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High-calorific bio-hydrogen production under self-generated high-pressure condition

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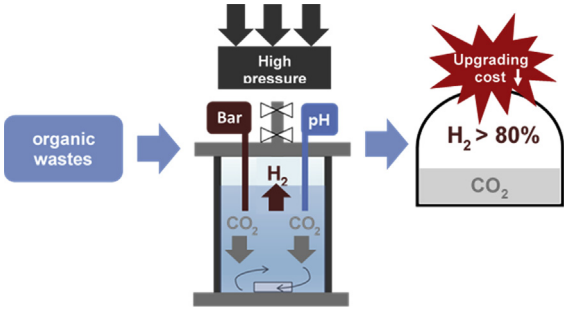
GRAPHICAL ABSTRACT



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ABSTRACT

For the use of biologically produced H_2, removal of CO_2 is an indispensable process. Unlike conventional CO_2 removal methods, this study proposed a self-generated high-pressure dark fermentation (HPDF) process as a novel strategy for directly producing high-calorific bio-H_2. The pressure was automatically increased by self-generated gas, while the maximum pressure inside fermenter was restricted to 1, 3, 5, 7, and 10 bar in a batch operation. As the pressure increased from 1 to 10 bar, the H_2 content increased from 55% to 80%, whereas the H_2 yield decreased from 1.5 to 0.9 mol H_2/mol hexose$_{added}$. The highest H_2 content of 80% was obtained at both of 7 and 10 bars. Increased lactate production with increased abundance of lactic acid bacteria was observed at high-pressure. Despite the lower H_2 yields at high-pressure conditions, HPDF was found to be economically beneficial for obtaining high-calorific bio-H_2 owing to the low CO_2 removal cost.

1. Introduction

Global warming caused by the excessive use of fossil fuels and the consequent greenhouse gas emissions is a critical global issue. To solve this problem, many researchers are paying attention to the development of clean alternative fuels (Scarlat et al., 2015). Hydrogen (H_2) is widely considered as a promising alternative to fossil fuels since it produces only water when combusted and has high energy density by mass (142 kJ/g) (Mazloomi and Gomes 2012). Currently, H_2 is exclusively made by gas reforming of hydrocarbons, and coal gasification, which require intensive energy (Kim et al., 2009). However, H_2 must be made from renewable resources under low energy requirement condition to reduce greenhouse gas level. Biological processes for H_2 production proceed under ambient temperature and pressure condition

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and are environmentally friendly approach with regards to carbon–-neutral characteristics (Ghimire et al., 2015; Kumar et al., 2017).

The biological H_2 production can be achieved by photo fermentation involving photosynthetic bacteria such as *Rhodobacter* sp. or dark fermentation with anaerobic bacteria such as *Clostridium* sp. and *Enterobacter* sp. (Budiman and Wu, 2018; Sivagurunathan et al., 2016b). Dark fermentative H_2 production using organic compounds (especially carbohydrates) has been considered a more economically-practical way because of its higher H_2 production rate and possible use of organic wastes (Ghimire et al., 2015; Sivagurunathan et al., 2016a). The major gaseous components in the produced biogas are H_2 and CO_2, and a trace amount of hydrogen sulfide (H_2S). The H_2 content usually falls in the range of 35 to 65%, depending on the substrate, reactor operational condition, and so on (Lin et al., 2012). Due to the presence of high CO_2 content in the bio-H_2 fermenter, the applications of biologically produced H_2 are often limited due to the low calorific value. For further application of bio-H_2 to fuel cells or electricity generation, the concentration of CO_2 needs to be reduced greatly (1–3%) (Petersson and Wellinger, 2009; Ryckebosch et al., 2011).

Recently, several attempts were made to directly produce high-calorific biogas (90% > CH_4) in a single anaerobic digester. This process is called in-situ biogas upgrading and considered to be economically advantageous compared to the conventional ex-situ biogas upgrading (Lecker et al., 2017). The main mechanisms applied here can be largely split into two: (1) supply of H_2 for CO_2 removal by hydrogenotrophic methanogenic reaction ($4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$), and (2) operation under high-pressure condition by self-generated biogas. In the latter method, due to the huge difference in the solubility between CO_2 and CH_4, high-calorific biogas containing 80–96% of CH_4 was attained (Lindeboom et al., 2011).

In bio-H_2 upgrading, physical and chemical processes have been applied (Bakonyi et al., 2013). For instance, Lin et al. (2007) used a physicochemical method (CO_2 absorber and a silica-gel desiccator) for removing CO_2 and obtained a high purity (99%) bio-H_2, from the biologically produced continuous H_2 fermenter. In another report, Bakonyi et al. (2015) investigated the simultaneous bio-H_2 production and upgrading in a membrane bioreactor system. The authors demonstrated that after upgrading, the H_2 content increased from 51 to 67%, whose content is far lower to the practical use. Instead of applying these conventional methods, there is a possibility of producing high-calorific bio-H_2 from single fermenter which is operated under high-pressure condition by self-generated bio-H_2. At the same temperature and pressure condition, the solubility of CO_2 is 31 times higher than that of H_2. Up to author's knowledge, the feasibility of high-pressure dark fermentation (HPDF) process has never been tested.

