Activated Carbons (AC) Prepared by Direct CO\textsubscript{2} Activation of\textit{ Parsea Americana} seeds Biomass for Supercapacitor Electrodes

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Abstract. Biomass converted into activated carbon (AC) by using physical activation method can form micro-meso pore structure and maintain the interconnected natural pore network of biomass. AC is prepared from the biomass of \textit{Parsea Americana} seeds (PAS) through a process of pre-carbonization, chemical activation, carbonization and physical activation which is activated at temperatures of 700˚C, 800˚C, and 900˚C. Characterization of physical properties of AC electrodes consisted of X-ray diffraction, Scanning Electron Microscope-Energy Dispersive X-ray and characterization of electrochemical properties of supercapacitor cells using Cyclic Voltametry. The results showed that the microstructure of the AC electrode has a semicrystalline structure characterized by the presence of two sloping peaks at an angle of 20 around 24˚ and 44˚ which corresponded to the hkl (002) and (100) planes, where the lowest Lc value was produced by the PAS-900 sample. The PAS-900 sample had aggregates or lumps with smaller size in small amounts in the presence of micro-mesopores and had the highest carbon content of 94.50% with the highest capacitance value of 203.12 F/g. The temperature of 900˚C is the best activation temperature in the process of manufacture AC electrodes from \textit{Parsea Americana} seeds biomass for supercapacitor cell applications.

1. Introduction
Electrochemical energy storage devices have attracted considerable attention due to the rapid development of sustainable energy and environmental pollution caused by excessive consumption of fossil fuels [1]. Supercapacitors are one of the sustainable energy storages that have the characteristics of high power density, fast charge and discharge rates, and long cycle life that can be applied to potential in hybrid electric vehicles, stand-by power systems, and portable electronic devices [2]. Currently, Carbon is the most widely used electrode material for supercapacitors due to its excellent thermal and chemical stability, high electronic conductivity, large specific surface area, and the structure can be maintained. Various carbon materials such as activated carbon [3], carbon nanotube [4], graphene [5], and carbon sheet [6].

Activated carbon (AC) is the main choice and is often used for supercapacitor cell electrode materials. Activated carbon has a high surface area, abundant raw material availability, relatively cheap price, and easy to obtain [7]. The raw material for making activated carbon comes from biomass waste. Biomass is a renewable organic compound in the form of waste from biological resources which includes grass, wood, agricultural or plantation waste, forest waste, and others. Activated
carbon can be made from a variety of biomass such as *Eucalyptus globulus* seeds [8], *Dautra metel* seed [7], *Polyalthia longifolia* seeds [9], *Xanthoceras sorbifolia* seeds [10] and *Wisteria sinensis* seeds [3]. In this research using biomass derived from *Parsea Americana* seeds.

*Parsea americana* (Avocado) is a fruit that is in great demand by the people of Indonesia. In general, *Parsea americana* have a thick yellowish green flesh with a brownish center seed [11]. People use *Parsea americana* on the flesh part used as a beauty, health, food, beverage and other products. *Parsea americana* seeds have not been used optimally, so there are still many *Parsea americana* seeds that are wasted and are considered as waste. One of the largest *Parsea americana* producing countries in the world is Indonesia, so it can increase the production of *Parsea americana* seed waste. *Parsea americana* seeds have the potential to be used as activated carbon for supercapacitor cell applications because it has a high enough carbon content.

Activated carbon (AC) was prepared from the biomass of *Parsea Americana* seeds using the physical activation method. Physical activation is an efficient method for producing porous carbon materials and non-corrosive. Physical activation has the main reagents, namely carbon dioxide, steam, and air. Carbon dioxide and steam usually have activation temperatures in the range of 700°C to 1000°C, while air has a lower activation temperature in the range of 350°C and 550°C [12 13]. Physical activation using CO₂ can form a meso-micro pore structure and also maintain the interconnected natural pore network of the biomass. The main objective of this research was to determine the effect of CO₂ activation on the physical properties of carbon electrodes and the electrochemical properties of supercapacitor cells.

