Effect of Activation Methods on the Supercapacitor Performance of Hydrochar Derived from Oil Palm Empty Fruit Bunch

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Abstract. In this study, the activated carbon (AC) derived from oil-palm empty fruit bunches (EFB) for using in effective supercapacitor application was carried out by two main steps namely hydrothermal carbonization and activation with three different activated agents steam, carbon dioxide and potassium hydroxide for increase of the AC’s specific area. The fabricated AC had surface area of 246.9 – 809.7 m²/g which were extremely higher as compared to the non-activated carbon i.e., 1.1 m²/g. It is concluded that the chemically AC afforded the best material and showed the high specific capacitance of 101.1 F/g at the scan rate of 5 mV/s with 1 M Na₂SO₄ as neutral electrolyte over the three-electrode cell. The study revealed that EFB could be considered as a promising potential electrode for supercapacitor.

1. Introduction
In Thailand, one of the main agricultural industry is oil-palm industry covering 8.96 million square meters of farmland which typically generates large quantities of agriculture waste called EFB with the amount of 1.68 million tons in 2019 [1]. In general, it can be used as fuel or fertilizer. However, EFB could be the starting material to produce high value-added product as porous activated carbon and used as working electrode in supercapacitor application which will play the very important role in the future.

The conversion of EFB into activated carbon was done by using EFB char which was obtained via many methods processes i.e., slow pyrolysis and hydrothermal carbonization (HTC) and used the obtained char through chemical activation with activation agents such as KOH, H₃PO₄, H₂SO₄, NaOH and etc., [2] or activated the char in physical activation under CO₂ or vapor, these methods aimed to increase specific surface area and pore volume which directly promoted the capacitancive performance [3]. R. Farma et al. studied about the production of fibers of EFB activated carbon and their electrochemical properties in monoliths form through low temperature carbonization and subsequent KOH activation at a KOH ratio (by weight) of 5% to 95% at 800 °C with residue time of 1-5 h [4], resulting to the increase of BET surface area from 448 to 1,704 m²/g and the high specific capacitance of 149 F/g. Moreover, Dieu HTT et al. had focused on conversion of EFB into AC with carbonization and chemical activation at 850 °C for 2 h, subsequently by Nitrogen-doping and they reported that the highest BET surface area of 2,774 m²/g which could enhance the specific capacitance of 217 F/g [5].
Nevertheless, all of these reports produced AC by carbonization process consuming more energy and power for operation than HTC. This research focuses on converting the EFB into AC through HTC followed by three different methods steam, CO$_2$ and KOH in order to investigate and compare the effect of activation methods. Furthermore, the area of cyclic voltammetry (CV) curve at scan rate of 5 mV/s was used to calculated the specific capacitance ($C_{sp}$).

2. Methodology

2.1 Material
EFB was provided by Suksomboon Palm Oil Co., Ltd, Chonburi Province, Thailand. The EFB were shredded and pre-dried before delivered to the experimental site. Then, the materials were further dried in a hot air oven at the temperature of 105 °C overnight, grinded into power form, and prepared for further experiment. The proximate analysis of EFB consisting in term of moisture, volatile matter, fixed carbon and ash are 2.39, 73.67, 18.68 and 5.26 wt%, respectively. The production of AC was completed in two steps: (i) HTC and (ii) physical or chemical activation in a vertical tubular reactor found in [6]. The schematic showing overall preparation of activated carbon is displayed in Figure 1.

2.2 Hydrochar fabrication
A 1-m$^3$ pilot-scale hydrothermal reactor was utilized to produce hydrochar from EFB. Roughly, 200 kg of EFB was manually added into the reactor from the top. After the reactor was sealed, the saturated steam was injected into the reactor. The treatment condition was 20 bar and 200 °C with the residence time of 30 min. After the process was finished, the steam in the reactor was released. Then, the hydrochar products were removed and the solid-phase products were collected and prepared for further experiment and analysis.

