POROUS CARBON FROM PINEAPPLE PEEL AS ELECTRODE MATERIAL OF SUPERCAPACITOR

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Abstract

Porous carbon from biomass has a great potential to be developed. Biomass as a resource is renewable, abundantly available, and cheap. One application of porous carbon is as an electrode material of supercapacitor due to its advantageous pore properties such as high specific surface area and pore volume. This research prepared porous carbon material from pineapple peel waste and tested it as a supercapacitor electrode. The research steps were material preparation, conversion of pineapple peel to porous carbon, and characterization, including material characterization and electrochemical characterizations. Pineapple peel (under 80 mesh size) was pre-carbonized by hydrothermal method at 1900C for 2 hours under a subcritical condition. After that, biochar was pyrolyzed at 9000C and activated using CO2/N2 (KB-900-50). As a reference, biochar was also pyrolyzed under a nitrogen atmosphere at 9000C without activation (KB-900). Produced porous carbon was characterized (i) pore structures, e.g., specific surface area, average pore diameter, and total pore volume using N2-sorption analysis, and (ii) electrochemical performance, e.g., cyclic voltammetry and galvanostatic method using 1 M H2SO4 electrolyte solution. The result showed that the activation process effectively increased the porosity of porous carbon. Material (KB-900-50) possesses a high surface area of 648 m2/g and a high capacitance value of 78 F/g.

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1. Introduction

Energy storage technology continues to evolve and has recently gained research interest. One energy storage technology that has attracted research interest is the supercapacitor, which has a fast-charging time and a long-life cycle. The supercapacitor has several advantages over conventional capacitors, including higher capacitance and a more comprehensive operating temperature range (Stenny Winata et al., 2020). Supercapacitors are divided into three types: electric double-layer capacitors (EDLC), pseudo-capacitors, and hybrid capacitors. The main component of the supercapacitor is the electrode which functions as energy storage. Materials such as porous carbon, graphene, and carbon nanotubes are commonly used as electrode materials for supercapacitors (Elaiyappillai et al., 2019; Rawat et al., 2022). Among them, porous carbon is the main choice for commercial production electrode material of supercapacitors because of its simpler production method, low cost, and availability of raw materials (Jain et al., 2016). Porous carbon can be produced from various types of resources such as coal, wood, synthetic polymers, and other biomass wastes (Stenny Winata et al., 2020; Prasetyo et al., 2013). In this case, the biomass waste in large quantities can be used as material for producing porous carbon using pyrolysis and hydrothermal processes (Saikia et al., 2020).

Biomass wastes are the best feedstocks for porous carbon production because they are cheap, abundant, and have high carbon content. Therefore, the use of biomass waste to produce low-cost porous carbon as the electrode material of supercapacitors is improving. Coconut shells, wood, melon peel, palm shell, candlenut shell, bamboo, rice husk, sawdust, and other biomass sources have been reported. The conversion of biomass into a valuable product such as porous carbon can be carried out in two steps: pre-carbonization to biochar and the activation process (Larasati et al., 2019). The pre-carbonization process using the hydrothermal method is one of the options which uses subcritical water to convert biomass into carbonaceous products called biochar (Jain et al., 2016).

In recent years, hydrothermal processes have attracted some attention as potential uses for biomass. Research and development were done to measure the potential and discover more potential applications. Lignocellulosic biomass has been studied in order to produce carbon-rich materials or biochar. Biopolymers in lignocellulosic can be degraded at different temperatures, hemicellulose at 180-290^{0}C, Cellulose at 240-350^{0}C, and lignin at 280-500^{0}C (Dimitriadis & Bezergianni, 2017). Typically, the hydrothermal method is carried out at a lower temperature range of 180-350^{0}C (Khan et al., 2019). The activation process is carried out to convert biochar to porous carbon which has more porosities. The activation process can be done either by chemical or physical activations (Lam et al., 2017). Ananas comosus, known as pineapple, is widely used for its fruits.

