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Nano Carbon Produced by Advanced Mild Hydrothermal Process of Oil Palm Biomass for Supercapacitor Material

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Abstract. Palm oil waste is an abundant biomass resource in Indonesia that is not well utilized as a raw material for producing high value-added materials. One product that is possible to be manufactured from oil palm biomass is activated nano carbon. Characteristics of high porosity and good conductivity will lead the activated nano carbon suitable as an electrode of supercapacitor material. Preparation of activated nano carbon is conducted by two main steps namely carbonization and activation. In this research, carbonization is done by hydrothermal process while activation is done by physico-chemical activation. This study focused on manufacturing activated nano carbon from empty fruit bunches of oil palm with hydrothermal carbonization for supercapacitor applications. The activation of mesopore area of the carbon has been taken place by using $ZnCl_2$ and $CaCl_2$ as a chemical activating agent during the hydrothermal process. The activated nano carbon produced from empty fruit bunches has a surface area of 41-1571 m^2/g and a pore size of 2.0–6.8 nm. In this study activated nano carbon is used as a working electrode in symmetric hybrid supercapacitor.

1. Introduction

Indonesia is one of the largest palm oil producer in the world with palm oil production reaches 31 million tons in 2015. The produced of palm oil is also produced a high amount of palm oil waste. One product that is possible to be manufactured from oil palm biomass is activated nano carbon. Activated nano carbon is an amorphous carbon material with high degree of porosity and an extended surface area [1]. Activated nano carbon preparations from wastes is vital for the regional economy when products of high value are obtained from low cost materials. These bring about the solution to problem of waste management [2]. Activated carbon is usually used as an adsorbent, energy storage application, synthesis carbon, catalyst support, etc [3]. One of interesting energy storage application is supercapacitor. Porous carbons are used as electrode material in supercapacitor because of high electrical conductivity, low cost and commercially available [4]. The pore size of activated nano carbon which is suitable for capacitor electrode is in the mesopore range (2-50 nm) [5]. Different raw material type and activation procedure has an important role in the physico-chemical characteristics of activated carbon e.g. surface area, porosity, and pore distribution, and surface functional groups which are all important properties for supports [6].

Preparation of activated nano carbon is conducted by two main steps namely carbonization and activation. The carbonization process is commonly conducted by pyrolysis method by heating the raw material at temperature range 300-600 °C in the total absence of oxygen condition and decomposes biomass into gas, liquid (bio-oil) and solid (bio-char). Another carbonization process which can be used



is a hydrothermal method. Hydrothermal carbonization (HTC) is a thermo-chemical process for recovery and valorization of biomass and organic waste that uses sub-critical liquid water as a reaction medium at mild temperature (180-250 °C) for converting feedstock into value added products [7]. The advantage of the hydrothermal process due to it used lower energy than pyrolysis process because the operation temperature is lower than pyrolysis process [8]. Study on activated nano carbon synthesis using biomass precursors has been done previously. Laginhas et al. (2016) have made activated carbon from chitosan by hydrothermal treatment at a temperature of 200 °C with surface area of about 852 m²/g. This research focused on manufacturing activated nano carbon from empty fruit bunches of oil palm with hydrothermal carbonization for supercapacitor applications by adding pre-treatment deashing raw material.

2. Experimental

2.1. Materials

Empty fruit bunch (EFB) was chosen as biomass samples. The sample was gathered from PT. Perkebunan Nusantara VIII in Bogor. EFB was cleaned using water and dried. After that, dried biomass is crushed using disc mill and sieved into coarse granules (35-80 mesh). The sample has been subjected to two different types of treatments in this study. The pretreatment processes are deashing and without deashing raw material. The pretreatment is leaching with 1M HF solution for an hour [9]. The samples were filtered off and washed with distilled water. The process of washing was continued until the wash-water remained neutral. Finally, the samples were dried at 105 °C in oven. Zinc chloride and calcium chloride was used as chemical activating agent.

