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Thermophilic bio-hydrogen production from corn-bran residue pretreated by calcined-lime mud from papermaking process

Jishi Zhang *, Junjie Zhang, Lihua Zang

School of Environmental Science and Engineering, Qilu University of Technology, Jinan 250353, China
Key Laboratory of Cleaner Production and Industrial Wastes Recycling and Resourcization in Universities of Shandong, Jinan 250353, China

HIGHLIGHTS

- Corn-bran residue (CBR) is an attractive, low-cost feedstock for H_2 production.
- CLMP pretreatment favored the H_2 evolution from CBR.
- CLMP disintegrated and gelatinized the crystalline construct of CBR.
- Maximum H_2 yield of 338.91 ml/g-VS was obtained after CLMP (10 g/L) treatment.
- CLMP pretreatment is an alternative approach to improve cellulosic H_2 production.

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ABSTRACT

This study investigated the use of calcined-lime mud from papermaking process (CLMP) pretreatment to improve fermentative hydrogen yields from corn-bran residue (CBR). CBR samples were pretreated with different concentrations (0–15 g/L) of CLMP at 55 °C for 48 h, prior to the thermophilic fermentation with heat-treated anaerobic sludge inoculum. The maximum hydrogen yield (MHY) of 338.91 ml/g-VS was produced from the CBR pretreated with 10 g/L CLMP, with the corresponding lag-phase time of 8.24 h. Hydrogen yield increments increased from 27.76% to 48.07%, compared to the control. The CLMP hydrolyzed more cellulose, which provided adequate substrates for hydrogen production.

1. Introduction

Energy shortages and environmental pollution have become the focus of world attention. Hydrogen has been widely recognized as available alternative energy carrier of future due to its effectivity, recycle and cleanness (Pan et al., 2011; Zhang et al., 2013a). It is mainly produced by the thermo-catalytic reformation of hydrogen-rich organic compounds, electrolysis of water and biological processes (Zhang et al., 2013a). Among them, bio-hydrogen production from biomass can recover energy and reduce dependence on fossil fuel, being lowly energy-intensive and friendly to environment (Zhang et al., 2013b). Furthermore, dark fermentative bio-hydrogen production from lignocellulosic feedstocks (e.g., agricultural and industrial organic wastes) is also a potentially promising method for constantly recovering hydrogen as a fuel (Zhang et al., 2013b, 2007). Moreover, lignocellulosic wastes are among the world's most abundant, providing renewable resources without competing with food supplies (Zhang et al., 2007). Lignocellulose-to-hydrogen conversion is a promising technology for the sustainable production of fuel, while major efforts should be made to improve its economic competitiveness.

Although lignocellulosic wastes have attractive, low-cost feedstocks for hydrogen production, direct biological conversion of them to hydrogen by anaerobic fermentation is very difficult due to the refractory of polysaccharide (cellulose and hemicellulose) (Öhgren et al., 2007). Therefore, the polysaccharide hydrolysis is the rate-limiting step for the whole bio-hydrogen production process. In order to make the carbohydrate polymers more accessible and more biodegradable to anaerobes or enzymes, many

* Corresponding author at: School of Environmental Science and Engineering, Qilu University of Technology, Jinan 250353, China. Tel.: +86 53189631680; fax: +86 531 89631163.
E-mail address: lyzhangjishi@163.com (J. Zhang).

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pretreatment approaches have been proposed to enhance the performance of hydrogen fermentation, such as steam explosion, thermal degradation, ammonia fiber explosion, acid and alkaline pretreatment (Cao et al., 2012; Hendriks and Zeeman, 2009). Among these promising approaches, alkaline pretreatment has received much attention due to its low-cost, easy operation and high efficiency (Cao et al., 2012) such as delignification, fiber expansion and increase of accessible surface area (Monlau et al., 2015). In general, alkaline pretreatment requires reduced pressures and temperatures compared to other pretreatment technologies, while it takes long residence time, usually in the order of hours or days rather than minutes (Reilly et al., 2014; Zhang et al., 2013a). During alkaline pretreatment, solubilization of lignin and modification in the crystalline state of the cellulose likely occur, which result in making the biomass more accessible for bacteria and enzymes (Zhang et al., 2007).

Following H_2SO_4 pretreatment at 120 °C for 90 min, a 125.11 ml H_2/g-VS was obtained from simultaneous saccharification fermentation of wheat straw solids, compared to 47.89 ml H_2/g-VS when using separate hydrolysis and fermentation (Quéméneur et al., 2012a). Interestingly, when alkaline pretreatment is to be followed by anaerobic fermentation, the pretreatment has more practical advantages than other pretreatment technologies (Cao et al., 2012). This can be explained by the fact that the alkaline remaining with the treated solid after pretreatment favor the following anaerobic digestion of biomass that generally requires alkalinity addition for pH control (He et al., 2008). Only in this way would the operational cost of lignocellulose-to-hydrogen bioconversion be significantly decreased. Although sodium hydroxide (NaOH) is most often used over other chemicals (e.g., $Ca(OH)_2$ and KOH) due to its high rate of chemical oxygen demand (COD) solubilization (Kim et al., 2003), the use of this reagent involves higher chemical costs and, therefore, a possible increase of pretreatment cost (Zhu et al., 2010). Some researchers provide a good review and discussion of the pretreatment methods in general bioconversion of biowastes, which apply for hydrogen, as well as for bioethanol and other fermentation processes (Baeyens et al., 2015). Compared with NaOH, calcined-lime mud from papermaking process (CLMP) is much safer and cheaper, and there are many pulp and papermaking enterprises that reuse the CLMP through lime kiln technology. Some studies on lime pretreatment were optimized at 100–200 °C, which could lead to high-cost and complicated operation (Chang et al., 2001). Besides, too drastic pretreatment conditions could cause inhibitory effects on the dark fermentation process (Gu et al., 2015; Zhu et al., 2010). However, by far no information is available on the feasibility of using CLMP pretreatment to improve bio-fuel production (e.g., H_2 and CH_4) from lignocellulosic biomass.

