



Impacts of different biochar types on hydrogen production promotion during fermentative co-digestion of food wastes and dewatered sewage sludge

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ABSTRACT

Pyrolysis and anaerobic digestion are two important strategies for waste management that may be combined for clean energy production. This article investigates the effects of 12 types of biochars derived from four feedstocks at three pyrolysis temperatures on H₂ production via fermentative co-digestion of food wastes and dewatered sewage sludge. The results show that feedstock type and pyrolysis temperature significantly influence biochar properties such as pH, specific surface area and ash contents. Despite the wide range of BET specific surface areas (1.2–511.3 m²/g) and ash contents (5.3–73.7(wt%)) of biochars produced, most biochars promoted the VFAs production process and altered the fermentative type from that of acetate type to butyrate type, which seemed to have a higher efficiency for H₂ production. Moreover, fitting of the results to the modified Gompertz model shows that biochar addition shortens the lag time by circa 18–62% and increases the maximum H₂ production rate by circa 18–110%. Furthermore, the biochar derived at higher pyrolysis temperatures enhances H₂ production dramatically over those derived at low temperatures. Principal components analysis demonstrated that the pH buffering capacity of biochar was critical to the promotion of fermentative H₂ production by mitigating the pH decrease caused by VFAs accumulation. Consequently, a sustainable integrated waste management strategy combining pyrolysis and anaerobic digestion is proposed for the efficient treatment of various bio-wastes.

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1. Introduction

Hydrogen gas (H₂) can be a sustainable and renewable fuel that produces no greenhouse gas (GHG). This could help to relieve the reliance on traditional fossil fuels and mitigate climate change (Turner, 2004). Currently, most H₂ is generated from non-renewable sources, which is counter to the aim of GHG emission reduction. Thus, in recent years, more sustainable and environmentally-friendly technologies have been developed for producing H₂ production, including photolysis, photo-fermentation and dark fermentation (Kalinci et al., 2009). Of these,

the dark fermentation, an H₂ production process via anaerobic microorganisms, requires not only minimal energy consumption but also has stronger operability for engineering applications. Additionally, dark fermentative H₂ production can be achieved using bio-wastes as sources to which could efficiently integrate organic waste management and cleaner energy production (Gioannis et al., 2013). In this way, many kinds of bio-wastes, such as food wastes, sewage sludge, and animal manures, could be degraded into volatile fatty acids (VFAs) and H₂ in anaerobic systems (Gilroyed et al., 2008; Han et al., 2016; Slezak et al., 2017). Therefore, the dark fermentative H₂ production strategy, which aims to reduce bio-wastes, produce valuable products and cleaner energy shows potential economic and ecological benefits.

Although fermentative H₂ production is a promising technology, several issues have limited its engineering application. First, fermentative H₂ production occurs within the acidification process of the anaerobic systems. Consequently, continuous VFAs

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production could cause a decrease in the pH, which is crucial for the metabolism of microbes and the metabolic pathways of H₂ production (Slezak et al., 2017). To overcome this problem, some buffering agents, such as lime mud and NaHCO₃, were added to stabilize pH in H₂ production systems (Lin & Lay, 2004). Additionally, to promote the H₂ yield and increase the biomass retention time, different types of carriers such as activated carbon, glass beads and expanded clay, could be added into the H₂ production system to enrich H₂ production bacteria (HPB) and to increase stability of the system (Barca et al., 2015).

As carbohydrate-rich and readily biodegradable materials, food wastes and other industrial bio-wastes from food production factories may be ideal substrates for fermentative H₂ production (Lin et al., 2012). However, for some kinds of lignocellulosic wastes that are recalcitrant to anaerobic degradation, other treatment strategies should be considered. Recently, studies on the pyrolysis of lignocellulosic wastes under oxygen-limited or oxygen-absent conditions are burgeoning, whereby these wastes are converted to biochar (Lehmann & Joseph, 2015). As a porous eco-compatible carbon-rich material, biochar has significant potential for environmental management, allowing carbon sequestration, GHG emission reduction, pollutant remediation, and soil amendment (Lehmann et al., 2011; Manyà, 2012; Woolf et al., 2010). Moreover, it is reported that biochar addition could promote anaerobic biogas (H₂/CH₄) production due to its unique properties, such as alkalinity characteristics for pH buffering (Wang et al., 2017) and high specific surface area (SSA) for biomass attachment (Luo et al., 2015). In a two-phase anaerobic digestion system for H₂ and CH₄ production, the maximum production rates of both H₂ and CH₄ increased as biochar was added (Sunyoto et al., 2016). In a single-phase methane production system for cattle manure anaerobic digestion, 1% biochar addition (dry substrate weight basis) increased biogas production by 31%, but a higher biochar dose addition did not result in any additional increase (Inthapanya et al., 2012). Biochar addition also mitigated mild ammonia inhibition and supported methanogen growth and metabolic functions (Lü et al., 2016). It is also reported that 10 g/L biochar addition both shortened the methanogenic lag phase by 11.4–30.3% and increased the maximum methane production rate by 5.2–86.6% (Luo et al., 2015). Furthermore, Meyerkohlstock et al. (2016) investigated the effects of biochar on the solid-state fermentation of bio-waste and reported that both biogas and methane yield increased by approximately 5% with 5% biochar addition.

