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Research Article

Influence of acidic catalysts in Hydrothemal Carbonization (HTC) process for synthesis of carbon nanomaterial prepared from horse manure

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Abstract

Horse manure (HM), which is a crucial waste material from livestock sector in Thailand. It consists of hemicellulose, cellulose and lignin that has a potential for carbon material production. In this research, carbon material was prepared from horse manure by hydrothermal treatment (HT) at 200ºC for 24 h with improvement of porosity and surface structure by acid catalyst that HNO_3, H_2SO_4, HCl and H_3PO_4 with ratio of 1, 3 and 5 wt%, respectively. Then, HT char was pyrolysed at 300ºC for 2 h to obtain the carbon nanomaterial. SEM image displayed that HCl catalyst shows highest porosity on char surface. The production yield treated by HCl 5 wt% is approximately 51.44 wt%. FTIR spectrum confirm that the functional group of biomass polymer was decomposed.

Keywords: carbon nanomaterial, biomass, horse manure, hydrothermal-carbonization, acid catalyst

Introduction

Biomass is organic matter derived from living, or recently living organisms. It is used as a source of energy and environment application. As an energy source, conversion of biomass to biofuel can be achieved by different methods such as thermal, chemical and biochemical and used for reduction of carbon dioxide even a low cost adsorbent (Reza et al., 2013; Nitsos et al., 2016). Horse manure (HM) is a biomass which is consist a carbon in its structure. Generally, carbon material such as biochar or activated carbon is synthesized via thermochemical conversion as pyrolysis, gasification, or hydrothermal treatment (HT) (Mosier et al., 2005; Ravindran & Jaiswal, 2016). Hydrothermal Carbonization (HTC) can be applied for biomass conversation. HTC is a low-temperature process (<300 °C) and it performs a high production yield. The HTC mechanism provided water molecules, heat and pressure to decompose bonding of biomass polymer; cellulose, hemicellulose and lignin result in increasing of porosity and surface area (Madenoğlu et al., 2016; Yan et al., 2016). These process obtained at 160-200 °C for 4-24 h, which can add acidic or base catalyst for development of the pore structure and surface area (Belver et al., 2002). However, temperature and time can not be

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increased surface area and pore size distribution as expectation. Acid catalyst is a basic chemical substance that can be used as co-solvent for developed biomass structure, increase in surface area and pore volume (Pandaa et al., 2010; Lynam et al., 2011; Huang et al., 2015; Aston et al., 2016; Fougere et al., 2016).

In this research, the study revealed the effect of acid catalyst (i.e. HCl, H_2SO_4, H_3PO_4 and HNO_3) on the morphology, surface area and porosity of produced carbon material from horse manure via hydrothermal carbonization process.

Materials and methods

Preparation of carbon nanomaterial

At first stage, 30 g of horse manure (size; 800 µm by sieving) was mixed with 60ml of DI water and 1, 3 and 5 wt% of acidic group (HCl, H_2SO_4, H_3PO_4 and HNO_3). The solution was transferred into telflon and stainless-steel reactor at 200°C for 24 h. Then, the hydrochar was quenched via water and dried at 80^{o}C for overnight. Finally, the samples was carbonized at 300°C for 2 h to obtain carbon nanomaterial. For characterization, proximate and ultimate analysis analysed the chemical and elemental compositions of horse manure followed standard method (Reza et al., 2013; Nitsos et al., 2016). Additionally, physical morphology and surface functional group of carbon nanomaterial were characterized by Scanning Electron Microscope (SEM) and Fourier Transform Infrared Spectroscopy (FTIR), respectively.

Results and discussion

The result on proximate analysis of horse manure shows in Table 1. It found that horse manure contains 15.33 wt% of fixed carbon content and ash content about 13.54 wt%. Furthermore, moisture is lower than 8.0% in weight. While, the volatile matter content is approximately 64 wt%. In addition, elemental analysis carried out to examine the C, H, N, O elemental composition. Results obtained in this study on C, H, N, O about 45.9%, 6.4%, 1.0%, 35.7%, respectively.

Table 1. Proximate and elemental analysis of horse manure.

Parameter	Horse manure
Proximate analysis (wt%)	
Moisture	7.79
Ash	13.54
Volatile matter	63.34
Fixed carbon[a]	15.33
Ultimate analysis (wt%)	
C	45.9
H	6.4
N	1.0
S	0.1
O[a]	35.7

[a] Oxygen (wt%) = 100 - (carbon + hydrogen + nitrogen + sulfur + ash).

