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Effect of hydraulic retention time on anaerobic hydrogenesis in CSTR

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Abstract

The objective of this work was to evaluate the production of hydrogen in a continuous system as a function of hydraulic retention time (HRT). The intermediates accumulated and other parameters of pH, oxidation–reduction potential were quantified. The heat treatment (103 °C for 24 h) of the compost from a cattle dung composting facility was able to select H_2-producing spores; this product was used as a seed for continuous systems. The brewery waste was used as substrate.

For the eight runs with combinations of five HRTs and four pHs, the results indicate that at pH = 5.5, a maximum H_2 production of 47% H_2 concentration, 43 ml H_2/g COD_{added}, and 3.1 l H_2/l reactor d was achieved at HRT = 18 h. Nevertheless, at HRT = 18 h, pH 5.5 was also the optimum pH for the maximum H_2 production among four pHs evaluated from 5 to 6.5. There was a significant accumulation of volatile acid and alcohols during the entire study.

Keywords: H_2; Acid accumulation; Ethanol; Anaerobic; Brewery

1. Introduction

Anaerobic production of hydrogen gas has received considerable attention lately, because of its energy value and non-pollutant nature. In traditional anaerobic processes, hydrogen produced through hydrolysis and hydrogenesis is immediately used up by hydrogen utilizing microbes, such as methane formers and sulfate reducing bacteria. Thus, the amount of H_2 present in the gas phase of either single or combined stage is insignificant (Kidby and Nedwell, 1991). If, however, in the absence or inhibition of hydrogen consuming bacteria, the H_2 concentration under appropriate conditions can be increased significantly, e.g., H_2 composition in the gas phase as high as 60% (Fang and Liu, 2002).

In addition to photosynthetic bacteria, many investigators have conducted experiments with different bacteria and substrates under a variety of conditions to generate H_2. The H_2 production is regulated by many factors, including the type and concentration of substrate (Okamoto et al., 2000), C/N ratio (Lin and Lay, 2004), pH (Fang and Liu, 2002; van Ginkel et al., 2001; Fan et al., 2004), temperature (Zhang et al., 2003), presence of H_2 consumers, e.g., lactic acid bacteria (Noike et al., 2002) and other inhibitors of sulfate and thiosulphate (Mizuno et al., 1998; Nandi et al., 2001). To have a practical sustainable application, studies in continuous-flow stirred-tank (CSTR) systems should be performed. Also, monitoring the intermediates is essential to elucidate the potential correlation between these intermediates and observed H_2 production. For example, the distribution of alcohols and volatile fatty acids (VFAs) may indicate the extent of H_2 production. Consequently, the main objective of the present study was to evaluate the effect of HRT of a CSTR system on H_2 production.

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2. Methods

2.1. Materials

The seeding material was obtained from the compost of a local cattle dung composting facility. The compost was first dried at 103 °C for 24 h; a given amount was added into 1 l of distilled water and mixed for 3 h by a mixer with 200 rpm, then the subsequent supernatant was filtrated and used as the seed. The bottom layer of a beer manufacturing plant after dilution at the desirable strength with supplemental nutrient addition was used as the feed solution in all experiments. To ensure adequate nutrient supply, inorganic solution was added to the brewery waste. The composition of the inorganic stock solution in 1 l solution is (Lay et al., 1999): 1 g NH_4HCO_3, 0.5 g KH_2PO_4, 50 mg $MgSO_4 \cdot 7H_2O$, 5 mg NaCl, 5 mg $NaMoO_4 \cdot 2H_2O$, 5 mg $CaCl_2 \cdot 2H_2O$, 7.5 mg $MnSO_4 \cdot 7H_2O$, and 1.38 mg $FeCl_2$. The feed concentration was controlled at about 50 g COD (chemical oxygen demand)/l.

