Bioresource Technology 141 (2013) 177–183

Contents lists available at SciVerse ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Feasibility of anaerobic digestion from bioethanol fermentation residue

Jeong-Hoon Park [a,b], Sang-Hyoun Kim [c], Hee-Deung Park [b], Dong Jung Lim [d], Jeong-Jun Yoon [a,*]

[a] Green Materials Technology Center, Korea Institute of Industrial Technology (KITECH), 35-3 Hongcheon-ri, Ipjang-myeon, Cheonan, Chungnam 330-825, Republic of Korea
[b] Department of Civil, Environmental and Architectural Engineering, Korea University, Anam-dong, Seongbuk-gu, Seoul 136-714, Republic of Korea
[c] Department of Environmental Engineering, Daegu University, Jillyang, Gyeongsan, Gyeongbuk 712-714, Republic of Korea
[d] Biolsystems Co. Ltd., Joong Pyung B/D 6F 64-1, Umyeon-dong, Seocho-gu, Seoul 137-900, Republic of Korea

HIGHLIGHTS

- Maximum CH_4 conversion rate of fermentation residue is 84.8% at 5 g COD/L of residue.
- Appropriate F/M ratio was significant on anaerobic digestion of fermentation residue.
- Inhibitory effects on anaerobic digestion can be overcome by increasing cell.
- Formic acid is strong inhibitor than levulinic acid on anaerobic digestion.

ARTICLE INFO

Article history:
Available online 16 March 2013

Keywords:
Red algae
Anaerobic digestion
Levulinic acid
Formic acid
Inhibition

ABSTRACT

The focus of this study was the reuse of red algal ethanol fermentation residue as feedstock for anaerobic digestion. Levulinic acid and formic acid, the dilute-acid hydrolysis byproducts, inhibited methanogenesis at concentrations over 3.0 and 0.5 g/L, respectively. However, the inhibition was overcome by increasing inoculum concentration. A series of batch experiments with the fermentation residue showed increased methane yield and productivity at higher inoculum concentration. The maximum methane conversion rate of 84.8% was found at 5 g COD/L of fermentation residue at 0.25 g COD/g VSS of food-to-microorganism (F/M) ratio. The red algal ethanol fermentation residue can possibly be used as a feedstock in anaerobic digestion at appropriate concentration and F/M ratio.

1. Introduction

Marine algal biomass has various advantages as a sustainable feedstock for bioenergy production (Kim et al., 2010). Marine algae grow faster and have greater carbon dioxide fixation ability than land plants (Lüning and Pang, 2003; Packer, 2009). Also, it can be cultivated easily without extra addition of nutrient or fertilizer such as nitrogen source (Buck and Buchholz, 2004). Furthermore, the lignin-free chemical structure would allow obtaining sugars without complex and expensive pretreatment such as lignin removal (Levin et al., 2004; Mosier et al., 2005).

More than 70% of red algal biomass, however, remains as fermentation residue in ethanol production (Park et al., 2012b). If the residue can be converted to methane by anaerobic digestion, ethanol could be supplied at lower prices. Furthermore, the net energy yield of ethanol fermentation would be enhanced. Already, numbers of research studies have investigated the feasibility of energy recovery from ethanol fermentation residue by anaerobic microbes. When used as feedstock for methane fermentation, the fermentation residue had a chemical oxygen demand (COD) of around 50 g COD/L (Hunter, 1988). In 1983–1985, Stover investigated the anaerobic digestion from 64 g COD/L of corn stillage with suspended-growth and fixed-film digester (Stover et al., 1983, 1984, 1985). In 2008, Schaefer used 100 g COD/L and 60 g VS/L of ethanol waste under thermophilic condition (Schaefer and Sung, 2008); however, most of these studies did not investigate in detail the effect of inhibition on anaerobic digestion. Inhibitory effect should be investigated because potential to decrease COD level can circumvent the expensive costs associated with directly processing water high in COD concentrations. Reducing COD levels will lower the cost of treatment; therefore, pretreatment via anaerobic digestion is a possible solution to achieve this reduction. Furthermore, this method will not only reduce cost but it can recover energy as well – further offsetting net treatment expenses.

This study investigated the feasibility of the red algal ethanol fermentation residue as a feedstock for anaerobic digestion. The effect of levulinic acid and formic acid as the potential inhibitors in the residue was examined. In addition, the residue was used as the feedstock for batch anaerobic digestion at various concentrations and food-to-microorganism (F/M) ratios.

* Corresponding author. Tel.: +82 41 589 8445; fax: +82 41 589 8580.
E-mail address: jjyoon@kitech.re.kr (J.-J. Yoon).

0960-8524/$ - see front matter Crown Copyright © 2013 Published by Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.biortech.2013.03.068

2. Methods

2.1. Inoculum sludge for anaerobic batch test

Granular sludge was taken from an anaerobic digester in a local brewery wastewater treatment plant. The pH, total suspended solids (TSS) and volatile suspended solids (VSS) concentration of sludge were 7.1, 52.6 and 49.2 g/L, respectively. Solids were analyzed by standard method from APHA (Eaton and Franson, 2005).

