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Hydrogen and Methane Production from Condensed Molasses Fermentation Soluble by a Two-stage Anaerobic Process

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Abstract

The treatment of condensed molasses fermentation soluble (CMS) is a troublesome problem for glutamate manufacturing factory. However, CMS contains high carbohydrate and nutrient contents and is an attractive and commercially potential feedstock for bioenergy production. The aim of this paper is to produce hydrogen and methane by two-stage anaerobic fermentation process. The fermentative hydrogen production from CMS was conducted in a continuously-stirred tank bioreactor (working volume 4 L) which was operated at a hydraulic retention time (HRT) of 8 h, organic loading rate (OLR) of 120 kg COD/m^3-d, temperature of 35^{o}C, pH 5.5 and sewage sludge as seed. The anaerobic methane production was conducted in an up-flow bioreactor (working volume 11 L) which was operated at a HRT of 24 -60 hrs, OLR of 4.0-10 kg COD/m^3-d, temperature of 35^{o}C, pH 7.0 with using anaerobic granule sludge from fructose manufacturing factory as the seed and the effluent from hydrogen production process as the substrate. These two reactors have been operated successfully for more than 400 days. The steady-state hydrogen content, hydrogen production rate and hydrogen production yield in the hydrogen fermentation system were 37%, 169 mmol-H_2/L-d and 93 mmol-H_2/g $\text{carbohydrate}_{\text{removed}}$, respectively. In the methane fermentation system, the peak methane content and methane production rate were 66.5% and 86.8 mmol-CH_4/L-d with methane production yield of 189.3 mmol-CH_4/g $\text{COD}_{\text{removed}}$ at an OLR 10 kg/m^3-d. The energy production rate was used to elucidate the energy efficiency for this two-stage process. The total energy production rate of 133.3 kJ/L/d was obtained with 5.5 kJ/L/d from hydrogen fermentation and 127.8 kJ/L/d from methane fermentation.

1 Introduction

The treatment of condensed molasses fermentation soluble (CMS) is a troublesome problem for glutamate manufacturing factory. However, CMS contains high carbohydrate and nutrient contents and is an attractive and commercially potential feedstock for bioenergy production. Anaerobic fermentation is an effective and energy saving process to generate energy from organic wastes. There were many reports on hydrogen and methane production by two-stage anaerobic fermentation process (Ueno et al., 2007 [1]; Antonopoulou et al., 2008 [2];

Chu et al., 2008 [3]). The aim of this report is to produce hydrogen and methane by two-stage anaerobic fermentation process.

2 Materials and Methods

2.1 Feedstock and hydrogen fermentation system (HFS)

Feedsctock, CMS and hydrogenogenic microflora were prepared according to the previous report (Lay et al., 2010 [4]). Two liter of the heat-treated microflora was inoculated into 2 L of CMS with 40 g COD/L in a continuously-stirred tank bioreactor (working volume 4 L). The cultivation was carried out at a hydraulic retention time (HRT) of 8 h, organic loading rate (OLR) of 120 kg COD/m^3-d, temperature of 35°C and controlled pH 5.5 by automatic titration with 4 N NaOH. The effluent from hydrogen producing fermentor was collected into a gas and liquid separator. The amount of biogas produced was measured using a wet-gas meter (Ritter, Germany, TG 1/5).

2.2 Methane fermentation system (MFS)

The anaerobic methane production was conducted in an up-flow bioreactor (working volume 11 L). Anaerobic granular sludge was collected from a fructose manufacturing industry in central Taiwan. The pH, volatile suspended solids (VSS, to express the biomass concentrations) and (total chemical oxygen demand, T-COD) concentrations of the seed sludge were 8.0, 37.68 g/L and 70.24 g/L, respectively. Ten percent of working volume of the up-flow bioreactor was filled with the anaerobic granular sludge. The operation was conducted at a HRT of 24 -60 hrs, OLR of 4.0-10 kg COD/m^3-d, temperature of 35^{o}C and pH 7.0. The effluent from HFS was used as the substrate. The two-stage anaerobic fermentation process was shown in Figure 1.