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Production yield of carbon nanomaterial show in Table 2. The results found that carbon nanomaterial prepared from hydrothermal process without the carbonization process had a yield about 68.37 wt%. The production yield of carbon nanomaterial produced by hydrothermal process adding HCl, H_2SO_4, H_3PO_4, HNO_3 is 51.44 wt% to 82.54 wt%, respectively. Increasing of HTC temperature and residence time become lower yield of char. After hydrothermal process, the char was performed through the carbonization at 300°C for 2 h. Carbon nanomaterial yields was ranged in 59.4 to 79.66 wt%.

Table 2. Production yield of carbon nanomaterials resulting from the HTC of horse manure.

Condition	HT Char (wt%)[a]			HTC Process (wt%)[b]		
HM-200-24	68.37			59.54		
	1wt%	3wt%	5wt%	1wt%	3wt%	5wt%
HCl	52.52	51.51	51.44	77.31	75.36	74.75
H_2SO_4	80.13	78.22	76.04	74.75	73.28	73.05
H_3PO_4	82.54	81.40	81.40	72.39	73.52	75.14
HNO_3	65.95	66.44	65.81	76.64	79.66	76.81

[a] Yield is defined as: Hydrochar by hydrothermal.

[b] Yield is defined as: carbon nanomaterial after carbonization at 300°C 2 h.

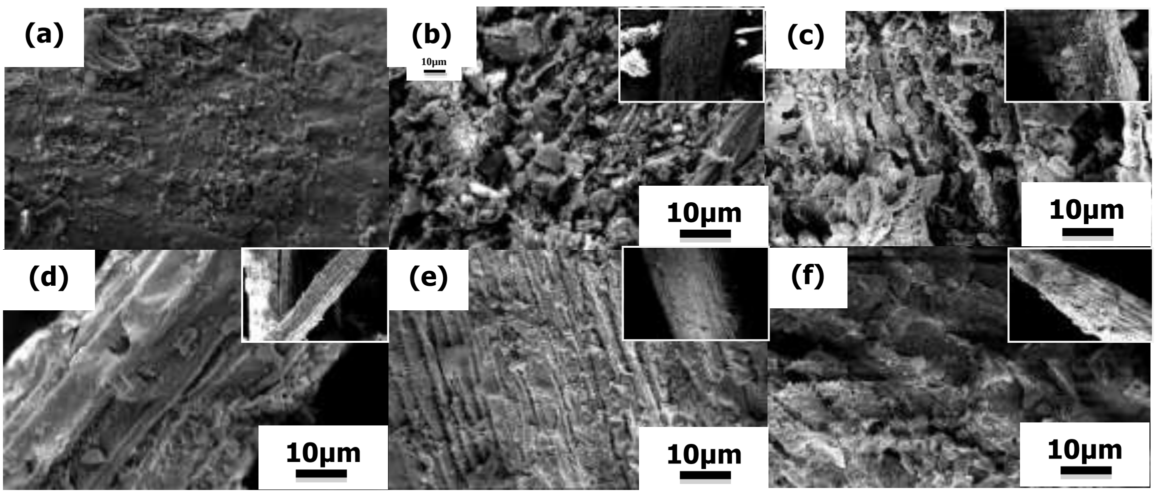

Figure 1. Scanning electron microscope (SEM) of (a) (1000x) horse manure, (b) carbon nanomaterial by hydrothermal at 200°C 24 h, (c) carbon nanomaterial adding HCl 5 wt%, (d) H_2SO_4 5 wt%, (e) H_3PO_4 5wt% and (f) HNO_3 5 wt%, recpectively.

SEM image displayed the surface appearance of horse manure and carbon nanomaterial samples (Figure 1). Feature of horse manure has size about 30 μm with smooth surface structure (Figure 1(a)). While, the size of carbon nanomaterials resulting from the hydrothermal carbonization of horse manure is approximately 20 μm (Figure 1(b)-1(f)).

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Carbon nanomaterial produced via hydrothermal at 200°C 24 h adding HCl 5 wt% has highest surface area. This is because of acid strength in one step dissociation of HCl and HNO_3 and 2 and 3 step dissociation of H_2SO_4 and H_3PO_4. The dissociation have positive charge leading to agglomerate of small particles. Therefore, carbon nanomaterial adding HCl have more porosity on surface than carbon nanomaterial treated by other acids (Pabst & Carta, 2007).