2.2. Red algal ethanol fermentation residue

Gelidium amansii obtained from a littoral area in Morocco was used as the feedstock for ethanol production. The *G. amansii* composition was as follows (%, dry base): cellulose (glucose) 14.9, galactose 23.1, 3,6 anhydrogalactose (3,6-AHG) 29.3, protein 15.6, ash 5.7 and others 11.4 (Park et al., 2011). The red algal biomass was washed using tap water to remove salt and milled to a size of <300 μm. Red algae powder was added with 1.0% (w/v) H_2SO_4 to a S/L ratio of 10% into a 30 L high-pressure reactor (depth; 50 cm, inner diameter; 28 cm). The slurry was pretreated at 150 °C and 2.5 ± 0.3 kg_f/cm^2 for 15 min and neutralized using $CaCO_3$ at a pH range of 6.0. Subsequently, the hydrolyzate was obtained by centrifuging at 3500 rpm for 10 min and used for the following ethanol fermentation (Park et al., 2012a). After the ethanol distillation process, fermentation residue was separated into liquid and yeast by centrifuging at 8000 rpm for 10 min to obtain the fermentation residue. The characteristics of the residue were as follows: COD, levulinic, and formic acid concentration were 74.0, 2.96, and 0.99 g/L, respectively.

2.3. Anaerobic batch test

Acetic acid (Acros, USA) and propionic acid (Acros, USA) of 3 g COD/L was used as the substrate of the feedstock in the inhibition study. The examined range of levulinic acid and formic acid were 0.5–5.0 g/L and 0.1–2.0 g/L, respectively. Two different levels of inoculum (4.5 and 20 g VSS/L) were tested. The equilibrium amounts of the substrate, the potential inhibitor, and the inoculum were added to a 160-mL serum bottle. The bottle was filled to 100 mL using distilled water, purged for 3 min with nitrogen gas, sealed, and then incubated at 35 ± 1 °C and 150 rpm.

Methane production from fermentation residue was performed in batches and each test had a working volume of 100 mL in a 160 mL serum bottle. The batch test was operated in an incubator in anaerobic conditions with the temperature maintained at 35 ± 1 °C and agitation at 150 rpm.

Sludge was filled up to 4.5 g/L. Subsequently, the serum bottle was purged for 3 min with nitrogen gas at 1 L/min to remove air. The effect of levulinic acid and formic acid on methane fermentation study was performed by using two different concentration (4.5 and 20 g/L) of granular sludge with a working volume of 300 mL in 500 mL medium bottles.

The initial acetic acid and propionic acid concentration was 3.0 g COD/L in all inhibitory batch tests using levulinic acid and formic acid. Other operation conditions such as temperature and rpm were the same as the conditions used in the previous fermentation.

2.4. Analysis

The methane contents in the biogas production was measured by gas chromatography (GC, Gow Mac series 580) using a thermal conductivity dectector (TCD) and a 1.8 m × 3.2 mm stainless-steel column packed with porapak Q (80/100 mesh) with helium as a carrier gas. The temperatures of the injector, detector, and column were kept at room temperature, 90 and 50 °C, respectively (Park et al., 2012b).

Methane correction was calculated as follows:

$$V_{CH_4}(\mathrm{STP}) = V_{CH_4}(\text{at } 35\ ^\circ\mathrm{C}) \times \frac{273}{(273+35)} \times \frac{(760-42.2)}{760} \quad (1)$$

where, 42.2: water vapor pressure at 35 °C (mmHg).

Levulinic acid, and formic acid were analyzed by high performance liquid chromatography (HPLC, YL9100 series, Korea) using a refractive index (RI) detector, an ultraviolet (UV) detector (210 nm), and a 300 mm × 7.8 mm Aminex HPX-87H (Bio-Rad, USA) ion exclusion column with H_2SO_4 of 5 mM as the mobile phase. The liquid samples were pretreated with a 0.45 μm membrane filter before injection to HPLC. The chemical oxygen demand (COD) and VS were measured according to Standard Methods (Eaton and Franson, 2005).

2.5. Assay

The methane production curve was fitted to a modified Gompertz equation (Lay et al., 1999) (2), which provides a suitable model for describing the methane production in batch tests:

$$M = P \times \exp\left[-\exp\left\{\frac{R_m}{P} \times (\lambda - t) \times e\right\} + 1\right] \quad (2)$$

where M is the cumulative methane production (mL), P is the methane production potential (mL), R_m is the maximum methane production rate (mL/day), λ is the lag-phage time (day), t is time (day) and e is the exponential 1.

3. Results and discussion

3.1. Effect of levulinic acid and formic acid on methane fermentation

The main components of fermentation residue were protein and inhibitory substrates (Fujishima et al., 2000; Park et al., 2011). Sugar was among the initial substrates, but it was completely fermented into ethanol. The chemical composition of *G. amansii* was analyzed in Section 2.2. Fermentation residue at high concentrations was shown to be a more efficient feedstock than at low concentrations for anaerobic digestion in the view of energy balance (Fujishima et al., 2000; Van Velsen, 1979). However, increase of the concentration of fermentable residue raised the concentrations of potential inhibitors. During the dilute-acid hydrolysis with high pressure and temperature, sugar is converted to 5-HMF, which is further degraded to levulinic acid and formic acid (Larsson et al., 1999). The inhibitory effect of the byproducts should be investigated to guarantee efficient and robust anaerobic digestion (Hashimoto, 1986; Koster and Lettinga, 1984, 1988). In a previous study, the effect of 5-HMF was investigated (Park et al., 2012b). The result of the study showed that concentrations of 5-HMF less than 5 g/L resulted in methane production by anaerobic digestion; however, concentrations above 5 g/L yielded no methane production. In these conditions, 5-HMF was generally removed by physicochemical method such as activated carbon adsorption (Chandel et al., 2011). On the other hand, levulinic acid and formic acid were not easily removed by physical methods; even though, these inhibitors are produced at a relatively lower concentrations than 5-HMF. For example, a previous study showed that fermentation residue were found to have concentrations of levulinic acid and formic acid below 2.0 and 0.5 g/L, respectively. However, these inhibitors could not be easily removed by physical method. Therefore, biological method should be investigated to overcome inhibitory substrates such as levulinic acid and formic acid. All batch experiments in this manuscript were conducted in duplicate. As a result, experimental