In this study, we operated batch mesophilic (37 ± 1 °C) HPDF system in which the maximum pressure allowed inside fermenter ranged from 1 to 10 bar. Gaseous products such as H_2 and CO_2, and pH were monitored during fermentation. The reasons for different H_2 yields obtained at different pressure conditions were elucidated by analyzing organic acids profile with thermodynamic calculation and microbial community change. In addition, a simple economic assessment was made to state the practical feasibility of HPDF.

2. Materials and methods

2.1. Inoculum and feedstock preparation

The inoculum for H_2 production was taken from an anaerobic digester in a local wastewater treatment plant in Korea. The pH, alkalinity, and volatile suspended solids (VSS) concentrations of the inoculum were 7.6, 2.4 g $CaCO_3$/L, and 26.2 g/L, respectively. The inoculum was shredded by a grinder to make a particle size smaller than 2.0 mm in diameter and was heat-treated at 90 °C for 30 min to inactive H_2-consuming methanogenic activity. Then, the certain amounot of inoculum was added to the fermenter at a final concentration of 10 g VSS/L. As a substrate, glucose was added to reach the chemical oxygen demand (COD) concentration at 6.0 g/L. To provide trace element, followings were added at (in mg L^{-1}): Na_2MoO_4 $4H_2O$, 5; H_3BO_3, 50, $MnCl_2$ $4H_2O$, 50; $ZnCl_2$, 50; $CuCl_2$, 30; $NiCl_2$ $6H_2O$, 92; $CoCl_2$ $6H_2O$, 50; Na_2SeO_3, 50 (Angelidaki and Sanders, 2004).

2.2. Experiment

Batch experiments were carried out using a stainless-steel fermenter equipped with a pH sensor and a pressure sensor. The effective volume of the fermenter was 700 mL with a total volume of 750 mL (diameter of 8 cm). The thickness of fermenter was 20 mm to withstand the pressure up to 15 bar. When the pressure reached the desired level (1, 3, 5, 7, and 10 bar) by self-generated bio-H_2, the gas was released to the gas holder by a controlled pressure regulator (Back pressure regulator, TESCOM, Supplementary information). Prior to fermentation, the pH was adjusted to 8.0 ± 0.1 by 10 N KOH solution, and the broth was purged with N_2 gas for 20 min to provide anaerobic condition. During the fermentation, pH was not controlled. The fermenters were agitated at 100 rpm using a magnetic stirrer and temperature was maintained at 37 ± 1 °C using water jacket. The produced gas, pH, and pressure data were monitored at 1–2 h intervals. The tests were carried out in duplicate and the results were averaged.

2.3. Analysis

Concentrations of VSS, COD, and alkalinity were measured according to Standard Methods (APHA, 2005). The amount of produced H_2 was calculated by summing the H_2 in the headspace of fermenter and gas holder, and adjusted to the standard condition of temperature (0°C) and pressure (1.0 bar) (STP). The H_2 and CO_2 contents in the bio-H_2 was analyzed by a gas chromatograph (GC, Gow Mac series 580) equipped with a thermal conductivity detector (TCD) and a 1.8 m × 3.2 mm (I.D.) stainless-steel column packed with a 5A molecular sieve with N_2 (99.999%) as a carrier gas. To determine the CO_2 concentration in the biogas, a GC (Gow Mac series 580) equipped with a TCD and a 6 ft × 1/8 in. (I.D.) stainless steel column packed with Porapak Q (80/100 mesh) was utilized. The temperatures of injector, detector, and column were kept at 50, 90, and 80 °C, respectively, in both GCs. Organic acids were analyzed by a high performance liquid chromatograph (HPLC) (LC-20A, Shimadzu Co, Japan) with an ultraviolet (216 nm) detector and a 100 mm × 7.8 mm Aminex HPX-87H column (Bio-Rad Lab. USA) using 0.01 M H_2SO_4 as a mobile phase. The liquid samples were pretreated with a 0.2 μm membrane filter before injection into HPLC.

2.4. Microbial community analysis

The samples (1 and 7 bar) for the bacterial community analysis were collected after the end of the fermentation. Deoxyribonucleic acid (DNA) was extracted using an Ultraclean Soil DNA Kit (Cat #12800–50; Mo Bio Laboratories, lnc., USA) and purified with an UltraClean Microbial DNA Isolation Kit (Mo Bio Laboratories, CA, USA). The preparation of libraries and PCR were performed as described elsewhere (Moon et al., 2015). The 16S universal primers 27F (5′GAGTTTGATC MTGGCTCAG3′) and 800R (5′TACCAGGGTATCTAATCC3′) were used for amplifying the 16 s rRNA genes. After the PCR products were purified and quantified, sequencing was performed using a 454 pyrosequencing Genome Sequencer FLX Titanium (Life Sciences, CT, USA), according to the manufacturer's instructions, by a commercial sequencing facility (Macrogen, Seoul, South Korea). Identification of operational taxonomic units (OTU), taxonomic assignment, community comparison, and statistical analysis were obtained by using the software MOTHUR with the sequences generated from pyrosequencing. To minimize the effects of poor sequence quality and sequencing errors, sequences were filtered and removed in part according to the previous