2.2. Hydrothermal

EFB with the specification ratio of biomass to water (1:3, 10 g biomass in 30 mL water) was fed into hydrothermal reactors containing water mixed with activating agent. The ratio of activating agent to the biomass was 2:1. The samples were held at the desired temperature (225, 250 and 275 °C) for 60 min. The obtained biochar was then filtered and dried at 105 °C for 24 hours.

2.3. Activation

The biochar which recovered from hydrothermal process loaded onto crucible and positioned inside the tubular furnace. The temperature was ramped to 800 °C at a rate of 10 °C/min under nitrogen atmosphere at a flow rate of 50 mL/min. After the temperature was reached, N₂ was replaced by CO₂ at a flow rate of 40 mL/min for two hours. Afterwards the furnace was cooled to room temperature in the presence of N₂. The product was added with HCl solution 0,1M and stirred for 30 minutes, then washed with demineralized water until rinsed water remained neutral. The product was dried at 105°C for 24 hours to obtained activated nano carbon.

2.4. Characterizations

Ash content of EFB determined by gravimetric analysis. FTIR analysis was conducted to get the qualitative and quantitative estimation of OFGs. The morphology of raw material and product was obtained by SEM. The surface area and pore diameter of activated nano carbon were calculated by applying the Brunauer-Emmet-Teller (BET) model using a gas sorption Quantochrome Instruments Nova 3200e.

Samples treated with chemicals used were named as AC-ZnCl₂ (activated nano carbon with ZnCl₂ as activating agent) and AC-CaCl₂ (activated nano carbon with CaCl₂ as activating agent).

2.5. Electrochemical Characterizations

The electrochemical analysis was conducted to observed activated nano carbon performance as a supercapacitor cell. Cyclic voltammetry, galvanostatic charge/discharge, and electrochemical

impedance spectroscopy were examined using Gamry V3000. Electrochemical analysis was performed by assembling in a symmetrical two-electrode configuration. The working electrodes were prepared from activated nano carbon which placed in 1 cm² of stainless steel mesh. Nafion 212 was sandwiched between two electrodes and then infiltrated with electrolyte solution (6 M KOH).

3. Results and Discussion

3.1. Effect of deashing treatments on empty fruit bunch-sample analysis

The proximate analysis of empty fruit bunch are reported in Table 1. Based on Table 1, it was the common characteristic of empty fruit bunch that growth in Indonesia.

Table 1. Proximate analysis of empty fruit bunch (EFB)

Sample	Moisture (wt%)	Volatile matter (wt%)	Fixed carbon (wt%)	Ash (wt%)
EFB	5.47	73.17	17,17	4.19

Fixed carbon and volatile matter content in empty fruit bunch is high so that this biomass suitable as a precursor material for activated nano carbon [10]. The deashing treatments is associated with the mass reduction in the original biomass feedstock. The ash-forming mineral content in biomass is removed by the use of a strong acid catalyst [11]. The percentage ash in the untreated and the treated EFB are presented in Table 2. It shows that treatment with HF can decrease the ash levels about 40%.

Table 2. Percentage of ash in treated EFB

	Untreated EFB (%)	Treated EFB (%)
Ash	4.19	2.86

3.2. Effect of hydrothermal treatment temperature

Table 3 shows the result of mass yield of activated nano carbon after hydrothermal carbonization and activation process. From Table 3, mass yield of activated nano carbon increase when temperature during hydrothermal increase from 225 °C to 275 °C.

Table 3. Mass yield of activated nano carbon

Activating agent	Mass yield of AC untreated EFB (g)			Mass yield of AC treated EFB (g)		
	225 °C	250 °C	275 °C	225 °C	250 °C	275 °C
ZnCl ₂	8.857	8.940	9.594	9.110	9.588	9.808
CaCl ₂	7.362	7.560	7.981	8.179	8.335	8.933

Higher temperature leads to extensive dehydration and an increase in the degree of condensation of the biochar. The effect of hydrothermal carbonization temperature (225, 250 and 275 °C) on the formation of OFG on EFB based biochar was observed that irrespective of temperature employed there was an increase in the OFG content in biochar compared to raw material [12].