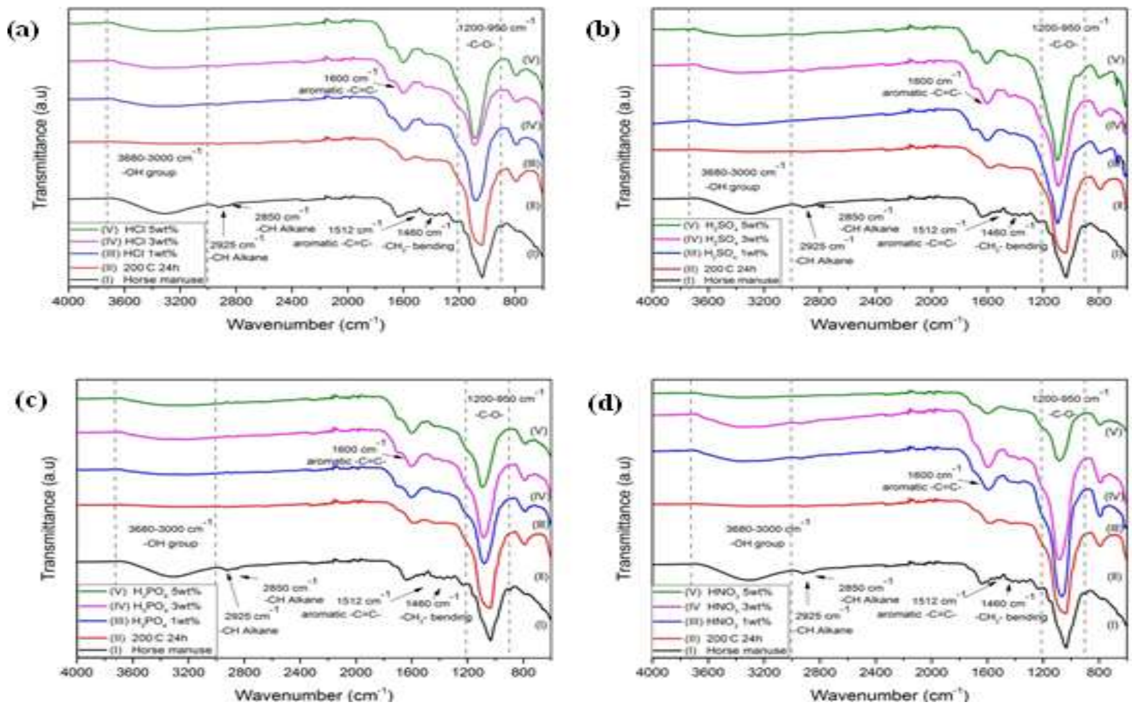

Figure 2. IR spectrum of produced carbon materials treated by a) HCl b) H_2SO_4 c) H_3PO_4 and d) HNO_3. *With Hydrothermal treatment, carbonized at 300 °C 2 h.

FT-IR spectra is displayed in Figure 2. The result reveals that the FT-IR patterns of carbon nanomaterial prepared from horse manure using HTC process.The broad band at 950-1200 cm^{-1} corresponded to C-O group, the band at 1,460 cm^{-1} corresponds to CH_2 bending, the band at 1,600 cm^{-1} and the band at 1,512 cm^{-1} attributed to C=C group. While, the peak at 1,740 cm^{-1} corresponds to C=O groups, the band at 2850 cm^{-1} and the peak at 2,925 cm^{-1} corresponds to CH alkane.The broad peak between 3,000-3,680 cm^{-1} corresponds to OH group (Aston et al., 2016). Moreover, Figure 2 showed the proportion of OH group, C=C group and CH_2 bending of carbon nanomaterial product. The functional groups were decreased since HTC process influenced the degradation of biomass polymer (i.e. hydrolysis, dehydration reaction. OH group was specifically declined owning to the decomposition of hemicellulose structure. After HTC process treated by acid catalyst, the band centered at 3,000-3,680 cm^{-1} corresponds to –OH group and the band at 2850 cm^{-1} to 2,925 cm^{-1} describes to –CH stretching. In addition, the band between 1,600 cm^{-1} - 1,512 cm^{-1} attributed to C=C group, the band at 1,460 cm^{-1}

corresponds to $-CH_2-$ bending, the band between 1200-950 cm^{-1} describes to C-O group. All functional groups were decreased with hydrothermal carbonization process in Figure 3.

