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Hydrogen Production by Anaerobic Digestion of Crude Glycerol from Biodiesel Fuel Manufacturing Process – Part II. Effects of Biodiesel Fuel-related Chemical Components on Hydrogen Production

Oozora Yamane[1] and Masaharu Komiyama[1,2*]

[1] Clean Energy Research Centre, University of Yamanashi, 4-3-11 Takeda, Kofu, 400-8511, Japan

[2] Center for Biofuel and Biochemical Research, Department of Chemical Enigneering, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Pera, Malaysia

Abstract

In order to utilize crude glycerol, a byproduct from biodiesel fuel production, its conversion through anaerobic fermentation was studied. Chemical components related to biodiesel fuel production were examined as substrates of anaerobic digestion. Glycerol was found to play a key role for the hydrogen production, while methanol, KOH and waste vegetable oil from which biodiesel fuel was made exerting synergetic effects.

Keywords: Biodiesel fuel, Crude glycerol, Anaerobic digestion, Hydrogen fermentation, Biodiesel fuel-related chemicals

1 Introduction

Biohydrogen production from waste biomass has been attracting wide attention [1]. The substrates for microbial hydrogen production include wastes from the food industry (such as bean curd waste, beer lees, corn starch hydrolysate and cheese whey) to agricultural waste (such as wheat straw and animal excrements). Among them crude glycerol, a byproduct of biodiesel fuel production, is in the spotlight [2]. The worldwide production of biodiesel fuel as of 2014 amounts to 29.7 billion L/yr [3], and simple estimate gives 3.2 billion L/yr crude glycerol production, since byproduct crude glycerol is discharged at a rate of ca. 10 wt% of the biodiesel fuel produced.

It is known that glycerol, when it is used as substrate of anaerobic fermentation, brings about hydrogen fermentation rather than methane digestion [4-9]. It is also known that byproduct crude glycerol from biodiesel fuel production process similarly enhances hydrogen production [4,5,10-16]. However, its effect, when compared to that of pure glycerol, was mixed. Selembo et al. reported that pure and byproduct glycerol gives similar hydrogen production with heat-treated mixed culture [5], while Ito et al. much less hydrogen production with *Enterobacter aerogenes* HU-101 [4]. To the authors' knowledge, no study has been performed to quantify the effect of constituents in crude glycerol on anaerobic fermentation. Instead, Rodrigues et al. [14] pretreated crude glycerol to remove some of the impurities while the addition of other components such as apple pomace hydrolysate [12] has been examined.

In the first part of this study, the authors reported the enhancement of hydrogen production and suppression of methane fermentation when crude glycerol was used as a substrate of anaerobic fermentation [17]. It is the objective of the second part of the study to identify the chemical components in the crude glycerol that are responsible for hydrogen production enhancement.

2 Experimental

2.1 Raw materials

The source of the crude materials employed in the present study follows the previous report [17]. Cattle excrement obtained from Yamanashi Prefectural Dairy Experimental Station, Hokuto City, Japan, was used as starting inoculum. Crude glycerol was obtained from the biodiesel production equipment (Nanko Co. Ltd., Japan, model ME-100, 100 L/day) installed at the Faculty of Engineering, University of Yamanashi. Byproduct crude glycerol was separated by sedimentation, and settled crude glycerol was withdrawn from the bottom of the reactor tank. The catalyst used for transesterification was KOH, and as a result, crude glycerol produced was highly alkaline. Its characteristics and compositions are listed in Table 1. The use of Inoculum B as a starting inoculum is to extract and highlight the characteristics of crude glycerol as substrate, since Inoculum B has stopped its initial fermentation stage already, and any activity observed with other substrate addition would be the direct consequence of the new substrate.

In order to determine the effect of the individual chemical component contained in the employed crude glycerol, pure chemical counterparts were purchased and used: glycerol (purity 99.0 %, Kanto Chemicals), potassium hydroxide (purity 99. 5 %, Wako Pure Chemicals) and methanol (purity 99.8 %, Wako Pure Chemicals).