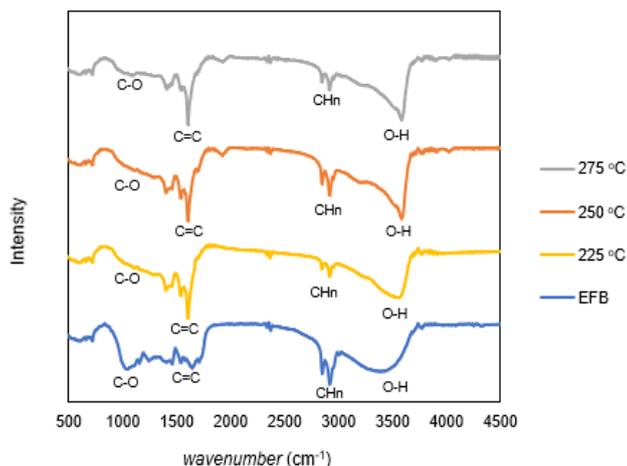


Figure 1. FT-IR spectrum of empty fruit bunch and biochar

Figure 1 shows FTIR spectrum from EFB and biochar. The peak around 1600 cm^{-1} attribute to aromatic groups (lignin and aromatic groups) which is formed during carbonization [13] where the intensity of bonds is not much different for the three samples. The intensity of OH-bonds decreased after the hydrothermal process. It is due to dehydration of biomass occurred so that water molecules within the biomass removed [14]. The intensity of the peak which is around $\sim 3500\text{ cm}^{-1}$ shows stretching vibration of OH-bonds (alcohol, phenol, and carboxyl groups).

3.3. Scanning Electron Microscopy (SEM) and BET Surface Area

Figure 2 shows the morphology of EFB and activated nano carbon after hydrothermal carbonization and activation process. Figure 2a indicate that EFB have a rough surface and closed pores. More pores are opened on EFB structure creating holes along the EFB surface, so that enhanced the porosity and the surface area of activated nano carbon.

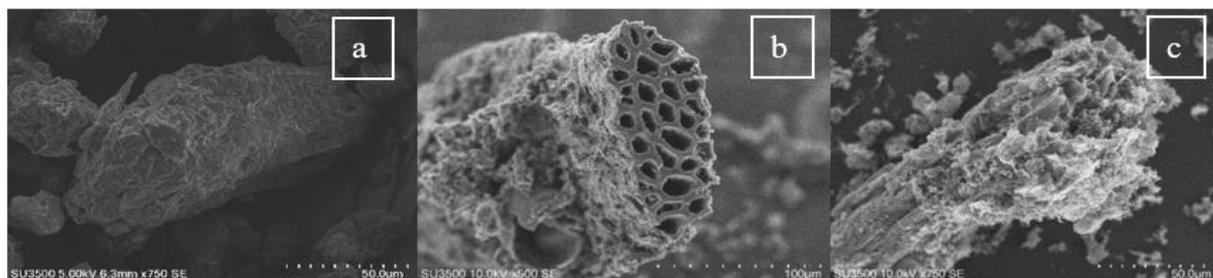


Figure 2. SEM result of (a) empty fruit bunch, (b) AC-ZnCl₂, and (c) AC-CaCl₂

The BET surface area of activated nano carbon which is produced at different process parameters is shown in Table 4. The surface area of activated nano carbon sample increase when temperature increase from $225\text{ }^{\circ}\text{C}$ to $275\text{ }^{\circ}\text{C}$. This may happen because some pores which are formed by the decomposition of organic components in materials increase when temperature of the hydrothermal process is increase. AC-ZnCl₂ shows the highest BET surface area. This is due to more effective dehydration in the addition of ZnCl₂ giving rise to higher OFG content and better activation. Likewise, ZnCl₂ which acts as an activating agent removes the oxygen and hydrogen content in biomass by forming water and could enhance the porosity of the material [15].