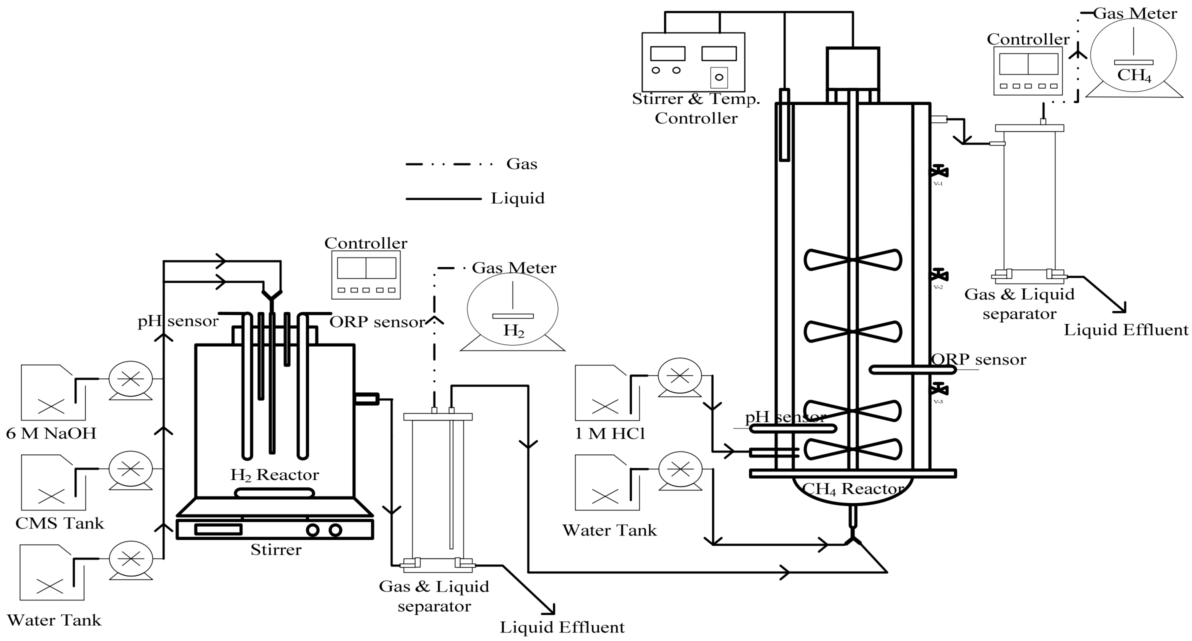

Figure 1: Schematic of the two-stage anaerobic biogas production fermentation system.

2.3 Analytical methods

The composition of product gas and the concentrations of ethanol and organic acids were measured as described previously (Lay et al., 2010 [4]). Analysis for the sampled broth for determination of residual sucrose concentration, pH, oxidation-reduction potential (ORP) and volatile suspended solid (VSS) concentration was carried out according to the previous report (Lin et al., 2010 [5]).

2.4 Monitoring

When a steady-state condition was reached, the hydrogen gas content and biogas production maintained stable, and the desired data obtained, the HRT was reduced. The monitoring parameters were pH, ORP (oxidation-reduction potential), alkalinity and gas production. The hydrogen production efficiency was evaluated using the hydrogen/methane productivity (the ability of converting carbohydrate and COD into hydrogen, respectively, HY and MY) and hydrogen/methane production rate (the rate of hydrogen/methane production from the reactor, HPR/MPR) and specific hydrogen/methane production rate (the rate of hydrogen/methane production from microflora, SHPR/SMPR). The total heating value could be calculated by Eq 1.

