Bioresource Technology 263 (2018) 437–443

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Enhancing fermentative hydrogen production with the removal of volatile fatty acids by electrodialysis

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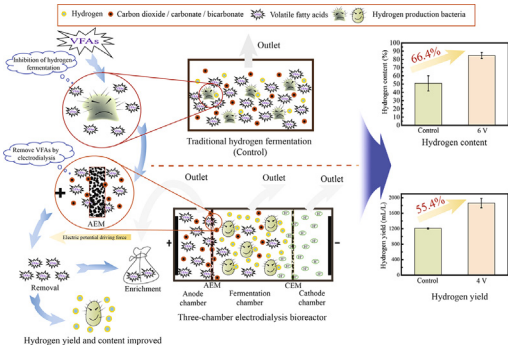
GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Hydrogen production
Fermentation
Volatile fatty acids (VFAs) removal
Electrodialysis
Bioreactor

ABSTRACT

A three-chamber electrodialysis bioreactor comprising fermentation, cathode and anode chambers was proposed to remove *in situ* volatile fatty acids during hydrogen fermentation. The electrodialysis voltage of 4 V resulted in a volumetric hydrogen productivity of 1878.0 mL/L from the fermentation chamber, which is 55.4% higher than that (1208.5 mL/L) of the control group without voltage applied. Gas production was not observed in the cathode and anode chambers throughout fermentation. By applying different voltages (0–6 V), the hydrogen content accumulated to 54.6%–84.7%, and it exhibited increases of 7.1%–66.4% compared with that of the control. Meanwhile, the maximum concentrations of acetate and butyrate in the fermentation chamber decreased to 10.3 and 13.1 mmol/L at a voltage of 4 V, respectively, which are 68.0% and 62.4% lower than that for the control.

1. Introduction

Hydrogen has received increasing attention on account of its clean combustion property and high calorific value by mass (142 MJ/kg) (Noblecourt et al., 2017; Xia et al., 2015). Many conventional methods exist for hydrogen production, such as steam reforming and water electrolysis (Cheng et al., 2012). Nevertheless, such methods may be accompanied by some disadvantages of high temperature, high pressure and high energy consumption (Holladay et al., 2009). In contrast, hydrogen production through dark fermentation of biomass wastes is

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https://doi.org/10.1016/j.biortech.2018.05.030
Received 16 April 2018; Received in revised form 6 May 2018; Accepted 7 May 2018
Available online 08 May 2018
0960-8524/

advantageous due to the low energy demand (Mamimin et al., 2017). Furthermore, a wide range of organic wastes can be degraded by dark fermentation, contributing to significant environmental benefits (Barca et al., 2016). However, the accumulated volatile fatty acids (VFAs), which are generated as a by-product in fermentation, can inhibit the metabolic activity of hydrogen-producing bacteria (HPB) and reduce hydrogen production (Bundhoo and Mohee, 2016; Elbeshbishy et al., 2017).

The inhibitory effects of VFAs and some control strategies have been investigated in a number of studies. For example, Zhang et al. studied the inhibitory effects of acetate (0–500 mmol/L) and butyrate (0–250 mmol/L) on dark fermentation using glucose as a substrate and *Clostridium bifermentans 3AT-ma* as the HPB (Zhang et al., 2012). They found that the hydrogen production trended to decrease with increased concentrations of acetate or butyrate. Compared with acetate, butyrate exhibited a more significant inhibition on fermentation. When acetate or butyrate was added to 20 mmol/L, the hydrogen production decreased by more than 15% and 20%, respectively (Zhang et al., 2012). Zheng and Yu studied the inhibitory effect of butyrate (4.2–25.1 g/L) on hydrogen production during fermentation (Zheng and Yu, 2005). They found that the hydrogen production decreased by 81.7% with 25.1 g/L of butyrate compared with that without the addition of butyrate (Zheng and Yu, 2005).

Tang et al. found that the hydrogen production gradually decreased with increasing acetate concentration. When the acetate concentration increased from 0 to 150 mmol/L, the hydrogen production decreased from 2.2 mol H_2/mol glucose to 0.6 mol H_2/mol glucose (Tang et al., 2012). Wang et al. studied the inhibitory effects of ethanol, acetic acid, propionic acid and butyric acid on fermentative hydrogen production at various VFAs concentrations ranging from 0 to 300 mmol/L. They concluded that the hydrogen production and production rate all trended to decrease with increased VFAs concentrations (Wang et al., 2008).