Previous research [14] manufacture activated carbon electrodes from Hybrid willow biomass with CO₂ activation temperature variations of 700°C, 750°C and 800°C, obtain the optimum specific capacitance value at a temperature of 800°C that is 92.7 F/g. Researcher [15] also manufacture activated carbon electrodes from Pine cone biomass with CO₂ activation temperature variations of 800°C and 900°C, obtain the optimum specific capacitance value at a temperature of 800°C which is 87 F/g. Researcher [16] also manufacture activated carbon electrodes from Walnut shells biomass with CO₂ activation temperature variations of 400°C, 500°C and 600°C, obtain the optimum specific capacitance value at a temperature of 500°C which is 76.89 F/g. In this research, the manufacture of activated carbon electrodes from *Parsea Americana* seeds biomass with CO₂ activation temperature variations of 700°C, 800°C, and 900°C.

2. Materials and Methods

*Parsea Americana* seeds as the basic material for manufacture AC electrodes are synthesized through a pre-carbonization process, chemical activation using 0.1M KOH activating agent. Subsequently, pellets were molded using a hydraulic press to produce activated carbon monoliths. The carbonization process at a temperature of 600°C under nitrogen gas flows at a heating rate of 3°C/minute for 1 hour. The physical activation process was activated at a temperature of 700°C, 800°C, and 900°C under carbon dioxide gas flow at a heating rate of 10°C/min for 2.5 hour. Physical activation aims to form micro-meso pore structure and also maintain the interconnected natural pore network of the biomass. The next process, the AC electrodes was neutralized using aquadest and dried at 110°C. The scheme for manufacture AC electrodes from *Parsea Americana* seeds biomass can be seen in Figure 1.

Characterization of the physical properties of AC electrodes consists of X-ray Diffraction and Scanning Electron Microscopy-Energy Dispersive Spectroscopy. X-ray diffraction to determine the crystallinity of AC electrodes using the XRD Shimadzu 700 instrument with a scattering angle of 2θ using a Cu k-α ray source and a wavelength of 1.5418 Å. Scanning Electron Microscopy to determine the surface morphology and pore distribution of AC electrodes using the instrument SEM, JEOL JSM-6510 LA and Energy Dispersive Spectroscopy to determine the elemental content of AC electrodes using the instrument EDX, JEOL JSM-6510 LA.

Characterization of electrochemical properties of supercapacitor cells using cyclic voltammetry method to determine the specific capacitance of AC electrodes. Cyclic Voltammetry was carried out using the Physics CV UR Rad-Far 5841 tool. The cyclic voltammetry measurement was carried out by
making supercapacitor cells using stainless Steel, chicken egg shell membrane, PAS AC electrodes and 1M H2SO4. Specific capacitance is measured from potential 0 to 1000 mV with a scan rate of 1 mV/s, 2 mV/s, 5 mV/s and produces a current and voltage density relationship curve.

Figure 1. The schematic illustration for the synthesis of activated carbon derived from *Parsea Americana* seeds

3. Results and Discussions

3.1 X-Ray Diffraction Analysis

Figure 2. X-Ray diffraction pattern of sample PAS
The microstructure of AC electrodes for all PAS samples showed the same diffraction pattern in semicrystalline form characterized by the presence of two sloping peaks at $2\theta$ angles around 24˚ and 44˚ which corresponded to the (002) and (100) hkl planes [17]. In Figure 2 there is a sharp peak indicating the presence of crystalline elements at the carbon electrode such as MgO$_2$ and CaCO$_3$. MgO$_2$ elements were found at angle of 37˚ (JCPDS No. 89-7746) and the compound CaCO$_3$ found at angles of 39˚ (JCPDS No.82-1690) [18]. The presence of these elements in small percentages at the carbon electrode because this element is the basic element of every biomass including *Parsea Americana* seeds [19].