To the best of the authors' knowledge, although the promotion of anaerobic biogas production by biochar addition is widely reported, studies on the effects of biochar' properties on the H₂ production process is rare. Thus, the intrinsic mechanism of fermentative H₂ production enhancement by biochar addition, which may be closely related to the properties of biochar, remains unclear. Generally, the feedstocks and highest treatment temperatures (HTTs) of biochar production are two important factors that significantly influence the properties of the derived biochar (Manyà, 2012). Nevertheless, the effects of biochar derived from different feedstock types at variable pyrolysis HTTs on fermentative H₂ production have never been studied. This lack of knowledge is addressed by examining the physiochemical properties of biochar produced from four feedstocks under three HTTs in the present study. Meanwhile, the effects of biochar addition on fermentative H₂ production are also elucidated, and the main derived property of biochar affecting the fermentative H₂ production process is determined. Finally, an integrated strategy for efficient and sustainable management of various bio-wastes is proposed.

2. Materials and methods

2.1. Biochar preparation

Four different types of biomass were used as feedstock materials. Sawdust (SD) was purchased from a local furniture factory, wheat bran (WB) and peanut shell (PS) were collected from a cropland in the suburb of Xi'an, Shaanxi Province, China, and sewage sludge (SS) was acquired from the Xi'an No.5 Wastewater treatment plant (WWTP). The feedstocks were air-dried at room temperature for five days. Subsequently, the feedstocks were placed into ceramic crucibles, covered with fitting lids, and pyrolyzed under oxygen-limited conditions in a muffle furnace (Shanghai Jing Hong Laboratory Instrument Co., Shanghai, China). Pyrolysis was carried out at HTTs of 300, 500, and 700 °C at a heating rate of approximately 15 °C min⁻¹ and then held at the given HTTs for 1 h. After the pyrolysis process was complete, the biochar samples were allowed to cool to room temperature and then pulverized to sieve to uniform size fractions of 0.25–1 mm. The biochar samples were then stored in plastic sealing bags until further analysis. The biochar samples were designated as SD3, SD5, SD7, WB3, WB5, WB7, PS3, PS5, PS7, SS3, SS5 and SS7, where the letters represent the feedstocks (SD, WB, PS and SS) and the numbers 3, 5 and 7 represent the HTT of 300 °C, 500 °C, and 700 °C, respectively.

2.2. Biochar property analysis

The biochar yields and proximate analysis were carried out according to ASTM D1762-84 (2013). The pH values of the biochars were measured in a 5% (w v⁻¹) suspension of deionized water prepared by shaking at 100 rpm under ambient temperature for 24 h using a pH meter (PHS-3C, Dapu Instrument Co., Shanghai, China). The BET (Brunauer-Emmett-Teller) SSA was measured via N₂ adsorption multilayer theory by a V-Sorb X800 surface area analyzer (Gold APP Instrument Co., Beijing, China). The elemental (CN/OH) analysis was carried out using an isotope ratio mass spectrometer (IRMS, IsoPrime100, Elementar, Germany). The surface morphology and textural properties of biochar were characterized via scanning electron microscope (SEM; JEOL, JSM-6510LV, Japan) with a tungsten filament. The surface functional group analysis of feedstocks and biochars were determined by Fourier transform infrared spectroscopy (FT-IR, ThermoFisher, USA) under an attenuated total reflectance (ATR) model. The spectrum was recorded in the wave number range of 500–4000 cm⁻¹. The feedstocks and biochar samples were pulverized without additional pretreatment. All the physiochemical analyses were carried out in duplicate.

2.3. Substrates and inoculum sources

Dewatered activated sludge (DAS) and food waste (FW) were used as substrates for co-digestion in the batch experiments. The DAS was collected from a sludge dewatering unit in Xi'an No.5 WWTP, Shaanxi Province, China. The FW sample was a synthetic preparation based on the characteristics of food waste in China, and the components are shown in supplementary materials. The ratio of FW to DAS based on wet weight was 4:1. The raw substrates were preserved at 4 °C before use.

The inoculum for the H₂ production experiments was collected from the biogas plant of a local brewery, which was steadily operated under mesophilic conditions. The inoculum was stored at 4 °C anaerobically for several weeks before use. The physio-chemical properties of the substrates and inocula were measured in duplicate and are listed in Table 1.

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