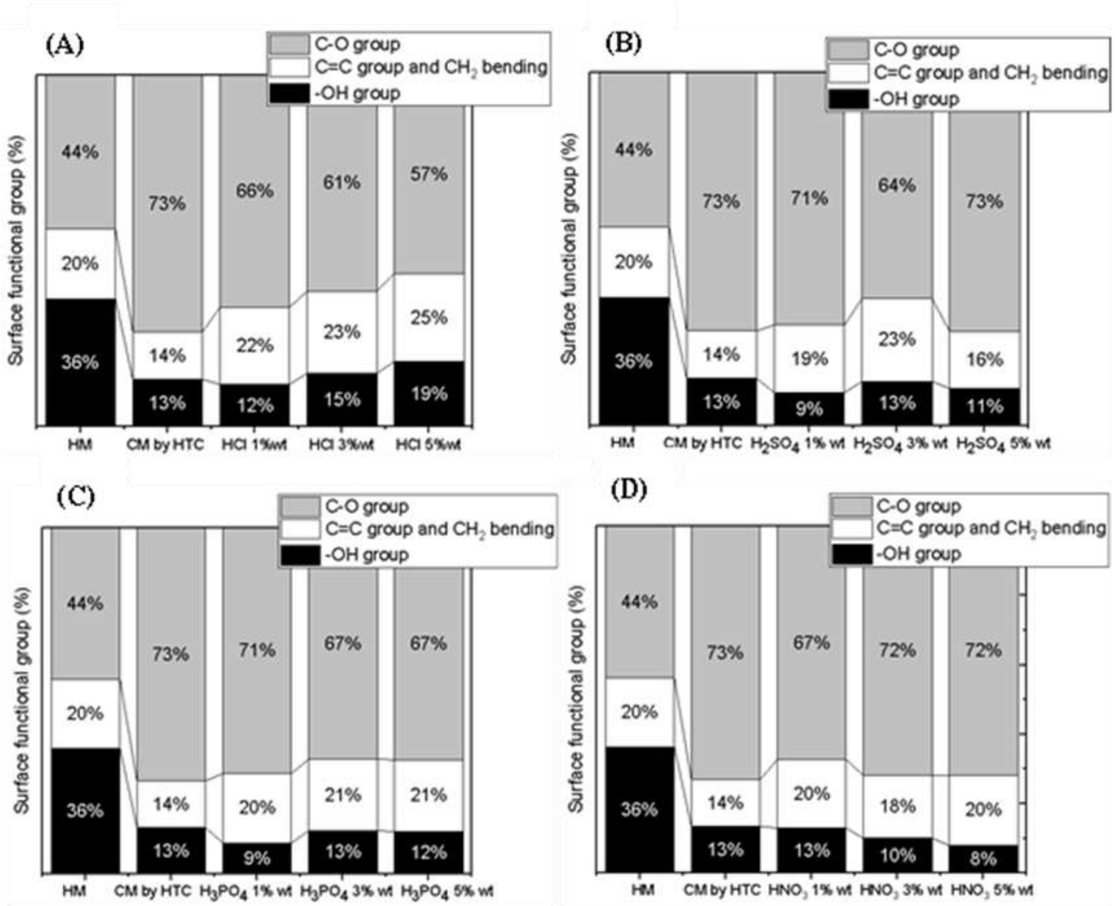

Figure 3. The proportion of OH group, C=C group, $-CH_2-$bending and CO group in carbon nanomaterial products.

Conclusion

Carbon nanomaterial was significantly influenced from acid catalyst in HTC process. The surface morphology of carbon nanomaterial was controlled by HTC process parameter. The samples produced at 200°C for 24h adding HCl 5 wt% with carbonization at 300°C for 2h reveal highest surface area. The production yield treated by HCl 5 wt% is approximately 51.44 wt%. FTIR spectrum confirm that the functional group of biomass polymer was decomposed. Therefore, the carbon content significantly increased. Carbon nanomaterial derived from horse manure could be a potential candidate as an alternative materials for several application such as catalyst supports for energy and environment applications and low cost adsorbent.

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