| Sample Code | 2θ (200) | 2θ (100) | $d_{002}$ (nm) | $d_{100}$ (nm) | $L_a$ (nm) | $L_c$ (nm) |
|-------------|----------|----------|----------------|---------------|------------|------------|
| PAS-700     | 23,81    | 44,03    | 3.73           | 2.05          | 99.41      | 13.34      |
| PAS-800     | 23.05    | 44,01    | 3.70           | 2.05          | 47.08      | 11.04      |
| PAS-900     | 24.56    | 44,06    | 3.62           | 2.05          | 44.40      | 9.80       |

The microcrystalline dimensions can be calculated using the Debye Scherrer equation. Table 1 shows that the lowest $L_c$ value is owned by the PAS-900 sample of 9.80 nm and the highest $L_c$ value is owned by the PAS-700 sample of 13.34 nm. The value of $L_c$ very influential on the surface area of the carbon electrode based on the empirical formula $SSA_{xrd}=\frac{2}{\rho_{xrd}L_c}$, where $\rho_{xrd}$ is obtained from the formula $\rho_{xrd}=\frac{d_{002}(\text{graphite})}{d_{002}(\text{sample})}\rho_{\text{graphite}}$. The $\rho_{\text{graphite}}$ and $\rho_{\text{grafit}}$ value are 0.33354 nm and 2.268 gr/cm$^3$ respectively [20, 21]. Based on this formula, the lowest $L_c$ value indicates a large surface area for carbon electrodes.

### 3.2 Scanning Electron Microscope-Energy Dispersive X-ray Analysis

**Figure 3.** The SEM images of AC electrode with magnification of 5000x (a) PAS-700°C, (b) PAS-800°C, (c) PAS-900°C, The SEM images of AC electrodes with magnification of 40.000x (d) PAS-700°C, (e) PAS-800°C, (f) PAS-900°C

The Scanning Electron Microscope characterization aims to determine the morphological structure and pore distribution of AC electrodes at different activation temperatures using a low resolution
magnification of 5μm (Figure 3a-c) and a high resolution of 0.5μm (Figure 3d-f). The SEM micrograph in Figure 3 (a-f) shows that the AC electrode consists of aggregates or lumps formed during the activation process [14]. In addition, the irregular structure of carbon particles in all samples is in agreement with XRD analysis. Figure 3a,d shows the SEM micrograph PAS-700 which has aggregates or lumps of different sizes with the presence of micropores. The PAS-800 sample also had aggregates or lumps of different sizes with the presence of mesopores. The PAS-900 sample had aggregates or lumps with smaller size in small amounts in the presence of micro-mesopores. This indicates that the activation reaction, which is essentially the gasification of biochar in carbon dioxide, is not the main reaction at temperatures above 700°C. The endothermic Boudouard reaction (carbon reacts with carbon dioxide and produces carbon monoxide) reaches equilibrium at a temperature of about 900°C. At this temperature, the sample yield did not change significantly after 150 minute of thermal processing. However, with increasing temperature up to 700°C-900°C, the reaction can increase the production of carbon monoxide and cause an increase in pore diameter, formation of new pores and an increase in surface area. The Boudouard reaction considers carbon as pure carbon, while the precursors of biomass and biochar in this research were composed of carbon and oxygen [22].

![Figure 3. The EDX image of AC electrode (a) PAS-650, (b) PAS-750, (c) PAS-850](image)

EDX characterization aims to determine the content of chemical elements contained in AC electrodes. AC electrodes have a percentage content of the elements carbon (C) and Oxygen (O2). The oxygen element is formed due to the use of CO₂ during the physical activation process which results in bonds between the carbon and oxygen elements through the gasification and Boudouard reactions as shown in equations 1 and 2 [14]. Figure 4 shows the sharpest peak possessed by the element carbon, so that the element carbon is the element that dominates the other elements in each sample. The carbon electrode which has the highest carbon element is owned by PAS-900 with a percentage value of 94.50% so that it can improve the performance of the supercapacitor [8].
\[ C(s) + CO_2(g) \rightarrow 2CO(g) \]  
\[ CO_2(g) + C(s) \rightleftharpoons 2CO(g) \]  

Table 2 shows the elemental content of the PAS-700, PAS-800 and PAS-900 samples which were activated at different temperatures of 700°C, 800°C, and 900°C. In general, all samples consist of domination carbon content and some oxygen content. The PAS-700 sample contains less carbon and more oxygen than the other samples due to the gasification reaction of biochar in carbon dioxide at temperatures below 700°C. Increased activation temperature can cause a occurred Boudouard reaction resulting in more carbon content and less oxygen content [16].

