

FUNDAMENTAL STUDY OF CARBON MATERIALS FROM EMPTY FRUIT BUNCH VIA HYDROTHERMAL CARBONIZATION WITH H_3PO_4 AND NaOH ACTIVATION

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Abstract

Lignocellulosic biomass has great potential as an energy source or feedstock for further conversion. Empty fruit bunches (EFBs) were agricultural waste materials from palm oil production. In this research, we aim to study the morphology of hydrochars derived from EFBs via hydrothermal treatments with phosphoric acid (H_3PO_4) and sodium hydroxide (NaOH) activation at different concentrations (i.e., 0.5, 0.7, and 1 M) at 200°C for 12 h, followed by carbonization at 700°C under nitrogen atmosphere for 2 h. The samples were characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy and specific surface analysis. After carbonization, the hydrochar activated by 1.0 M H_3PO_4 possessed the highest surface area of 590 m²/g with the dominance of micropores. Hydrothermal carbonization with acid–base activation showed an effective method in preparing high porous activated carbon from EFB.

Keywords: Hydrothermal carbonization, empty fruit bunch, hydrochar, acid/base activation

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Introduction

Thailand is the agricultural country where there are a lot of agricultural crops, such as sugarcane, cassava, rice husk and palm oil. Palm oil is known as major economic crops. Empty fruit bunch (EFB) is the agricultural residue and available in abundance and no economical value from palm oil industries (Katamanee, 2006). Hydrothermal carbonization (HTC) is a thermochemical process to convert biomass into a coal-like material with higher carbon content at temperature between 180°C and 250 °C in a pressure vessel for several hours. The products obtained from HTC are composed of solid hydrochar, a water-soluble and a gas consisting of carbon dioxide (Matson *et al.*, 2011; Libra *et al.*, 2011; Falco *et al.*, 2013).

Activated carbon is a common term used to describe carbon-based materials that have developed high surface area with an internal porous structure and have a wide spectrum of oxygenated functional groups (Gonzalez, 2018). Activated carbon is widely used for many applications, such as separation of gases, recovery of solvents and adsorbents in various industrial sectors. In general, the activated carbons are prepared either by physical or chemical activation (or both). For physical activation, the raw material is carbonized (carbonization step) and the prepared char subsequently reacted with steam or CO₂ (activation step) (Caturla *et al.*, 1991; Torregrosa *et al.*, 1991; Botha *et al.*, 1993). In contrast, chemical activation can complete in a single step by carrying out thermal decomposition of raw material mixed with chemical reagents, such as H₃PO₄, KOH, NaOH, and Na₂CO₃ (Nethaji *et al.*, 2011). Among several acid reagents, activation by

H₃PO₄ can be achieved at lower temperatures with higher yield. In addition, most of H₃PO₄ can be recovered after the process is finished (Castro *et al.*, 2000). For base reagents, NaOH activation has several advantages over other base reagents, such as (i) lower dosage, (ii) cheaper, (iii) more environmentally friendly, and (iv) less corrosive (Tseng, 2006). Therefore, H₃PO₄ and NaOH were herein chosen as acid and base reagent for chemical activation.

In this work, EFB was employed as a precursor in the synthesis of carbon materials via HTC process with H₃PO₄ and NaOH activation. The temperature, time, and concentration of acid–base used in hydrothermal reaction were in the range of 0.5–1.0 M at 200°C and 12 h, respectively. The subsequent carbonization of hydrochars was carried out at 700°C for 2 h under nitrogen atmosphere. The effects of concentration acid–base hydrothermal and carbonization conditions on the properties of carbons synthesized were characterized by several techniques, including scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy and surface area analysis.

