Effect of temperature and times by hydrothermal carbonization process from sawdust and bagasse for carbon materials supporter

Peerawith Sumtong¹*, Nuwong Chollacoop² and Apiluck Eiad-ua¹

¹College of Nanotechnology, King Mongkut’s Institute of Technology Ladkrabang, Bangkok, Thailand
²National Metal and Materials Technology (MTEC), Pathum Thani, Thailand
*E-mail: p.sumtong@gmail.com

Abstract
Carbon supporter from biomass has been fabricated by hydrothermal carbonization due to this process changes the structure of lignocellulose including cellulose, hemicellulose and lignin. The applications from carbon support are gaining in importance due to decreasing supply of fossil fuels and growing environmental concerns. Hydrothermal carbonization process was used to upgrade biomass such as sawdust and bagasse varying temperature at 160 to 200 °C and varying times at 4 to 24 hr with deionized water 120 ml and 60 ml, respectively. The biochars from sawdust and bagasse under hydrothermal carbonization conditions were characterized by Fourier transform infrared spectroscopy (FT-IR). It showed that the most hydroxyl group from this samples was decreased due to cellulose and hemicellullose from biochars were decomposed over than 200°C. The Biochars yield from sawdust and bagasse by hydrothermal carbonization conditions was determined from weight loss after hydrothermal carbonization process, which is Biochars yield were decreased with increasing hydrothermal carbonization temperature because lignocellulose was decomposed at high temperature and time. The morphology of Biochars were investigated by scanning electron microscope (SEM). It represented the porous structure was inflated to increasing hydrothermal carbonization temperature.

Keywords: hydrothermal carbonization, biomass, sawdust, bagasse, carbon supporter

Introduction
The fossil fuel consumption rate has been increased to industry and household by using from coal, petroleum and natural gas. From this fuel, the disadvantage to environment such as toxic pollution will be causing the global warming. Moreover, the energy derived from fossil fuel will decreasing nowadays and high cost. So, it was interesting trends in the renewable energy are numerous.

The waste biomass was interesting in recent years because the lignocellulose has enormous potential as a feedstock for the production of fuel, heat and electrical power approximate to coal (Liu et al., 2017). Biochemical and thermochemical conversion are two parts techniques used to lignocellulose from waste biomass. Compared with biochemical conversion technique, thermochemical has several advantages such as short processing times and high product yields (Tekin et al., 2014). In addition, thermochemical conversion methods, direct combustion and co-combustion have less risk and inexpensive. From reviews on waste biomass direct combustion conclude that is not a satisfying option due to natural properties of biomass feedstocks such as high moisture and oxygen contents. For example, during combustion to biomass, the high moisture will affect to lowers combustion temperature as well as increase carbon monoxide (CO) emission (Khan et al., 2009; Haykınc-Açma, 2003) causing serious air pollution in atmosphere.

Hydrothermal carbonization is thermochemical conversion for transformation lignocellulose structure including cellulose, hemicellulose, lignin and extractives in waste biomass to obtain biochars with high temperature between 140-220 °C (Liu et al., 2013; Tekin et al., 2014) and vary times, pressure approximate 10 mbar. It can be generate liquid (bio-oil), gaseous (mainly carbon dioxide), aqueous, and solid products (biochar) (Akhtar & Amin, 2011). In present most attention is paid to the liquid and gaseous products, but the bio-oil from hydrothermal carbonization cannot be used directly because it is
the high acidity, complex composition and viscosity. Compared to bio-oil and gaseous products, only a few investigations have been carried out on solid biochar. The biochar is generally produced as a byproduct from waste biomass and high hydrophobicity (Liu et al., 2013; Tekin et al., 2014).

Sawdust is a byproduct of sawmilling. It is a fine powder and toxic waste in factory. Moreover, it can be utilized for example Paul blakeney and fir trees that reacts with NaOH and Na₂CO₃ adsorption of copper (Cu) and zinc (Zn). Moreover, coconut trees that reacts with H₂SO₄ absorbs nickel (Ni) and mercury (Hg) (Ngah & Hanafiah, 2008). Bagasse is a similar fiber. It used in the biofuel or the paper industry. In this work, we study the effect of hydrothermal carbonization by varying temperature and time from sawdust and bagasse for carbon supporter.

Materials and methods

Materials

Sawdust and bagasse were selected as the representative waste biomass. The biomass was crushed to less than 5 mm and dried at 90 °C for 24 hr for hydrothermal carbonization process.

Preparation

The biochars from waste biomass (sawdust/bagasse) was prepared by around 30 g and 15 g was loaded with 120 ml and 60 ml deionized water into reactor for hydrothermal carbonization. This process was varying temperatures at 160 to 200 °C and times at 4 to 24 hr. After that the biochars were quickly cooled down at room temperature and dried at 90 °C for 24 hr.

