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Conversion of sewage sludge to clean solid fuel using hydrothermal carbonization: Hydrochar fuel characteristics and combustion behavior

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HIGHLIGHTS

- The hydrothermal carbonization of sewage sludge process is developed.
- Hydrochars are solid fuels with less nitrogen and sulfur contents.
- The first order combustion reaction of hydrochars is derived.
- Main combustion decomposition of hydrochars is easier and more stable.
- Formation pathways of hydrochars during hydrothermal carbonization are proposed.

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ABSTRACT

Conventional thermochemical treatment of sewage sludge (SS) is energy-intensive due to its high moisture content. To overcome this drawback, the hydrothermal carbonization (HTC) process was used to convert SS into clean solid fuel without prior drying. Different carbonization times were applied in order to produce hydrochars possessing better fuel properties. After the carbonization process, fuel characteristics and combustion behaviors of hydrochars were evaluated. Elemental analysis showed that 88% of carbon was recovered while 60% of nitrogen and sulfur was removed. Due to dehydration and decarboxylation reactions, hydrogen/carbon and oxygen/carbon atomic ratios reduced to 1.53 and 0.39, respectively. It was found that the fuel ratio increased to 0.18 by prolonging the carbonization process. Besides, longer carbonization time seemed to decrease oxygen containing functional groups while carbon aromaticity structure increased, thereby rendering hydrochars highly hydrophobic. The thermogravimetric analysis showed that the combustion decomposition was altered from a single stage for raw sludge to two stages for hydrochars. The combustion reaction was best fitted to the first order for both raw sludge and hydrochars. The combustion of hydrochars is expected to be easier and more stable than raw sludge because of lower activation energy and pre-exponential factor.

1. Introduction

The treatment of sewage sludge (SS) produced from wastewater treatment plants (WWTPs) is still an important global issue due to its high moisture content and poor dewaterability. At present, SS has attracted great attention as a promising feedstock for the production of renewable biofuels [1]. Pyrolysis-based concept is the main stream of research in converting SS into energy carriers [2,3] and adsorption materials [4]. As an alternative, the hydrothermal treatment technology is developed to harness energy from SS in the presence of water to avoid the energy-intensive prior drying. The desired products mainly depend on the hydrothermal conditions. Previous studies on hydrothermal processing focused on the production of heavy oil through hydrothermal liquefaction at 250–380 °C [5] and enhanced H_2 yield using catalytic hydrothermal gasification under 380 °C and 23 MPa [6]. It is not until recently that the hydrothermal carbonization (HTC) regains great attention as a promising technology for efficient wet biomass conversion to biocarbons, although it has been used to simulate natural coalification for over a century [7].

HTC is defined as a thermochemical process used to convert organic feedstock into carbonaceous product (hydrochar) in the presence of water under moderate temperatures (180–350 °C) and

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pressures (2–10 MPa) [8]. After HTC, the hydrochars obtained exhibit moderate calorific value, high aromaticity structures and mesoporous textures. In addition, hydrochars are biologically sterilized due to thermal treatment [9] whereas aqueous by-product can be efficiently separated from hydrochars. Consequently, HTC extends the potential feedstocks for hydrochar production to biomass materials with high moisture content [10].

Currently, many biomass substrates, including cellulose [11], microalgae [12,13], anaerobically digested maize silage [8], municipal solid waste [14–16], distiller's grains [17], and black liquor [18], have been applied in HTC to gain fuels or materials. Previously, Yoshida and Antal [1] carbonized SS with moisture content up to 30% in order to produce biochar for land utilization. According to heavy metals elution results, the biochar could be acceptable for land use. In another study, Park et al. [9] enhanced the stability and dispersibility of coal-sludge-water slurry using SS hydrothermally pretreated at 200 °C. More recently, Meng et al. [19] examined the hydrothermal dewatering and drying of SS at 160–200 °C. Their experimental results showed that the moisture content of treated SS was reduced to less than 20% with an evaporation rate of four times higher than untreated SS.

In general, carbohydrates and proteins comprise the main organic components in SS whereas lignin accounts for only a small amount. Carbohydrates and proteins can be hydrothermally decomposed at above 180 °C while lignin is degraded at 280–500 °C [20,21]. During HTC, two distinct phases, i.e., solid and liquid, are formed. The evolved gas is small and mainly consists of carbon dioxide [14]. However, an immiscible liquid-phase was observed during HTC of municipal waste streams at 250 °C [14], which indicated that hydrothermal liquefaction occurred and lower carbonization temperature was desired. In addition, carbonization time can also affect the products of HTC. Zhang et al. [22] showed that prolonged liquefaction time did not promote liquefaction process while it could raise the yield of residues. Therefore, in this study, an HTC process using stainless steel Teflon-lined reactor under lower temperature and different carbonization times was employed to recover solid fuel from SS with minimized liquefaction and corrosion issues.

