Journal of Environmental Management 201 (2017) 52–62

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Research article

Hydrothermal co-carbonization of sewage sludge and pinewood sawdust for nutrient-rich hydrochar production: Synergistic effects and products characterization

Xiaojuan Zhang [a], Lei Zhang [a, b, *], Aimin Li [a, **]

[a] School of Environmental Science & Technology, Dalian University of Technology, Key Laboratory of Industrial Ecology and Environmental Engineering (MOE), Dalian, 116024, Liaoning, China
[b] State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin, 150090, China

A R T I C L E I N F O

Article history:
Received 8 March 2017
Received in revised form
7 June 2017
Accepted 8 June 2017

Keywords:
Hydrothermal carbonization
Biomass
Different mixing ratio
Synergism
Nutrient elements

A B S T R A C T

The aim of this study is to explore the synergistic effects of hydrothermal co-carbonization of sewage sludge and pinewood sawdust on hydrochar production. Firstly, the effects of mixing ratios on hydrothermal carbonization were investigated, and then, the hydrochar was characterized by diverse analytical techniques. The mass balance results indicated that a significant synergistic enhancement occurred in terms of the increased hydrochar yield, organic and carbon retentions. By combining sewage sludge and pinewood sawdust at the mass ratio of 1:1, 58.11 ± 0.91% of hydrochar yield was obtained with high synergistic coefficients (8.41% for hydrochar yield, 13.09% for carbon retention, and 14.92% for organics retention). The hydrochar properties of nutrients, such as nitrogen and phosphorus, and surface functional groups were improved by hydrothermal co-carbonization approach. The FT-IR spectra, CP-MAS ^{13}C NMR and SEM results further indicated that hydrothermal co-carbonization promoted the development of aromaticity and surface structure. Our findings suggested that hydrothermal co-carbonization is a promising strategy to tailor high-performance hydrochar for different applications.

1. Introduction

Biochar is a porous and carbonaceous material generated through the thermo-chemical conversion of renewable biomass under a depleted oxygen atmosphere (Liu et al., 2015). The produced biochar could be utilized for numerous purposes. For example, biochar is utilized as an alternative to fossil fuels due to its high-energy density (Liu et al., 2013). Furthermore, biochar can be used for wastewater purification taking advantage of its adsorption capability towards inorganic, organic and microbial contaminants (Ahmad et al., 2014). Recently, using biochar as a soil conditioner has become an attractive research and application field. Biochar in agricultural soil can store carbon, thus reducing greenhouse gases emission (GHGs) (Lehmann et al., 2006). In addition, biochar has the potential to improve soil fertility by supplying and/or retaining nutrients for crop production (Atkinson et al., 2010).

Generally, biochar is produced from biomass either by slow or fast pyrolysis, gasification, torrefaction and hydrothermal carbonization. Pyrolysis is one of the most typical processes to produce biochar (Ahmed et al., 2016). It has a high carbon content and high aromatic degree. However, pyrolysis process for biochar production has some disadvantages. Firstly, a substantial heat input (an endothermic process) and inefficient heat transfer leads to a high-energy consumption (Bridgwater, 2012). Another issue is that the yield (30% for slow pyrolysis, 10% for fast pyrolysis) and the surface functional group density of biochar are relatively low. In addition, the biochar may also contain a considerable amount of polycyclic aromatic hydrocarbons (PAHs) and dioxins which pose a threat to soil amendment application (Hale et al., 2012). Therefore, the development of advanced biochar production process is still a challenging task.

Recently, the conversion of waste biomass into biochar (referred to as hydrochar) by using hydrothermal carbonization (HTC) process attracts widespread attention. Hydrothermal carbonization is a thermo-chemical process, which takes place in subcritical water under a moderate temperature and pressure, to improve the

* Corresponding author. School of Environmental Science & Technology, Dalian University of Technology, Key Laboratory of Industrial Ecology and Environmental Engineering (MOE), Dalian, 116024, Liaoning, China.
** Corresponding author.
E-mail addresses: zhanglei78@dlut.edu.cn (L. Zhang), leeam@dlut.edu.cn (A. Li).

http://dx.doi.org/10.1016/j.jenvman.2017.06.018
0301-4797/

properties of raw biomass for further use (Hoekman et al., 2011; Xiao et al., 2012). Compared to pyrolysis process, hydrothermal carbonization process has some advantages. It could be directly employed to high-moisture biomass like food waste, sewage sludge and algae without pre-drying. More importantly, it produces much higher yields of hydrochar (45–70%) than pyrolysis process (10–30%) (Kambo and Dutta, 2015). The hydrochar produced from HTC process has a high heating value and good combustion performance due to an increased carbon content and lower oxygen content (Berge et al., 2011; He et al., 2013). In addition, the energy efficiency of HTC process is much higher than that of pyrolysis process due to the exothermic reaction. The HTC process is an exothermic process and it can liberate energy throughout dehydration to form the condensed carbons (Maria et al., 2007). Funke and Ziegler (2011) reported that the amount of energy released progressively increased with stronger carbonization caused by severe reaction conditions, i. e. higher temperature and longer residence time. They also found that the type of feedstocks affected the released heat of reaction, e.g. 1.06 MJ/kg_{daf} for glucose, 1.0 MJ/kg_{daf} for cellulose and 0.76 MJ/kg_{daf} for wood at conditions of 240 °C, solids loading of 20%, pH 7. Although the liberated heat might not compensate for the energy loss in industrial application, the exothermic behavior could save the energy input.

