Analysis of Characteristics of Activated Carbon from Cacao (Theobroma cacao) Skin Waste for Supercapacitor Electrodes

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Abstract. The production of activated carbon from the cacao (Theobroma cacao) skin waste was investigated to be used as a super capacitor electrode. This study was conducted in order to obtain the characteristics of the activated carbon electrodes of cacao skins. Activated carbon electrodes were made by a combination of chemical and physical activation methods. Samples were pre-carbonized at 250°C for 2.5 hours, whereas chemical activation was performed using KOH activators of 0.3M and 0.4M, with physical activation temperatures of 700°C, and the particle size of the activated carbon used is smaller than 38 µm. Then it was characterized by X-ray diffraction (XRD), the CiklicVoltammetric (CV) method, and Scanning Electron Microscopy (SEM). Hence, the analysis was carried out on the specific dimensions, density and capacitance. It was found that the mass, diameter, thickness, and density of the electrodes have decreased, and the specific capacitance of the electrodes has increased along with the increase in KOH concentration from 0.3 M to 0.4 M. The specific capacitance value at a concentration of 0.3 M was 90.2 F/gr with a density of 0.850 gr/cm³ and a concentration of 0.4 M was 140.2 F/gr with a density of 0.802 gr/cm³. The X-ray diffraction curve data showed that the value of Lc and the lattice distance (d002) of C0.4 samples was smaller than the C0.3 sample. From the obtained results, the surface area of the C0.4 sample was greater than the C0.3 sample. It was clear that the chemical activation of 0.4M produces electrodes with better performance than 0.3M.

1. Introduction

Indonesia is the third country in the world in cacao producing besides Ghana and Ivory Coast. Cacao is one of the productive plants that produces fruit and can bear fruit throughout the year [1]. Cacao fruit consists of three main components, namely fruit skin, placenta, and seeds (Figure 1). Fresh cacao skins consist of 73% skins, 24.2% seeds, and 2% placenta [1-3], and makes the cacao skins becoming the most waste of all cacao plants, which is about 75% of its fresh skins [4]. One ton of dried cacao beans is equivalent to 10 tons of fresh cacao skins. To overcome the high production number, effective handling of waste is needed so that it does not interfere with the production process and the environment around the processing plant.

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Various alternatives have been made to deal with the final disposal of cacao fruit waste. One of them is creating valuable products, such as antioxidants in cosmetic products [6], additives [3], as animal feed [7], adsorbents of Rhodamin B dyes [8], absorbent heavy metals [9-10], corrosion inhibitors [11], restoration of mechanical properties of mild steel after corrosion [5], activated carbon [12], absorbent amoxicillin [13], paper production [14], and many others.

Biomass materials can be used as raw material to make activated carbon, because biomass is composed of lignocellulose, cellulose, and hemicellulose which are organic carbon. Activated carbon can be made from all carbon-containing materials, both organic and inorganic carbon with the condition that the material has a porous structure and meets the requirements of the Indonesian National Standard (SNI) No. 06-3730-1995. Some of utilized biomass such as wood, lignite, bones, palm shells, oil palm bunches, agricultural waste such as coffee fruit skins, cacao fruit husks, rice husks, straw, cob and cornstalks, fruit skins, fruit seeds, grain skins, and others [14].

Cacao skin is one of the biomass wastes that meets the requirements to become activated carbon. This research was set up to make activated carbon from cacao shell using KOH activator with variations in concentration at a temperature of 700°C. By processing cacao skin waste into carbon electrodes as a basic material for super capacitors, not only is the environment protected from pollution, but it will also reduce the number of carbon electrodes imported by industry in Indonesia.

2. Research Method

The making of activated carbon from biomass cacao skin until printed into pellets has been described in previous publications [15]. Carbon pellet moulding was carried out using a hydraulic press at 8 tons pressure. The next step was the carbonization process using furnaces, starting from room temperature to 305°C, and held for one hour. Then proceed to a maximum temperature of 600°C in the N₂ gas environment and continued to physics activation at 700°C using CO₂ gas. The 305°C temperature resistance was taken from durian skin’ temperature resistance, due to the similar texture of cacao fruit and durian skin after experiencing the dehydration process [16]. Dimension measurements carried out include the measurements of mass, diameter, thickness of each pellet prior to and after the physics’ carbonization-activation [15].

