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Hydrogen Production from Alcohol Wastewater by Upflow Anaerobic Sludge Blanket Reactors under Mesophilic Temperature

Thipsalin Poontaweegeratigarn, Sumaeth Chavadej, Pramoch Rangsunvigit

Abstract**—**In this work, biohydrogen production via dark fermentation from alcohol wastewater using upflow anaerobic sludge blanket reactors (UASB) with a working volume of 4 L was investigated to find the optimum conditions for a maximum hydrogen yield. The system was operated at different COD loading rates (23, 31, 46 and 62 kg/m^3d) at mesophilic temperature (37 ºC) and pH 5.5. The seed sludge was pretreated before being fed to the UASB system by boiling at 95 ºC for 15 min. When the system was operated under the optimum COD loading rate of 46 kg/m^3d, it provided the hydrogen content of 27%, hydrogen yield of 125.1 ml H_2/g COD removed and 95.1 ml H_2/g COD applied, hydrogen production rate of 18 l/d, specific hydrogen production rate of 1080 ml H_2/g MLVSS d and 1430 ml H_2/ L d, and COD removal of 24%.

Keywords**—**Hydrogen production, Upflow anaerobic sludge blanket reactor (UASB), Optimum condition, Alcohol wastewater

I. Introduction

THE world has faced to insufficient global energy and the majority of the energy consumed today is derived from fossil fuels. When fossil fuels are burned, carbon dioxide and other pollutants are generated [1]-[2]. Excess carbon dioxide in atmosphere causes global warming due to the greenhouse effect. Thus, it is necessary to find alternative energy sources that are renewable and environmentally friendly to replace the use of fossil fuels. Hydrogen is one of the alternative energy sources, which is a clean energy, possessing a high energy yield (122 kJ/g), and does not contribute to the greenhouse effect [3]-[5]. Moreover, hydrogen is an odorless, colorless, tasteless, and non-poisonous gas [6]. There are a lot of advantages of hydrogen utilization, such as its high conversion efficiency, its ability to be recycled, and its non-pollution. When hydrogen is used as a fuel, it produces only water, thus reducing carbon dioxide emission [7]-[8]. From these reasons, hydrogen has been an unrealized "fuel of the future". Hydrogen can be produced via various process technologies, such as fossil fuels processing or by electrolysis using solar power or gasification.

Thipsalin Poontaweegeratigarn., Sumaeth Chavadej and Pramoch Rangsunvigit The Petroleum and Petrochemical College, Chulalongkorn University, Soi Chula 12, Phayathai Road, Pathumwan, Bangkok 10330, Thailand (e-mail: bomalt_bm@hotmail.com)

Sumaeth Chavadej Center for Petroleum, Petrochemical, and Advanced Materials, Chulalongkorn University, Bangkok 10330, Thailand (Phone: +66-2-218-4139, fax: +66-2-218-4139, e-mail: sumaeth.c@chula.ac.th)

But these processes are highly energy intensive, expensive and not environmentally friendly, whereas the biological hydrogen production is more attractive (and even more attractive if waste/wastewater is used as a raw material) [9].

Biological hydrogen production is the most challenging area of biotechnology with respect to environmental problems. The biological process mainly includes photosynthetic hydrogen production and fermentative hydrogen production [10]-[11]. Most studies have been related to fermentative hydrogen production. The scarcity of information related photosynthetic hydrogen production is due to two reasons: (a) it is difficult to control light penetration and its uniform distribution, and (b) the process is likely not cost-effective unless the free sunlight can be used as the light source [12]. Moreover, fermentative hydrogen production has the advantages of rapid hydrogen production rate and simple operation [13]-[14]. In addition, it can utilize various organic wastes as substrates for fermentative hydrogen production. Comparing with the photosynthetic hydrogen production, fermentative hydrogen production is more feasible and widely used [15].