*Corresponding author.
E-mail address : masaharu@yamanashi.ac.jp, masaharu.komiyama@utp.edu.my

Table 1 Characteristics and Compositions of Crude Glycerol Employed in the Present Study

pH	12.7
glycerol / wt%	43
methanol / wt%	13
water / wt%	2.5
palmitate / wt%	4.1
oleate / wt%	20
steroids / wt%	0.3
ash / wt%	8.6
potassium / wt%	4.2
sodium / wt ppm	72
phosphorous / wt ppm	10
Other impurities / wt%	8.5

2.2 Inoculum preparation

Inoculum preparation also follows preceding report [17], viz., the cattle excrement was first sieved with a screen with 1.7 mm opening in order to remove straw mulching and other debris. The sieved cattle excrement was mixed with water of the same weight. in a 10 L polyethylene tank. The air in the head space was replaced with nitrogen, a Tedlar bag is connected and shaking of the entire assembly was started with temperature-controlled water bath shaker at 37 °C. The amount of gas produced was measured once a day by water displacement method, until when the substrate in the inoculum is almost exhausted, i.e., gas production has levelled off. Total solids shown in Table 2 is measured as the residue after heating at 105 °C for 24 h, and volatile solids after heating at 550 °C for 24 h.

Table2 The Inoculum Employed in the Present Study

	Preparation method	Total solids / wt%	Volatile solids / wt%
Inoculum B	Cattle excrement is sieved (2 kg after sieving) and mixed with 2 L water, then methane fermented under anaerobic condition at 37 °C for ca. 150 h until biogas production has levelled off.	5.33	4.54

2.3 Procedures

Experimental procedure also follows the preceding paper, viz., the inoculum prepared as above was divided into smaller batches, typically 50 mL in a 100 mL flask, and crude glycerol or other biodiesel fuel-related chemical components were added. Again, the air in the head space of each reactor (flask) was replaced with nitrogen, a Tedlar bag was connected and shaking of the entire assembly was started with temperature-controlled water bath shaker. Throughout the present experiment, mesophilic digestion temperature of 37 °C was employed. The amount of gas produced was measured at the appropriate interval by water displacement method. Gas composition analysis was done by using a Shimadzu GC-8A gas chromatograph equipped with a thermal conductivity detector. An activated carbon column operated at 70 °C was used for gas separation with Ar carrier gas.

The substrates tested here are listed in Table 3 for single component testing and Table 4 for multiple component testing. The amount of each chemical component added as a substrate was determined to reflect the composition of crude glycerol, but not to the exact amount. The starting pH varied from 6.4 to 7.6 in the case of Table III experiments and 6.4 to 7.2 in the case of Table IV experiments due to the acidity/basicity of added substrate, while after the reaction all the reactors show the same pH of 6.4.

Table 3 Biodiesel Fuel-Related Chemical Components Examined as Substrate

Run #	Amount of Inoculum B / g	Biodiesel fuel-related components added / g					
		Crude glycerol	Pure glycerol	MeOH	KOH	Waste vegetable oil	Biodiesel fuel
B1	100.0	10.0	-	-	-	-	-
B2	100.0	-	6.0	-	-	-	-
B3	100.0	-	-	2.5	-	-	-
B4	100.0	-	-	-	0.26	-	-
B5	100.0	-	-	-	-	2.0	-
B6	200.0	-	-	-	-	-	4.0

* Two times larger reactor was used, with two times as much inoculum as well as the substrate

Table 4 Two Component Biodiesel Fuel-Related Chemical Combinations Examined as Substrate

Run #	Amount of Inoculum B / g	Biodiesel fuel-related components added / g				
		Pure glycerol	MeOH	KOH	Waste vegetable oil	Biodiesel fuel
C1	100.0	5.8	2.5-	-	-	-
C2	100.0	5.8	-	0.26	-	-
C3	100.0	5.8	-	-	2.0	-
C4*	200.0	11.6	-		-	4.0

* Two times larger reactor was used, with two times as much inoculum as well as the substrate

3 RESULT AND DISCUSSION

3.1 Effect of various substrates related to biodiesel fuel production on biohydrogen production with Inoculum B

The single-component (Table 3) fermentation results are shown in Figure 1. The difference in fermentation time among the samples (see caption of Figure 1) is due to the fact that fermentation was terminated when incremental gas production became zero. As it may be apparent from the figure, except crude glycerol and pure glycerol, no other biodiesel fuel-related components tested here produced a significant amount of hydrogen. From this data, it may be safely concluded that glycerol is the essential component that brings about the hydrogen production under the current experimental conditions.