Pineapple is one of the potential horticultural commodities to be developed and produced in Indonesia. Pineapple plants in Indonesia are almost evenly distributed in all corners of the region because the Indonesia region has a diversity of agroclimatic, making it possible to develop various types of plants, including one of them being the pineapple commodity. Unfortunately, pineapple peels are disposed of unused without real benefit, most of which were disposed of as natural waste. In this research, the conversion of pineapple peel to porous carbon was performed with a thermochemical transformation process of hydrothermal treatment. This research aims to determine material characteristics and electrochemical performance of the material as the electrode material of supercapacitors. Pineapple peel was chosen since it is abundantly available and is not utilized. It is expected that pineapple is peeled 1 million tons/per year produced in Indonesia.

2. Methodology

2.1 Materials

The raw material of pineapple peel was gathered from a pineapple seller in Sleman, Yogyakarta. Isopropyl alcohol (purity of 99%, purchased Merck), Nafion solution (purity of 5%, purchased from Sigma-Aldrich), H_2SO_4 (96%, Merck), and distilled water (aquadest).

2.2 Material Preparation

The pineapple peel was cleaned with water and then dried for approximately four days. Afterward, the dried pineapple peel was crushed using a grinding machine and sieved using an 80-mesh sieve. The use of an 80-mesh sieve can produce smaller and more delicate particle sizes to facilitate a better contact area between water molecules and pineapple peel powders.

2.3 Biochar Production

The thermochemical conversion technique of hydrothermal treatment was used to decompose and hydrolyze organic compounds from pineapple peel into solid and liquid products. The pineapple peel powder (90 g) and distilled water (ratio 1:12) were placed in a hydrothermal reactor. The reactor contents were maintained at the desired temperature of 190^{0}C for 120 minutes. The selection of temperature at 190^{0}C since it is in the range of optimal hydrothermal reaction temperature, while the selection of residence time for 120 minutes refers to previous research conducted by Jain et al., (2015). The biochar obtained was then filtered and dried at 60^{0}C for 48 hours.

2.4 Biochar Activation Process

The biochar obtained from the pre-carbonization process was then physically activated with CO_2 in a tube furnace at 900^{0}C with a heating rate of 3^{0}C/min under a nitrogen atmosphere at a flow rate of 50 mL/min (Larasati et al., 2019). After reaching the desired temperature, CO_2 flowed as an activator at a flow rate of 50 mL/min for 2 hours. The ratio of CO_2 and N_2 was 1/1 vol/vol. After the activation process was completed, the furnace was cooled to room temperature. Afterward, the porous carbon material is ready to be characterized. The obtained porous carbon was named KB-900-50.

While for carbon without activation, biochar is pyrolyzed in a tube furnace at 900^{0}C with a heating rate of 3^{0}C/min under a nitrogen atmosphere at a flow rate of 50 mL/min for 2 hours (Larasati et al., 2019). The porous carbon obtained was coded as KB-900. With these two samples, a comparison of carbon with and without can be carried out in Table 1.

Table 1. Porous carbon naming

Temperature (^{0}C)	Carrier Gas, N_2 (mL/min)	Activator, CO_2 (mL/min)	Sample Code
900	50	50	KB-900-50
900	50	–	KB-900

2.5 Material Characterization

Lignocellulosic and proximate analyses were carried out by gravimetric analysis (STA PT1000, Linseis, Germany). The porous carbon's specific surface area, average pore diameter, total pore volume, adsorption isotherm, and pore size distribution were obtained from N_2 adsorption-desorption analysis (NOVA 2000, Quantachrome, USA).

2.6 Electrochemical Characterization

Electrochemical performance testing from electrode material was performed using cyclic voltammetry to determine the capacitance value. The cyclic voltammetry method was performed using a three-electrode system configuration in Figure 1. A three-electrode system is selected because all components for the experimental setup are simple in assembling an electrochemical cell to collect data during experiments. The electrode materials were made by mixing 10 mg of porous carbon with 20 µL Nafion solution 5% as a binder and adding 1 mL of Isopropyl alcohol and then ultrasonication for 30 min so that a homogeneous mixture was produced. After that, 10 µL ink was taken and dripped on the working electrode. Finally, it dried at room temperature until the working electrode was dried. Cyclic voltammetry tests were performed at a scan rate of 10 mV/s - 200 mV/s at a potential window of -0.2 V to 0.7 V using a H_2SO_4 1 M electrolyte.

