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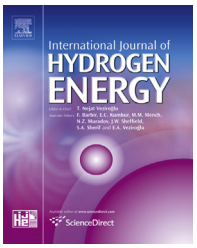

Directional enhancement of fermentative coproduction of hydrogen and acetic acid from glucose via control of headspace pressure

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ABSTRACT

Headspace pressure is a critical factor affecting hydrogen and acetic acid (HAc) generation. However, few studies have determined how to improve the coproduction of biohydrogen and HAc to increase the utilization efficiency from glucose by controlling headspace pressure. Here, we examined hydrogen and HAc coproduction by mesophilic fermentation with decreasing headspace pressures in a half-continuously running reactor. At 20 kPa, the glucose degradation rate was above 90%. HAc was the main soluble metabolite products (SMPs), with productivities of 1.74 mol/mol $glucose_{degraded}$, accounting for 93.95% of total SMPs, respectively. Maximum hydrogen productivity was 13.39 mM/d, and 70.11% of added glucose was converted into hydrogen and HAc with a total productivity of 133.72 g chemical oxygen demand/mol $glucose_{added}$ L d. Thus, hydrogen and HAc coproduction was achieved; however, homoacetogenesis was not completely inhibited by low headspace pressure, and the ratio of actual to theoretical hydrogen productivity was only 43.99%.

Introduction

Anaerobic fermentation is a key technology applied for sustainable waste and wastewater management. Fermentation products at all stages are chemical substances and energy materials with higher-added value, such as hydrogen, lactic acid (HLa), short-chain fatty acids, alcohols (EtOH), and methane. Among these, hydrogen production has been emphasized because it is clean and does not cause pollution. Additionally, as one of the primary final products of soluble metabolic product (SMP) degradation by acetogenesis, acetic acid (HAc) has been a major focus of researchers, as a basic reagent used to prepare many compounds.

However, hydrogen productivity is very low. Theoretically, 2–4 mol of hydrogen can be produced from 1 mol of glucose by conversion into HAc or HBu [27]. In reality, the actual hydrogen yield is less than 50% of the theoretical maximum because of thermodynamic limitations, the existence of non-hydrogen-producing bacteria, and the acetogenic hydrogen-consuming reaction [21]. HAc fermentation is also limited by two complications, i.e., low productivity and difficulties with HAc purification owing to the coproduction of various SMPs. For example, in the presence of high HAc concentrations, the activity of microorganisms is inhibited, and the electron

Abbreviations: HAc, acetic acid; HLa, lactic acid; SMP, soluble metabolite product; HPr, propionic acid; HBu, butyric acid; HVa, valeric acid.

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transfer pathway is altered [29], resulting in incomplete degradation of organic matter and reduced HAc productivity. Additionally, the coproduction of organic matter, including EtOH, HAc, propionic acid (HPr), butyric acid (HBu), iso-butyric acid, lactic acid (HLa), and valeric acid (HVa) [18], leads to increased diversity of microbial community, resulting in the coexistence of multiple metabolic pathways and promoting metabolite diversification.

The partial pressure of hydrogen is a critical factor affecting the productivities of hydrogen and HAc. Studies have shown that as the pressure decreases, hydrogen synthesis decreases, metabolic pathways shift, and acetogenesis is thermodynamically favorable [27,28], leading to increase in productivity of hydrogen and HAc, production and proportions of SMPs, and ratio of HAc to HBu [6,15,23]. As the pressure increases, metabolic pathways shift to production of more reduced substrates such as EtOH, HLa, acetone, and butanol [2,3]. Additionally, regulation of hydrogen partial pressure can also modulate homoacetogenesis and the acetate oxidation reaction, thereby altering HAc and hydrogen productivity [9,20,25,35].

Some researchers have examined the effects of hydrogen partial pressure on HAc and hydrogen. Yerushalmi et al. (1985) [36] reported that as hydrogen partial pressures increases, butanol and ethanol fermentation from pure cultures of *Clostridium acetobutylicum* increase. Lamed et al. (1988) [22] increased the headspace pressure to 2.5 atm and found that fermentation shifted toward EtOH production. Lee et al. (2012) [23] reported that HBu and HAc are the two primary SMPs, accounting for 85–99% of total SMPs found in reduced-pressure processes. However, other studies have shown that although HAc productivity is increased by the optimization of fermentation parameters and control of hydrogen partial pressure, this productivity accounts for only 50–70% of the total SMPs [3]. In addition, hydrogen productivity increases by 30–271% when the pressure is reduced [14,23,36]; even a slight vacuum of −0.03 atm can dramatically improve hydrogen productivity [19]. Thus, as described above, changes in hydrogen, HAc, and HBu production are related to changes in hydrogen partial pressure.