Nevertheless, it should be noted that pure glycerol alone does not show hydrogen production activity compared to that of crude glycerol. Apparently, some synergetic mechanism among crude glycerol components was working to give such high hydrogen production when crude glycerol was added to Inoculum B.

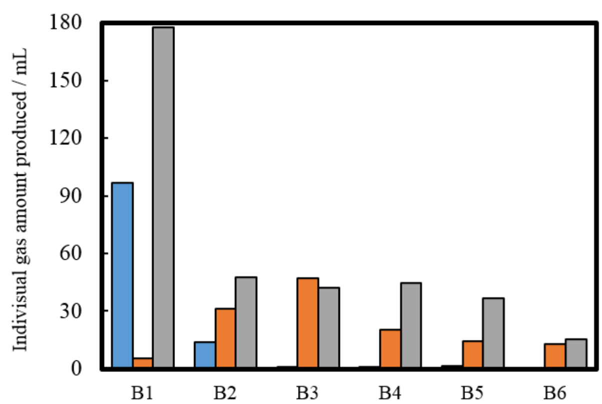

Figure 1 Biogas compositions produced with Inoculum B and various amount of biodiesel fuel-related chemical components as substrate (For substrates added, see Table 3). Blue bar: H_2, orange bar: CH_4 and gray bar: CO_2. Fermentation time was; B1, B3, B4 : 259 h, B2: 188 h, B5, B6: 138 h. For Run B6, the amount of gas produced was devided by 2 (see footnote on Table 3).

3.2 Effect of biodiesel fuel-related chemical component combinations on biohydrogen production with Inoculum B

Figure 2 shows the gas composition obtained from anaerobic fermentation of each chemical combinations listed in Table IV. For the ease of comparison, B1 and B2 experiments from the previous section are also reproduced in this figure.

From the figure it is obvious that the presence of methanol (Run C1), KOH (Run C2) and waste vegetable oil (which are the source of biodiesel fuel production, Run C3) all enhance the nature of pure glycerol (Run B2), increasing hydrogen production (blue bars). Among the three biodiesel fuel-related chemical components, KOH (Run C2) gives highest synergetic effect. However, suppression of methane production (orange bars) is observed only in Run C1 (pure glycerol + MeOH) and Runs C2 and C3 show methane production comparable to hydrogen. Apparently, these results are still short of explaining the high hydrogen production when crude glycerol was used as substrate (Run B1).

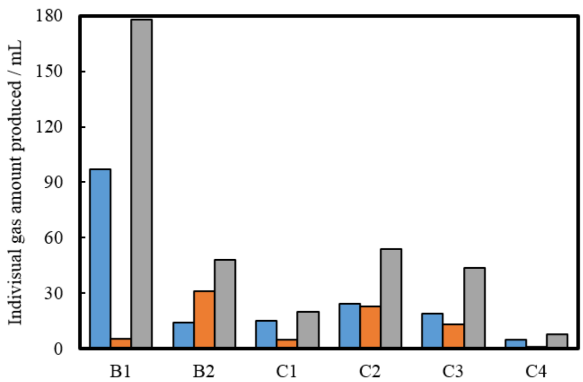

Figure 2 Biogas compositions produced with Inoculum B and various combinations of pure glycerol and biodiesel fuel-related chemical components as substrate. Fermentation time were; B1: 259 h, B2: 188 h, C1 through C4: 138 h. Blue bar: H_2, orange bar: CH_4 and gray bar: CO_2.

4 CONCLUSIONS

Peculiar anaerobic fermentation characteristics of biodiesel fuel production byproduct crude glycerol, enhancement of hydrogen production, was examined using biodiesel fuel-related chemical components as anaerobic digestion substrate. Glycerol was found to play a key role for the hydrogen production, while methanol, KOH and biodiesel fuel reactant waste vegetable oil exerting a synergetic effect.

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