Table 4. Surface area of activated nano carbon

Activating agent	BET Surface area untreated EFB (m ² /g)			BET Surface area treated EFB (m ² /g)		
	225 °C	250 °C	275 °C	225 °C	250 °C	275 °C
ZnCl ₂	740	1048	1229	1006	1240	1571
CaCl ₂	41	406	528	268	454	723

Surface area of activated nano carbon which produced with treated EFB is higher than activated nano carbon which produced with untreated EFB. The treatment with HF is more effective to remove some of the ashes contained in EFB, because HF is known to be effective to remove compounds such as carbonates, oxides and silica [16]. Average pore size diameter of activated nano carbon shown in Table 5.

Table 5. Activated nano carbon pore size

Activating agent	Average pore size untreated EFB (nm)			Average pore size area treated EFB (nm)		
	225 °C	250 °C	275 °C	225 °C	250 °C	275 °C
ZnCl ₂	2.18	2.01	2.50	2.63	2.94	2.13
CaCl ₂	2.88	2.79	4.97	6.81	5.53	5.63

The AC-CaCl₂ has bigger pore size than AC-ZnCl₂. The contact between activating agent and EFB is more intense and resulted the porosity of the activated nano carbon enhanced. Activating agent to the raw material ratio which is used in this research drive the micropore formation and pore widening simultaneously. Even though activated nano carbon has mesoporous size, it close to micropore size [17]. The different activating agent is used for activated nano carbon manufacturing has also affected the character of activated nano carbon characteristics [18].

3.4. Electrochemical characterization

Electrochemical analysis was performed to analyze the performance of activated nano carbon while was applied in supercapacitor cell. Figure 3a shows the voltammogram has a tendency to form a slope and not in rectangular shape, that indicates charging-discharging process through high resistance inside the supercapacitor cell [19]. Furthermore, from the voltammogram was suspected that corrosion reaction occurred in electrode due to the dielectric material used was too thin.

Figure 3b shows galvanostatic charge/discharge of activated nano carbon has a triangle and symmetric shape which indicate the supercapacitor cell has good capacitive performance [20]. This result shows that the capacitance of supercapacitor cells made from AC-CaCl₂ is greater than AC-ZnCl₂ which is suitable with the results from calculations performed by cyclic voltammetry (CV) analysis

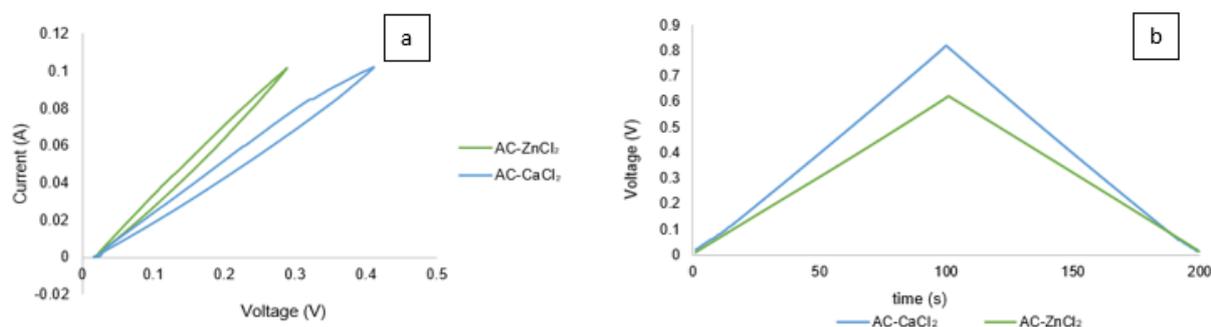


Figure 3. (a) Cyclic voltammogram and (b) Galvanostatic charge/discharge diagram

The specific capacitance of the produced activated nano carbon can be calculated from voltammogram according to the following Equation (1): [21]

$$C = \frac{\sum |I| \cdot \Delta t}{m \Delta V} \quad (1)$$

with $\sum |I| \cdot \Delta t$ is the area of the current $|I|$ (A) against time (s); m (g) is the mass of active material in the electrode; and ΔV (V) is the potential window.