**Table 2. Elemental analysis of the samples**

| Elements (%) | Samples | PAS-700 | PAS-800 | PAS-900 |
|-------------|---------|---------|---------|---------|
| Weight (%)  | Atom (%) | Weight (%) | Atom (%) | Weight (%) | Atom (%) |
| Carbon      | 92.31   | 94.12   | 92.33   | 94.13   | 92.80   | 94.50   |
| Oxygen      | 7.69    | 5.88    | 7.67    | 5.87    | 7.20    | 5.50    |
| Total       | 100%    |         |         |         |         |         |

### 3.3 Cyclic Voltametric Analysis

**Figure 5.** a) Cyclic Voltametry curve of sample PAS b) Cyclic Voltametry curve of PAS-900 at different scan rate c) specific capacitance vs scan rate of sample PAS
Figure 5a shows the cyclic voltammetric curve of the PAS sample for each activation temperature variation using a scan rate of 1 mV/s at the same potential. The CV curve of all samples has a relatively regular shape and is shaped like a rectangle which is a characteristic of EDLC supercapacitors [24]. The curve area of the PAS-900 sample is larger than that of the other two samples, indicating a higher specific capacitance. A larger area of the curve indicates a large charge and discharge current due to the large amount of charge of the electrolyte ions accumulating on the surface of the carbon electrode.

| Sample Code | Ic (A)   | Id (A)   | Csp (F/g) |
|-------------|----------|----------|-----------|
| PAS-700     | 0.000466 | -0.00004 | 50.68     |
| PAS-800     | 0.000653 | -0.00044 | 172.53    |
| PAS-900     | 0.001015 | -0.00061 | 203.12    |

Table 3 shows that the specific capacitance of PAS-900 has the highest capacitance among the other samples due to the increase in the physical activation temperature. Increasing activation temperature will produce micro-meso pores, increase the pore volume and surface area caused by the Boudouard reaction rapidly and stably. The PAS-900 sample has the largest specific surface area and pore volume consisting of micro-meso pores so that the charge accumulation in the EDLC is more or has a large capacity than other samples [14]. Micro-pores function as a storage medium for electrolyte ions and meso-pores function as a diffusion medium for electrolytic ions. AC electrode which has a combination of micro-meso pores can improve the performance of the supercapacitor [23].

Figure 5b shows the curve of cyclic voltammogram sample-900 with various scan rates of 1mV/s, 2 mV/s and 5mV/s. The scan rate can affect the specific capacitance value obtained. Figure 5c shows that the smaller the scan rate used, the greater the capacitance value obtained for each sample. This is because the low scan rate can make the ions diffuse at a very slow speed so that it takes a long time to accumulate charge on the surface of the carbon electrode so that it produce a large amount of charge. The high scan rate can make the ions diffuse at a very fast speed so that it takes a fast time to accumulate charge on the surface of the carbon electrode so that it produces a small amount of charge [24].

4. Conclusion

Parsea Americana seeds has the potential to be used as AC electrodes for supercapacitor cell applications with CO₂ activation temperature variations. Parsea Americana seeds are the first biomass waste reported as a source for the manufacture of AC electrodes without adhesive and chemical doping. The results showed that the microstructure of the AC electrode had a semicrystalline structure characterized by the presence of two sloping peaks at an angle of 26 around 24° and 44° which corresponded to the hkl (002) and (100) planes, where the lowest Lc value was produced by the PAS-900 sample. The PAS-900 sample had aggregates or lumps with smaller size in small amounts in the presence of micro-mesopores, and had the highest carbon content of 94.50% with the highest capacitance value of 203.12 F/g.

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