After measuring the density, the carbon pellet sample was polished to a diameter of ± 8 mm and a thickness of ± 0.3 mm, then washed until the pH of the washing water became neutral. Then neutral carbon electrodes were immersed in 1 M sulphuric acid (H₂SO₄) solution which functioned as an electrolyte in super capacitor cells.

The electrochemical properties of carbon electrodes were tested by assembling a super capacitor cell. The specific capacitance value of the super capacitor can be calculated using the CiclicVoltamentry (CV) method at an induced rate of 1 mV/s to 100 mV/s [15].

3. Results and Discussions

3.1 Physical properties

During the drying process, the skin of cacao fruit experienced a reduction in water content by 84.47%, where the water content of fresh cacao skin was 70.582%, and became 10.964% when it dried.
carbonization process causes the decomposition of organic material in cacao shells, and releases volatile substances, where most of the non-carbon elements will be released into the air [17]. The space left by these non-carbon elements forms a pore, nevertheless the pore volume and surface area formed is usually small below the standard of activated carbon. As a result of the release of volatile elements, the carbon produced has decreased. The percentage of mass depletion of cacao shells to carbon ranges between (19.3-34.2)%. The physical observations of carbon from cacao shells to carbon pellets can be seen in Figure 2.

The low water content because of the smaller surface of activated carbon contains fewer polar functional groups so that the interaction between polar water vapour is also small [18-19]. Low level of this water content also indicates that the substance evaporates, and other compounds in the activated carbon the skin of cacao is more easily released, so that the surface area of activated carbon is getting bigger and the pores of charcoal are increasing.

The measurement results of mass dimensions (m), diameter (d), thickness (t), and density (ρ) in each variation, before and after carbonization-activation of physics can be seen in Table 1, and 2. The increase on KOH concentration from 0.3 M to 0.4 M stimulated a decrease in the dimensions and density of carbon pellets. These results were in accordance with previous studies conducted by ErmanTaer (2016) on the manufacture of super capacitor electrodes from rubber wood using chemical activation of KOH and HNO₃. The reduction in density on the carbon electrode is due to the addition of the pore structure from the combination of activation [20]. Analysis of the dimensional shrinkage and density of activated carbon in both variations is presented in Tables 1 and 2.

Table 1. Percentage of the electrodes shrinkage with a 0.3M KOH activator at temperature of 700°C

| No | Variable     | Beginning | Ending | Losing | Shrinking (%) |
|----|--------------|-----------|--------|--------|---------------|
| 1  | Massa (gram) | 0.703     | 0.256  | 0.447  | 63.6          |
| 2  | Diameter (cm)| 1.985     | 1.480  | 0.505  | 25.3          |
| 3  | Thick (cm)   | 0.254     | 0.187  | 0.067  | 26.9          |
| 4  | Density (gram/cm³) | 0.918 | 0.850  | 0.038  | 9.9           |

Figure 2. Preparation of activated carbon electrodes for cacao skin husks(a) cacao skin skin, (b) after dehydration, (c) after pre-carbonization, (d) after sifting, (e) after printing, (f) pellets after carbonization and activation, and (g) pellets after polishing.
Table 2. Percentage of the electrodes shrinkage with a 0.4M KOH activator at temperature of 700°C

| No | Variable      | Beginning | Ending | Losing | Shrinking (%) |
|----|---------------|-----------|--------|--------|---------------|
| 1  | Massa (gram)  | 0.689     | 0.231  | 0.458  | 64.1          |
| 2  | Diameter (cm) | 1.978     | 1.486  | 0.492  | 29.8          |
| 3  | Thick (cm)    | 0.240     | 0.187  | 0.763  | 25.0          |
| 4  | Density (gram/cm³) | 0.950 | 0.802  | 0.148  | 18.6          |

The mass loss occurring in the 0.4 M sample with activation temperature of 700°C was greater than the mass loss in the 0.3 M sample with the same activation temperature, however it was not too significant. It is because the carbonization process causes the decomposition of organic material in the cacao skin and releases volatile substances such as water vapour during the carbonization and activation process. The dominant mass loss will impact on the diameter and thickness. There was a significant difference in the thickness dimension, the shrinkage of thickness in the 0.3 M sample with a temperature of 700°C which was much greater than in the 0.4 M sample with the same temperature. On the other hand, the diameter dimension showed an adjacent value. The physical parameter values would clearly produce lower densities in carbon after activation than carbon before carbonization [13].