In this work, biohydrogen production via dark fermentation from alcohol wastewater by using upflow anaerobic sludge blanket reactors (UASB) was investigated. The system was operated at different COD loading rates (23, 31, 46 and 62 kg/m^3d) at mesophilic temperature (37 ºC) and controlled pH 5.5.

II. Experimental

A. Seed Sludge Preparation

Seed sludge was obtained from the UASB reactor treating an alcohol wastewater of Sapthip Lopburi Co., Ltd., Thailand. It was boiled at 95 °C for 15 min to eliminate methane-producing bacteria before being introduced as a seed sludge into the UASB reactors [16].

B. Substrate Preparation

The ethanol wastewater was also obtained from Sapthip Lopburi Co., Ltd., Thailand. It had a chemical oxygen demand (COD) value about 45,000 mg/l and the ratio of COD: nitrogen: phosphorous of 100:2:0.4 which is sufficient amount for anaerobic degradation (the theoretical ratio of COD: nitrogen: phosphorous is 100:2:0.4).

C. UASB Operation

The upflow anaerobic sludge blanket (UASB) reactors were constructed from borosilicate glass with a 4 L working volume. The temperature and pH were controlled by a water jacket system with a circulating heating bath and a pH-controller, respectively. The schematic of the UASB unit is shown in Figure 1. The ethanol wastewater was fed into the reactor from the feed tank using a peristaltic pump. The feed was pumped into the bottom of the reactor (in upward direction) and passed through the microorganism sludge. A three-phase separator was used for preventing outflow of flocculants and separating the gaseous products and the overflown liquid effluent. The effluent was adjusted to pH 5.5 using a 5 wt.% NaOH solution and was recycled to the UASB at a recycle 1:1. The temperature of the UASB reactor was maintained at 37 ºC by using the water jacket with a circulating water bath.

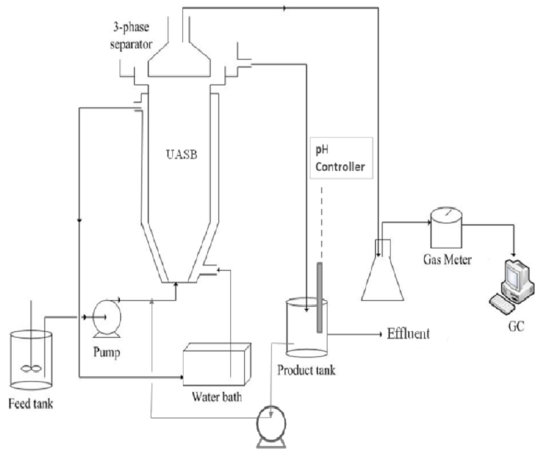

Fig. 1 Flow diagram of UASB process

Ethanol wastewater was fed into the UASB reactor with an initial feed COD value of 45,000 mg/l at different COD loading rates from 23 to 62 kg COD/m^{3}d, corresponding to the feed flow rate and hydraulic retention time (HRT), as shown in Table 1. The gas composition, gas production rate, hydrogen production rate, COD removal, specific hydrogen production rate and hydrogen yield, were determined after the system reached steady state.

TABLE I
FEED FLOW RATES AND HRT AT DIFFERENT COD LOADING RATE

COD loading rate (kg/m^3 d)	Feed Flow Rate (l/d)	HRT (d)
23	2.07	1.93
31	2.76	1.45
46	4.14	0.96
62	5.52	0.72

D. Analytical Methods and Measurements

The volume of gas produced in the bioreactor was recorded daily using the water replacement method by a gas counter.

