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The Open Fuels & Energy Science Journal, 2015, *8*, 81-85

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Bio-hydrogen Production from Beer Wastewater in an Internal Circulation (IC) Reactor

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Abstract: An internal circulation (IC) using hydrogen-producing anaerobic granular sludge as seed sludge and beer wastewater as substrate was employed to evaluate the effect of hydrogen production and the performance of reactor. Running at the temperature of 35±1 °C, the pH value of influent controlled is 5.5 and organic loading rate (OLR) from 30 kg COD/(m3•d) to 42 kg COD/(m3•d), the IC reactor presents a high hydrogen production ability as the hydrogen production rate (HPR) maximized at 6.0-6.83 m3/(m3•d). Hydrogen volume content was estimated to be 42-46% of the total biogas and the biogas was free of methane throughout the study. COD removal efficiency could reach 20-30% and the dissolved fermentation products were predominated by ethanol with the concentration of 900-950 mg/L, which accounts for 45%-56% of the total liquid products. These values may imply that the IC reactor is a kind of feasible fermentative hydrogen production equipment.

Keywords: IC reactor, hydrogen production, Beer wastewater, Ethanol-type fermentation.

1. INTRODUCTION

Hydrogen is considered as an important future energy source for it has high energy density, clean and versatile [1]. Among all hydrogen-producing processes, hydrogen production by bio-fermentation is considered as the most promising one for its outstanding features of mild process conditions, low energy consumption and abundant raw materials. It has become an increasingly popular hot spot among researchers around the globe [2,3]. The key factors of biological hydrogen production technology for industrial applications are developing efficient bio-hydrogen reaction equipment, improving energy recovery efficiency and reducing production costs. At present researches of hydrogen production by bio-fermentation mostly concentrate on continuously stirred tank reactor (CSTR) [4-6], Up-flow Anaerobic Sludge Bed (UASB) [7] and expanded granular sludge bed (EGSB) [8]. IC reactor is the third generation of effective anaerobic reactor, which has some outstanding characteristics such as high volume loading rate, less occupied area, strong ability for resisting shock loading and wide application in high concentration organic wastewater treatment [9, 10]. However, the application of IC reactor in hydrogen production has not been discussed. In this study, IC reactor with hydrogen-producing anaerobic granular sludge as seed sludge is developed for fermentative hydrogen production from beer wastewater. The results will provide technical basis for the engineering application of fermentative hydrogen production.

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2. MATERIAL AND METHODS

2.1. Reactor

This lab-scale IC reactor was made of Plexiglas with a column section of 140 mm internal diameter, 1500 mm in length and 1260 mm in reaction zone height (Fig. **1**). The reactor had a working volume of 18.46 L and the three-phase separator capacity of 6.16 L. The out part of the reactor was covered with a black soft film for dark .The process was operated at 35±1℃ by uniformly enwinding heating thread out part of the reactor. A continuous culture was introduced by feeding substrate to the bottom of the reactor with a peristaltic pump. The biogas generated was collected with water seal and measured by wet gas meters (Model LML-1, Changchun Filter Co. Ltd., Changchun, China) which were filled with acidified saturated salt solution in order to prevent the biogas from dissolution.

2.2. Experimental Wastewater and Seed Sludge

The experimental wastewater containing a high concentration of organic matter was obtained from China resources Snow breweries (Zhengzhou). Influent COD was about 10000 mg/L, pH value varied from 5.0 to 6.0.