The main purpose of this study was to develop an HTC process that can be applied to convert SS to an alternative clean fuel. The specific objectives were to: (1) investigate the fuel characteristics of hydrochars; (2) interpret the formation pathways of hydrochars; (3) discuss the effect of carbonization time on the characteristics of hydrochars; and (4) analyze the combustion behavior of hydrochars and evaluate the feasibility of hydrochars as alternative clean fuels.

2. Materials and methods

2.1. Materials

Dewatered SS was collected from Ulu Pandan Water Reclamation Plant in Singapore. The sludge was derived from treatment of domestic wastewater followed by anaerobic digestion and thickened to approximately 85.7 wt.% moisture content. The SS was stored at 4 °C and used as received in HTC experiments. With regard to the characterization of samples, the SS was air-dried for two weeks and ground into fine powders. The air-dried sludge powders (here labeled as DS) were sealed in a dry glass bottle.

2.2. HTC experiments

HTC experiments were conducted in a non-stirred 125 mL stainless steel Teflon-lined reactor (Parr Instrument Co., USA). Since the stainless steel surface can be easily attacked by halogen and sulfur in feedstocks under hot-compressed water [23], Teflon-liner was employed to avoid the corrosion of stainless steel reactor wall. In each batch experiment, approximately 10.3 g of the dewatered SS was loaded into the vessel and sealed. The reactor was placed in a muffle furnace and heated up to 200 °C under autogenous pressure. When the pre-set temperature was reached, five carbonization times of 4, 6, 8, 10, and 12 h were maintained, respectively. After the desired carbonization time elapsed, the reactor was removed from the furnace and placed in a 4 °C cold room to quench the reactor rapidly.

After hydrothermal carbonization process, the liquid was poured out of the vessel since the dewaterability of SS was greatly enhanced. The liquid was collected in a sampling vial and weighed to determine the weight of liquid phase. The remaining solid/liquid mixture was washed out of the vessel into a beaker. Then, the solid product was washed with distilled water for several times and separated using a vacuum filtration apparatus through microfiltration filter paper. Finally, the solid product was collected in a beaker. The suspended solid in the beaker was oven-dried at 105 °C overnight and weighed to obtain the weight of hydrochars. The hydrochars were marked as HC-4, HC-6, HC-8, HC-10, and HC-12 in accordance with carbonization time. All the experiments were carried out in triplicate. Hydrochar yield and corresponding approximate equilibrium moisture content were calculated using the following equations.

$$\text{Hydrochar yield } (\%) = \frac{\text{Hydrochar weight}}{\text{Dry sludge weight}} \times 100\% \tag{1}$$

$$\text{MC}_e = \frac{W_1 - W_2}{W_0} \times 100\% \tag{2}$$

where MC_e is the approximate equilibrium moisture content, W_1 is the weight of moisture in the loaded sludge, W_2 is the weight of liquid phase, and W_0 is the weight of the loaded sludge.

2.3. Solid fuel characterization

2.3.1. Chemical and physical properties analyses

Test methods for ash and volatile matter (VM) were performed based on ASTM D3174 and D3175, respectively. The fixed carbon (FC) percentage was determined by difference. The elemental compositions of the raw sludge and hydrochars were determined using elemental analyzer (vario EL cube CHNOS, Germany). The higher heating values (HHVs) of the samples were measured by IKA C2000 BASIC bomb calorimeter. The FTIR spectra were obtained using a Perkin Elmer spectrum GX FTIR spectrometer. Briefly, hydrochars were ground into fine particles and mixed with KBr powders in order to prepare pellets. Samples were scanned from 4000 cm^{-1} to 400 cm^{-1} with a resolution of 4 cm^{-1}. A constant sample to KBr ratio of 2 mg:280 mg was used to compare corresponding intensities of functional groups in samples semi-quantitatively. The background was subtracted from the spectra of samples. Surface morphologies of the raw sludge and hydrochars derived at different carbonization times were examined by JEOL JSM-7600F Field Emission Scanning Electron Microscope (FE-SEM).

2.3.2. Surface properties analyses

Zeta potential measurements were conducted to investigate the surface charge of hydrochars. Zeta potential values were measured at 25 °C under pH values ranging from 2 to 7 using Malvern Zeta Sizer Nano Series, which was equipped with a rectangular electrophoresis cell. The pH value of solution was adjusted by titrating 0.05 M H_2SO_4 into 0.1 M NaOH bulk solution. Then, 20 mL solution was added into a flask containing 0.01 g sample to make a 0.05 wt.% suspension. The surface oxygen containing functional groups are mainly composed of carboxylic ($-$COOH), lactone ($-$C=O), and phenolic ($-$OH). Boehm titration method was used