2.2. Experiment

The study was conducted in a continuous flow system. An acrylic-made tank (effective volume 2 l) with a four-blade mixer (150 rpm) was used as the completely stirred tank reactor (CSTR). The reactor was housed in a constant temperature chamber controlled at 37 ± 1 °C. However, the feeding tank was stored in a refrigerator at 4 °C. pH was automatically adjusted with 1 N KOH or 1 N HCl to the set value. The monitoring instruments of pH, ORP (oxidation–reduction potential) and temperatures were directly inserted into the reactor. The CSTR experiments consisted of eight runs in which five of them were controlled with different HRTs (staring from 48 h and stepwise reduced to 8 h) at constant pH 5.5. The other three designed with the same HRT based on the optimum HRT from the previous five runs but varying with three pH values (5.0, 6.0, and 6.5) to observe pH effect on H_2 production. Experimental conditions are summarized in Table 1. After changing experimental conditions, a period of four HRTs was allowed for the system to reach stable. The samples were then taken after at least one HRT after reaching the stable conditions for the analysis of VFAs, alcohols, and other parameters. The gas output rate was measured via wet-gas meters (Sinagaw W-NK 05A), and gas samples were taken from sampling ports of the reactor for the analysis of H_2 and CH_4 concentrations.

2.3. Analysis

The H_2, CO_2 and CH_4 were monitored in a GC (Shimadzu Model 8A), equipped with a thermal conductivity detector (TCD). For H_2 measurements, a 2-m glass column (Porapak Q, 50/80 mesh) was installed and the operating temperatures of the injection port, the oven, and the detector were 100, 60, and 100 °C, respectively. Nitrogen gas was used as the carrier gas at a flow rate of 30 ml/min. For CO_2 and CH_4 measurements, a 2-m column (Molecular Sieve, 80/100 mesh) was used and the corresponding temperatures at the injection port, oven, and TCD were 120, 60, and 120 °C, respectively. Helium was used as the carrier gas at a flow rate of 30 ml/min.

VFAs (acetic acid, propionic acid, butyric acid and iso-butyric acid) were measured in another GC-flame ionization detector, FID (Shimadzu, Model 14B). The capillary column was packed with SGE BP20 and the operating temperatures for the injection port and the FID were the same, about 170 °C. The temperature in the oven was gradually increased from 100 to 130 °C at a rate of 5 °C/min. Alcohols, including methanol, ethanol, propanol and butanol, were monitored in the same GC-FID. The column was packed with Gaskuropack 54 (60/80 mesh) and the temperature was controlled at 110 °C for both the injection port and the FID. Nitrogen was the carrier gas for both volatile acids and alcohol analyses at a flow rate of 30 ml/min. The correlation coefficients (R^2) for the standard calibration curves of all these VFAs and alcohols were >0.998.

Analyses of other parameters including COD and volatile solids (VS) essentially followed those prescribed in the Standard Methods (APHA, 1995).

3. Results and discussion

3.1. Effect of HRT

The pseudo-steady state results of H_2 concentrations (%), H_2 production (l/d) as well as H_2 yield (ml/g COD_{added}) and ORP as a function of HRT at a constant pH 5.5 are shown in Fig. 1a. In the present study, no CH_4 gas was detected that indicated the absence of CH_4 formers and the effectiveness of the heat treatment. All parameters were affected by the HRT employed, e.g., H_2 composition varied from 21% to 47% and H_2 output from 2.1 to 6.1 l/day. There appears an optimum HRT (18 h) among five HRTs studied for the highest H_2 concentration (47%) as well as the maximum H_2 production (6.1 l/d). The HRT 18 h also corresponded to the lowest ORP (−490 mV). For comparison, the ORP values ranged from −500 to −550 mV in a pure culture of a *Clostridium* strain using glucose as substrate (Kataoka et al., 1997). At higher HRTs, the H_2 production was significantly reduced, probably due to byproduct inhibition. Fang and Liu (2002) reported that as high as 64% H_2 composition could be obtained at HRT = 6 h and pH = 5.5 with H_2 yield 2.1 mol/mol glucose and production rate of 4.6 l H_2/g VSS d.