Corn-bran residue (CBR), a by-product in the starch-sugar industry, mainly consists of fiber and starch, and a small amount of sulfite ion (SO_3^{2-}) (Zhang and Zheng, 2015). Therefore, the utilization of CBR is usually confined within the fields of animal feeding and anaerobic fermentation (Zhang and Zheng, 2015). CBR can also be pyrolyzed to produce biochar that is a potential adsorbent for pollutants (Zhang and Zheng, 2015). In addition, lime mud from papermaking process (LMP), which is an inorganic waste from the kraft process, is rich in $CaCO_3$ and soluble inorganics (Zhang et al., 2013b), making it extremely difficult to handle or reuse. Thus, the common method of LMP disposal is landfill (Zhang et al., 2013b, 2015). Lately there is an increased interest regarding eco-processing of this waste, particularly by anaerobic digestion, during which it can not only act as a buffering material but also supply inorganic nutrients and active sites for anaerobic reactions (Zhang et al., 2014, 2015).

This study aimed at investigating the effects of hydrothermal-CLMP treatment on CBR solubilization and hydrogen production. The possible enhancement mechanisms of hydrogen fermentation from CBR pretreated by CLMP were also clarified through the structural and compositional changes of CBR. A better understanding for the effects of hydrothermal-CLMP prehydrolysis on hydrogen fermentation would be useful from both a scientific and an engineering point of view.

To the best of our knowledge, fermentative hydrogen from CLMP pretreated CBR is reported here for the first time.

2. Methods

2.1. Preparation of inoculum and substrates

Sewage sludge (SS) was obtained from a municipal wastewater treatment plant in Jinan, China, treating about 50 kilotons of wastewater and generating approximately 250 tons of SS daily. The SS, whose average water content was 80%, was incubated under thermophilic (55 °C) and anaerobic conditions with addition of a nutrient stock solution. The incubation process lasted 20 d until the biogas production phase finished. Then the incubated SS was treated at 80 °C for 30 min in order to eliminate interspecies hydrogen transfer and to restrain methanogenic activities. After that, the SS cooled to 55 °C was cultivated in a medium containing glucose (5000 mg/L), peptone (200 mg/L), and yeast extract (25 mg/L) at 55 °C for 36 h before inoculation, maintaining anaerobic condition. The inoculum characteristics are as follows: pH: 7.3 ± 0.2, mixed liquor suspended solids (MLSS, mg/L): 50 ± 5.0, mixed liquor volatile suspended solids (MLVSS, mg/L): 22 ± 2.0, ammonia nitrogen (NH_4^+-N, mg/L): 30 ± 5.0, and soluble chemical oxygen demand (SCOD, mg/L): 3000 ± 50.

The corn-bran residue (CBR) was obtained from Xiwang Group in Shandong (China) where corn was deeply processed to produce starch. It consists of starch (18.52%), cellulose (10.54%), hemicellulose (40.57%), lignin (1.06%), protein (14.38%), lipin (3.54%), ash (6.34%) and water (5.05%). After the CBR sample was dried at 80 °C in a fan-assisted oven for 2 days, it was milled into fine particles, whose sizes range from 125 to 250 μm. The physical and chemical properties of the CBR used in the present study had been characterized in our previous study (Zhang and Zheng, 2015). The relatively low content of dissolved matter makes pretreatment necessary, in order to improve the chemical oxygen demand (COD) solubilization of CBR. Thus, a higher efficiency of the bio-hydrogen fermentation must be achieved.

2.2. Preparation of calcined-lime mud from papermaking process

The generation, composition and microstructure of the lime mud from papermaking process (LMP) which was used in the present study, had been determined as previously described (Zhang et al., 2013b). The specific surface area (SSA) of the LMP is 3.388 m^2/g, and its thermo-gravimetric analysis (TGA) is shown in Fig. 1. The LMP was calcined in the operating furnace at 850 °C for 3 h, which was marked as CLMP. The main reaction was shown in Eq. (1).

$$CaCO_3 = CaO + CO_2 \uparrow \quad (1)$$

As shown in Fig. 1, the LMP began to decompose at 637.8 °C, which was 182.2 °C lower than the reported value for bulk calcite ($CaCO_3$) (Liu et al., 2003). Moreover, the weight residual rate of the LMP at 850 °C was 55.23%, and the major component of the residue was calcium oxide (CaO). The results showed that LMP consisted of mainly amorphous structures, and contained a small quantity of impurities. Therefore, CLMP could provide a cheap alkaline substance and some trace elements for improving the performance of hydrogen fermentation.