Green synthesis of Supercapacitor electrodes activated carbon from *Veitchia Merilli* Seed waste by a two-stages pyrolysis in integration

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Abstract. Pyrolysis process consists of two-stages in integration aims to carbon purification, evaporates volatile compounds so that it enlarges the pore diameter, and increases the surface area of the activated carbon. This research used *Veitchia Merilli* seed (VMS) waste by optimizing the stages-carbonization to obtain a high specific capacitance. Initial preparation begins with the pre-carbonization process at a temperature of 200°C, the activated carbon powder is converted into a monolith form using a Hydraulic Press and followed by a pyrolysis process in the stages-carbonization with temperature variations of 500°C, 600°C, and 700°C and the stages-physical activation at temperature of 800°C. The results showed that the thermal resistance temperature of the carbon powder was 287°C. The lowest density value occurs in the VMS-600 sample of 0.591 gr/cm³ and Microstructure analysis shows that the carbon electrode is amorphous which is characterized by the presence of peaks at 2θ angles around 24º and 44º with the highest Lc value of 15.069 nm, with the highest specific capacitance value of the supercapacitor cell of 210,442 F/g. Temperature 600°C is the optimum temperature carbonization in the process fabrication of carbon electrodes from VMS waste for supercapacitor cell application.

1. Introduction
Human need for energy continue to increase, these needs depends on energy sources from fossil flues, natural minerals, crude oil, natural gas and nuclear fuel [1]. Indonesia is one of the developing countries that requires high-capacity energy because Indonesia has a large population. The energy crisis occur throughout the world, especially Indonesia, Energy sources in Indonesia come from fossil energy which has decreased production every year. Energy use in Indonesia has reached 114 MTOE consisting of 40% transportation sector, 36% industry, 16% household, 6% commercial and 2% other sectors [2]. Renewable energy sources such as biomass waste are needed to overcome the energy crisis in Indonesia. Biomass is an organic compound derived from living things such as agricultural waste, plantation crops, forestry and animals that can be used as raw material for the manufacture of activated carbon. Activated carbon is a porous solid that has 85-95% carbon produced from materials containing carbon through a high-temperature heating process using gas, water vapor, and chemicals to open the
pores. Activated carbon can be used as an electrode for supercapacitor applications because it is porous, easy to synthesize, light weight, abundant raw materials and economical [3].

Supercapacitors are a new breakthrough in the world of electrical energy storage devices that have a large charge storage capacitance, large energy density and power density, fast and durable charge-discharge process when compared to other storage devices [4]. Supercapacitors consist of four parts namely electrodes, electrolytes, separator and current collector. The supercapacitor electrode is the main part to determine the performance of the supercapacitor which is influenced by the manufacturing process. The process of making activated carbon electrodes through the process of pre-carbonization, chemical activation and pyrolysis. The pyrolysis process consists of carbonization and physical activation stages which aims to carbon purification, evaporates volatile compounds so that it enlarges the pore diameter, and increases the surface area of activated carbon. The stages-carbonization is carried out for water removal or dehydration, evaporation of cellulose, lignin, hemicellulose, and carbon purification. The stages-carbonization uses a temperature of 300°C-900°C, if the temperature is above 1000°C it will cause a lot of ash to form so that it can cover the surface area and make the absorption decrease. The stages-carbonization is carried out in the furnace and in the flow of nitrogen gas (N₂) [5]. Nitrogen gas is an inert gas which will reduce ashing and oxidation in carbon pyrolysis and further heating. Nitrogen gas also has an affordable price when compared to other gases.

