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Effects of operating parameters on hydrogen production from raw wet steam-exploded cornstalk and two-stage fermentation potential for biohythane production

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ABSTRACT

Biohythane (biohydrogen + biomethane) production from agricultural residue is a win–win solution for the supply of renewable energy and valorization of waste biomass. This study reported the first investigation on hydrogen fermentation directly using raw wet steam-exploded cornstalk (SC) without any further processing for drying or detoxification. The effects of key operating parameters (feedstock concentration, initial pH and heat treatment of seed sludge) were systematically studied. The suitable conditions for hydrogen fermentation from the wet SC were the feedstock concentration at 200 g L^{-1} (TS, 6–8%), pH at 6.5 and seed sludge without heat treatment. In addition, compared to one-stage biomethane fermentation, the two-stage biohythane fermentation by integrating hydrogen fermentation with biomethane production from SC led to the hydrogen and methane yields of 12 and 195 L kg^{-1} TS^{-1}, respectively, corresponding to an increased energy recovery of 26%, reduced fermentation time and facilitated conversion of volatile fatty acids. These results demonstrated the feasible energy-efficient biohydrogen or biohythane production from the wet steam-exploded cornstalk, implying the promising potential of this method for harvesting clean hythane vehicle fuel from agricultural biomass.

1. Introduction

The energy crisis is becoming a global issue. Hydrogen, as a clean and efficient renewable energy, is considered to be the best alternative to fossil fuels [1–4]. However, commercialization of hydrogen energy is hampered by a cost-intensive process. Hythane, a mixture of hydrogen and methane, has attracted significant attention as a transit form of pure hydrogen in the near term [5]. With the addition of hydrogen to methane, hythane has been noted to exhibit obvious advantages over compressed natural gas as a vehicle fuel, such as extended flammability range, shortened quenching distance, reduced greenhouse gas emissions, and improved fuel efficiency [6]. Hythane could be sustainably produced from biomass through microbial fermentation (biohythane) [7,8]. With the development of agriculture, the yield of agricultural residues has increased up to about 700 million tons a year in China [9]. Therefore, utilization of agricultural residues for the production of biohythane through two-stage anaerobic fermentation is an important way to valorize the agricultural waste, reduce environmental pollution, and, to some extent, complement the constrained energy supply.

Lignocellulosic agricultural biomass, such as cornstalk, has natural recalcitrance with a highly rigid three-dimensional structure mainly consisting of cellulose, hemicellulose, and lignin, making it very difficult to degrade and transform [10]. Steam explosion has already been recognized as an efficient approach to breaking up the structure of lignocelluloses, where the changes in the water forms serve as the main factor [11,12]. However, the hydrolysate obtained after steam explosion contains many

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fermentation inhibitors, including phenolic compounds, furfural and acetic acid [13]. An additional step of detoxification is generally needed to remove these inhibitors, including the use of milk of lime [14], organic solvent extraction [15], activated carbon adsorption [16], concentration under vacuum [17], and ion exchange [18]. Moreover, steam-exploded cornstalk (SC) always needs to be dried before the use in the subsequent bioprocess, thus making the whole process energy-intensive, water-unsustainable, and industrially undesirable. It is therefore of crucial importance to study the possibility of directly utilizing wet SC in anaerobic fermentation. However, so far there is no report on the effects of the wet steam-exploded cornstalk on anaerobic fermentation for the production of either biohydrogen, biomethane or biohythane.

The purposes of the current study were to (1) investigate the feasibility of hydrogen fermentation directly using wet SC without detoxification and drying; (2) evaluate the influence of process parameters (feedstock concentration, initial pH and heat treatment of seed sludge) on hydrogen fermentation by using a normal-pressure batch bioreactor; and (3) examine the biohythane production potential from wet SC by using two-stage anaerobic fermentation.

2. Materials and methods

2.1. Seed sludge, substrate and medium

The anaerobic sludge, sampled from an anaerobic digester of Xiaohongmen Wastewater Treatment Plant (Beijing, China), was used as the seed sludge. Three different SC were used as substrates: a dried one (TS, >90%; VS/TS, 84–86%) taken from a factory in Shandong (SDSC); a wet one (TS, 28–30%; VS/TS, 76–80%) directly taken from Laihe Company (LHSC). The concentrations of HMF and FUR in LHSC were in ranges of 90–150 and 60–165 mg L^{-1}, respectively; and another dried one (TS, >90%; VS/TS, 90–96%) taken from Prof. Chen Hongzhang's Laboratory (Institute of Process Engineering, Chinese Academy of Sciences) (LASC). The medium contained the following (L^{-1}): yeast extract, 2.0 g; $(NH_4)_2SO_4$, 1.3 g; KH_2PO_4, 1.5 g; $K_2HPO_4{\cdot}3H_2O$, 2.9 g; $CaCl_2$, 0.075 g; $MgCl_2{\cdot}6H_2O$, 0.2 g; and $FeSO_4{\cdot}7H_2O$, 1.25 mg. The pH of all the substrates was 6–6.5 unless otherwise stated.

