Available at www.sciencedirect.com

ScienceDirect

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

Biological fermentative hydrogen and ethanol production using continuous stirred tank reactor

Wei Han [a], Hong Chen [a], Anying Jiao [a], Zhanqing Wang [a], Yongfeng Li [a,b,c,*], Nanqi Ren [c,**]

[a] School of Forestry, Northeast Forestry University, Harbin 150040, China
[b] College of Chemistry and Chemical Engineering, Shanghai University of Engineering and Science, Shanghai 201620, China
[c] School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090, China

ARTICLE INFO

Article history:
Received 2 December 2010
Received in revised form
24 March 2011
Accepted 6 April 2011
Available online 29 September 2011

Keywords:
Fermentative hydrogen production
Organic loading rate
Energy conversion rate
Continuous flow

ABSTRACT

Hydrogen and ethanol are promising biofuels and have great potential to become alternatives to fossil fuels. The influence of organic loading rates (OLRs) on the production of fermentative hydrogen and ethanol were investigated in a continuous stirred tank reactor (CSTR) from fermentation using molasses as substrate. Four OLRs were examined, ranging from 8 to 32 kg/m^3·d. The H_2 and ethanol production rate in CSTR initially increased with increasing OLR (from 8 to 24 kg/m^3 d). The highest H_2 production rate (12.4 mmol/h l) and ethanol production rate (20.27 mmol/h l) were obtained in CSTR both operated at OLR = 24 kg/m^3 d. However, the H_2 and ethanol production rate tended to decrease with an increase of OLR to 32 kg/m^3 d. The liquid fermentation products were dominated by ethanol, accounting for 31–59% of total soluble metabolities. Linear regression results show that ethanol production rate (y) and H_2 production rate (x) were proportionately correlated which can be expressed as $y = 0.5431x + 1.6816$ ($r^2 = 0.7617$). The total energy conversion rate based on the heat values of H_2 and ethanol was calculated to assess the overall efficiency of energy conversion rate. The best energy conversion rate was 31.23 kJ/h l, occurred at OLR = 24 kg/m^3 d.

1. Introduction

With the inevitable depletion of the world's energy supply, there has been an increasing worldwide interest in alternative sources of energy [1]. Ethanol can be supplemented for gasoline as a fuel for transportation and also can be used as a substrate for biodiesel production. Hence, bioenergy technology focuses heavily on converting biomass feedstock to bioethanol and/or biodiesel at this moment [2,3].

Hydrogen is considered an ideal and clean energy carrier for the future because of its high conversion, recyclability and non-polluting nature [4]. Fermentative hydrogen production has attracted increasing attention recently due to its high rate of hydrogen evolution and its applicability to different types of organic wastes and wastewaters from industrial processes. Furthermore, using organic wastes reduce waste disposal problems [5,6]. In addition to H_2 production, anaerobic fermentation also produces a significant amount of alcohols (such as ethanol).

Due to the conversion of hydrogen to methane in the anaerobic fermentation process, the blocking of the methanogenesis in the anaerobic pathway is one of the key

* *Corresponding author*. School of Forestry, Northeast Forestry University, Harbin 150040, China. Tel.: +86 13903614476; fax: +86 451 82192120.
** *Corresponding author*.
E-mail addresses: dr_lyf@163.com (Y. Li), dr_hit@163.com (N. Ren).

0360-3199/$ – see front matter
doi:10.1016/j.ijhydene.2011.04.048

considerations. The inhibition of the methanogenic activity can be achieved by controlling various parameters, such as the pH [7], aerobic pretreatment [8] and the solids retention time (SRT) [9], for acidogenesis. Of the various parameters, the aerobic pretreatment is considered to be useful and economic. In general, the inhibition of methanogens can be achieved by using aerobic pretreatment for 30–40 days [10].