The manufacture of supercapacitor electrodes with variations in carbonization temperature has been carried out by various researchers including Farma et al (2013) making activated carbon electrodes from oil palm empty fruit bunches waste with temperature variations of 600°C, 700°C and 800°C, getting a specific capacitance of 80 Fg⁻¹ at a temperature optimum 800°C. Researchers Cheng et al (2020) made activated carbon electrodes from Laminaria Japonica waste with various carbonization temperatures of 600°C, 800°C, 1000°C, and 1200°C, getting a specific capacitance of 192 Fg⁻¹ at a temperature optimum 800°C. In this study, the manufacture of activated carbon electrodes from Veitchia Merilli seeds waste with various carbonization temperatures of 500°C, 600°C, and 700°C.

Veitchia Merilli (Princess Palm) is one type of palm that is widely available in Indonesia., especially in Pekanbaru. Veitchia Merilli is currently used as an ornamental plant in parks, schools, offices and many more. Its beautiful and attractive shape makes Veitchia Merilli relatively expensive compared to other types of palms. Veitchia Merilli fruit can become waste when it falls and left unattended. Veitchia Merilli fruit has seeds that have the potential to be used as activated carbon for supercapacitor cell applications because they contain flavonoid compounds. Flavonoid compounds are polyphenolic compounds that have 15 carbon atoms arranged in a 6-3-6 configuration, consisting of two groups of 6 substituted benzene rings connected by a three-carbon aliphatic chain [8].

2. Experimental Section

Veitchia Merilli seeds waste is cleaned and dried in the sun for 5-6 days. The pre-carbonization process at 200°C produces a self-adhesive carbon powder. The carbon powder was converted into a monolith using a hydraulic press and followed by a pyrolysis process consisting of a stages-carbonization with a temperature variation of 500°C, 600°C, and 700°C flowing with N₂ gas at a heating rate of 3°C·min⁻¹ and a stages-physical activation at a temperature of 800°C flowed with CO₂ gas at a heating rate of 10°C·min⁻¹. The stages-carbonization is carried out for water removal or dehydration, evaporation of cellulose, lignin, hemicellulose, and carbon purification. The next process, the carbon electrode is neutralized using aquades and dried at 110°C. The scheme for making carbon electrodes from Veitchia Merilli seed waste can be seen in Figure 1.

Thermogravimetry characterization using the Shimadzu TGA-50 instrument at a temperature of 600°C with nitrogen gas flowed to determine the thermal resistance temperature of carbon powder from Veitchia Merilli seeds waste. Density measurements were carried out before and after the pyrolysis process. Density measurements were carried out by measuring the diameter and thickness using a digital caliper and the sample mass using a digital scale. X-ray diffraction characterization
using the XRD Shimadzu 700 instrument with a scattering angle of \(2\theta (10^\circ-60^\circ)\) using a Cu k-\(\alpha\) light source and a wavelength of 1.5418.

Electrochemical characterization of supercapacitor cells using the Physics CV UR Rad-Far 5841 tool at a voltage of 1 V with variations in the scanning rate of 1 mV/s, 2 mV/s, 5 mV/s, and 10 mV/s. Manufacture of supercapacitor cells consist of electrodes, electrolytes, separators, and current collectors. The VMS carbon electrode has a diameter of 7 mm and a thickness of 3 mm which is immersed in a sulfuric acid electrolyte solution for two days which is separated by a chicken egg membrane and the charge of the ions will be stored in the current collector.

![Fabrication of carbon electrodes from Veitchia Merili seeds waste](image)

**Figure 1.** Fabrication of carbon electrodes from *Veitchia Merili* seeds waste

3. Results and Discussions

3.1 Thermogravimetry Analysis

Figure 2 shows the mass shrinkage of carbon powder from Veitchia Merilli seeds waste to temperature or the Thermogravimetry (TG) curve and rate of mass shrinkage to temperature or the Differential Thermal Gravimetry (DTG) curve.

