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Production of char from sewage sludge employing hydrothermal carbonization: Char properties, combustion behavior and thermal characteristics

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ABSTRACT

A comprehensive study was conducted on the properties of chars which derived from hydrothermal carbonization (HTC) of sewage sludge (SS) while varying the operation parameters as reaction temperature 180–300 °C, reaction time 30–480 min. The properties of chars derived from municipal sewage sludge HTC were evaluated by Elemental analysis, FTIR spectra and thermogravimetric analysis. Elemental analysis showed that O/C and H/C atomic ratios reduce to 0.07 and 1.84, respectively at 300 °C, 30 min due to dehydration and decarboxylation reactions were significant during HTC process. Higher heating values of the chars have improved 1.02–1.10 times of SS (10.97 MJ/kg) when reaction temperature rose to 260 °C with holding time between 30 min and 90 min. The approximate equilibrium moisture content becomes stable at 48.5% after 60 min reaction. The FTIR spectra determined that the HTC reaction improved dehydration on the —OH band in SS. Higher temperature improved carbon aromaticity during HTC of SS. The thermogravimetric analysis is an effective means to analyze combustion behavior and thermal characteristics. It was also used to determine combustion kinetics of SS and chars. The result shows that the ignition temperature of chars was higher and has better performance on safe handling, storing and transportation than SS.

1. Introduction

With the rapid development of urban construction, the quality of effluent treatment standards was improved more stringent. It results in the production of sewage sludge (SS) increased drastically in recent years, and it expected to 34 million metric tonnes in 2015 [1]. In general, SS has been deemed as a resource to generate renewable biofuels by its high biodegradable organic matter, which can be used as energy source and fertilizer in agriculture [2,3]. Nevertheless, it cannot be ignored that SS has the character of high moisture content, poor dewaterability and is often contaminated with heavy metals [4]. Moreover, pathogens and hazardous organic substances can result in the potential harm to soil, vegetation, animals and humans simultaneously due to unsuitable treatment. Currently, less than 20% of the sewage sludge in China has been treated safely, most of the SS has been disposed by conventional ways include composting, land/ocean disposal and incineration. Those methods are gradually limited by the rigorous requirement of environmental protection. At present, some recycling technologies for disposal of SS have been widely advocated including anaerobic digestion/aerobic composting [5], soil amendments [6], sludge pyrolysis [7] and hydrothermal carbonization (HTC) for solid fuel [8]. By considering the low cost and high resource recovery rate of hydrothermal carbonization, it has been deemed as a promising technology for wet biomass treatment. Many biomasses, including cellulose [9], wasted crops [10], municipal solid waste [11], maize silage [12] and corn stover [13] can be converted into fuels or materials via HTC process.

Organic feedstocks are converted into carbonaceous product (char) using water as a carbonization medium at moderate temperatures (180–350 °C) under self-generated pressure (2–10 MPa)

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[12,14]. It can simultaneously increase the dewaterability of SS [10] and been biologically sterilized by thermal treatment [15]. In addition, the liquid by-product can be efficiently separated from chars. While these studies mainly focused on the hydrothermal gasification or liquefaction of organic compounds, only a few published literature focused on the solid product under low temperature HTC process of SS. Menget al. [16] investigated the drying effect of SS product at 160–200 °C by hydrothermal drying. The results showed that the hydrothermal dying improved the dewaterability of SS and not affected by the different type of sludge samples. Zhao et al. [17] focused on energy recovering from SS by producing solid biofuel with HTC process. Hydrothermal temperature of 200 °C and holding time of 30 min were suggested to produce solid biofuel from SS with an energy recovery rate of 50%. During the HTC process, solid and liquid products were the main distinct phases. A few gas generated and it mainly consists of carbon dioxide [18]. However, Liang et al. [19] stated that the volume based heating value of municipal solid waste was improved at around 6.4–9.0 times at 220 °C and 2.4 MPa for 30 min, which indicated that lower carbonization temperature can produce higher solid yield in a certain range. In addition, Zhang et al. [20] reported that HTC process could promote the yield of char with the increase of reaction time. However, there are few investigations on the combustion behavior of char obtained from SS after treated by HTC.

Therefore, the goal of clean production has played an important role in studies on the characteristics of by-products from HTC process. It is meaningful to develop the study on fuel quality for combustion under different conditions. The main objectives of this study are to investigate the effect of HTC reaction temperature and reaction time on the properties of char, discuss the chemical changes after HTC process. Analyze the combustion behavior and thermal characteristics of SS and chars as alternative solid fuels.