2.3 Activated carbon production

2.3.1 Physical activation. 25 g of washed hydrochar was loaded into the reactor. Then, 0.1 L/min of N$_2$ was fed through the reactor in order to eliminate O$_2$ and prevent the hydrochar from combustion. The reactor was externally heated to 800°C with holding time of 1 h and the heating rate of activation was 10 °C/min. Once the reactor reached the target temperature, 0.1 L/min of steam flow generated by high-temperature autoclave was fed through the reactor. After finishing, the system was cooled down in N$_2$ atmosphere. CO$_2$ was carried out by switching the steam to CO$_2$ with equal flow. The AC products were defined as AC-S (steam) and AC-C (CO$_2$).

2.3.2 Chemical activation. 25 g of hydrochar was immersed in 5M KOH solution with ratio of 1:3 %w/w. The KOH-impregnated hydrochar was stirred for 2 h, centrifuged for solid-liquid separation, and dried for 12 h. For activation process, the activation condition is same as physical activation mentioned above. After the activation was done, the obtained AC was washed and neutralized with distilled water and 3M HCL solution before oven dried at 105 °C for 1 d. The dried sample was ground, sieved, and prepared for further experiment. The obtained oil-palm EFB chemically activated carbon was named as AC-CH.

![Figure 1. Schematic preparation of activated carbon](image-url)
2.4 Characterizations

Proximate analysis was conducted by Simultaneous Thermal Analyzer (STA) Model 449F3. BET surface area of materials was analyzed by Micromeritics ASAP 2020 Surface & Porosity Analyzer. The porosity was examined using adsorption/desorption isotherm. The electrochemical properties of ACs were analyzed using an Autolab-PGSTAT302N in three-electrode cell using 1 M Na$_2$SO$_4$ as electrolyte under room temperature. The working electrode was done by coating well-mixed homogeneous paste which contained 70 wt.% AC, 20 wt.% carbon black and 10 wt.% PVDF dissolved in N-Methyl-2-pyrrolidone (NMP) into nickel foam, and dried for 6 hours at 60 °C in vacuum oven in order to prevent nickel foam from oxidation. Ag/AgCl and Pt wires were applied as the reference electrodes and the counter electrode, respectively. The CV plot of electrodes were operated at a voltage range of 0 to 1 V at scan rates of 5, 10, 20, 50, 70 and 100 mV/s; the galvanostatic charge-discharge GCD curved was examined at current density of 3 A/g.

Electrochemical impedance spectroscopy (EIS) was record in frequency range of 0.1 to 100,000 Hz. The specific capacitance ($C_s$) of examined electrode in the three-electrode cell can be calculated by the area under CV curve as follows:

$$C_s (F/g) = \int \frac{IdV}{mv\Delta V}$$  

where $IdV$: CV curve’s area, $m$: active mass (g), $v$: scan rate (mV/s), and $\Delta V$ is the range of voltage (V).

The yield percentage was calculated thus:

$$\% \text{ Yield} = \frac{M^* \times 100}{M^{**}}$$

Where $M^*$: initial mass of hydrochar and $M^{**}$: mass of the obtain AC in dry basis.

3. Results and discussion

3.1 Effect of activation methods

The result of mass yield of AC for AC-S, AC-C and AC-CH are 22.69, 55.33 and 29.80%, respectively, the activating agents produced different changes in the mass yield of AC. AC-C displayed the highest yield indicating that some volatile substances were remained in the pore which leaded to undergo lower surface area and pore volume. While AC-S and AC-CH showed lower yield as compare to AC-C. As the same activation temperature, both samples were likely to perform higher surface area than AC-C. According to the concentration of 5 M KOH and the ratio of 1:3, higher KOH ratio reduced the carbon yield percentage because of the KOH impregnation destroyed the carbon structure in the micro and nano-scale. [7]