![Thermogravimetry characterization results curve (DTG, TG) carbon powder from VMS](image)

**Figure 2.** Thermogravimetry characterization results curve (DTG, TG) carbon powder from VMS
The curve on the dotted line is a Thermogravimetry (TG) graph with 3 times the difference. The first shrinkage occurred at a temperature of 150.0°C with a mass loss percentage of 5.70%, this was due to the evaporation of water vapor in *Veitchia Merilli* seeds. The second shrinkage occurred at a temperature of 350.8°C with a mass loss percentage of 43.86%, this was due to the simultaneous decomposition of lignocellulosic compounds in the biomass. At a temperature of 550.0°C third shrinkage of 59.97% occurred, this was due to the decomposition of the lignin. These results are in accordance with the research of Yang et al (2007) which stated that lignin will undergoes decomposition at a temperature of 150-900°C. Chen et al (2019) stated that hemicellulose will decomposition at a temperature of 200-340°C. Cellulose is thermally degraded at a higher and narrower temperature range than hemicellulose, which is 300-400°C.

The curve with a line is the Differential Thermal Gravimetry (DTG) curve, there is one peak that shows the maximum rate of mass loss occurs at a temperature of 286.5°C with a rate of 0.876 mg/min. At this temperature, cellulose, hemicellulose, and lignin compounds evaporate simultaneously and a high percentage of mass loss occurs. The peak of the DTG curve concludes that the temperature of 286.5°C is the thermal resistance temperature for *Veitchia Merilli* seeds which is used as the resistant temperature in the pyrolysis process.

### 3.2 Density Measurement Analysis

Figure 3a shows the comparison of the density values before and after the pyrolysis process, before the pyrolysis process all samples had an average density of 0.922 gr/cm³. The decrease in density after pyrolysis is due to the evaporation of lignocellulosic compounds during carbonization, such as the release of hydrogen and oxygen in the form of gas, resulting in carbon purification with an open pores structure [11]. The density values after the pyrolysis process of the samples VMS-500, VMS-600 and VMS-700 were 0.611 gr/cm³, 0.591 gr/cm³, and 0.619 gr/cm³, respectively.

![Density graph before and after pyrolysis](image_url)

**Figure 3a.** Density value of carbon electrode VMS, b. Density shrinkage of carbon electrode VMS.

Figure 3b shows the density shrinkage that occurs at the VMS-500, VMS-600 and VMS-700 carbon electrodes after the pyrolysis process is 33.383%, 37.326% and 31.564%, respectively. The highest density shrinkage occurred in VMS-600, which was 37.326%, this happened because the higher carbonization temperature, the oxygen, hydrogen and carbon bonds become weak, this makes it easy for nitrogen gas (N2) to release oxygen and hydrogen to be released from carbon. This reaction caused by the reduction of oxygen and hydrogen in the carbon electrode so that mass shrinkage occurs. The electrodes on VMS-700 experienced smaller shrinkage compared to VMS-600, this is because the higher the carbonization temperature will damage the carbon electrode caused by the excessive deossation process[7]. The carbonization temperature of 600°C is temperature optimum to get a low density value so that a high porosity value is obtained at the *Veitchia Merilli* seeds carbon electrode.
3.3 Microstructure Analysis
The result of X-ray diffraction pattern in Figure 4 shows that the carbon electrode of the *Veitchia Merilli* seeds has an amorphous structure, this is indicated by the hkl (002) and (100) planes which are located at an angle of 2θ around 24°-44. The sloping peak shape shows the amorphous structure of the biomass material [12].

![X-ray diffraction pattern of carbon electrode VMS](image)

Figure 4. X-ray diffraction pattern of carbon electrode VMS

The N_p value in Table 1 indicates the number of layers on the electrode carbon. VMS-600 has the highest N_p value of 4.137. The highest L_c value is owned by VMS-600 of 15.069Å, while the lowest L_c value is owned by VMS-700 of 8.96Å. The larger surface area of the electrode carbon, the greater the L_c [13]. According to [14] a high L_c value indicates a large aspect ratio (L_c/L_a), meaning that the greater the L_c/L_a value, the higher the surface area. Carbon electrode structure shrinkage regularly causes high Lc and Np values so that the gap between crystals gets wider which causes an increase in surface area. [15].

