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Hydrogen-rich gas production by steam gasification of hydrochar derived from sewage sludge

Chao Gai [a], Yanchuan Guo [b], Tingting Liu [a], Nana Peng [a], Zhengang Liu [a,*]

[a] Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 18 Shuangqing Road, Beijing 100085, China

[b] Key Laboratory of Photochemical Conversion and Optoelectronic Material, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, 29 Zhongguancun East Road, Beijing 100190, China

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ABSTRACT

Hydrothermal carbonization is an effective pretreatment for further thermal conversion of high moisture biomass without a high cost of a dehydration process. The current paper concerns the properties of hydrochar derived from hydrothermal carbonization of sewage sludge, and the feasibility of steam gasification of hydrochar for hydrogen-rich gas production was investigated. Sewage sludge derived hydrochar was characterized using scanning electron microscopy, Fourier transform infrared spectroscopy, and inductively coupled plasma atomic emission spectroscopy to evaluate its feasibility for gasification application. The effect of reaction temperature, steam to biomass mass ratio, and addition of alkali catalysts on steam gasification characteristics of raw sewage sludge and corresponding hydrochar were evaluated, in terms of major composition of the produced gas, gas yield, gasification efficiency and energy density. The results showed that sewage sludge derived hydrochar was rich in hydrophilic functional groups and increased Fe, Ni, alkali and alkaline earth metals (i.e. K, Na, Ca, Mg), resulting in a higher hydrogen yield and energy efficiency than direct steam gasification of sewage sludge under identical conditions. In addition, hydrogen-rich gas production was also favored with the presence of alkali catalysts, especially for the hydrochar. The present study demonstrates that hydrothermal carbonization provides an effective pretreatment of sewage sludge for production of hydrogen-rich gas via steam gasification.

Introduction

Hydrogen has been widely recognized as a zero-emission fuel. Steam reforming of natural gas is one of the primary industrial methods to produce hydrogen. Exhaustible reserves of fossil fuels have promoted alternative technologies to generate hydrogen from renewable sources like biomass [1]. As a by-product from municipal or industrial wastewater, sewage sludge is a kind of abundant biomass in developed and developing countries. Landfill, incineration and anaerobic digestion are traditional treatments for sewage sludge, which

* *Corresponding author*. Tel./fax: +86 10 62915966.
E-mail address: zgliu@rcees.ac.cn (Z. Liu).
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suffer from secondary pollution or long processing period [2]. In comparison with these treatments, gasification appears a promising recycling approach for producing hydrogen from sewage sludge in a shorter period of time [3–5].

Syngas from the gasification process consists mainly of hydrogen, carbon oxides, light hydrocarbons and heavy condensates as tars. The hydrogen concentration and yield are affected by various factors such as biomass property, temperature, and gasifying agents. According to Gil-Lalaguna et al. [6], steam as the gasifying agent enhanced hydrogen yield compared to air gasification or air-steam gasification. To further increase hydrogen yield in the steam gasification process, various catalysts have also been employed such as dolomite, alkali catalysts, and noble metals like Ni-based catalysts [7,8]. Combined different catalysts have also been proved to be effective promoting hydrogen production. For instance, Gong et al. [9] reported that with addition of 3.33 wt.% Ni and 1.67 wt.% NaOH, the hydrogen yield of 4.8 mol/(kg organic matter) was almost five times as much as that without catalyst. In addition to catalytic gasification, higher purity hydrogen gas can be achieved by *in situ* removal of CO_2 by CaO-based absorbents such as calcined dolomite [10]. Fermoso et al. have recently reported that a high yield (80–93%) of high purity hydrogen (99.9%) was achieved by the addition of Pd/Ni–Co catalyst coupled with calcined dolomite as the CO_2 acceptor in the steam gasification process of chestnut wood sawdust [11].

