

CHARACTERIZATIONS OF CARBON MATERIALS PREPARED FROM BIOMASS CHARCOALS

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ABSTRACT

Carbon materials derived from biomass charcoals were prepared by a simple carbonization technique as follow with a ball milling process and hydrothermal method. The biomass charcoals were carbonized from a wide variety of low cost raw materials (such as corncob, coconut shells, cassava tuber, and bamboo stalk) from agricultural wastes, easily available and sustainable materials in local farmland. An additional ball milling process was introduced after carbonization to obtain charcoal powder for further procedures. Then, the carbon material was synthesized via a hydrothermal method using charcoal powder as a carbon source and precursor. The morphology and chemical functional groups of the as-prepared biomass charcoal was determined by scanning electron microscopy (SEM) and fourier transform infrared spectroscopy (FTIR). The variations of biomass raw materials had an influence on morphology, microstructure and chemical composition of the as-prepared biomass charcoal. In this research, a comparison study was drawn based on the types of biomass charcoal using hydrothermal methodology to produce carbon materials. Physical characteristics and properties of synthesized carbon were also studied throughout this work such as crystallinity by X-ray diffraction (XRD), elemental composition by CHNO-S analyzer, and pore structure by N₂ adsorption analysis.

1. INTRODUCTION

As an element, carbon is part of a countless number of natural or synthetic organic molecules. As the materials used in industry, the well-known forms of carbon are graphite and diamond. Graphite has been used as a pencil lead while diamond is usually used in the production of jewelry. However, carbon materials are

widely use and have many applications in different forms. (Flandrois, 2002). Traditional carbon materials are mostly prepared from non-renewable sources of precursors such as coal, coal tar, and asphalt (Li, et al., 2015). Recently, biomass such as agricultural waste has been known as important sources of precursors for the production of carbon (Skodras, et al., 2007). For example, Li, et al.(2015) prepared nanoporous carbon having superconductor behavior from corn straw by the KOH activated method. Tao, et al.(2015) reported the preparation of sulfonated carbon catalysts using biomass waste from willow catkins and its use for esterification. Furthermore, Wu, et al. (2015) prepared graphene-like bamboo charcoal through the high-temperature treatment of phenolic resin in the bamboo charcoal. Absorbent activated carbon was prepared from grape industrial processing waste (Saygılı, et al., 2015).

Corn cob, coconut shell, cassava tuber and bamboo stalk are example of biomass produced from agricultural activities in Thailand. This research is concerned with the conversion of agricultural byproduct into value added materials. Thus, the present paper investigates the preparation method of carbon material from biomass charcoal powder by a hydrothermal approach. The as-prepared products were characterized and the effect of precursors were also studied.

2. EXPERIMENT

2.1 Preparation method

2.1.1 Preparation and characterization of biomass charcoal

The agricultural wastes used as materials for the preparation of biomass charcoal were collected from

local field in Kanchanaburi province, Thailand. The selected biomass species are corncob, coconut shell, cassava tuber and bamboo stalk. The collected materials were cleaned and dried before carbonization using the traditional technique for 2 hours. An additional ball milling process was introduced after carbonization for 1 hour to obtain charcoal powder (CHP) for the carbon precursor. The microstructure of the as-prepared charcoal was determined using a field emission scanning electron microscope JEOL JSM-6335F FE-SEM) operating at 15 kV. Fourier transform infrared spectrometer (510 Nicolet FT-IR) using a KBr pellet technique operated in the range of 400–4000 cm^{-1} was used to identify the chemical functional groups of biomass charcoal.

2.1.2 Preparation and characterization of carbon materials

Carbon materials were prepared by hydrothermal method using charcoal powder produced from corn stalk and cassava tuber as carbon sources and precursors. For hydrothermal method, 0.500 g corncob CHP was mixed in 30 ml de-ionized water and then transferred to a Teflon-lined stainless-steel autoclave (80 ml capacity). The autoclave was tightly closed, heated and maintained at 200 °C for 24 hours and naturally cooled to room temperature. The black precipitates were separated by filtration, washed in de-ionized water and absolute ethanol, and dried at 60 °C for 6 hours for further characterization. In order to study the effect of raw materials on the composition of the as-prepared carbon, cassava tuber CHP was used as a carbon precursor instead of corncob CHP.