Specially, hydrothermal carbonization process has a unique advantage for the functionalization of carbonaceous materials. It can generate high-performance carbonaceous materials with special morphologies (such as hollow-sphere structure), rich surface functional groups (such as hydroxyl, carbonyl, or carboxylic), high hydrophilic property and strong chemical reactivity (Hu et al., 2010). Some researchers have adopted hydrothermal carbonization process in controlled chemical reactions to tailor the structure of carbonaceous materials for some specific applications (Titirici and Antonietti, 2010). Considering the fact that hydrothermal carbonization technology is an effective way to produce functional carbonaceous materials, the hydrochar produced from HTC process might be a promising soil amendment with multiple-nutrient and good adsorption properties.

Previous studies indicated that hydrochar from lignocellulosic biomass via hydrothermal carbonization had a high hydrochar yield and rich oxygen-containing functional groups (Kang et al., 2012). In contrast, the hydrochar obtained from sewage sludge, which was comprised of carbohydrates, lipids and proteins, had a relatively low yield. However, sewage sludge had a high level of nutrients such as nitrogen, phosphorus and potassium as compared to lignocellulosic biomass (Kim et al., 2014). As the functionality of hydrochar could be varied by the type of feedstock and concentration, considering the different characteristics of two materials, the hydrothermal co-carbonization might have some benefits in several ways. For example, woody biomass is rich in organic components, especially lignin which could provide a skeleton for the growth of small particles on it, and protein in the sewage sludge could help in the functionalization of the carbon materials. The intermediates from hydrothermal treatment of lignocellulosic biomass, like furfural, ketone and aldehydes, were highly reactive, which could be beneficial for the hydrochar production by forming some humins like residue.

Furthermore, the nutrients, i.e. nitrogen, phosphorus, sulfur, potassium and sodium could be partially retained in the solid residue which makes it suitable for soil amendment applications. As sewage sludge has relatively lower carbon content and higher ash content, hydrothermal co-carbonization with lignocellulosic biomass will improve the properties of the hydrochar, such as an increases in carbon content and decreases ash content (Taya et al., 2001). On the basis of the above considerations, this study aims to explore the feasibility of producing a high-quality hydrochar via hydrothermal co-carbonization (Co-HTC) of two typical materials, sewage sludge and pinewood sawdust. The explicit objectives are: (1) to investigate the influence of mixing ratios on hydrothermal co-carbonization performance in terms of solid yield, carbon retention; (2) to determine the physicochemical properties of hydrochar (the composition, nutrients and surface functional group density); (3) to characterize the molecular structural and morphological properties of the hydrochar; (4) to explicate the synergistic effects during the Co-HTC process of sewage sludge and pinewood sawdust.

2. Experimental

2.1. Materials

Pinewood sawdust (PS) obtained from a wood processing plant, Dalian, China, was selected as a representative lignocellulosic biomass. PS was dried at 105 °C for 24 h and then sieved (less than 2.80 mm). Dewatered sewage sludge (SS) was taken from a domestic wastewater treatment plant (WWTP) in Dalian, China. The metal concentrations in sewage sludge were 384, 289, 138 and 975 mg/kg for Cr, Cu, Pb and Zn, respectively. As, Cd and Hg concentrations were under the detection limit. These metal concentrations meet the control standards for pollutants in sludges from agricultural use (neutral and alkaline soil) (China National Standard, GB 4284-84).

The raw dewatered sewage sludge was stored at 4 °C and then directly used for further hydrothermal carbonization experiment within 15 days. The raw sewage sludge contained 88.18 ± 0.02 wt% of moisture content. For some analysis (elemental analysis, SMT, FTIR, etc.), the dried sewage sludge was prepared by the drying of the raw sewage sludge at 65 °C overnight. The sewage sludge contains a high amount of minerals: SiO_2 (84.52 mg/g), CaO (33.80 mg/g), P_2O_5 (32.92 mg/g), Al_2O_3 (14.83 mg/g), Fe_2O_3 (13.71 mg/g), K_2O (6.48 mg/g), MgO (5.43 mg/g). Other characterization parameters for both feedstocks are shown in Table 1 in the following section.

2.2. Hydrothermal co-carbonization (Co-HTC) procedure

Co-HTC experiment of SS and PS was carried out in a 250-mL stirred batch reactor (Nickel alloy 625, GCF-type, Dalian Controlled Plant, China). In this study, the reaction temperature of 220 °C was chosen according to Kim et al. (2014), Funke and Ziegler (2010) and our previous data. Kim et al. (2014) reported that 220 °C was the optimum temperature for hydrothermal carbonization of anaerobically digested sludge. Under hydrothermal conditions of lower than 200 °C, in general, the hydrolysis of lignocellulosic biomass occurred other than carbonization (Funke and Ziegler, 2010). In addition, we found that at a higher temperature of 250 °C the yield of hydrochar was greatly decreased. Thus, in this study, 220 °C was selected as the hydrothermal carbonization temperature.

In each test, 102 g of feedstock was loaded into the reactor with mass ratio 7.5:1 (90 g water, 12 g dry matter). The SS and PS were weighed and manually mixed with the ratios of 1:0, 3:1, 1:1, 1:3 and 0:1 on dry basis. Nitrogen gas was purged to the sealed reactor in order to remove the oxygen. Then the reactor was heated up to a designated temperature. At the end of reaction, the reactor temperature was rapidly cooled down to below 180 °C by using cool water within 3–5 min and then took 2–3 h to cool down to room temperature. When the reactor temperature reached the room temperature, the product gas was collected by a gas sample bag and then measured by water displacement. The liquid-solid mixture was poured into a beaker and then separated by vacuum filtration