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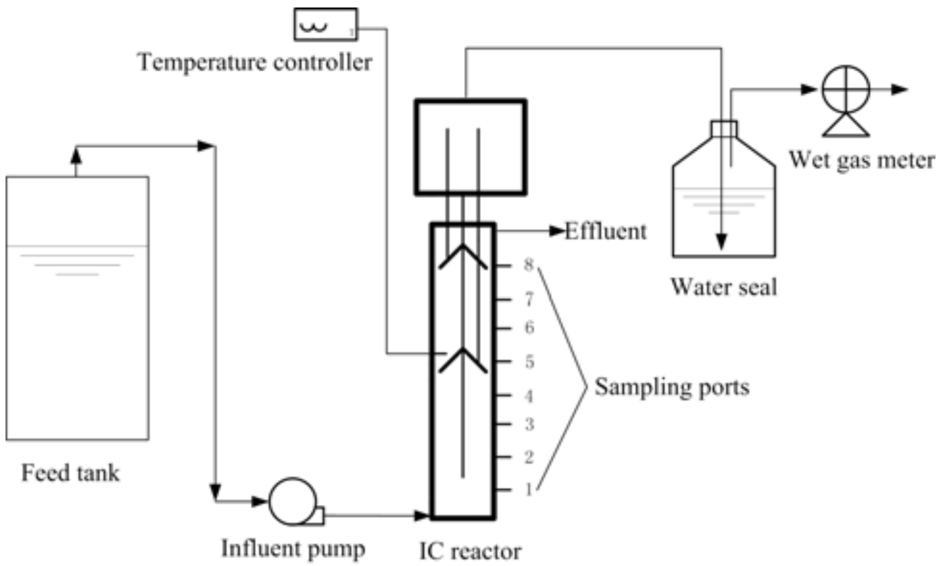

Fig. (1). Schematic diagram of the IC reactor.

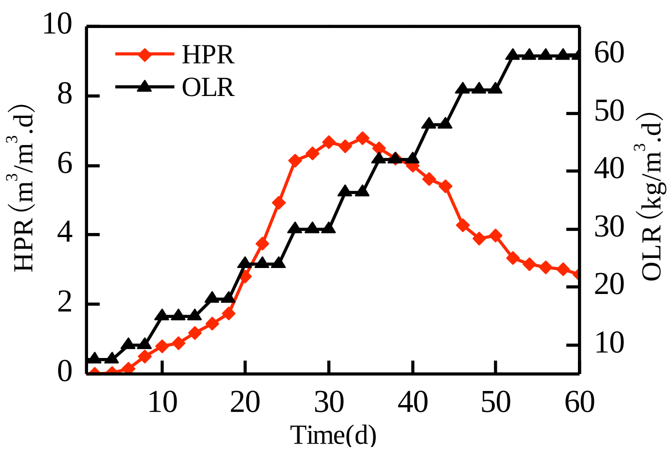

Fig. (2). Hydrogen production rate and OLR variation.

The feed sludge was fresh hydrogen-producing anaerobic granular sludge obtaining from fermentative hydrogen-producing IC reactor, with diameter of 0.5-2.0 mm, volatile suspended solids (VSS) of 10.5 g/L.

2.3. Bioreactor Start-up and Operation

The initial influent was diluted by tap water to control the COD around 2500 mg/L. In the first fifteen days, OLR increased gradually from 7.5 kg COD/(m^3•d) to 15 kg COD/(m^3•d) by keeping influent COD at 2500 mg/L and reducing the hydraulic retention time(HRT) from 8 h to 4 h step by step; In the sixteenth to sixtieth day, OLR increased gradually from 15 kg COD/(m^3•d) to 60 kg COD/(m^3•d) by keeping HRT at 4 h and increasing influent COD from 2500 mg/L to 10000 mg/L little by little.

2.4. Analytical Methods

The COD and pH were measured according to standard methods [11], Hydrogen content in the biogas was determined by gas chromatography (GC, Agilent 4890, American).

Ethanol and volatile fatty acid concentrations (VFA) were assessed using Gas Chromatography (GC-14, Shimadzu, Japan).

3. RESULTS AND DISCUSSION

3.1. Reactor Performance of Hydrogen Production

The hydrogen production rate (HPR) has generally been considered as an important parameters to evaluate the reactor performance of hydrogen production. Fig. (**2**) depicts the HPR variations with OLR.

Fig. (**2**) showed that from the 1st to the 34th day HPR increased as OLR increased, while HPR showed a downward trend as OLR continued to increase after the 34th day. In the start-up stage (1st to the 12th day), OLR was 7.0-15 kg COD/(m^3•d), the corresponding HPR was less than 1.0

Table 1. Comparison of HPR from some other studies.