One major disadvantage of steam gasification of sewage sludge is that a dehydrating pretreatment is required for steam gasification process. However, this is a high energy-intensive consumption process and thus increases the cost of pretreatment since the moisture content of sewage sludge is averagely as high as 90% [12]. Hydrothermal processing is one of important conversion techniques, which can enhance the transformation of biomass to fuels and chemical feedstocks in a water-rich phase at mild temperatures (180–500 °C) and at sufficient pressures [13,14]. It offers potential advantages in terms of high conversion efficiency, high throughputs, and the ability to use diverse feedstock without drying process [15,16]. Based on operation conditions, hydrothermal technology can be divided into different processes such as hydrothermal carbonization (HTC), hydrothermal gasification (HTG) and hydrothermal liquefaction (HTL) [17–19]. Among these processes, HTC is effective for production of carbonaceous materials from biomass [20]. Recently, Escala reported that conducting HTC and drying the hydrochar have energetic advantages compared with drying the sewage sludge for thermal disposal treatment [21].

Therefore, one promising alternative of conventional steam gasification of sewage sludge for hydrogen production is the steam gasification of the hydrochar derived from sewage sludge via hydrothermal carbonization pretreatment. Álvarez-Murillo et al. [22] investigated the steam gasification characteristics of hydrochar derived from HTC of olive stone as a representative of lignocellulosic biomass. It was observed that hydrochar of olive stone provided improved gasification characteristics. Dissimilar with lignocellulosic biomass, sewage sludge is mainly composed of proteins and lipids. However, few study has been concerned about the influence of hydrochar from HTC of sewage sludge on subsequent catalytic gasification behavior. The principal objective of this study was to investigate the feasibility of steam gasification of the hydrochar derived from sewage sludge for hydrogen-rich gas production. The effects of operating conditions, including reaction temperature and the mass ratio of steam to biomass on gasification characteristics of sewage sludge and hydrochar were experimentally evaluated in terms of product distribution, gas composition, gas yield, gasification efficiency and energy density. Besides, additions of alkali catalysts in steam gasification of the hydrochar were also performed to identify the effect of hydrothermal treatment on catalytic steam gasification of sewage sludge.

Experimental procedures

Hydrothermal carbonization

The sewage sludge was collected from an urban sewage treatment plant in Shandong, China (118°10′ to 120°01′ E, 35°32′ to 37°26′ N). Hydrothermal carbonization of sewage sludge was carried out using a stainless autoclave with 2000 mL capacity. A 1000 mL feedstock slurry of sewage sludge with water was loaded into the reactor and sealed. The reactor was heated to 180 °C and kept for 1 h. It should be noted that a temperature range of 180–250 °C is generally applied for hydrochar production *via* hydrothermal carbonization [23,24]. Based on a production practice, a relatively low temperature (180 °C) was applied in the current study. The corresponding pressure at final reaction was 1.5 MPa. Then the reactor was rapidly cooled by flowing tap water. The solid fraction was separated from the resultant mixture by centrifugation and was oven dried at 105 °C for 24 h, which is regarded as the hydrochar derived from sewage sludge. Dried sewage sludge and the hydrochar were both milled and then sieved. The fraction of 100–120 mesh was reserved for the experimental runs. All the experiments were repeated for three times, and hydrochars were mixed to reduce the error.

Hydrochar characterization

Volatile matter and ash contents of sewage sludge and hydrochar were determined following standard ASTM D3175-07 and ASTM D3174-12. Elemental analysis (C, H, O, N, S) was conducted on an elemental analyzer (CE-440, Exeter Analytical Inc., North Chelmsfor, MA). The Higher Heating Values (HHV) of sewage sludge and hydrochar were measured at a bomb calorimeter (Model 1281, Parr Instrument Co., USA).

The textural, structural and chemical properties of the feedstock greatly affect the gasification reactivity [25]. In this study, the concentration of inorganic elements, surface morphology, crystallographic structures and surface functionalities of sewage sludge-based hydrochar were investigated by different analytical techniques. The absolute concentration of inorganic elements (Ni, Fe, K, Na, Ca, Mg, Si, Al, Cu, Zn, Sn, Ti) in the sewage sludge and hydrochar were determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). The procedure involved a digestion of sample (0.1 g) in a $HNO_3/H_2O_2/HClO_4/HF$ mixture (2:2:1:2), and the solution was analyzed by ICP-AES (Leeman Prodigy, USA).