The mass shrinkage was high in number caused by the evaporation of material other than carbon during the carbonization and activation process. Whereas the shrinkage in diameter and thickness was caused by heating which directly presented the empty space between carbon atoms, so that bonds or carbon atoms form stronger bonds [21]. Shrinkage of mass was more dominant than shrinkage of diameter and thickness, this condition would clearly produce a lower density on activated carbon than green carbon [21].

3.2 XRD analysis

X-ray diffraction analysis (XRD) utilized a 2θ diffraction angle that was in the 10º-100º angle range. Previous publications have explained the pattern of XRD activated carbon of cacao skin with concentrations of 0.3M and 0.4M KOH activators [15].

The difference in the electrode structure of 0.3 M and 0.4 M at 700°C could be observed from the peak height and width half the height of the the peak of the XRD diffractogram which were 95.380 nm and 15.176 nm for the 0.3 M sample with a temperature of 700°C. As for the 0.4 M sample with a temperature of 700°C were 194.64 nm and 6.8725 nm [15]. The shift in peak height and width half the height of the peak indicated the rearrangement of carbon atoms.

The XRD data fitting results from each sample were obtained at the lattice distance d_{002} and d_{100}, as shown in Table 4. The largest Lc / La ratio number was obtained on the 0.3M electrode sample and the smallest on the 0.4M electrode sample at the same temperature 700°C.

Table 3. Results of data fitting of X-ray diffraction data of cacao skin electrodes

| Kode Elektroda | 2θ_{002} (°) | 2θ_{100} (°) | d_{002} (Å) | d_{100} (Å) | Lc (Å) | La (Å) |
|---------------|--------------|--------------|-------------|-------------|--------|--------|
| C 0.3 M       | 23.569       | 44.781       | 3.771705    | 2.022225    | 20.01669 | 11.93877 |
| C 0.4 M       | 24.747       | 44.634       | 3.594769    | 2.028543    | 3.256256 | 30.3769 |

Based on the empirical formula used, to produce a higher surface area of carbon electrodes a smaller lattice distance (d_{002}) and smaller dimensions of microcrystalline (Lc) are required [15]. The X-ray diffraction curve data in Table 4 shows that the C 0.4M sample has a smaller Lc value and the lattice distance (d_{002}) than the C 0.3M sample, so it can be indicated that the surface area of the C 0.4M sample is greater than sample C 0.3M.
3.3 Scanning Electron Microscopy (SEM) analysis

The scanning electron microscope (SEM) analysis aims to determine the morphology of the carbon electrodes of cacao skins by looking at the distribution of the portions. The sample observations in Figure 3 were carried out at 5000 X magnification.

![Figure 3. Observation of SEM carbon electrode temperature of 700°C, magnification of 5000 Xa) 0.3M, and b) 0.4M.](image)

Figure 3a shows the surface morphology of the activated carbon of the cacao skins. Pores between particles are spread almost evenly on the surface of the sample, some have elongated and irregular shapes. There are still small particles on the surface of the sample which indicate the presence of material other than carbon in the 0.3M 700°C sample or free particles that do not evaporate completely during the carbonization and activation process. The particles are clearly more visible and there are pores in between these particles that are spread evenly with various shapes and sizes.

In Figure 3b shows the morphology of 0.4M carbon electrode 700°C, where the pores between particles are larger than the carbon electrode sample 0.3M 700°C, with irregular size and shape. It is also seen chunks on the surface of the carbon electrode which shows a denser electrode sample structure. There are particles formed more clearly having quite large pore shaped with uneven size in between them. Compared with the morphology of durian skin carbon electrodes with the same magnification and physical activation time, it shows that the carbon particles are relatively dense, elongated and irregular in shape, and the pores between the particles have formed. Closed pores cause the density of carbon electrodes to increase, resulting in small specific capacitance [20].