Materials and Methods

Preparation of Carbon Materials from Efb's Via HTC

EFBs were obtained from the Krabi province of the Southern Thailand. EFBs were dried at 90°C overnight and then reduced their size using a blender machine, followed by sieving with a 700 µm mesh. 10 g of grinded

Table 1. Experimental conditions for hydrothermal process

Condition	Temperature (°C)	Time (h)
0.5 M H ₃ PO ₄	200	12
0.7 M H ₃ PO ₄	200	12
1.0 M H ₃ PO ₄	200	12
0.5 M NaOH	200	12
0.7 M NaOH	200	12
1.0 M NaOH	200	12

EFBs was mixed with 100 mL of DI water and transferred into a Teflon-lined stainless-steel reactor. The hydrothermal reaction was performed at temperatures of 200°C for 2 h under acid and base conditions (0.5–1.0 M concentration of H_3PO_4 and NaOH). The resultant hydrochars were quenched in water and dried at 90°C overnight. The experimental conditions and the respective samples prepared are shown in Table 1.

Characterization

The proximate and ultimate analyses were carried out to evaluate the chemical and elemental compositions of EFBs according to the standard method (Jamari and Howse, 2012). SEM images were taken on a Zeiss EVO 50 microscope operated at an accelerating voltage of 10 kV. The presence of functional group on samples was confirmed with a Thermo Scientific Nicolet 6700 FTIR spectrometer. N_2 adsorption–desorption isotherms were measured on a 3Flex Micromeritics surface analyzer at liquid N_2 temperature (-196°C) to investigate textural structure, including specific surface area, pore volume and pore size distribution. Prior to the measurement, all samples were degassed at 150°C for 6 h under vacuum. The specific surface area was determined by the Brunauer–Emmett–Teller (BET) method at relative pressures (p/p_0) between 0.05 and 0.30. The pore volume and pore size distribution were determined by the Barrett–Joyner–Halenda (BJH) method. Raman spectra were recorded on a Thermo Scientific DXR SmartRaman spectrometer with a laser-excitation wavelength of 532.1 nm.

Results and Discussion

The results of proximate and ultimate analyses of EFB showed that as-received EFB was mainly composed of moisture of 63.49 ± 0.53 wt% and volatile of 32.56 ± 0.24 wt% as two major components, while fixed carbon and volatile were found to be only 2.96 ± 0.08 wt% and 1.00 ± 0.04 wt%, respectively. In case of

EFBs after drying, C, H, N, and O obtained from elemental analysis were 43.78 ± 0.05 wt%, 6.06 ± 2.02 wt%, 0.56 ± 0.01 wt% and 49.67 ± 0.04 wt%, respectively.

The SEM images of EFB and hydrochars after carbonization are displayed in Figure 1. Based on the results obtained in the previous report by Yu *et al.*, the percentage of fixed carbon content was decreased when the carbonization temperature increased to 800 – 900°C (Yu *et al.*, 2014). Therefore, carbonization was performed at 700°C for 2 h in this work. From the SEM images, it was clearly observed a significant difference in morphology of hydrochars hydrothermally treated at different H_3PO_4 and NaOH concentrations. A major change was observed at the surface of the hydrochars particles activated by H_3PO_4 , where sphere-like microparticles adhered to the surface of hydrochar in Figures 1(c)–2(e). This feature suggests the decomposition of the lignocellulosic structure of EFB (Sevilla and Fuentes, 2009). Figures 1(f)–2(h) show that the macrocellular morphology of base hydrochars remain unchanged with appearance of smooth and large pores on the surface.

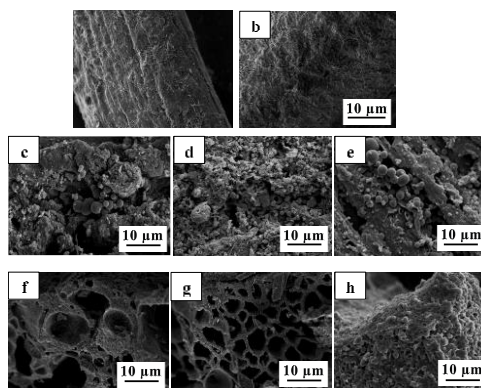


Figure 1. (a) SEM images at a magnification of $500\times$ of EFB. (b) SEM images ($1,000\times$) of EFB via carbonization. SEM images at a magnification of $1,000\times$ of EFB hydrothermally treated at different acid and base concentrations after carbonization: (c) $0.5\text{ M H}_3\text{PO}_4$, (d) $0.7\text{ M H}_3\text{PO}_4$, (e) $1.0\text{ M H}_3\text{PO}_4$, (f) 0.5 M NaOH , (g) 0.7 M NaOH and (h) 1.0 M NaOH