From the analysis above, it is theoretically feasible to coproduce hydrogen and HAc in anaerobic fermentation by controlling hydrogen partial pressure. However, most studies have focused on how to increase hydrogen production by controlling hydrogen partial pressure, not generating HAc by forming predominant fermentation pathways. Therefore, based on the effects of hydrogen partial pressure on fermentation pathways and SMP distributions, we aimed to control headspace pressure in order to increase HAc productivity, improve the proportion of HAc of the total SMPs, and coproduce hydrogen to maximize the energy conversion rate.

Materials and methods

Inoculum and fermentation medium

Seed sludge was obtained from an operating anaerobic reactor that had been used to treat pig manure for 3 years. The sludge was filtered and thermally pretreated at 100 °C for 30 min to inactivate methanogen. Finally, the concentration of volatile solids (VSs) and volatile suspended solids (VSSs) of seed sludge were 12.56% and 6.50%, respectively, and the pH was 7.12. The reactors were initially inoculated at a rate of 40% (v/v).

In this study, glucose was used as the sole carbon source. The medium used for fermentation contained 3 g/L glucose and sufficient amounts of inorganic supplements, including 3 g/L $C_6H_{12}O_6$, 3 g/L NaCl, 2 g/L $(NH_4)_2SO_4$, 1.5 g/L KH_2PO_4, 0.2 g/L $CoCl_2 \cdot 6H_2O$, 0.2 g/L $FeSO_4$, 0.1 g/L $CaCl_2 \cdot 2H_2O$, 0.1 g/L $MnCl_2 \cdot 6H_2O$, 0.05 g/L $ZnCl_2$, 0.1 g/L Na_2MoO_4, 0.05 g/L $MgSO_4$, and 0.01 g/L $NiCl_2 \cdot 6H_2O$.

Fermentation process setup and operation

Hydrogen production experiments were conducted in serum bottles with a working volume of about 1.0 L. One reactor was equipped with a vacuum pressure controller connected with a pump to control the headspace pressure in the reactor (Fig. 1). Headspace pressure was set in five control ranges: 100 ± 1 kPa, 80 ± 1 kPa, 60 ± 1 kPa, 40 ± 1 kPa, and 20 ± 1 kPa. At each stage, the reactors were operated for 9 days to reach a steady state at every headspace pressure tested (as shown in former experiments, the steady state was defined as the state at which the standard deviations of chemical oxygen demand [COD] removal efficiencies were within 10%, and this state appeared when the reactor operated for 5–6 days at a constant headspace pressure). The bottles were incubated in a heated water jacket (35 ± 0.5 °C). After loading the inoculum and substrate, the bottles were flushed with nitrogen for 30 s to remove oxygen from the headspace.

Fermentation experiments were carried out in the half-continuous mode, and substrate was added to the serum bottles once per day, with a hydraulic retention time (HRT) of 2 days. Gas and liquid samples were collected once a day before the substrate was added.

Analytical methods

COD, VSSs, and VSs were determined according to standard methods [1]. The biogas yield was measured using a wet gas flow meter (W-NK-0.5; Shinagawa, Japan), and the gas volumes were calibrated to 25 °C and 760 mmHg.

Volumetric biogas composition, including CH_4, CO_2, N_2, and H_2 (mainly H_2 and CO_2), was analyzed using a gas chromatograph (FULI; GC9790II; China) equipped with a thermal conductivity detector and packed column (Porapak Q column [3 m × 3 mm] cascading with a TDX-01 column [2 m × 3 mm]). The carrier gas was helium. The injector, oven, and detector temperatures were 150, 200, and 120 °C, respectively. Volumetric hydrogen and methane yields were calculated by multiplying the total yield by the corresponding volume percentages.

The SPMs, including HAc, HPr, HBu, HLa, and EtOH, were measured using the same gas chromatograph equipped with a flame ionized detector (FID) and column (Kromat, KB-Wax; 30 m × 0.32 mm × 0.33 μm). The carrier gas was nitrogen at a flow rate of 75 mL/min. The inlet and detector temperatures were both 250 °C. The oven temperature was originally 80 °C and was increased to 200 °C at a rate of 20 °C/min.

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