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Gasification characteristics of hydrochar and pyrochar derived from sewage sludge

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A B S T R A C T

Two types of the biochars, pyrochar and hydrochar derived from low temperature pyrolysis (LTP) and hydrothermal carbonization (HTC) of sewage sludge were prepared and characterized. Their gasification properties were further experimentally evaluated. The results showed that the hydrochar was more hydrophobic than the pyrochar. The hydrochar was rich in nitrogen-containing functional groups and increased nickel, iron, alkali and alkaline earth metallic species compared to the raw sludge and pyrochar. It enhanced the interactions between the carbon surface and hydrogen bonding as well as gasification reactivity of the hydrochar, thus resulting in a higher hydrogen concentration and yield than the pyrochar under identical conditions. Additionally, the hydrochar had a more porous structure on the surface, facilitating the pores better accessible for condensable hydrocarbon molecules and thus improved the gas production and gasification efficiency. Although the energy recovery efficiency of LTP-gasification method was higher than that of HTC-gasification approach, the total energy consumption during the HTC pretreatment combined with subsequent gasification was lower than the energy evolved in the corresponding product gas in most gasification conditions. This study demonstrates that the integration of HTC pretreatment and subsequent gasification has promising potential for hydrogen-rich syngas production from sewage sludge.

1. Introduction

The depletion of fossil-fuel reserves and increasing environmental pollution caused by the large-scale application of fossil fuel make hydrogen an attractive alternative energy carrier and for the production of chemical products (e.g., methanol, ammonia) [1]. Currently, hydrogen is mostly generated from steam reforming of natural gas for industrial application. To achieve the goal of sustainable hydrogen production, the dependence away from fossil-fuel to renewable alternatives, such as biomass resources, is a step in the right direction [2]. As a byproduct from municipal or industrial wastewater treatment processes, sewage sludge is a kind of abundant waste biomass, which contains large amounts of organic components. Until recently, sewage sludge is usually disposed by landfill or incineration, which suffers from secondary pollution and low energy recovery rate [3].

Green Chemistry aspires to reduce consumption of nonrenewable resources and at the same time produce high-quality products in an environmental-friendly manner from renewable resources. Gasification of sewage sludge may be one of the promising sustainable approaches for hydrogen-rich syngas production. However, raw sludge is unsuitable for direct gasification due to the high water content and thus pretreatment is necessary to improve its quality prior to further gasification process [4]. Applying proper thermochemical pretreatment can also improve the energy efficiency and diversify the energy utilization pathways.

As one of the typical thermochemical pretreatment, low temperature pyrolysis (LTP) [5,6] converts biomass into pyrochar under an inert atmosphere with low heating rate. The pyrochar has improved physical and chemical characteristics, and it has been extensively used for soil amendment, wastewater pollution remediation, carbon sequestration and bioenergy production [7]. An alternative to LTP is hydrothermal carbonization (HTC) [8–10], which converts biomass into hydrochar in aqueous phase under facile temperatures and self-generated pressure. HTC offers several potential advantages such as high conversion efficiency and the

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ability to use diverse feedstock without drying pretreatment, which is especially suitable for high water content of biomass like sewage sludge.

The physical properties and chemical functionalities on the surface of the pyrochar and hydrochar are significantly different from each other, both of which thus have respective advantages in various industry applications. Escala et al. [11] reported that conducting HTC and drying the hydrochar have energetic advantages compared with drying the sewage sludge for thermal disposal treatment. In addition, the HTC-pretreated sewage sludge is reported to have improved combustion properties compared to the pyrochar and raw sludge [6,9,12,13]. In terms of gasification of the biochar, Álvarez-Murillo et al. [5] studied the steam gasification characteristics of the hydrochar derived from olive stone as a representative of lignocellulosic biomass. It was observed that the hydrochar modified the gas profiles during gasification, improving H_2 and CO production as well as the heating value. Erlach et al. [14] also concluded that pretreating the lingocellulosic biomass with HTC produced a hydrochar that was better suited for entrained flow gasification than raw biomass. These studies successfully verified the improved gasification behavior of lignocellulosic biomass after the hydrothermal pretreatment.