The phase and crystallinity of products were studied by an X-ray diffractometer (Bruker D8 Discover XRD) using the $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) operating using a step size of $0.02^\circ/\text{step}$ from 5° to 80° . The as-prepared carbon was then examined by an elemental analyzer to determine the contents of C, H, N. Nitrogen adsorption was analyzed by a multipoint BET surface area and pore size analyzer (Quantachrome Autosorb 1) with outgassing at 150 °C for 6 hours before taking the measurement. The BET surface area (S_{BET}), total pore volume (V_{tp}) and pore size distributions (D_p) were determined from nitrogen adsorption-desorption data by Quantachrome software.

3. RESULTS AND DISCUSSION

3.1 Biomass charcoal (precursor) characterization

After carbonization and without ball milling, the fractured surfaces of biomass charcoal were observed using field emission scanning electron microscopy (FESEM). The FESEM images (Fig. 1) revealed different natural structures of biomass charcoal surfaces and the products composed of carbon in solid form. These results are in accordance with the FTIR analysis presented in Fig. 3.

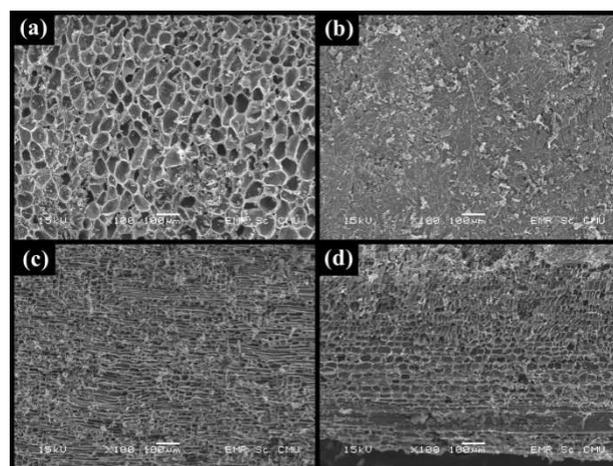


Fig. 1 SEM images of biomass charcoal after carbonization of (a) corncob (b) coconut shell (c) cassava tuber and (d) bamboo stalk

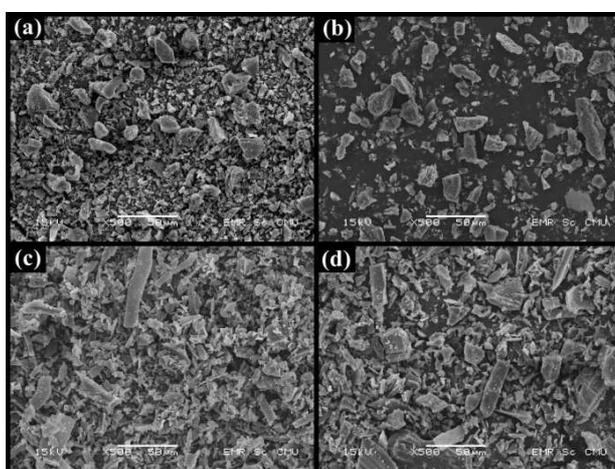


Fig. 2 SEM images of ball milled charcoal powder (a) corncob (b) coconut shell (c) cassava tuber and (d) bamboo stalk

The fractured surface of corncob charcoal displayed the largest holes on the cross section surface as seen in Fig 1a, while the cassava tuber and bamboo stalk charcoal displayed smaller hole structures in Fig 1c and d, respectively. On the other hand, there was no apparent hole in the fractured coconut charcoal surface (Fig 1b). The images in Fig. 2 show the morphology of biomass charcoal powder after ball milling for 1 hour. The milled charcoal powder showed irregular granules with uniform pore size.