To investigate the presence of functional groups, the FTIR spectra of EFB and hydrochars after hydrothermal treatment at different acid and base concentrations were collected and are shown in Figures 2(a) and 3(b). A weak and broad band at 3,000–3,600 cm^{-1} are visible for both acid and base conditions, confirming the presence of hydroxyl groups. The weak broad peak around 2,000–2,400 cm^{-1} in acidic condition can be attributed to the carbon–oxygen and ketene groups. The band near 1,615–1,700 cm^{-1} corresponds to carbonyl stretching C=O for acetyl groups in hemicellulose and carbonyl aldehyde in lignin (Kazayawoko *et al.*, 1997; Guo *et al.*, 2007). The band at 1,170–1,300 cm^{-1} can be assigned to C=O stretching of the carboxylic groups in hemicellulose (Mwaikambo and Ansell, 2002). The emergence of bands at between 950 and 1,000 cm^{-1} in acidic condition is associated with the C–H vibration in aromatic group in lignin (Himmelsbach *et al.*, 2002; Lili *et al.*, 2010; Ru *et al.*, 2012).

Figure 3(a) and 3(b) present the FTIR spectra of hydrochars after carbonization at different concentrations of acid and base. Compared to those before carbonization due to evaporation and decomposition of function groups into volatile products at high temperature (Sakina *et al.*, 2000; Román *et al.*, 2013). This also proves that the activation process have taken place successfully (Wang *et al.*, 2010).

To further evaluate more detailed information on the structure of carbons, Raman spectroscopic analysis was carried out, as shown in Figures 4(a) and 5(b). The Raman spectra of carbonized samples were comprised of two pronounced peaks centered at 1,360 and 1,600 cm^{-1} , which are related with the D band and G band, respectively. The D band is related to the breaking of symmetry caused by structural disorders and defects, whereas the G band refers to the in-plane bond stretching motion of the pair of sp^2 carbon atoms (Schwan *et al.*, 1996; Sevilla *et al.*, 2009). These two characteristic peaks had low intensity with broad feature, indicating an amorphous nature of carbons. Additionally, it

was seen that the intensity of both D and G bands increased at higher H_3PO_4 and NaOH concentrations. This result confirmed that activation by higher concentration of acid and base could lead to more graphitization of carbon samples.

Furthermore, surface area, pore volume and pore diameter of carbonized hydrochars

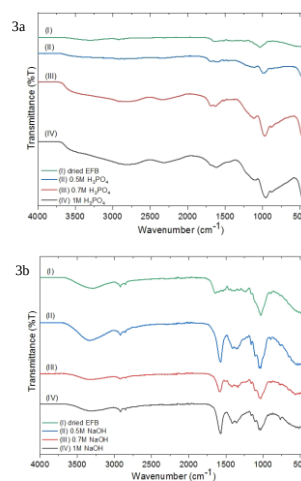


Figure 2. FTIR spectra of EFB and hydrochars hydrothermally treated at 200°C for 12 h with: (a) H_3PO_4 and (b) NaOH activations

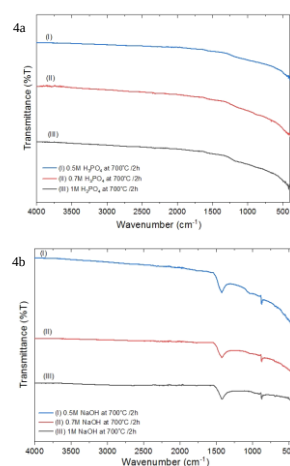


Figure 3. FTIR spectra of carbonized hydrochars with (a) H_3PO_4 and (b) NaOH activations