Total energy (kJ) = $\sum V \times \frac{P}{R \times T} \times H_{H_2 \, or \, CH_4} = V \times \frac{1}{0.082 \times 298} \times H_{H_2 \, or \, CH_4}$ Eq 1

V is the H_2 or CH_4 production efficiency (L/L-reactor); P is the measurement pressure of the gas (1 atm); R is the gas constant (0.0821 L atm/mol K); T is the measurement temperature of the gas (273+25 K); H is heating value (kJ/mol). The heating values of hydrogen and methane are 285.8 and 896 kJ/mol, respectively.

3 Results

3.1 Performance of hydrogen fermentation system

Table 1 summarizes the experimental results obtained during the 491 days of fermentation. ORP value was about -420 mV which is close at the optimal value of -400 mV for HFS (Hippe et al., 1992 [6]; Kumar et al., 1995 [7]). The S-COD degradation was low (7.8%), because Organic material was converted into soluble metabolic products such as ethanol, acetate, propionate, butyrate. The carbohydrate was a good substrate for hydrogen producing bacteria (Koskinen et al., 2008 [8]). Therefore, the carbohydrate degradation was 65.9%. Figure 1 illustrates the daily variations at HRT of 8 h. The results shows the HPR, SHPR and HY were 162 mmol-H_2/L-d, 36 mmol-H_2/g VSS-d and 89.3 mmol-H_2/g Carbohydrate, respectively. The HPR value is similar with our previous study (Lay et al., 2010 [4]).

Table 1: The performance of hydrogen fermentation system at HRT 8 h.

OLR (kg COD /m^3-d)	ORP (-mV)	VSS (g/L)	S-COD (mg/L)			S-Carbohydrate (mg/L)		
			Influent (mg/L)	Effluent (mg/L)	Degradation (%)	Influent (mg/L)	Effluent (mg/L)	Degradation (%)
120±18.4	422±25	4.4±1.2	41,341±5,899	41,341±5,899	7.8	10,311±1,952	3,512±1,098	65.9

*OLR: organic loading rate

3.2 Performance of methane fermentation system

In our previous study (Lin, 2005 [9]), the optimal substrate concentration for methane fermentation of 10 g COD/L was obtained. However, the effluent concentration of the HFS was about 40 g COD/L. Therefore, the effluent of the HFS was diluted before seeded into the MFS. The MFS was started-up at HRT of 24 h with the fermentor performance enhanced successfully at HRT of 60 h. Table 2 shows the ORP was constant at -480 mV which is the optimal value for methane production (Dirasian et al., 1963 [10]). VSS was increased with increasing OLR. The S-COD and carbohydrate degradations were from 45.2 to 64.7% (Table 2).

Table 2: The performance of methane fermentation system at varied HRT.

HRT (h)	OLR* (kg COD /m³-d)	ORP (-mV)	VSS (g/L)	S-COD (mg/L)			S-Carbohydrate (mg/L)		
				Influent (mg/L)	Effluent (mg/L)	Degradation (%)	Influent (mg/L)	Effluent (mg/L)	Degradation (%)
60	4±1.4	478±5	0.8±0.4	8,762±3,454	3,092±661	64.7	990±671	419±138	57.7
48	5±1.2	472±6	10.3±5.8	11,802±2,399	4,303±873	63.5	1,233±383	545±162	55.8
24	10±2.1	484±28	16.3±10	11,122±2,054	5,213±1,082	53.1	949±164	482±93	49.2
12	20±2.0	485±36	2.1±0.3	10,813±1,024	5,928±809	45.2	913±102	485±58	46.9

*OLR: organic loading rate

Figure 2 illustrates the daily variations in MPR, MY and SMPR at various HRTs. When the OLR was increased stepwise, the MPR increased along with the increasing OLR. The peak MPR of 151 mmol CH_4/L-d and MY of 313 mmol CH_4/g COD at 20 kg COD/m^3-d and HRT 12 h were 5 and 6-fold higher than 28 mmol CH_4/L-d and 51 mmol CH_4/g COD (at 4 kg COD/m^3-d and HRT 60 h). This value is 50% higher than HPR of 208 mmol H_2/L-d at HRT 4.4 h from molasses in CSTR (Liu et al., 2008 [11]).