Table 6. Specific capacitance of activated nano carbon electrode

Material	Capacitance (F/g)
AC-ZnCl ₂	2.452
AC-CaCl ₂	4.305

The results of specific capacitance in Table 6 show that the specific capacitance of AC-CaCl₂ electrode is greater than AC-ZnCl₂ electrode. The results show the contradiction to the average pore size of activated nano carbon. The capacitance is not affected by the surface area of materials. The lower specific capacitance could be caused due to imperfect interphase connection, cell resistance and cell sealing system not optimal [22]. This imperfect cell sealing system could cause the presence of reactive and unstable oxygen functional groups which can interfere the ion transfer process [23]. In addition, side reactions between carbon, electrolyte and impurities could also decrease cell capacitance [24].

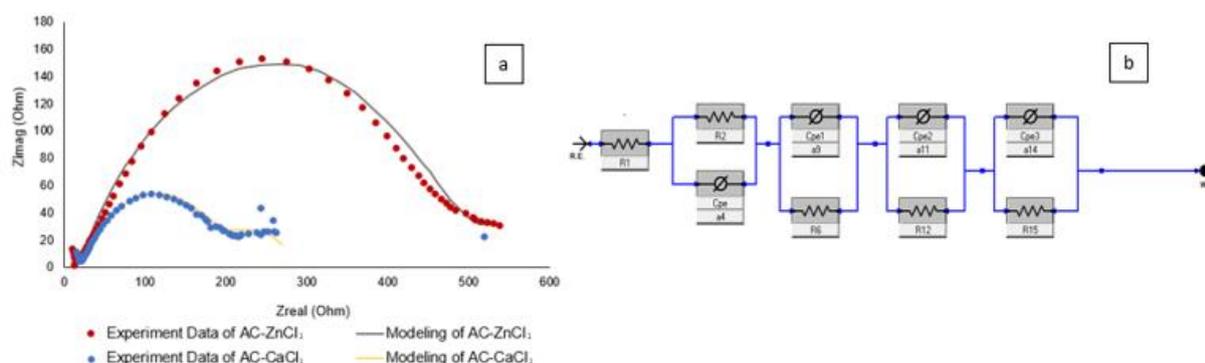


Figure 4. (a) Nyquist Curve and (b) Equivalent circuit of Supercapacitor from activated nano carbon

The result of EIS analysis is represented in a Nyquist curve which is modelled with equivalent circuits to obtain the impedance value of the supercapacitor cell. Figure 4a and Figure 4b show the Nyquist curve and equivalent circuit, respectively.

The Nyquist curve of activated nano carbon supercapacitor has two semicircle curve which indicates cell impedance is affected by charge transfer and mass transfer.

Table 7. Impedance parameters of carbon electrode

Parameter	Value	Unit	Parameter	Value	Unit
R1	1.13×10^{-1}	Ohm	Cpe2	5.55×10^{-4}	S*s ^a
R2	19.04	Ohm	a11	5.76×10^{-1}	
Cpe	6.80×10^{-8}	S*s ^a	R12	128.3	Ohm
a4	9.83×10^{-1}		Cpe3	2.37×10^{-2}	S*s ^a
R6	57.51	Ohm	a14	6.47×10^{-1}	
Cpe1	3.41×10^{-4}	S*s ^a	R15	80.12	Ohm
a9	8.13×10^{-1}				

Table 7 shows the parameters of the equivalent circuit modelling against the experimental data. Ohmic resistance (R1) is a parameter which is related to the electrolyte resistance. Based on the EIS analysis, the interphase resistance of activated nano carbon supercapacitor causes the capacitance of supercapacitor cell becomes smaller which is suitable with the results from calculations performed by cyclic voltammetry (CV) analysis.

4. Conclusion

Activated nano carbon as an electrode material of supercapacitor can be obtained from palm oil waste through the hydrothermal carbonization and activation process. Increasing temperature during the hydrothermal carbonization process could increase the surface area of activated nano carbon. The capacitance of supercapacitor is 4.305 F/g for activated nano carbon using CaCl₂ as activating agent (AC-CaCl₂).

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