Reactor Type	Maximum HPR	Substrate Types	Reference Source
CSTR	4.77	Glucose	[12]
CSTR	2.25	Sucrose	[13]
UASB	2.39	Sucrose	[14]
EGSB	7.43	molasses	[15]
IC	6.83	Beer wastewater	This study

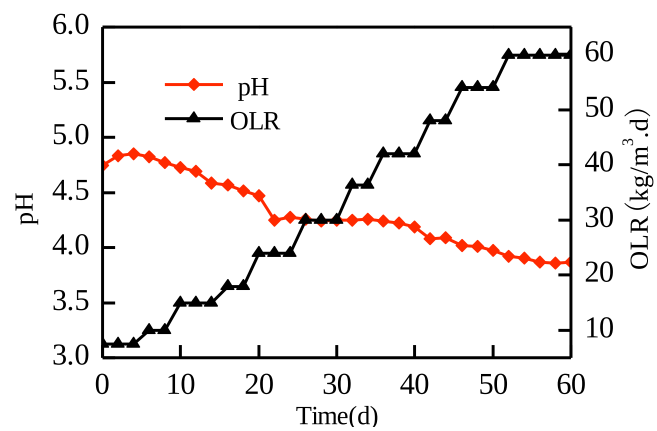

Fig. (3). pH of effluent variations with OLR.

$m^3/(m^3\bullet d)$; When OLR increased to 30-42 kg COD/($m^3\bullet d$), the corresponding HPR was about 6.0-6.83 $m^3/(m^3\bullet d)$; when OLR continued to increase to 48-60 kg COD/($m^3\bullet d$), the corresponding HPR was about 2.8-4.2 $m^3/(m^3\bullet d)$. The maximum HPR of 6.83 $m^3/(m^3\bullet d)$ was observed with an OLR of 36 kg COD/($m^3\bullet d$). During the gas production process of the 1^{st} to the 24^{th} day, hydrogen volume content increased over time and was estimated to be 5-35% of the total biogas. After 24^{th} day, hydrogen volume content kept the level of 42％-46％. According to the analysis, OLR has a significant influence on the effect of hydrogen production of IC reactor. In order to obtain a preferable fermentative hydrogen-producing effect of beer wastewater, the OLR of IC reactor should not exceed 45 kg COD/($m^3\bullet d$).

The comparison of HPR from continuous flow hydrogen production reported in the previous researches were summarized in Table **1**. According to Table **1**, IC reaction in this research have a relative high level of HPR, which proved that IC reactor can obtain a preferable hydrogen-producing efficiency under high OLR and have pretty good development prospects as biological hydrogen-producing process.

3.2. Variations in PH

Environmental pH was proved to play an important role in fermentative hydrogen production performance. Acid-producing fermentation bacteria had great pH adaptability. The optimal pH range for most bacteria was 5.0~8.5, some acid-producing fermentation bacteria can exist under pH of 4.0. pH has great effect on the bio-hydrogen production process, which would not only influence certain enzyme activity and the growth rate of bacteria but also change the status and amount of dominant bacterial populations in reactor and would further change the fermentation pathway and affect the hydrogen-producing effect of acid- producing fermentation bacteria populations. Ren [16] pointed that the optimal pH range of hydrogen production from ethanol type fermentation was 4.2~4.5, which used molasses wastewater as influent. Lay [17] pointed that the optimal pH range of hydrogen production from butyric acid type fermentation was 6.7. In this study, pH of influent was controlled around 5.5. Fig. (**3**) depicts pH of effluent variations with OLR.

Fig. (**3**) showed that pH of effluent presented a downward trend as OLR increased. When influent OLR was less than 42 kg COD/($m^3\bullet d$), pH of effluent maintained between 4.2-4.8. While influent OLR increased to more than 54 kg COD/($m^3\bullet d$), pH value of effluent dropped to below 4.0. According to the variation of HPR, it maintained at a relative high level when OLR between 30-42 kg COD/($m^3\bullet d$), meanwhile, pH value of effluent reached 4.2-4.3. The result was in accordance with the study of Ren [16]. During the whole process, no methane gas was detected, which indicated that low pH effectively inhibited methanogenesis.

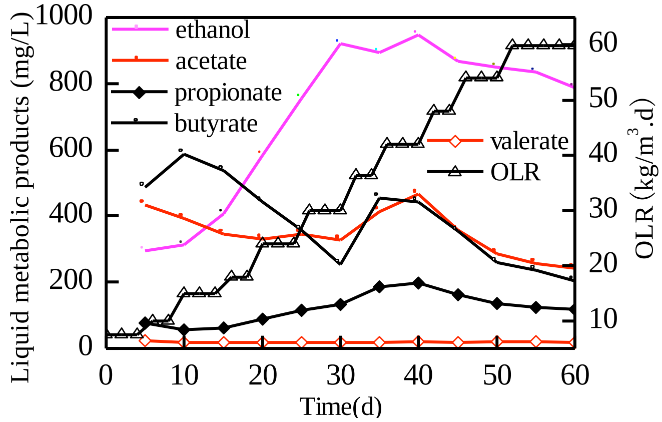

Fig. (4). Liquid metabolic products and OLR variation in the IC reactor.