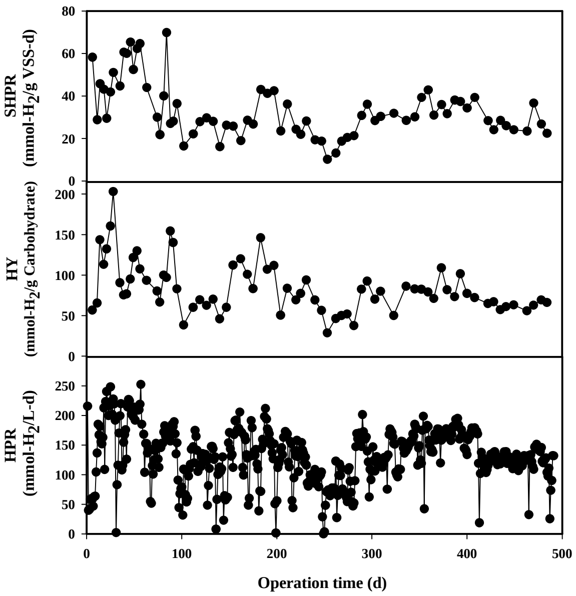

Figure 2: Hydrogen production rate, hydrogen yield and specific hydrogen production rate at HRT 8 h.

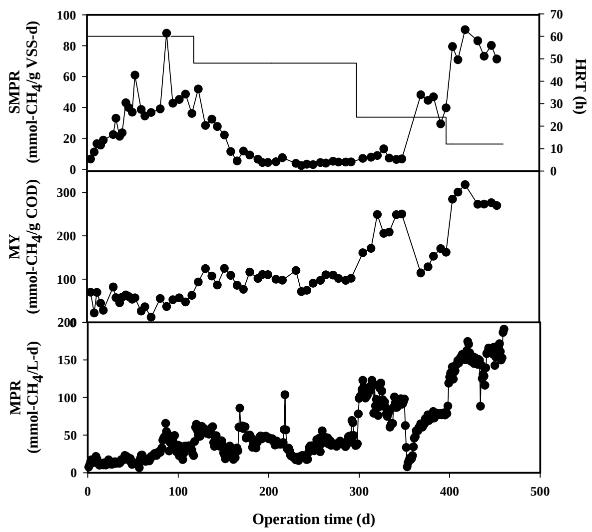

Figure 3: Daily evolution of methane production rate, methane yield and specific methane production rate.

3.3 Total energy production of two-stage anaerobic process

Table 3: Bioenergy production of two-phase bioenergy fermentation system.

Reactor	HRT (h)	HPR (mmol-H_2/L-d)	MPR (mmol-CH_4/L-d)	HY (mmol-H_2/g Carbohydrate)	MY (mmol-CH_4/g COD)	EPR (kJ/L-d)		EY (kJ/g Carbohydrate)	EY (kJ/g COD)
HFS	8	162	-	89.3	-	46.3	-	25.5	-
MFS	60	-	23.8	-	51.2	-	21.3	-	45.9
	48	-	46.9	-	120.2	-	42.0	-	107.7
	24	-	86.8	-	189.2	-	77.8	-	169.5
	12	-	151.1	-	312.8	-	135.4	-	280.3

Table 3 lists the total energy production calculated from hydrogen and methane production from the two-stage anaerobic process. The energy production rate (EPR) of 46.3 kJ/L-d and energy yield of 25.5 kJ/g carbohydrate were obtained from HPR of 162 mmol-H_2/L-d and HY of 89.3 mmol-H_2/g carbohydrate, respectively. The peak EPR in methane fermentation system was 135.4 kJ/L-d and the peak EY was 280.3 kJ/g COD at HRT 12 h. However, the total EPR of 181.7 kJ/L-d and EY of 305.8 kJ/g substrate for this two-stage anaerobic fermentation process were carried out at hydrogen fermentation system at HRT 8 h and methane fermentation system at HRT 12 h.

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