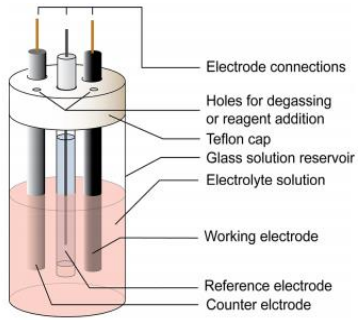

Figure 1. Three-electrode system (Elgrishi et al., 2018)

The capacitance value of the electrode materials was calculated from a cyclic voltammetry curve according to using the following equation:

$$C = \frac{1}{2.m.v} \text{ x } \frac{A}{(V_2 - V_1)} \quad (1)$$

Where, *C* refers to the capacitance value, *A* is the area of the cyclic voltammetry curve, $(V_2 - V_1)$ is the potential limits at the low and high levels during CV tests, *m* is the mass of porous carbon material in the electrode, and *v* is the scan rate.

3. Results & Discussion

3.1 Lignocellulosic Analysis

The lignocellulosic analysis is needed to show the composition contained in the biomass. The lignocellulosic analysis of pineapple peel biomass is presented in Table 2.

Table 2. Lignocellulosic analysis of pineapple peel

Components	Value (%)
Cellulose	21.6
Hemicellulose	21.6
Lignin	2.91

Based on the Table 2 of lignocellulosic analysis, it can be seen that pineapple peel has a more dominant hemicellulose content of 47%, followed by cellulose at 21.65% and lignin of 2.91%. Knowing the composition of organic compounds contained in pineapple peel biomass can be used as a reference in determining the operating conditions of 190ºC according to literature (Dimitriadis & Bezergianni, 2017).

3.2 Hydrothermal Treatment of Pineapple Peel

The results of the carbonization process using the hydrothermal method are shown in Figure 2. The biochar product was 36.66% of the original mass of dried pineapple peel.

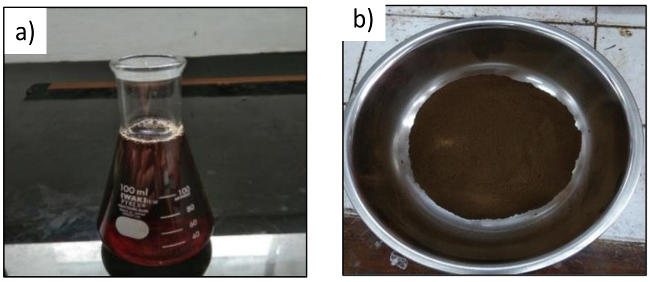

Figure 2. (a) Bio-oil (b) Biochar

Figure 2 shows that the bio-oil product's hydrothermal process results have a dark brown color and the biochar has a brownish color, indicating that the organic compounds in the biomass were successfully dissolved in the liquid phase to produce bio-oil and biochar. The color of biochar and bio-oil are similar to other biomass hydrothermal products (Xu & Li, 2021; Wa & Michalik, 2021). Water in subcritical conditions and smaller particle size facilitated easier water penetration into the biomass matrix, making the disintegration of organic compounds in biomass easier (Stenny Winata et al., 2020).

3.3 Proximate Analysis

The quality of biochar obtained after pre-carbonization was determined using proximate analysis. Table 3 shows the proximate analysis of biochar.

Table 3. Proximate analysis of biochar

Proximate analysis (%)			
Fixed Carbon	Volatile Matter	Moisture	Ash
68.92	27.31	0.03	3.72

The proximate analysis results show that biochar's fixed carbon and volatile matter content are high and have low moisture. Fixed carbon and moisture content in biochar determine the quality of biochar produced; high fixed carbon with low moisture content indicates the better quality of biochar (Iskandar & Rofiatin, 2017). In manufacturing porous carbon, a good precursor has a high fixed carbon and volatile matter content and low ash (Canales Flores et al., 2018).

3.4 N_2 Adsorption-Desorption

The carbon material's structural characteristics, including specific surface area, average pore diameter and total pore volume obtained from N2-sorption analysis, are presented in Table 4.

Table 4. Pore analysis of porous carbon

Material	Characteristics		
	Specific Surface Area (m²/g)	Average Pore Diameter (nm)	Total Pore Volume (cc/g)
Biochar	7	3.12	0.056
KB-900	9	3.04	0.075
KB-900-50	648	2.32	0.37

Table 4 shows the significant effect of the activator in the specific surface area enhancement. The highest specific surface area and total pore volume produced were 648 m^2/g and 0.37 cc/g for porous carbon KB-900-50. Specific surface area is one factor that can support better electrochemical performance. The isotherm curve and pore size distribution on porous carbon are shown in Figure 3 and Figure 4.