2. Experimental

2.1. Materials preparation

Dewatered SS was taken from a wastewater treatment plant in Changsha, China. The initial moisture content of sludge was 89.32%. SS was dried in an oven kept at 105 °C for at least 24 h to remove the water completely, and subsequently grounded into fine powders (<0.25 mm) and stored in a dry glass bottle.

2.2. Hydrothermal carbonization reaction process

HTC experiments were conducted in a 500 mL 316 stainless steel reactor equipped with an automatic temperature controller and auto-stirred. SS powder was homogenously mixed with deionized water at a ratio of 1:9 after loaded into the reactor. One of the HTC experiments were performed at 180, 220, 260 and 300 °C and maintained for the reaction time of 30 min, while the another were performed at 60 min, 90 min, 360 min and 480 min and maintained for the reaction temperature of 260 °C. The heating rate was proximately of 4 °C/min. At the end of preset time, the reactor was allowed to cool down in room temperature. Solid and liquid products were separated by vacuum filtration apparatus with microfiltration filters. After that, the chars were taken in a beaker and oven-dried at 105 °C over night until its weight was stable, which as the weight of chars. The chars produced were referred as temperature-residence time, e.g. the char which called as 180–30 stands for the sample obtained at 180 °C and 30 min residence time. The yield of char and corresponding approximate equilibrium moisture content were calculated using the following equations:

$$\text{Char yield} \quad (\%) = \frac{\text{Char weight}}{\text{Dry SS weight}} \times 100\% \tag{1}$$

$$MC_e = \frac{W_1 - W_2}{W_2} \times 100\% \tag{2}$$

where MC_e meant the approximate equilibrium moisture content, W_1 is the mass of the loaded sludge (with moisture) and W_2 is the dry mass of loaded sludge.

2.3. Analysis of chars

The elemental analysis of SS and chars was performed by 2400 Series II CHNS Analyzer, PerkinElmer, USA. Table 1 presents the physical and chemical characteristics associated with these feedstocks. Fourier Transform Infrared Spectroscopy was done by FTIR-8400S Spectrometer, USA. The dry sample mix with KBr then pressed to disk to detect. It was investigated in the 4000–400 cm^{-1} region with 100 scans per sample. The baseline of the raw data was adjusted and then the modified data was normalized, recorded background was subtracted from the spectrum of SS and chars. A thermogravimetric analyzer (STA 409, NETZSCH, Germany) was used to measure thermal characteristics of the chars, the heating temperature range from 30 °C to 800 °C at a heating rate of 15 °C/min with air (N_2 = 80%, O_2 = 20%) and inert atmosphere (N_2 = 100%) flow.

3. Results and discussion

3.1. General properties of SS and chars

Proximate and ultimate analysis of SS and the derived chars are summarized in Table 1. The percentages of H and N in SS are 4.21% and 4.86%, respectively. However, the results declined to 3.22–3.92% and 1.12–1.64% after HTC process at different conditions due to some surface functional groups which consist of H and N have lost with volatile matters during HTC process. It also complies with the FTIR analysis in Section 3.3. Since the element C can exist in the form of fixed carbon and gas, the decrease of C is not significant while the increased ash content of chars are great after HTC process, indicating that a few carbon in SS formed hydrocarbon compounds as gas and then lost into the air or converted into liquid [18]. Higher heating values (HHVs) have been calculated with elemental composition. The HHVs formula was developed by Perry and Chilton based on the Dulong formula. The results show that HHVs can be improved under appropriate HTC conditions. The HHVs of chars increased to 11.79 MJ/kg with temperature rise to 260 °C. However, it obtained lower HHVs when the reaction time spans of longer than 90 min are considered. As the HHVs results, it indicated that the value of HHVs was higher than SS when reaction temperature at 260 °C with reaction time not exceeded 90 min, which were 1.02–1.10 times of SS. Besides, it reached the maximum value (12.06 MJ/kg) of 260–60.

Van Krevelen diagram can clearly visualize the carbonization degree of SS to chars. As shown in Fig. 1, the atomic ratio of H/C and O/C reduced in different degree after HTC process, from 2.02 and 0.46 to 1.99 and 0.15 when reaction temperature rise to 180 °C, respectively. Then, the ratio of H/C decreased to 1.84 and O/C dropped at 0.07 while the reaction temperature rose to 300 °C. On the other hand, H/C and O/C have been more affected in dehydration and demethanation by prolonging reaction time from 30 min to 480 min, which from 1.94 and 0.23 to 1.84 and 0.33, respectively. It is worth noting that the minimum H/C and O/C atomic ratios were 1.80 and 0.07, respectively of 260–60 and 300–30. The reduction of H/C and O/C was similar to the lignocellulosic biochars [22] and pyrolysis biochars [23]. The effect of