The amount of gas composition was determined by a gas chromatograph (Auto System GC, Perkin-Elmer) equipped with a thermal conductivity detector (TCD). The organic contents in the cassava wastewater and the effluent samples of both UASB units were quantified by using the chemical oxygen demand method (COD). The microbial concentration in the UASB bioreactor was measured by taking the whole sludge in the bioreactor at the end of operation for each COD loading rate. The sludge sample was filtered, and the filtered solids were dried at 110°C to obtain MLSS (mixed liquor suspended solids) and further burnt at 550°C to obtain MLVSS (mixed liquor volatile suspended solids) to represent the microbial concentration in the system. The analytical methods of COD and VSS were followed the standard methods. The amount of volatile fatty acid in mg as acetic acid per liter was determined by a distillation-titration method. The effluent sample was distillated and titrated with 0.1 M NaOH aqueous solution using phenolphthalein as an indicator [17].

III. RESULTS AND DISCUSSION

A. Gas Production Rate and COD Removal

The gas production rate and COD removal efficiency at different COD loading rates are shown in Figure 2. Both the gas production rate and COD removal efficiency increased with increasing COD loading rate and then decreased. A maximum gas production rate and COD removal efficiency were 64 l/d and 24%, respectively at a COD loading rate of 46 kg/m^{3}d. The results can be explained in that high amount of organic compounds in the reactor at a high COD loading rate provided higher substrates available for microbes to convert into higher quantities of gaseous products [18]. However at a very high COD loading rate, both gas production rate and COD removal decreased due to the microbial was washed out from the system as a result of the increasing toxicity from the VFA accumulation in the system which will be discussed later.

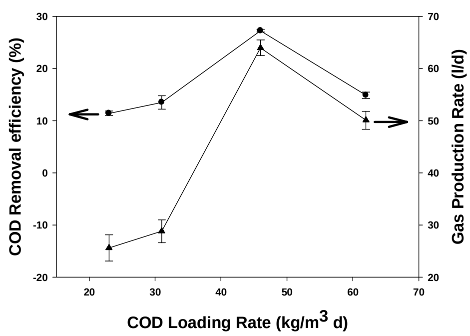

Fig. 2 COD removal efficiency and gas production rate as a function of COD loading rate at 37ºC and pH 5.5

B. Hydrogen Production Rate

The hydrogen production rate is calculated from the gas production rate and hydrogen composition. Figure 3 shows the effect of COD loading rate on gas composition and hydrogen production rate. The hydrogen production rate increased with increasing COD loading rate and then decreased with further increased COD loading rate. The maximum hydrogen production rate of 18 l/d was found at a COD loading rate of 46 kg/m^{3}d. For the gas composition mainly consisted of hydrogen and carbon dioxide. The hydrogen percentage increased with increasing COD loading rate and reached a maximum at a COD loading of 46 kg/m^{3}d. After that, the hydrogen percentage decreased to 25% with further increasing COD loading rate. The results can be explained in that more microbial cells were washed out from the system as a result from the toxicity of VFA accumulation [19]. When the COD loading rate increased from 46 to 62 kg/m^{3}d, the carbon dioxide content showed an opposite trend with the hydrogen content. Fang et. al., [20] found the same results that the produced gas comprised of mostly hydrogen and carbon dioxide and the carbon dioxide had an opposite trend with hydrogen.

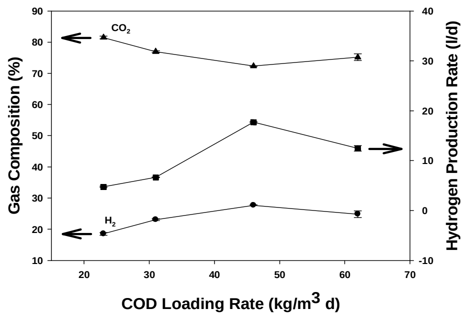

Fig. 3 Gas composition and Hydrogen production rate as a function of COD loading rate at 37ºC and pH 5.5

C. Specific Hydrogen Production Rate

Specific hydrogen production rate (SHPR) is defined as the hydrogen production rate per unit weight of the microbial cells in the bioreactor or per unit volume of the bioreactor. Figure 4 shows the specific hydrogen production rate at different COD loading rates. The results showed that with increasing COD loading rate, the SHPR increased and reached a maximum value of 1080 ml H_2/g MLVSS d, or 1430 ml H_2/ L d at a COD loading rate 46 kg/m^{3}d correspond to the highest microbial concentration in the system which will be discussed later. When the system was operated at a higher COD loading rate than 46 kg/m^{3}d, the SHPR decreased markedly. The decreasing in SHPR at further increased COD loading rate results from the toxicity from VFA accumulation in the bioreactor, which can inhibit the growth of hydrogen-producing bacteria.