The suitable control of VFAs levels during fermentation can contribute to enhanced hydrogen production. Noblecourt et al. used a submerged membrane anaerobic bioreactor to avoid VFAs accumulation (Noblecourt et al., 2017). The component of VFAs has similar molecular weights as monosaccharides and amino acids, rendering the effective separation of substrates and by-products difficult. As a result, this technology could cause a significant loss of small molecules (such as amino acids and monosaccharides), which are favourable substrates for HPB. There are a few literatures indicate that use of electrodialysis technology can remove VFAs and avoid the loss of small molecules of organic components (Arslan et al., 2017; Jones et al., 2017; Tang et al., 2014). Jones et al. employed conventional electrodialysis to remove and recover VFAs from model solutions and fermentation broths, resulting in high VFAs removal efficiencies up to 99% at a voltage of 18 V during 60 min of the removal process (Jones et al., 2015). The hydrogen production increased from 0.24 mol H_2/mol hexose to 0.90 mol H_2/mol hexose using conventional electrodialysis (Jones et al., 2017). It should be noted that conventional electrodialysis was used for conducting post-treatment on the fermentation effluent, and the fermentation liquor was subsequently circulated to the fermentation reactor. Such a system includes the fermentation unit and the *ex situ* VFAs removal unit, which cannot directly control the concentration of VFAs in the fermentation reaction zone and may increase the system complexity. However, previous studies were mainly focused on the batch VFAs removal in a separated electrodialysis reactor. Continuous *in situ* VFAs removal during dark fermentation by electrodialysis has yet been reported.

In this paper, a novel three-chamber electrodialysis bioreactor with *in situ* electrodialysis was proposed, for the first time, to simultaneously remove VFAs continuously and to control the concentration of VFAs in fermentation reaction zone directly, thereby enhancing hydrogen fermentation. The aims of this study are to:

- Assess the VFAs removal characteristics using synthetic fermentation liquor.
- Compare the performance of hydrogen fermentation at various voltages.
- Analyse the changes in concentrations of VFAs during hydrogen fermentation.

2. Materials and methods

2.1. Bioreactor

A three-chamber electrodialysis bioreactor was constructed using polymethyl methacrylate. The inner length, width and height of the reactor are 12, 4 and 5 cm, respectively. This bioreactor has a total volume of 240 mL. It comprises an anode chamber (inner length, width and height are 3, 4 and 5 cm; 60 mL), a cathode chamber (inner length, width and height are 3, 4 and 5 cm; 60 mL), and a fermentation chamber (inner length, width and height are 6, 4 and 5 cm; 120 mL) separated by an anion exchange membrane (AEM, 20 cm^2) and a cation exchange membrane (CEM, 20 cm^2). AEM and CEM were purchased from Hangzhou Green Environmental Protection Technology Co. LTD (Hangzhou, China). Graphite electrodes were used as the anode and cathode with a thickness of 2 mm and an area of 20 cm^2 (Beijing Electric Carbon Plant, Beijing, China). A programmable DC power supply (ARRAY 3646A, Bost Electronic Instrument Co. LTD, Shenzhen, China) was used as an external power supply for the electrodes.

2.2. Inoculum and medium

The mixed HPB was isolated and acclimated from the anaerobic digestion sludge derived from a rural digester treating straw and manure in Chongqing, China. The sludge was heated at 100 °C for 30 min to inactivate methanogens and hydrogen consumers, and subsequently enriched three times (3 d each time) to enrich the spore-forming HPB (Xia et al., 2015). The composition of the acclimation medium was described in a previous study (Cheng et al., 2012).

2.3. Experimental procedures

The three-chamber electrodialysis bioreactor was used to assess the VFAs removal characteristics by using a synthetic VFAs solution with an initial acetic acid concentration of 20 mmol/L or a butyric acid concentration of 20 mmol/L. Eighty millilitres of synthetic VFAs solution was added to the fermentation chamber, and 40 mL of deionized water was added to the anode and cathode chambers to ensure an equal liquid surface level in the fermentation chambers.

For hydrogen fermentation, 8 mL of acclimated HPB and 72 mL of deionized water mixed with 0.8 g of glucose were added to the fermentation chamber. For all reactors, glucose was used as the substrate at a concentration of 10 g/L. Forty millilitres of deionized water was added to the anode and cathode chambers, respectively. The initial pH value of the fermentation chamber was adjusted to 6.5 ± 0.1 using 6 mmol/L HCl or NaOH solution.

The voltage was set at 0–6 V by a programmable DC power supply in the VFAs removal experiments and hydrogen fermentation. A single chamber bioreactor (without voltage and ion-exchange membrane) was used as the control, which was operated with 80 mL of fermentation medium with HPB. A three-chamber electrodialysis bioreactor without substrate addition (no glucose) was used as the hydrogen fermentation blank (as shown in Table 1). All fermentation chambers were purged with nitrogen gas for 5 min to ensure an anaerobic environment. The headspace of the fermentation chamber was 40 mL. All bioreactors were kept in a thermostat water bath maintained at 35 °C for 96 h. The gas produced was discharged from the headspace of the fermentation chamber and subsequently collected using a graduated container. The gas and liquid samples were collected at a time interval of 12 h for further analysis, and the pH value of the fermentation solution was