were examined using N_2 adsorption–desorption isotherm. For the samples activated with NaOH, their surface area was found to be very low about 1–4 m^2/g . Their low surface area indicates that pore structure was not developed. However, when H_3PO_4 concentration increased to 1.0 M, the surface area of activated sample immediately increased to 589 m^2/g . This confirms that hydrothermal treatment with high H_3PO_4 concentration is greatly required for the pore development of carbon samples. The N_2 adsorption–desorption isotherms of hydrochars after carbonization are displayed in Figure 5. It exhibited type II or IV isotherms with a hysteresis feature, indicating its hierarchical pore structure, including of non-porous or meso and macropores materials. From the t -plot of carbon with H_3PO_4 activation at 1.0 M, the micropore and external (meso and macropores) surface areas were estimated to be 319.5 and 279.3 m^2/g , respectively. This result indicates that its surface area is dominated by microporous structure. Significant improvement of surface area at high H_3PO_4 concentration can be explained that H_3PO_4 is assumed as a dehydration agent role during activation. With a satisfactory high concentration, it can inhibit the formation of tars and any other liquids, thus

facilitating the pore development of the samples. Moreover, the movement of volatiles through the pore channels will not be hindered and volatiles will be released easily from the carbon surface during activation. The surface area, mean pore size and pore volume of all samples and some commercial activated carbons are summarized in Table 2. Although surface area of porous carbons obtained in this study is still relatively low when compared to most of commercially available activated carbons (Kaiser *et al.*, 2007; Martins *et al.*, 2015). it shows the opportunity to further improve surface area of porous carbons through the optimization of acid concentration, carbonization temperature and hydrothermal conditions.

Conclusions

The concentration of acid and base in HTC process are the significant factors in controlling physicochemical properties of carbon products. The FTIR spectra confirmed that the functional groups on hydrochars were disappeared after carbonization, indicating both dehydration and decarboxylation at high temperature. The Raman spectroscopy data showed that carbons became more graphitized at high concentration of acid

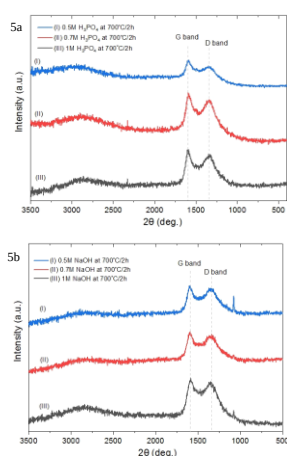


Figure 4. Raman spectra of carbonized hydrochars with (a) H_3PO_4 and (b) NaOH activations

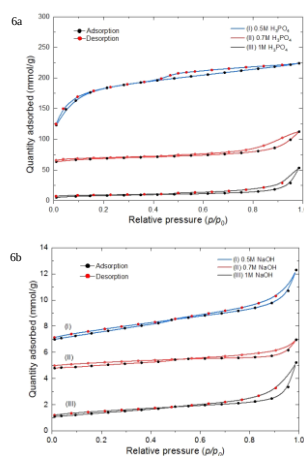


Figure 5. (a) N_2 adsorption–desorption isotherms of hydrochar after carbonization with (a) H_3PO_4 and (b) NaOH activations

Table 2. Experimental BET data of hydrochars carbonized at 700°C and commercial activated carbons

Sample	Surface area (m ² /g)	Mean pore size (nm)	Pore volume (cm ³ /g)
0.5 M H ₃ PO ₄	27.5	18.0	0.077
0.7 M H ₃ PO ₄	54.1	10.9	0.080
1.0 M H ₃ PO ₄	589.8	2.4	0.122
0.5 M NaOH	4.1	7.7	0.008
0.7 M NaOH	1.4	9.1	0.003
1.0 M NaOH	1.9	13.0	0.006
Fagron	514	-	0.990
Panreac	296	-	0.540
Kothmex AM-1131	1131	-	0.403
Challenge OAM-1001	1140	-	0.457
Zorflex FM-10	939	-	0.561

and base; however, they were mainly composed of amorphous phase. Among a series of conditions investigated, we found that hydrothermal process of 1.0 M H₃PO₄ at 200°C for 12 h and further carbonization at 700°C for 2 h is an optimal condition to obtain porous carbon with high surface area of 590 m²/g. We anticipate that porous carbon materials prepared from EFB via HTC with H₃PO₄ activation can potentially applied for adsorbents for dye removal or related applications.

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