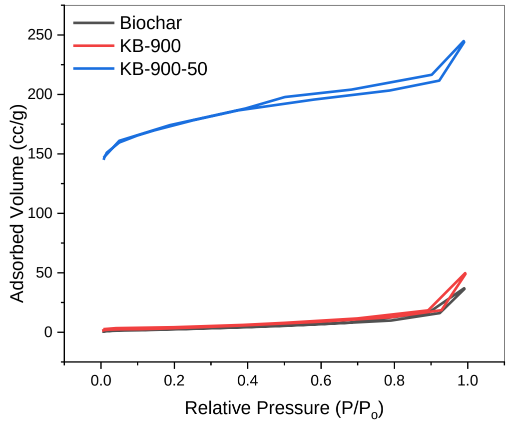

Figure 3. Isotherm Curves of Biochar KB-900 and KB-900-50

Figure 3 shows the adsorption isotherm of biochar, KB-900, and KB-900-50, respectively. The carbon material obtained has an adsorption isotherm type IV based on the IUPAC classification. Type IV isotherm has a hysteresis loop in the area around P/P_0 0.4-1 (Elaiyappillai et al., 2019). Based on the isotherm curve, it can be seen that the same type of material can produce different dominant pore structures. KB-900-50 shows the more dominant mesoporous structure. The enhancement in the adsorbed volume on the carbon material indicates the presence of more porosity which was achieved during activation process (Ajay et al., 2021).

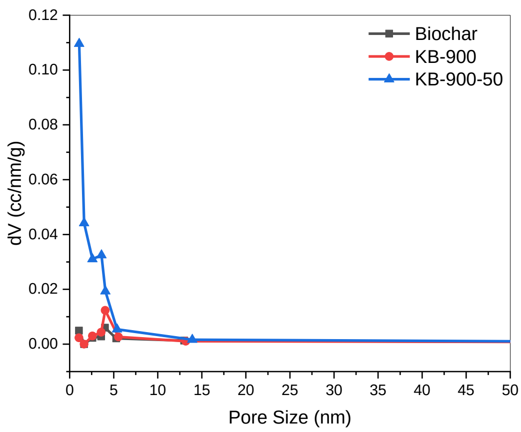

Figure 4. Pore size distribution curves of biochar, KB-900 and KB-900-50

Figure 4 shows the pore size distribution curves of biochar, KB-900, and KB-900-50, respectively, which suggests that the carbon material has apparent peaks in the micropore range of 1-2 nm and mesopore range of 2-5 nm. A broad porosity was obtained, which agrees with the literature as typical carbon from biomass (Elaiyappillai et al., 2019).

3.5 Electrochemical Characterization

Electrochemical testing on carbon material can provide information regarding the capacitance value, which is an important parameter for energy storage (Ajay et al., 2021). Cyclic voltammetry testing for the three-electrode materials was carried out at a scan rate of 10 mV/s - 200 mV/s, as shown in Figure 5.

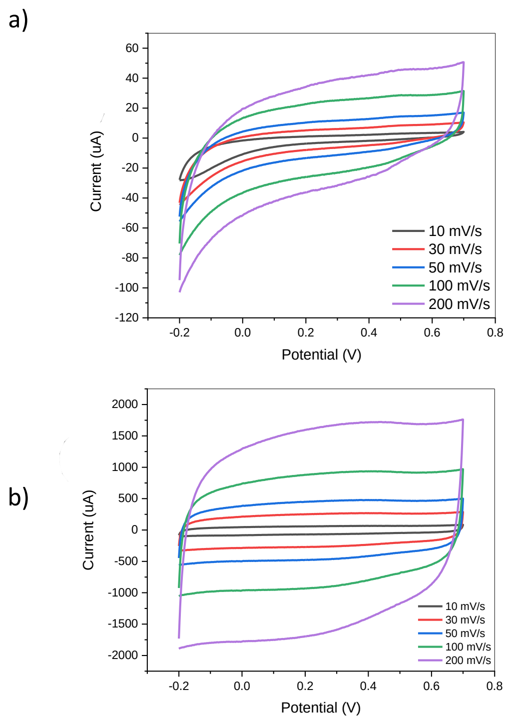

Figure 5. CV Curves (a) KB-900 (b) KB-900-50

Figure 5b shows the cyclic voltammetry curve has a rectangular profile, indicating that the electrode material has ideal capacitive performance (Vinayagam et al., 2021). The electrode material KB-900-50 has a higher current indicating better electrochemical performance.

