Rosi, et al., 2013). After soaking, then carbon was treated with ultrasonic waves irradiation and un-irradiation. After treating irradiation and un-irradiation of ultrasonic waves, the carbon then burned in a kiln at a temperature of 350 °C for 1 hour. This was done to eliminate impurities on activated carbon. Activated carbon obtained with and without irradiation of ultrasonic waves then characterized.

Surface Morphology Analysis of Bagasse Activated Carbon

The surface morphology of bagasse activated carbon was done by using Scanning Electron Microscope (SEM) Tescan Vega3 Bruker.

![Figure 3. SEM image of activated carbon bagasse on a scale of 2 μm (a) without irradiation of ultrasonic waves, (b) the irradiation of ultrasonic waves](image)

Figure 3 shows the results of SEM of bagasse activated carbon with magnification on a scale of 2 μm. In both types of activated carbon either treated with irradiation or not, pores formed due to the evaporation of volatile components as well as the release of inorganic compounds that cause the formation of pores in activated carbon. A regular porous formation was also discovered in the rice husk based activated carbon (Nasir et al., 2014)

There is a clear difference between irradiated activated carbon and un-irradiated activated carbon. Based on the known pore image formed on the irradiated activated carbon has a diameter size of 1.5 to 2 μm. While the un-irradiated activated carbon has a pore diameter of 1.6 to 3 μm. In the irradiated activated carbon, more equitable distribution of pores, more number of pores, and the pore sizes tend to be smaller than the pores in un-irradiated activated carbon. In addition, the pores in irradiated activated carbon are formed up to the inside of the carbon. In contrast to un-irradiated activated carbon, which pores are formed not too good and only formed at the surface of the carbon. Better pore distribution proved that ultrasonic irradiation treatment cavitation effect, which occurs on the bubble formation and breakdown of activated carbon to form more number of pores in the irradiated carbon than un-irradiated activated carbon.
Surface Area Analysis of Irradiated and Un-irradiated Bagasse Activated Carbon

Table 2. Data of irradiated and un-irradiated bagasse activated carbon surface area

<table>
<thead>
<tr>
<th>Sample</th>
<th>Absorbance</th>
<th>Final conc. (ppm)</th>
<th>Initial conc. (ppm)</th>
<th>Volume (L)</th>
<th>Carbon Weight (g)</th>
<th>$X_m$ (mg/g)</th>
<th>$(Na.a)/Mr$</th>
<th>S (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Un-irradiated activated carbon</td>
<td>4,388</td>
<td>22,69791</td>
<td>300</td>
<td>0.05</td>
<td>0.3</td>
<td>46,21700</td>
<td>3,706</td>
<td>171,2802</td>
</tr>
<tr>
<td>Irradiated activated carbon</td>
<td>4,412</td>
<td>21,81770</td>
<td>300</td>
<td>0.05</td>
<td>0.3</td>
<td>46,19620</td>
<td>3,706</td>
<td>171,2030</td>
</tr>
</tbody>
</table>

Results of surface area determination with methylene blue method showed that the irradiated activated carbon bagasse provide a larger surface area of 171.2802 m²/gram than un-irradiated bagasse activated carbon of 171.2030 m²/gram, although the difference was not significant which only amounted to 0.0772 m²/gram. This proves that ultrasonic waves irradiation affect the surface area of activated carbon. Irradiated activated carbon experience the effects of cavitation where bubbles are forming and breaking. Bubble breaking then formed more pores in the activated carbon, so that the surface area of irradiated activated was bigger than the un-irradiated activated carbon. These data correspond to pore characterization with SEM on the previous discussion, where the smaller the pore size, the more pores are formed, so that the value of the surface area of activated carbon increases.

Determination of Spesific Capacitance of Bagasse Activated Carbon

Bagasse activated carbon had been synthesized then made into electrodes and printed to create a simple electrochemical capacitors.

Electrochemical capacitors shaped like a sandwich, where there were two layers of electrodes sandwiching a layer of hydrogel electrolyte. Electrochemical capacitors were made had a diameter of 3.5 cm, with a thickness of 0.6 cm, and weight of 3.3 grams, shown in Figure 4.

Figure 4. Electrochemical capacitors of bagasse activated carbon

Electrochemical capacitors that have been made subsequently storage capacity measured using LCR-meter, so it obtained the storage capacity data of irradiated and un-irradiated bagasse activated carbon shows in Table 3.
Table 3. Data of specific capacitance of irradiated and un-irradiated bagasse activated carbon

<table>
<thead>
<tr>
<th>Electrochemical capacitor samples</th>
<th>Storage capacitance (F/gram)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Un-irradiated activated carbon</td>
<td>0.4624 x 10^{-5}</td>
</tr>
<tr>
<td>Irradiated activated carbon</td>
<td>0.3284 x 10^{-5}</td>
</tr>
</tbody>
</table>

Table 3 shows the specific capacitance value of the electrochemical capacitors which the un-irradiation activated carbon has a bigger storage capacitance value than the irradiated bagasse activated carbon although the difference was not too significant. This indicates that ultrasonic waves irradiation affect the value of specific capacitance of activated carbon storage as a capacitor electrode. This may be influenced by the chemical content in the activated carbon due to the effect of cavitation on irradiation ultrasonic treatment.

CONCLUSION

Ultrasonic wave irradiation treatment gives effect to the pore morphology on bagasse activated carbon. Irradiated activated carbon had smaller pore structure, a lot, and distributed evenly than un-irradiated activated carbon.

The surface area of irradiated bagasse activated carbon in optimum condition at a temperature of 30 °C for 60 minutes is 171.2802 m²/g with a specific capacitance value of 0.3284 x 10^{-5} F/gram, while the surface area of the un-irradiated activated carbon was 171.2030 m²/g with a specific capacitance value of 0.4624 x 10^{-5} F/gram.

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