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# Value-adding conversion and volume reduction of sewage sludge by anaerobic co-digestion with crude glycerol

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## HIGHLIGHTS

- Anaerobic co-digestion of sewage sludge and a crude glycerol was evaluated.
- Co-digestion yielded methane, hydrogen, and 1,3-PDO as value-added products.
- Increasing glycerol levels significantly increased hydrogen and 1,3-PDO production.
- By adjusting glycerol content, hydrogen and methane fermentation was controlled.
- Addition of crude glycerol promoted the solubilization of sewage sludge.

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## ABSTRACT

In this study, conversion of sewage sludge to biogas by anaerobic co-digestion with crude glycerol was examined. When 0.126 g/L crude glycerol was added to the reactor, only methane was produced. Upon addition of 5.04 g/L crude glycerol, hydrogen production occurred, and a significant amount of 1,3-propanediol (1,3-PDO) was generated in the liquid phase. On day 6, the dry weight was largely composed of organic acids (48%) and 1,3-PDO (17%), which are water-soluble. Degradation of 1,3-PDO was very slow, which is advantageous for recovery. Crude glycerol, which contains alkaline substances, promoted organic matter degradation by microorganisms, which possibly affected biogas and 1,3-PDO production. Addition of 0.630–2.52 g/L glycerol initially led to hydrogen production, followed by methane production a few days later, which stabilized within 1 week. In conclusion, adjustment of the crude glycerol concentration allows controllable conversion to value-added products for co-digestion.



## 1. Introduction

Sewage sludge production has increased worldwide with the expansion of the sewerage network and installation of new wastewater treatment plants. The sludge must be treated before it can be safely disposed into the environment. The cost of sewage sludge treatment and disposal is estimated to account for half of the total cost of wastewater treatment (Davis and Hall, 1997). Therefore, minimizing the negative impact of sewage sludge on the environment is desirable, but remains a major challenge.

Anaerobic digestion is an appropriate technique for reducing the volume and weight of excess sludge before final disposal, and it is employed worldwide as the oldest and most important process for sludge stabilization. Additionally, anaerobic digestion can partly recover bioenergy from the sludge through methane production (Parkin and Owen, 1986). However, conventional anaerobic digestion is rather inefficient because of low organic content (volatile-to-total solids ratio, VS/TS) in a combined sewer system. Co-digestion with waste containing a high organic content, such as food waste, could be a reliable option to enhance the activity of anaerobic microorganisms. A proper mixture provides complementary and synergistic effects that offset the lack of carbon sources in sewage sludge and dilute harmful or excessive substances that inhibit that activity of anaerobes in food waste (Kim et al., 2007).

Crude glycerol is the major by-product of biodiesel fuel (BDF) production. With increasing concerns about global warming, the production of crude glycerol is expected to expand with increasing BDF usage. In general, crude glycerol is generated from the transesterification of vegetable oils, using alkaline catalysts, and contains multiple impurities such as alcohols, fatty acids, esters, alkalis in the form of alkali soaps and hydroxides, and heavy metals (Rivero et al., 2014). Owing to these impurities, costly and

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energy-intensive purification steps such as distillation and extraction (Chi et al., 2007; Rehman et al., 2008) are usually required before the crude glycerol can be used in downstream food, cosmetic, and medical industries. Therefore, much attention has been focused on disposal of the surplus crude glycerol from BDF production.

Anaerobic co-digestion is an attractive method for the disposal of crude glycerol because of the concurrent conversion of the glycerol to bioenergy and useful materials and the volume reduction of inoculum. Several studies have reported co-digestion of crude glycerol and sewage sludge (Athanasoulia et al., 2014; Rivero et al., 2014), cattle manure (Robra et al., 2010; Baba et al., 2013; Castrillon et al., 2013), pig manure (Amon et al., 2006; Astals et al., 2012), and organic fractions of municipal solid wastes (Fountoulakis and Manios, 2009). It has been reported that co-digestion of sewage sludge and crude glycerol boosts methane production (Fountoulakis et al., 2010; Nartker et al., 2014; Silvestre et al., 2015).

Anaerobes can biotransform glycerol into hydrogen and 1,3-prodanediol (1,3-PDO), which is a hydrogen precursor (Barbirato et al., 1996; Biebl et al., 1998; Chatzifragkou et al., 2010; da Silva et al., 2009; Zeng and Biebl, 2002). Hydrogen is a promising alternative to fossil fuels because it has a high energy yield (122 kJ/g) and produces water rather than greenhouse gases when combusted. In addition, 1,3-PDO has important applications; it can be used as a solvent, monomers for cyclic compounds, and monomers for condensation to produce plastics. Most studies on fermentation methods have focused on the use of pure microbial cultures because of higher yields than those with mixed cultures (Johnson and Rehmann, 2016; Vivek et al., 2016). In these studies, bacterial strains in the genera *Citrobacter, Enterobacter, Ilyobacter, Klebsiella, Lactobacillus, Pelobacter*, and *Clostridium* were used (Pagliaro et al., 2007). However, methods using pure bacterial strains involve expensive equipment and complicated protocols. In contrast, methods involving mixed cultures are easy to implement and incur lower costs and fewer contamination problems. Therefore, several approaches exist to improve the productivity of mixed-culture methods (Gallardo et al., 2014). In a previous study, we investigated the co-digestion of sludge and pure glycerol and found that the addition of a fermentation promoter induced the conversion of glycerol to hydrogen and 1,3-PDO (Tokumoto and Tanaka, 2012).