Different from lignocellulosic biomass (mainly composed of biopolymers cellulose, hemicellulose and lignin), the main composition of sewage sludge is protein and lipid. Therefore, different gasification behavior of hydrochar derived from sewage sludge is expected to that of the hydrochar from lignocellulosic biomass. Our previous study [15] investigated the gasification behavior of the hydrochar derived from sewage sludge by hydrothermal carbonization. It was observed that compared to the raw material, the hydrothermally treated sewage sludge had improved gasification characteristics in terms of hydrogen-rich syngas production. However, the lack of understanding on the effect of different pretreatments on the gasification behavior of the same sewage sludge under identical conditions is making the investigation on thermochemical treatment of sewage sludge difficult to go to a more profound level. Therefore, the primary goal of this study is to investigate the gasification properties of pyrochar and hydrochar derived from sewage sludge by LTP and HTC, respectively. Previous literature [16–18] have shown that steam as the gasifying medium has been proved effective for enhancing hydrogen yield compared to air gasification or air-steam gasification. In this work, the effects of operating conditions, including reaction temperature and the mass ratio of steam to biomass on gasification characteristics of the pyrochar and hydrochar were experimentally evaluated in terms of gas composition, heating value, gasification efficiency and energy recovery efficiency.

2. Experimental section

2.1. Biochars preparation

Sewage sludges were collected from a municipal sewage treatment plant in Beijing, China. The collected raw sludge still contains high content of water. Prior to the LTP reaction, the raw sludge was centrifuged, oven dried at 105 °C for 12 h and then ground into powders. However, no dewatering and drying pretreatment was conducted for the HTC treatment.

Reaction temperature and retention time are two significant factors affecting the properties of the biochars. A recent study [19] investigated the effect of temperature (180–250 °C) on the characteristic of hydrochar derived from anaerobically digested sludge, and it was concluded that 220 °C was the optimal reaction temperature with the highest energy recovery efficiency (93.1%). Danso-Boateng et al. [20] evaluated the kinetics of HTC of different biomass, and it was reported that temperature had a more pronounced effect on hydrochar production than retention time and increasing the retention time beyond 1 h did not significantly improve hydrochar yield. Therefore, for both fundamental and practical interests, we used a temperature of 220 °C and retention time of 1 h for the hydrochar production.

Hydrochar of sewage sludge was prepared using a stainless autoclave. A feedstock slurry of raw sludge with DI water was loaded into the reactor and kept the solid:liquid ratio of 1: 9 (w/w). The reactor was sealed and heated to 220 °C for 1 h, and the corresponding pressure at final reaction was 1.9 MPa. Then the reactor was rapidly cooled down to room temperature by flowing tap water. Solid hydrochar produced from HTC was separated from the resultant mixture by centrifugation, and was oven dried at 105 °C for 12 h before the subsequent gasification test.

To make a comparison, the pyrochar derived from sewage sludge was produced under the same temperature (i.e., 220 °C) by the approach of LTP. The LTP experiment was conducted in a quartz tubular reactor under atmospheric pressure. Five grams (5 g) of the dried sewage sludge were packed in the middle of the reactor and then heated by an electric furnace under a constant N_2 (99.9%) flowing of 200 ml/min. After being held at 220 °C for 1 h, the electric furnace was turned off and the samples were cooled to ambient temperature. All the LTP and HTC experiments were conducted in duplicates. The pyrochar and hydrochar derived from sewage sludge were both ground into powders less than 0.5 mm for the characterization and subsequent steam gasification experiments.

2.2. Steam gasification experiments

Steam gasification of the pyrochar and hydrochar was carried out in a laboratory-scale fixed-bed reactor system [15]. It is mainly composed of a quartz tubular reactor, steam generation kit, N_2 line, and a gas purification unit. The inner diameter and length of the quartz tube are 60 mm and 1000 mm, respectively. Schematic illustration of biochar preparation and steam gasification for the production of hydrogen-rich syngas is shown in Fig. 1.

As the beginning of each test, 1 g of feedstock was weighed and then placed onto the quartz boat. Nitrogen (99.9%) with a flow rate of 100 ml/min was fed to the reactor to produce an anoxic atmosphere. The quartz tube was heated to the desired temperatures by an electric furnace, followed by turning on the steam generation kit. After 20 min, the quartz boat was injected into the heating zone of the tube by the rod, and the nitrogen gas was switched off. The produced gas passed through the gas purification unit to remove tar and water, then the clean, cool and dry gas was collected using a gas sampling bag in the entire reaction time. The main gas composition (H_2, CH_4, CO, CO_2) was analyzed using a gas chromatograph (GC 3420A) equipped with a thermal conductivity detector (TCD) and two columns, including 5A and GDX-104. Argon was adopted as the carrier gas, and standard gas mixtures were applied for quantitative calibration. Gasification characteristics of the pyrochar and hydrochar were evaluated in terms of hydrogen yield, lower heating value (LHV) of the product gas and gasification efficiency [15,21]. Besides, an index of energy recovery efficiency (ERE) [22] was used in this work to evaluate the effect of two different pretreatments on the entire energy balance, which is calculated as:

$$ERE^{i}_{\mathrm{Pre}} = \frac{HHV^{i}_{biochar} \times W^{i}_{biochar}}{HHV_{dry\ sludge} \times W_{dry\ sludge}} \quad (1)$$