Table 5. The capacitance of electrode material

Material	Scan Rate (mV/s)	Capacitance (F/g)
KB-900	10	2
KB-900-50	50	78

The electrochemical performance of the electrode materials in Table 5 shows that the electrode material KB-900-50 has the highest capacitance value compared to electrode material KB-900. Regarding the correlation between the specific surface area with capacitance value is proportional, the higher the specific surface area of the porous carbon material, the more electrolyte ions (cations and anions) can be adsorbed or accumulated on the electrode material so that the capacitance value increases. The pore size also influences the capacitance value. Therefore, the highest specific surface area followed by the pore size in the mesoporous range is very important to facilitate a better electrolyte ion transfer (Chen et al., 2017).

Electrolytes are important for supercapacitor performance. The electrolyte used determines the potential window of a supercapacitor. Aqueous and organic electrolyte are commonly used types of electrolytes. The aqueous electrolytes such as H_2SO_4 can improve the capacitance value but limit the potential window. Meanwhile, organic electrolytes such as $LiPF_6$ can expand the potential window up to 3 V (Mone et al., 2022).

The correlation of scan rate with capacitance value is shown in Figure 6 for KB-900 and KB-900-50.

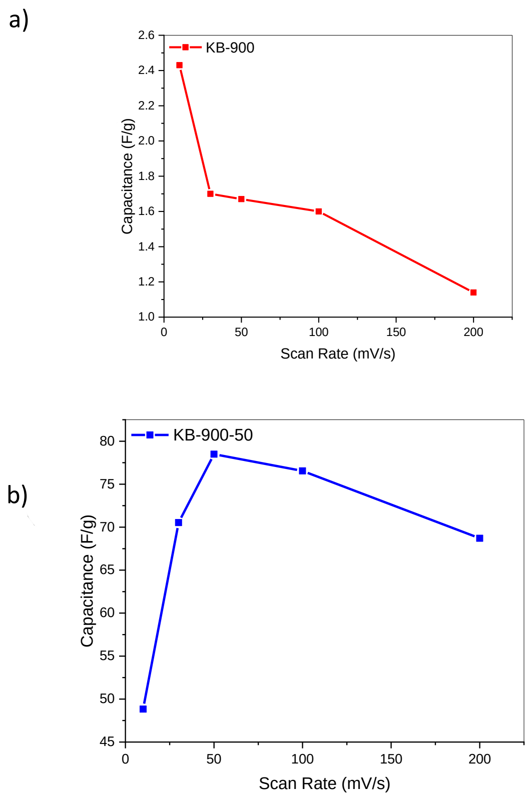

Figure 6. Correlation of scan rate with capacitance (a) KB-900 (b) KB-900-50

For KB-900, the capacitance value decreases as the scan rate increases. The highest capacitance value is shown at the lowest scan rate of 10 mV/s. This is because the high scan rate makes the voltage flow rate fast; as a result, the time available for the electrolyte ions to diffuse into the pores of the carbon electrode is shorter, and the formation of a double layer tends to be less. Meanwhile, at a low scan rate, the time available for the electrolyte ions to diffuse into the pores of the carbon electrode is longer, and the formation of a double layer tends to be more KB-900-50, showing a different character. The highest capacitance value is shown at a scan rate of 50 mV/s. At a low scanning rate, it is possible that ions are not fully charged to the carbon surface.

4. Conclusion

Porous carbon as an electrode material of the supercapacitor was obtained from the conversion of pineapple peel by pre-carbonization and activation processes. The best material characteristics and electrochemical performance are shown by porous carbon with a specific surface area of 648 m^2/g and a capacitance value of 78 F/g produced by activation using CO_2 at 900^0C. Considering its abundance and derived from renewable resources, pineapple peel can be used as a feasible raw material for the production of porous carbon as an electrode material of supercapacitors.

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