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Biohydrogen from molasses with ethanol-type fermentation: Effect of hydraulic retention time

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ABSTRACT

Though ethanol-type fermentation has many advantages for improving hydrogen production rate (HPR) in continuously mode hydrogen producing system, information on this fermentation is very deficient. The effect of hydraulic retention time (HRT) on biohydrogen production and operational stability of ethanol-type fermentation was investigated in a continuous stirred tank reactor (CSTR) using molasses as substrate. Five HRTs were examined, ranging from 4 to 10 h. At HRT 5 h, the highest HPR of 12.27 mmol L^{-1} h^{-1} was obtained from ethanol-type fermentation in the pH range of 4.3–4.4. During the whole operation process, ethanol, butyrate and acetate were the predominant metabolites. A total COD concentration of ethanol and acetate accounted for above 73.3% of total soluble microbial products. Linear regression showed that HPR and ethanol production rate were proportionately correlated at all HRTs which could be expressed as $y = 0.9821x - 3.5151$ ($r^2 = 0.9498$). It is meaningful that the proposed recovery of both hydrogen and ethanol from fermentation process can improve energy production rate and economic profit. Results demonstrated that the best energy production rate was 15.50 kJ L^{-1} h^{-1}, occurred at HRT = 5 h.

1. Introduction

Energy is vital to the economic development, yet dependence on fossil fuels as our primary energy source contributes to global climate change, environmental degradation, and health problems [1]. Hydrogen as a clean, renewable fuel has attracted a great deal of attention since it produces only harmless water when combusted and possesses a high energy yield (286 kJ mol^{-1}). Current hydrogen production methods can be broadly divided into physicochemical and biological processes. Among biological hydrogen production processes, dark fermentation is known to be less energy-intensive and more environmental friendly, for it can be carried out at ambient temperature and pressure [2]. On the other hand, utilizing wastes to produce hydrogen is a possible alternative in terms of current waste disposal methods. So the dark fermentation for hydrogen production can serve a dual purpose of the exploitation of clean energy resources and the disposal of organic wastewaters.

To produce hydrogen from dark fermentation process, the blocking of the methanogenesis in anaerobic pathway is one of the key considerations, due to the conversion of hydrogen to methane in this step. The inhibition of methanogenic activities can be achieved by controlling many parameters [3], such as pH, HRT, and organic loading rate (OLR). Of various parameters, most researchers have focused on the role of pH

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and the inhibition of methanogens has been reported under weak acid pH conditions. In fact, the HRT is also a very important parameter. As HRT is related to the amount of organics that can be handled per unit time, it has a direct impact on economical operation [4]. Generally, hydrogen producing bacteria prefer short retention time; since the main hydrogen producing bacteria, Clostridium sp., tend to produce volatile fatty acids (VFAs) with hydrogen at the exponential growth phase while they produce alcohols at the stationary growth phase [5]. It is also generally held that short HRT prohibits methanogenic growth, since the growth rate of methanogens is much lower than that of hydrogen producing bacteria [4,6,7].

Another important consideration for hydrogen production from anaerobic fermentation is the type of fermentation. In many papers, butyrate-type fermentation has been depicted as the most common pathway for fermentative hydrogen production [8–10]. Although Ren et al. [11] and Hwang et al. [8] have investigated some suitable environmental factors for ethanol-type fermentation, but suggested no operational guideline for a reactor with regard to the production of hydrogen. Despite ethanol-type fermentation having many advantages for hydrogen production, information on this fermentation is very deficient, as the researches on this fermentation pathway focused on the production of ethanol as a fuel [12,13].

Until now the dark fermentation process for sequential hydrogen production has been operated with various types of organic substrates such as glucose [3], food waste [14], cheese whey wastewater [12], sugary wastewater [15] and coffee drink manufacturing wastewater (CDMW) [16]. Although a few substrates were very efficient and effective as a carbon source for the hydrogen production process, there is still a need to search more cost-effective substrates for industrial application of this process. Molasses as one of commercially available organic substrates has been used as a nutrient source for fermentative production of hydrogen [17–19] for the reason that it contains a high concentration of sugars such as glucose, sucrose and fructose as well as nutrient minerals. To the best of our knowledge, however, there are few papers on the utilization of molasses as a sole carbon source for hydrogen and ethanol production in a mixed microbial community culture.

The objective of this study was to examine the performance of sequential hydrogen production from ethanol-type fermentation at different HRTs using molasses as substrate for anaerobic fermentation process in CSTR reactor. On the basis of experimental data obtained at various HRTs, the ethanol-type fermentation in this study realized the dual recovery of two most important bioenergy products, hydrogen and ethanol, which could effectively improve the energy production rate.

2. Methods

2.1. Feeding

The molasses used as substrate for hydrogen production was collected from local sugar refining industry. The characteristics of molasses are shown in Table 1. The molasses, containing a high concentration of carbohydrates including sugars, was diluted by water to a certain concentration (8 g COD L^{-1}) and minimum 45% (w/w) of molasses corresponded to readily fermentative sugars. The chemical oxygen demand (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.

2.2. Hydrogen-producing sludge

The seed sludge used in this study was the anaerobic sludge obtained from a local municipal wastewater treatment plant (Harbin, China). The sludge was first sieved through mesh with a diameter of 0.5 mm in order to eliminate large particulate materials that could cause pump failure. Then the seed sludge was aerated for 35 days using molasses as the substrate to inactivate hydrogen-utilizing bacteria, especially methanogens. During the aerobic cultivation process, biological activity of hydrogen-producing bacteria was examined by analyses of glucose consumed. After enough cultivation, the hydrogen-producing sludge with suspended solids (SS) of 12.81 g L^{-1} and volatile suspended solids (VSS) of 8.35 g L^{-1} was inoculated into the CSTR.

2.3. Analytical methods

Biogas generated from the CSTR was collected using a wet gas meter (Model LML-1, Changchun Filter Co. Ltd., Changchun, China) calibrated to a temperature of 25 °C and pressure of 1 atm condition. Effluent samples from the reactor were also collected for metabolites analyses over the entire period of reactor operation.

COD, pH and alkalinity were monitored and measured daily according to Standard methods [20]. The oxidation–reduction potential (ORP) was measured by a pHS-25 acidity voltmeter. Hydrogen was 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 40 mL/min. Detection of VFAs in the fermentation solution was analyzed by another gas chromatograph (GC 112, shanghai Anal. Inst. Co.) with a flame ionization detector (FID). A 2-m stainless steel column was packed with the supporter GDX-103 (60–80 meshes). The

Table 1 – Composition of the normal molasses.

Component	Percentage (%, w/w)	Component	Percentage (%, w/w)
Total sugar	45–58	P_2O_5	0.02–0.07
Dried materials	78–85	SiO_2	0.1–0.5
TOC	28–34	Al_2O_3	0.05–0.06
TKN	0.2–2.8	Fe_2O_3	0.001–0.02
CaO	0.15–0.8	MgO	0.01–0.1
K_2O	2.2–4.5	Ash content	4–8

TOC: total organic carbon; TKN: total Kjeldahl nitrogen.