Biohydrogen production from wastewater through fermentation is carried out by anaerobic acidogenic bacteria with highly diverse fermentation characteristics and hydrogen production capabilities [11]. Fermentation performance is dependent on a number of factors [12], such as temperature, pH and hydrogen partial pressure. Hariklia et al. [13] showed that the most suitable temperature for biological hydrogen production was 35 °C. Moon et al. [14] indicated that pH in the fermentation process would drop rapidly with the abundant soluble microbial products (especially acetate) and pH 4.0 was regarded as the operational limit for the anaerobic biohydrogen production process. Mizuno et al. [15] studied the continuous stirring of the anaerobic culture and the removal of the hydrogen by supplying another gas (such as nitrogen) could help to keep a low hydrogen partial pressure and thus result in enhanced hydrogen production rate and yield. The variations of these factors result in diverse microbial communities, which lead to different hydrogen yields [16]. However, most studies have been focused on the mechanism of hydrogen production by pure cultures from single carbohydrates, insufficient information is available on biological fermentative hydrogen and ethanol production from molasses in a mixed microbial community culture.

In this study, using molasses as the sole carbon substrate, the performance of continuous H_2 and ethanol production rate was investigated at different organic loading rates (OLRs) for CSTR. The objective of this work was to develop innovative fermentation technology for dual production of two most critical biomass energy products, H_2 and ethanol.

2. Materials and methods

2.1. Experimental set-up

Continuous culture was performed in a 12.5 L continuous stirred tank reactor (CSTR) with an effective volume of 5.4 L (Fig. 1). The reactor, operated in a continuous flow mode, was completely mixed by a variable speed stirred with a gear shift.

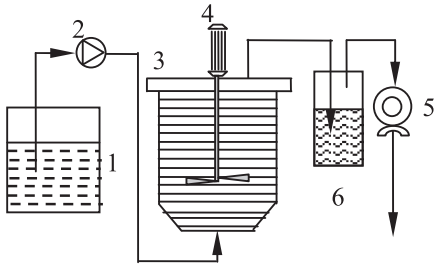

Fig. 1 – Schematic diagram of the CSTR reactor for biohydrogen production from molasses wastewater. 1. waste water box. 2. feed pump. 3. reactor. 4. agitator. 5. biogas meter. 6. water lock.

Temperature was automatically kept at the level of 35 ± 1 °C using an electric jacket. The influent flow rate was controlled by a feed pump. Biogas generated during the reactor operation was collected by a water displacement method through an outlet provided at the top of the reactor. The hydrogen collection system consisted of a water separator.

2.2. Hydrogen-producing sludge and cultivation

The seed sludge used in this study was obtained from a local municipal wastewater treatment plant. Prior to use, the sludge was first sieved through mesh with a diameter of 0.5 mm in order to remove waste materials that could cause pump failure. The sludge settled at room temperature for 10 days, was aerated for 30 days to inhibit the methane-producing bacteria activity and then was added into the CSTR. Afterward, the diluted molasses with chemical oxygen demand (COD) of 4000 mg/L was fed into the CSTR continuously at the HRT of 6 h. At the beginning of the start-up period, the biomass in the reactor was approximately 17.74 gMLVSS/L.

2.3. Feeding

Normal molasses, containing about 53% sugars, was diluted by water to certain loading rate (8–32 kg COD/m^3 reactor/d). The molasses used throughout the study was collected from a local sugar refining industry and its characteristics are given in Table 1. The COD: N: P of the influent was maintained at a ratio of 1000:5:1 by adding synthetic fertilizer in order to supply microorganisms with adequate nitrogen and phosphorus.

2.4. Analytical methods

COD, biogas yield and its constituents were measured and monitored daily in the CSTR. These analyses were performed according to Standard Methods [17].

Biogas yield was measured at room temperature by a wet gas meter (Model LML-1, Changchun Filter Co. Ltd., Changchun, China), while its constituents were analyzed using a gas chromatography (SC-7, Shandong Lunan Instrument Factory). The gas chromatography was equipped with a thermal conductivity detector (TCD) and a stainless steel column (2 m × 5 mm) filled with Porapak Q (50–80 meshes). Nitrogen was used as the carrier gas at a flow rate of 30 ml/min. A dose of injected sample was 0.5 ml each time. Based on the percentage of hydrogen in biogas, the hydrogen yield could be calculated.

Table 1 – Composition of the normal molasses.

Component	Percentage (%, w/w)	Component	Percentage (%, w/w)
Dried materials	78–85	MgO	0.01–0.1
Total sugar	48–58	K_2O	2.2–4.5
TOC	28–34	SiO_2	0.1–0.5
TKN	0.2–2.8	Al_2O_3	0.05–0.06
P_2O_5	0.02–0.07	Fe_2O_3	0.001–0.02
CaO	0.15–0.8	Ash content	4–8