3.2 BET surface area

Although, the steam activation showed lower yield percentage, it could provide the higher BET surface area and total pore volume which was mainly from the macropores in comparison with CO$_2$ activation which mostly created the micropores. Moreover, the average pore size found in CO$_2$ activation appeared wider. KOH was a major key for the formation of pore structure. During the activation, metallic potassium which is not found in physical activation was formed and was in charge of further gasification and released of some gases, i.e., CO$_2$, CO and H$_2$[8]. The textural properties of samples are presented in Table 1.
Table 1. Pore structure parameters of activated carbon

| Sample    | BET Surface Area (m²/g) | t-plot Micropore Area (m²/g) | Total Pore Volume (cm³/g) | Average Pore Diameter (nm) |
|-----------|-------------------------|------------------------------|---------------------------|---------------------------|
| Hydrochar | 1.14                    | 4.00                         | 0.004                     | 10.57                     |
| AC-S      | 388.50                  | 350.63                       | 0.206                     | 4.91                      |
| AC-CO     | 246.90                  | 245.88                       | 0.131                     | 7.91                      |
| AC-CH     | 809.71                  | 511.23                       | 0.526                     | 5.67                      |

Steam and CO₂ activation exhibit the porosity development as well as an increase of the surface area of hydrochar [9]. In comparison to chemical activation at the same temperature, these areas were relatively low at. Likewise, the electrochemical performance discussed in next topic verified that the chemical activation was more appropriate method for AC production from EFB.

The N₂ isotherms are shown in Figure 2. According to BBDT classification, AC-S and AC-C isotherms correspond to type I and H4 loop, indicating that both of them were microporous materials and a slight characterization of mesopore was observed [10]. As a non-activated material, hydrochar exhibited low adsorption/desorption properties. The N₂ adsorption-desorption isotherms of AC-CH displayed the type IV and H3 loop at the range of relative pressure from 0.45 to 0.95, indicating meso/macropores capillary condensation [11].

![Figure 2. adsorption/desorption isotherms of samples](image)

3.3 Electrochemical characterization

The electrochemical performance via CV plots of AC-S, AC-C and AC-CH at scan rate of 100 mV/s in 1M Na₂SO₄ shown in Figure 3a. The current density of AC-CH electrode was obviously higher than AC-S and AC-C electrode, resulting from its high surface area. The all of CV curves displayed no apparent reduction peaks, specifying that all of them were normal electric double layer capacitance (EDLC) electrode materials [12]. In comparison to AC-S and AC-C, the integral area of AC-CH was extremely larger and its shape was more rectangular indicating a better capacitance performance while the CV of AC-S and AC-C electrode exhibited an irregular and resistive voltammogram which was due to the appearance of many impurities. Figure 3b exhibits the CV plots of AC-S at different scan rates from 5 to 100 mV/s, presenting that no any redox peaks with the increase scan rate was observed.
confirming for its EDLC behavior. The specific capacitance of AC-S, AC-C and AC-CH calculated with equation (1) at scan rate of 5 mV/s were 4.2, 1.1 and 101.1 F/g respectively. Figure 3c showed the GCD behaviors of AC-S, AC-C and AC-CH electrodes in the voltage range from 0 to 1 V. The result displayed close triangular shape at every curves, suggesting that these electrodes showed perfectly EDCL behavior [13], which is in consistent with the CV curve in Figure 3a. The Nyquist plots for AC-S, AC-C and AC-CH electrodes is presented in Figure 3d. According to the electrochemical impedance spectroscopy (EIS) curves, the internal resistance (Rs) is approximate from the intercepts of the real part and the charge transfer resistance (Rct) can be acquired by the semicircular radius [14]. The AC-CH electrodes exhibits Rs related to the electron conductivity of 2.77 Ω and shows Rct involved to the chemical reactions of 39.3 Ω. Moreover, no semicircular was found in AC-S and AC-C suggesting pure EDLC behavior [15].

![Figure 3](image.png)

**Figure 3.** (a) CV curves, (b) CV curves of AC-CH at various scan rates, (c) GCD curves at current density of 3 A/g and (d) Nyquist plot

**4. Conclusions**

In this study, AC derived from EFB-hydrochar was produced by steam, carbon dioxide and KOH chemical activations. Chemical activation showed better efficacy than both physical activations with increase of the BET surface area, total pore volume and the improvement of porosity. Furthermore, the AC obtained from chemical activation method exhibited the highest specific capacitance of 101.1 F/g at scan rate of 5 mV/s. According to the results, the AC produced from EFB-hydrochar were promising as electrode for supercapacitor application.
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