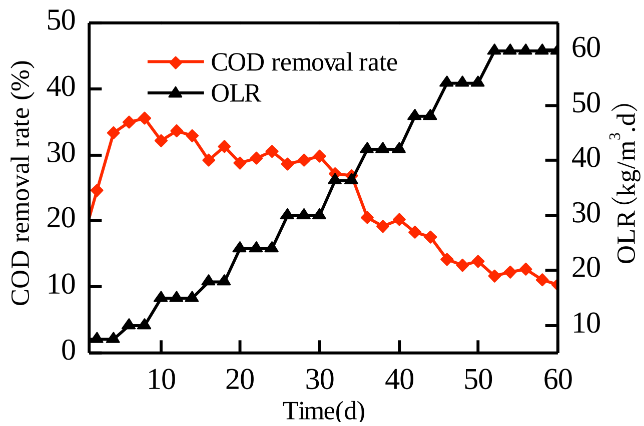

Fig. (5). COD removal rate and OLR variation in start-up stage.

3.3. Composition of Liquid end Production

Anaerobic fermentative hydrogen production is divided into 3 types: butyric acid type fermentation, propionic acid type fermentation and ethanol type fermentation. In many papers, butyrate-type fermentation has been depicted as the most popular pathway for fermentative hydrogen production [5, 18]. In this process, Liquid metabolic products and OLR variation in the IC reactor were shown in Fig. (**4**).

According to Fig. (**4**), in the first 15 days from start-up, butyric acid accounted for the largest amount of liquid end production, followed by acetic acid and ethanol; as the OLR increased, the ethanol concentration in liquid end production kept rising and reached 756 mg/L at day 25, which accounted for 47.45% of total VFAs. This indicated that bacteria producing hydrogen, acid, and ethanol had the dominant position in the reactor. When OLR continued to increase to 60 kg COD/(m^3•d), ethanol was always the main product of fermentative production, which indicated that the main type of reactor was ethanol type fermentation. When OLR was 30-42 kg COD/(m^3•d), ethanol concentration reached maximum of 900-950 mg/L accounting for 45%-56% of total VFAs. Combining this with HPR variation (Fig. **2**), it showed that variation of ethanol concentration and HPR were positively correlated.

3.4. COD Removal Rate

In this process, influent COD was gradually increased from 2500 mg/L to 10000 mg/L and COD removal rate is shown in Fig. (**5**). According to Fig. (**5**), when influent OLR was gradually increased from 7.5 kg COD/(m^3•d) to 30 kg COD/(m^3•d), COD removal rate maintained at 30%~35%; when OLR was 30~42 kg COD/(m^3•d), COD removal rate maintained at 20%~30%. When influent COD was increased to 8000~10000 mg/L, OLR reached 48-60 kg COD/(m^3•d), COD removal rate gradually decreased from 20% to 10.35%. The result indicated that COD removal rate could reach 20%~30% under the condition of high hydrogen-producing effect in IC reactor.

CONCLUSION

Using fermentative hydrogen production with beer wastewater as substrate showed that when the condition of OLR was at 30-42 kg COD/(m^3•d), HPR was about 7.0-7.8 m^3/(m^3•d) and hydrogen content was 42-46%; COD removal rate was up to 20-30%, maximum HPR was 7.83 m^3/(m^3•d) with corresponding OLR of 36 kg COD/(m^3•d). During the whole operation process, the main fermentation type in IC reactor was ethanol type fermentation. At the stage of high

HPR, ethanol was the main products of liquid end production with the concentration of 900-950 mg/L, accounting for 45%-56% of total VFAs.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

ACKNOWLEDGEMENTS

This study was supported by the scientific and technological project of the Education Department of Henan Province (No.12A610008).

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Received: October 16, 2014 Revised: December 23, 2014 Accepted: December 31, 2014