Characterization

The morphology of biochars (sawdust and bagasse) were characterized by scanning electron microscope (SEM) on EVO® MA10. The functional group were determined by Fourier transform infrared spectroscopy (FT-IR) technique in the wave number range of 4000-400 cm⁻¹. The yield of biochars were calculated from weight lossed of biochars under hydrothermal carbonization process compared with weight of raw biomass. Finally, the carbon content of biochars were investigated via CHN analyser.

Results and discussion

The Morphology of biochars under hydrothermal carbonization were characterized by SEM images. Figure 1 and Figure 2 show SEM images of sawdust biochar and bagasse biochar with different temperature from 160-200°C for 24 hr. Change in temperature were found to affect the morphology such as larger porous structure at increase temperature and time (Deng et al., 2016). This is because of increasing temperature and time in process will decompose the lignocellulose in biomass (Tekin et al., 2014). Cellulose and hemicellulose structures can be eliminated from the surface by hydrolysis reaction (Zhao et al., 2014; Kapu and Trajano, 2014) in hydrothermal process.

![SEM images](image.png)

**Figure 1.** The biochars (sawdust) from hydrothermal carbonization conditions at (A) raw, (B) 160°C, (C) 180°C, and (D) 200°C for 24 hr.
Figure 2. The biochars (bagasse) via hydrothermal carbonization conditions at (A) raw, (B) 160°C (C) 180°C, and (D) 200°C for 24hr.

The functional group in biochars were investigated by Fourier transform infrared spectroscopy (FT-IR). Figure 3 show the functional group of sawdust and bagasse at different hydrothermal carbonization from 160-200°C for 24 hr. At 3680-3000 cm\(^{-1}\) was indicated to OH group of cellulose, hemicellulose and lignin. At 2917 cm\(^{-1}\) indicated to \(-\text{CH}\) alkane group of lignin peak. At 1715 cm\(^{-1}\) indicated to C=O group of hemicellulose. At 1634-1328 cm\(^{-1}\) indicated to lignin peak. At 1210-1080 cm\(^{-1}\) indicated to bending of C-O peak in hemicellulose. Increasing of time and temperature resulted in hydroxyl group, Lignin and C-O peak decreased. The hydroxyl group (-OH) of cellulose, hemicellulose and lignin were decreased with hydrothermal temperature due to deoxygenation and dehydration reaction. It can be eliminated O\(_2\) and H\(_2\)O contents for biochar production. As a result biochars are increase hydrophobicity (Liu et al., 2013). Lignin peak at 1634-1328 cm\(^{-1}\) is slightly change from aromatization reaction because lignin consists of the most aromatic rings is high stability and degradation approximate 300°C. While bending of C-O peak of hemicellulose at 1210-1080 cm\(^{-1}\) was reduced dramatically due to hemicellulose is less stable than lignin. Moreover, the C-O peak component are depend on the type of biomass.

Figure 3. FT-IR spectrum after hydrothermal carbonization conditions by vary times and temperatures (A) sawdust and (B) bagasse.
The biochars yield from sawdust and bagasse in Figure 4 were slightly decreased with increasing of hydrothermal carbonization temperature from 160 to 200 °C and time from 4 to 24 hr. Due to cellulose and hemicellulose contents in lignocellulose were decomposed and eliminated during hydrothermal carbonization by hydrolysis reaction. Hydrolysis can be destroyed structure and chemical composition of cellulose and hemicellulose (polymers structure) to monomer structure (Zhao et al., 2014; Kapa & Trajano, 2014). Furthermore, the loss yields from biochars with hydrolysis reaction can be converted to solid liquid and gas (Tekin et al., 2014).

**Figure 4.** Yield of biochars from hydrothermal carbonization with different temperature and time (A) sawdust and (B) bagasse.

The CHN element of biochars were reported about increasing carbon content via using hydrothermal carbonization. In Figure 5, carbon content of bagasse conditions (raw and 200 °C 24 hr) were 43.35% and 57.53%, respectively while sawdust conditions were 43.23% and 54.65%, respectively. Increasing carbon content is due to the different chemical composition of sawdust and bagasse also cellulose, hemicellulose and lignin (Garrote et al., 1999).

**Figure 5.** CHN elemental analyzer of biochars with hydrothermal carbonization.

**Conclusion**

Biochars from using sawdust and bagasse have been successfully produced with hydrothermal carbonization process. Yield of biochars under hydrothermal carbonization were decreased due to cellulose and hemicellulose in lignocellulose were almost totally decomposed with increasing temperature and time. Deoxygenation and dehydration reaction causes biochars to have hydroxyl group decreased.
But lignin content has slightly changed because the temperature is too low. Finally, the optimum conditions from hydrothermal carbonization is bagasse 200°C for 24 hr because it is the less hydroxyl group, C-O peak of hemicellulose and carbon content.

Acknowledgements
This work was financially supported by the Research and Researcher for Industry (RRi), The Thailand Research Fund (TRF) and also thankful to Nanoporous Materials Research Laboratory at College of Nanotechnology, King Mongkut’s Institute of Technology Ladkrabang for their supporting.

References