The FT-IR spectrum demonstrated the existence of functional groups in the ball milled charcoal powder which corresponded with chemical compounds in the biomass that has been reported by various researchers. The peaks at $873\text{-}875 \text{ cm}^{-1}$ are related to out of plane bending vibrations of aromatic C-H group (Isahak, et al., 2013). The bands at $1577\text{-}1591 \text{ cm}^{-1}$ are related to C-C stretching vibrations (Saygılı, et al., 2015). The peaks located at $1690\text{-}1701 \text{ cm}^{-1}$ are ascribed to C=O stretching which confirms the existence of a carboxylic acid group in the structure. The peak originated from aliphatic C-H

asymmetric stretching vibration appears at 2927 cm^{-1} (Haafiz, et al., 2015) and the broad peak in coconut shell CHP at 3429 cm^{-1} was produced by O-H hydroxyl group. The band around $1438\text{--}1441\text{ cm}^{-1}$ and $1380\text{--}1384\text{ cm}^{-1}$ are due to C-H deformation vibration in CH_3 (Wang, et al., 2015). The bands at lower wave numbers from corncob CHP, including $459, 694, 796, 1083$ and 1167 cm^{-1} are characteristic bands associated with Si-O-Si vibration mode (Ning, et al., 2004). As a result, the chemical compositions of as-prepared charcoal powder are slightly different depending on the biomass raw materials.

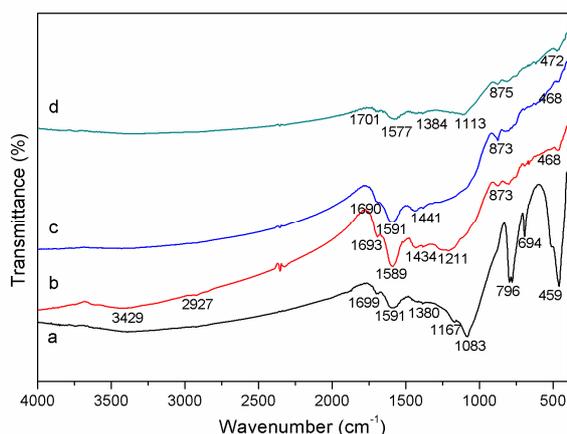


Fig. 3 FT-IR spectrum of ball milled charcoal powder (a) corncob (b) coconut shell (c) cassava tuber and (d) bamboo stalk

3.2 XRD of carbon materials

Phase and crystalline structures of the as-synthesized samples were characterized by X-ray powder diffraction (XRD) as shown in Fig. 4. The XRD pattern of the sample derived from cassava tuber CHP was rather broad and low intensity peaks were observed at 23.5° and 43.09° which could be identified as peaks of carbon materials for (002) and (100) plane, respectively (Dobiašova, et al., 1999).

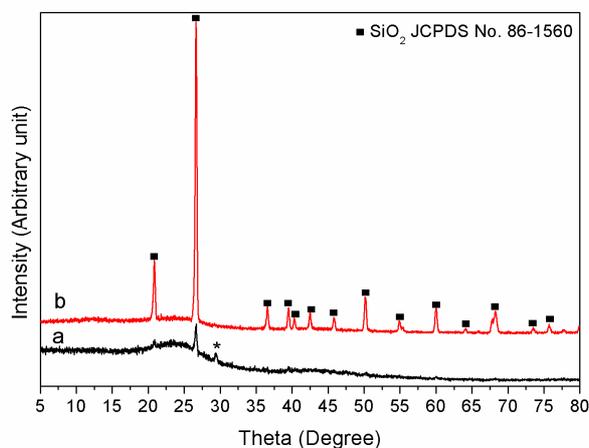


Fig. 4 XRD patterns of as-prepared products using two different precursors: (a) cassava tuber CHP (b) corncob CHP.

Additional XRD peaks were detected as the SiO_2 impurity at 26.68° with an unidentified peak (*) indicating the presence of the trace elements within the raw material (Wang, et al., 2015). When corncob CHP was used instead of cassava tuber CHP as a carbon precursor, XRD patterns were found to correspond with the hexagonal SiO_2 quartz phase of the JCPDS database No. 86-1560 (Powder Diffraction File, 2001). XRD pattern of carbon could not be found in this product. Combined with FTIR analysis, it is known that the raw material was contaminated with Si; therefore the choice of biomass raw materials had an influence on phase and chemical composition of the as-prepared carbon materials.

3.3 CHN analysis of carbon material

The effect of raw materials on the chemical composition of the as-prepared products was also investigated by elemental analysis. The results show higher carbon content in the product derived from cassava tuber CHP precursor, and therefore is the most suitable raw material for the preparation of carbon compared to the corncob CHP as in table 1. Moreover, an elemental analysis could identify the presence of carbon material in the product prepared from corncob CHP that was not able to detect by XRD technique.