The aims of the current study were to: (1) assess the potential of bioconversion by co-digestion of sewage sludge and crude glycerol, especially with regard to value-added products such as hydrogen and 1,3-PDO, (2) evaluate the volume of crude glycerol in co-digestion required for practical residence time, and (3) estimate the mechanism of co-digestion, based on the change in total solids composition after the process.

## 2. Materials and methods

### 2.1. Seed sludge

The sewage sludge inoculum used in this study was sampled from waste-activated sludge in the Senboku sewage disposal plant (Sakai, Japan). The water content of the sewage sludge was 99.5% and the sewage sludge contained 4.57 g/L volatile solids. The inoculum was collected on the same day the anaerobic experiment was started to prevent decay, which occurs within a few days. The sludge was dewatered by centrifugation to a water content of 95.0%, 97.5%, and 99.5%.

### 2.2. Carbon sources

Crude glycerol was derived from BDF by transesterification of waste cooking oil obtained from the cafeteria at our university. The characteristics of the crude glycerol are shown in Table 1. The total organic carbon (TOC) content of the sewage sludge was measured with a TOC analyzer (TNM-1; Shimadzu, Kyoto, Japan).

### 2.3. Glycerol digestion in sewage sludge under anaerobic conditions

All fermentation experiments were conducted in auto-sampler vials (20-CV; PerkinElmer, Waltham, MA, USA) with butyl rubber and aluminum seals at 37 °C. Glass vials with a capacity of 21.6 mL were filled with a mixture of 4 mL of sewage sludge with various water contents and 1 mL of crude glycerol. Crude glycerol concentrations in the final reactor were adjusted to 0.126, 0.630, 1.26, 2.52, 5.04, and 7.57 g/L by dilution in water. The head spaces of the vials were purged with 100% nitrogen under 1.2 atm. In total, 13 vials were prepared for each glycerol treatment. Total solids (TS) were determined as a sum of the dry weight of sewage sludge and the initial crude glycerol weight. The dry weight was measured after drying for 1 day in an oven at 105 °C.

### 2.4. Gas-phase production

During the fermentation reaction, 0.5-mL samples of gas in the headspaces of the vials were removed, using a 2.5-mL gas-tight syringe (Ito Co., Shizuoka, Japan). Gas samples were removed daily for the first 7 days and every other day thereafter, for a total of 14 days. The gas composition ($H_2$, $N_2$, $CH_4$, and $CO_2$) was analyzed by gas chromatography (GC-8APT; Shimadzu, Kyoto, Japan), using a stainless steel 80/100 mesh Porapak Q column (3 m × 3.0 mm; GL Sciences, Tokyo, Japan) and a thermal conductivity detector. Argon was used as the carrier gas at a rate of 20 mL/min. The injector, oven, and detector temperatures were 100 °C, 70 °C, and 100 °C, respectively. An 80% $N_2$/20% $CO_2$ gas mixture, $H_2$ gas, and $CH_4$ gas were used as the standard gases. We measured three independent samples for each condition.

### 2.5. Liquid-phase production

Liquid-phase products were sampled every day for the first 5 days and every other day thereafter, for a total of 20 days. The concentration of organic acids was determined by high-performance liquid chromatography (HPLC), using a Shimadzu LC-10AD VP pump equipped with two ion-exclusion chromatography columns (Shim-pack SCR-102H; 8 × 300 mm; Shimadzu), with post-column pH-buffered conductivity detection (CDD-6A; Shimadzu). The mobile phase consisted of 5 mM *p*-toluenesulfonic acid (PTSA) solution at a flow rate of 0.8 mL/min. Mixtures of 5 mM PTSA and 100 mM ethylenediaminetetraacetic acid were used as post-column reagents, both at flow rates of 0.8 mL/min. The column temperature was maintained at 40 °C. The total organic acid content was determined as the sum of the concentrations of maleic acid, citric acid, malic acid, succinic acid, glycolic acid, lactic acid, formic acid, acetic acid, levulinic acid, pyroglutamic acid, propionic acid, butyric acid, *iso*-butyric acid, valeric acid, and *iso*-valeric acid.

**Table 1**
Characteristics of crude glycerol.

| Parameter | Value |
|---|---|
| pH (–) | 12.6 |
| Glycerol (wt%) | 45.0 |
| Methanol (wt%) | N/D |
| TOC (g/L) | 482.4 |
| Total solids (wt%) | 4.26 ± 0.06 |
| Water content (wt%) | 95.7 ± 0.06 |