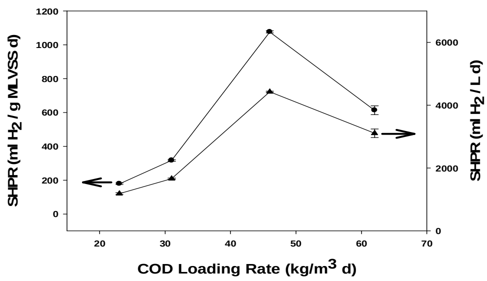

Fig. 4 Specific hydrogen production rate (SPHR) as a function of COD loading rate at 37°C and pH 5.5

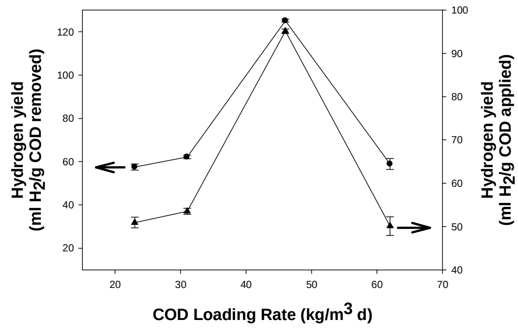

Fig. 5 Hydrogen yield as a function of COD loading rate at 37°C and pH 5.5

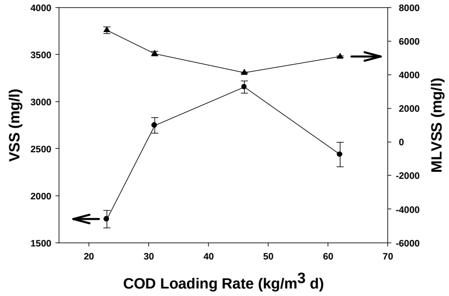

Fig. 6 MLVSS and effluent VSS as a function of COD loading rate at 37°C and pH 5.5

D. The amount of volatile fatty acid (VFA)

Figure 7 shows the effect of COD loading rate on amount of VFA. The amount of VFA increased remarkably with increasing COD loading rate. From the results, it can be concluded that a higher COD loading rate (>46 kg/m^{3}d), there is high VFA accumulation which is the cause of the decrease in hydrogen production performance.

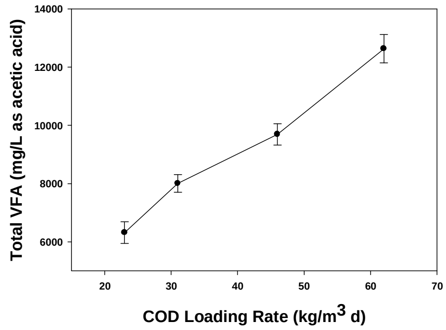

Fig. 7 The amount of volatile fatty acid as a function of COD loading rate at 37ºC and pH 5.5

IV. CONCLUSIONS

The biohydrogen production from alcohol wastewater by using upflow anaerobic sludge blanket reactors (UASB) was investigated under mesophilic temperature (37 ºC) and pH 5.5. From the results, the maximum hydrogen production was achieved at a COD loading rate of 46 kg/m^{3}d. At this condition, the highest hydrogen content (27%), hydrogen yield

(125.1 ml H_2/g COD removed and 95.1 ml H_2/g COD applied), hydrogen production rate (18 l/d), specific hydrogen production rate (1080 ml H_2/g MLVSS d and 1430 ml H_2/ L d), and COD removal (24%) were obtained.

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