Table 1 Elemental analysis of the as-prepared products using different precursors

Sample	Elemental composition (wt%)		
	C	H	N
Corncob CHP	43.37	1.791	0.7233
Cassava tuber CHP	66.01	3.113	1.818

3.4 N_2 adsorption-desorption isotherm

N_2 adsorption-desorption analysis revealed the S_{BET} , V_{tp} and D_p values of the as-prepared products using the hydrothermal method. The obtained results are presented in Table 2. According to XRD and elemental analysis, the product derived from cassava tuber CHP exhibited a higher S_{BET} , V_{tp} and D_p than that derived from corncob CHP due to adsorption of major carbon materials in the product.

Table 2 Textural properties of as-prepared products using different precursors

Samples	Textural characteristic		
	S_{BET} (m^2/g)	VT (cm^3/g)	D_p (nm)
Corncob CHP	51.37	0.06005	4.676
Cassava tuber CHP	61.27	0.08904	5.813

CONCLUSION

In this work, carbon materials were prepared through the hydrothermal method in de-ionized water without chemical activation of biomass charcoal. The products derived from cassava tuber and corncob charcoal powders (CHP) had a carbon composition of 66.01 %wt

and 43.38 %wt, respectively. The carbon content from cassava tuber CHP was greater than that from corn cob CHP. This implied that the variations of biomass raw materials played greater role in the formation of carbon materials. However, the SiO₂ impurity was detected in all products due to the trace amount of the element in raw materials.

REFERENCES

Dobiašová L., Stary V., Glogar P., Valvoda V., Analysis of carbon fibers and carbon composites by asymmetric X-ray diffraction technique, *carbon*, Vol 37, pp. 421-425, 1999.

Flandrois S., *Carbon molecules and materials*, Taylor & Francis Inc, London, 2002.

Haafiz M.K.M., Hassan A., Khalil H.P.S.A., Khan I., Inuwa I.M., Islam Md.S., Hossain Md.S, Syakir M.I., Fazita M.R.N., Bionanocomposite based on cellulose nanowhisker from oil palm biomass-filled poly(lactic acid), *Polym. Test.*, Vol 48, pp. 133-139, 2015.

Isahak W.N.R.W., Hisham M.W.M., and Yarmo M.A., Highly Porous Carbon Materials from Biomass by Chemical and Carbonization Method: A Comparison Study, *J. Chem.*, Vol 2013, Article ID 620346, 6 pages

Li S., Sun L., Wang L., Wang Y., Preparation and electrochemical performance of corn straw-based nanoporous carbon, *J. Porous Mater.*, Vol. 22, Issue 5, pp.1351-1355, 2015.

Ning C.Q., Greish Y., El-Ghannam A., Crystallization behavior of silica-calcium phosphate biocomposites: XRD and FTIR studies, *J. Mater. Sci. Mater. Med.*, Vol 15, pp. 1227-1235, 2004.

Powder Diffract File, JCPDS-ICDD, 12 Campus Boulevard, Newtown Square, PA, 19073-3273, U.S.A. 2001.

Saygılı H., Güzel F., önal Y., Conversion of grape industrial processing waste to activated carbon sorbent and its performance in cationic and anionic dyes adsorption, *J. Clean Prod.*, Vol 93, pp. 84-93, 2015.

Skodras G., Diamantopoulou Ir., Zabaniotou A., Stavropoulos G., Sakellaropoulos G.P., Enhanced mercury adsorption in activated carbons from biomass materials and waste tires, *Fuel Process. Technol.*, vol 88, pp. 749-758, 2007.

Tao M., Guan H., Wang X., Liu Y., Louh R., Fabrication of sulfonated carbon catalyst from biomass waste and its use for glycerol esterification, *Fuel Process. Technol.*, vol. 138, pp. 355-360, 2015.

Wang K, Zhao N, Lei S, Yan R, Tian X, Wang J, et al, Promising biomass-based activated carbons derived from willow catkins for high performance supercapacitors, *Electrochim. Acta*, Vol 166, pp. 1-11, 2015.

Wu F., Liu W., Qiu J., Li J., Zhou W., Fang Y., Zhang S., Li X., Enhanced photocatalytic degradation and adsorption of methylene blue via TiO₂ nanocrystals supported on graphene-like bamboo charcoal, *Appl. Surf. Sci.*, Vol. 358, pp. 425-435, 2015.



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