2.2. Experimental system and procedure

The experiment device was a normal-pressure bioreactor system, consisting of 250-ml glass flask with a working volume of 150 ml, gas-tight plastic tubes, sampling valve, and gas balloon. The glass flask served as the anaerobic vessel for fermentation, the produced gas was measured using the gas sampling valve and collected by gas balloon, and the fermented broth was sampled by the sampling port embedded in the flask. The feasibility study of hydrogen fermentation from the wet SC was first investigated by examining the effects of key operating parameters, including SC types and concentration, initial pH and heat pretreatment of seed sludge. The flask bioreactors containing substrate were degassed with pure nitrogen for 30 min to reach anaerobic conditions prior to use. To determine the influence of substrate concentration, 40, 100, 200, 400, and 800 g L^{-1} of substrate were tested, respectively. To evaluate the effect of pH on anaerobic fermentation, the medium with initial pH of 5.5, 6.5, and 7.5 was prepared. With regard to detection of the effect of heat pretreatment of seed sludge, the experiments were performed using a water bath with temperatures controlled at 50, 80, and 100 °C, respectively. 7% (w/v) of the boiled anaerobic sludge (70 g L^{-1}) was inoculated in a flask culture for biohydrogen production [19].

The biochemical potential for coproduction of hydrogen and methane (biohythane) [7] from SC was then investigated under the optimized conditions compared to one-stage biomethane process. The one-stage biomethane experiment was carried out using an initial pH of 7.5, whereas the two-stage fermentation for biohythane production was performed using an initial pH of 6.5 for hydrogen fermentation, followed by adjusting pH to 7.5 for the subsequent methane fermentation when hydrogen production was ceased in the same flask culture system.

2.3. Analytical methods

Gas samples were analyzed by using a gas chromatograph equipped with a thermal conductivity detector (TCD) and a column packed with TDX-01 (GC112A, China) [20]. The detected gases included hydrogen, oxygen, and methane. Metabolic intermediates during microbial fermentation were analyzed by a high performance liquid chromatography (HPLC; Shimadzu 10A) equipped with a refractive index detector (RID) and a Shodex RSpak KC-811 column. $HClO_4$ (1 g L^{-1}) was used as the mobile phase at a flow rate of 1 ml min^{-1}. The samples were centrifuged (12,000 rpm, 10 min) and the supernatant was filtered using a 0.22-mm membrane filter before use. The detected intermediates included volatile fatty acids (VFAs) and ethanol.

The concentrations of soluble sugars were measured by employing the phenol–sulfuric acid method [21]. Cellulose, hemicelluloses, and lignin in the pretreated and fermented cornstalks were evaluated according to the procedures reported by National Renewable Energy Laboratory (NREL) [22].

The utilized glucose equivalent was calculated based on carbon balance during microbial fermentation, and its detailed description has been given elsewhere [19]. Energy recovery was calculated by dividing the combustion values of hydrogen and methane produced by that of cornstalk [19]. The combustion values of hydrogen, methane, and glucose are 280, 864, and 2870 kJ mol^{-1}, respectively, and a detailed description has been given elsewhere [19].

3. Results and discussion

3.1. Hydrogen fermentation using SC

3.1.1. Effects of SC types and concentrations on hydrogen fermentation

Table 1 shows the comparison of hydrogen productivity using different SC as feedstocks. LHSC achieved a maximum hydrogen yield of 10.21 L kg^{-1} TS^{-1}. Compared with the dried SC, such as SDSC and LASC, LHSC contained more soluble sugar and VFAs, which contributed to more hydrogen production.

The effect of feedstock concentrations on hydrogen fermentation was then studied using LHSC. With the increase in the substrate concentration from 40 to 200 g L^{-1}, the hydrogen yield increased up to 10.41 L kg^{-1} TS^{-1}. However, the hydrogen production ceased when the substrate concentration was 400 g L^{-1} and 800 g L^{-1}. A similar phenomenon was observed through the analysis of metabolites after fermentation. When the substrate concentration was increased up to 200 g L^{-1}, acetic acid reached its maximum (5.54 mM), whereas decreased VFAs were observed when the substrate concentration reached 400 g L^{-1}. Substrate concentration is an important factor for anaerobic fermentation. The current results demonstrated that 200 g L^{-1} was a suitable concentration for hydrogen fermentation. The substrate at high concentration (400 or 800 g L^{-1}) might result in uneven mass transfer and contain a high amount of fermentation inhibitors, thereby suppressing hydrogen fermentation according to the study by Li and Chen [13].