3.4 X-ray Dispersive Energy (EDX) analysis

Composition analysis with X-ray energy dispersion (EDX) represents the percentage of elemental content contained in carbon electrode samples, as seen in Table 4.

| Contents | C 0.3M 700°C Massa % | Atom % | C 0.4M 700°C Massa % | Atom % |
|----------|----------------------|--------|----------------------|--------|
| C        | 87.05                | 91.02  | 87.87                | 91.49  |
| O        | 10.12                | 7.95   | 9.65                 | 7.54   |
| Mg       | 0.75                 | 0.39   | 0.94                 | 0.48   |
| Ca       | 2.07                 | 0.65   | 1.55                 | 0.48   |
| Total    | 100%                 |        |                      |        |
Table 4 shows that the elements contained in carbon electrode samples consist of Carbon, Oxygen, Magnesium and Calcium. At the activation of 0.3 M and 0.4 M, the percentage of carbon element content is higher than other elements, namely 91.02% at 0.3 M and 91.49% at 0.4 M. The high content of C indicates that carbon electrode samples has a very high purity. Element O has the second highest percentage after element C, and occurred when carbonization of oxygen content in carbon samples is not completely decomposed or bonds are formed in the activation process [11]. Ca content is presence because it is found in the composition of the skin of cacao fruit. Mg element is indicated to derive from unclean steel balls when ball milling.

The quantity of element C in the 0.4 M carbon electrode sample at 700°C temperature is greater than that of the 0.3 M carbon electrode sample at the same temperature. This specifies that the 0.4 M KOH sample contains more carbon than the 0.3 M KOH sample. The addition of KOH activator concentration from 0.3 M to 0.4 M results in the decomposition of non-carbon content, so that the element C produced is higher.

3.5 Electrochemical properties

Cyclic Volta metric (CV) measurement data is stated in the specific capacitance curve (Csp) of the voltage in the scan rate of 1 mV/s. The CV curve demonstrates the graph of current strength against voltage at KOH concentrations of 0.3 M and 0.4 M, as shown in Figure 4.

Figure 4 points out the CV curve for 0.4 M KOH treatment having a better capacitive response than the 0.3 M KOH sample. This is characterized by a wider middle potential area, so as to increase the number of pores of carbon electrodes. The increase in the number of pores is in line with the increase in the number of ions flowing into the electrodes marked by the width of the charge-discharge curve, as shown in Figure 4. The wider the charge-discharge curve, the greater the specific capacitance produced by the activated carbon electrode.

![Figure 4. CV curve of activated carbon with KOH 0.3 M and 0.4 M.](image_url)

0.4 M carbon electrode sample temperature of 700°C has a better capacitive response, this is characterized by a wider central potential area, a greater charge process at 0 V and a horizontal discharge curve shape when compared with the sample 0.3 M 700°C. The shape of the CV curve of 0.4 M 700°C is square, known as the most ideal form for activated carbon electrodes. An increase in the value of specific capacitance (Csp) improves as the increase of KOH concentration from 0.3 M to 0.4 M, as seen in Figure 5. It is illustrated within the value of specific capacitance (Csp) at concentrations of 0.3 M and 0.4 M with an average mass of 0.0132 and 0.0112 is 90.2 F/gr and 140.2 F/gr.
4. Conclusions
The activated carbon of cacao skins has the potential to be used as a basis for super capacitor electrodes. Analysis of dimensions, density and specific capacitance on the cacao skin carbon electrodes with variations in concentration showed the diameter and thickness of the carbon electrode pellets decreased. Shrinkage of mass and an increase in KOH concentration result in a decrease in the density value of carbon electrodes namely 0.850 gr/cm$^3$ for C 0.3M and 0.802 gr/cm$^3$ for C 0.4M. XRD analysis indicates that the surface area of the C sample of 0.4 M is greater than the C sample of 0.3M, because the 0.4M C sample has smaller Lc value and lattice distance (d$_{002}$) than the C 0.3 sample. The specific capacitance value (Csp) increases in line with the increase on KOH concentration from 0.3M to 0.4M, which is from 90.2 F/gr to 140.2 F/gr.

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