| Sample Code | 2θ (002) | 2θ (100) | d_(002) (Å) | d_(100) (Å) | L_a (Å) | L_c (Å) | L_c/L_a | N_p |
|-------------|----------|----------|-------------|-------------|---------|---------|---------|-----|
| VMS-500     | 24,146   | 44,932   | 3,683       | 2,016       | 15,836  | 9,036   | 0,570   | 2,454|
| VMS-600     | 24,414   | 46,441   | 3,643       | 1,952       | 4,025   | 15,069  | 3,744   | 4,137|
| VMS-700     | 23,524   | 45,685   | 3,778       | 1,984       | 17,925  | 8,960   | 0,500   | 2,373|

3.4 Cyclic Voltammetry Analysis
The resulting voltammogram curve is shaped like a rectangular which is a typical EDLC with good performance. Charging and discharge current can affect the width of the curve formed, this is because the larger the charging current curve, the wider the discharge current curve, so the specific capacitance value produced is higher [16]. Figure 5a show that red curve is the curve that has the largest area of the VMS-600 sample. Table 2 shows that the optimum specific capacitance value of supercapacitor cells with carbon electrodes from *Veitchia Merilli* seed waste is owned by the VMS-600 sample of 210,442 F/g. VMS-600 has the highest number of layers and density shrinkage with the highest percentage, so that more pores on the carbon electrode are formed and has a great opportunity to accommodate more anions and cations in the charging and discharging process. The more ions trapped...
in the pores, the higher the specific capacitance value in the supercapacitor cell. While the carbon electrode pores that are not filled with ions will produce a small current curve and produce a low specific capacitance value [17].

| Sample Code | Ic (A)   | Id (A)   | Csp (F/g) |
|-------------|---------|---------|-----------|
| VMS-500     | 0.000557| -0.00054| 155.042   |
| VMS-600     | 0.001299| -0.00108| 210.442   |
| VMS-700     | 0.000411| -0.00034| 99.733    |

Figure 5b shows a cyclic voltammogram with different scan rates of 1 mV/s, 2 mV/s, 5 mV/s and 10 mV/s on the VMS-600 sample. The scan rate is greatly affected the shape of the voltammogram curve and the specific capacitance value obtained, the higher the scan rate value, the lower the specific capacitance value. At a scan rate of 1 mV/s with a voltage of 0-1000 mV it will take 1000 seconds for the electrolyte ions to enter the pores of the carbon electrode completely, while for a scan rate of 10 mV/s with the same voltage it will take 100 seconds for ions electrolyte ions enter the pores of the carbon electrode completely, so it is clear that there is a difference in the time for the ions to enter the electrode pores between giving a small scan rate and a large scan rate. The low scan rate causes the ions to have a long time to diffuse to the meso and micro pores of the carbon electrode. On the other hand, if the scan rate is high, the ions will only reach the macro pores [18]. Figure 5c shows the effect of the scanning rate on the specific capacitance value at each carbon electrode, the greater the scan rate value, the smaller the specific capacitance value, the highest specific capacitance value was obtained at the VMS-600 electrode at a scanning rate of 1 mV/s.

![Figure 5](image-url)
4. Conclusion

Veitchia Merilli seeds have the potential to be used as electrodes for supercapacitor cells by varying the carbonization temperature. Veitchia Merilli seeds are the first biomass waste reported as a raw material for making carbon electrodes without template methods, composites and the addition of other synthetic materials. The results showed that the thermal resistance temperature of the carbon powder was 287°C which was used as the thermal resistance temperature in the pyrolysis process. The lowest density value occurs in the VMS-600 sample of 0.591 gr/cm^3 and Microstructure analysis shows that the carbon electrode is amorphous which is characterized by the presence of two sloping peaks at an angle of 20 around 24º and 44º with the highest Lc value of 15.069 nm, with the highest specific capacitance value of the supercapacitor cell of 210,442 F/g.

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