Research Article

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Biological conversion of CO_2 to CH_4 using hydrogenotrophic methanogen in a fixed bed reactor

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Abstract

BACKGROUND: Biological conversion of CO_2 to useful carbonic compounds such as methane is a potentially attractive technology for reducing its concentration in the atmosphere. One of the advantages of this technology over chemical conversion is that it requires much lower energy for reduction of CO_2. In this article, biological conversion of CO_2 to CH_4 using hydrogenotrophic methanogens was examined in a fixed bed reactor inoculated with anaerobic mixed culture from the anaerobic digestor of a sewage treatment plant.

RESULTS: Methane formation commenced on the first day of operation of the fixed bed reactor. CO_2 fed to the reactor was reduced with H_2 by hydrogenotrophic methanogens. The feed ratio of CO_2 to H_2 is an important factor in determining the conversion rate of CO_2. When the feed ratio is 4, methane is produced at the expected rate according to the chemical equation. The CO_2 conversion rate was 100% when the gas retention time was 3.8 h in the fixed bed reactor.

CONCLUSIONS: The results show that the fixed bed reactor employing hydrogentrophic methanogens has the potential to be effective in converting CO_2 to CH_4 with a conversion rate of 100% at 3.8 h retention time.

Keywords: hydrogenotrophic methanogens; CO_2 conversion; methane; fixed bed reactor

INTRODUCTION

The conversion of CO_2 to a useful carbonic compound may contribute to CO_2 reduction in the atmosphere. However CO_2 is a thermodynamically stable compound and its reduction requires high energy and electroreductive processes.[1] Various CO_2 reduction methods using chemical and biological reactions have been proposed and investigated, for example catalytic hydrogenation, electrolytic reduction and photosynthesis by algae.[1–6] The potential of catalysts for CO_2 conversion has been discussed in recent reviews.[1] In the presence of noble metals such as Rh, Ru, and Pd CO_2 can be reduced with reducing agents including hydrogen or electron-rich chemicals. However, the inert property of CO_2, together with lower reactivity in various reactions, needs energy-intensive operating conditions including high temperature (300–600 °C) and high pressure (higher than 10 atm).[1]

Biological conversion of CO_2 requires only mild operation conditions. Biological fixation using the photosynthetic function of microalgae *Chlorella* and *Synechocystis* sp. can save energy compared with catalytic conversion requiring energy-intensive reaction conditions.[2,6] The reaction conditions for photosynthetic fixation are mild requiring about 30 °C and 1 atm. However light has to be provided for photosynthetic reaction, making reactor design difficult. And most important, the microalgae system requires land, water, and climate resources that are seldom found near CO_2 generating plant.

Instead of using the photosynthetic function of microalgae, methanogens which are known to have the capability to utilize CO_2 as electron acceptor are proposed in this study. Methanogens have been classified as methylotrophic, acetoclastic, and hydrogentrophic.[7] Methylotrophic methanogens are known to use methyl compounds such as dimethyl sulfide, trihalomethanes, chloromethanes, etc. Acetoclastic methanogens produce methane from acetate that is a major intermediate produced from anaerobic digestion of organic matter. Meanwhile, hydrogenotrophic methanogens can produce methane from a hydrogen–carbon dioxide mixture without other organic carbon sources.

Only little attention has been given to the development of an effective process using hydrogenotrophic methanogens.[7,9,10] Hydrogenotrophic methanogens are known to use CO_2 as an electron acceptor and H_2 as an electron donor. Conventional studies of methanogens have tended to concentrate on their habitat, as all methanogens are strict anaerobes.[8] A recent study reported that hydrogenotrophic methanogens were able to be enriched in an electrochemical bioreactor.[7] In this study, hydrogenotrophic methanogens were enriched in a fixed bed

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reactor by feeding a gas mixture of carbon dioxide and hydrogen. The biological conversion reaction can be described by the following equation. According to the stoichiometry, 4 mol of H_2 is needed to reduce 1 mol of CO_2.

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2\,H_2O$$

This study examines the biological conversion of CO_2 into CH_4 by hydrogenotrophic methanogens enriched in a fixed bed reactor. A fixed bed reactor was designed and operated continuously by feeding gas mixture of carbon dioxide and hydrogen in the laboratory. According to the chemical equation, the mole ratio of H_2 to CO_2 of feeding gas is important in determining the conversion rate of CO_2 and the production rate of CH_4. Thus it was varied from 1 to 8. In order to obtain engineering data for reactor design, the gas retention time in the fixed bed reactor was changed by varying the flow rate of gas mixture of CO_2 and H_2.

MATERIALS AND METHODS

Continuous operation of anaerobic fixed bed reactor

The experimental system is given in Fig. 1. It is composed of an up-flow anaerobic fixed bed reactor (7.8 L working volume) and gas cylinder (CO_2 and H_2). Internal diameter and height of the fixed reactor are 10 cm and 100 cm, respectively. The fixed bed reactor was packed with reticulated polyester urethane sponge (10 pores per inch). The sponge has density 28–30 kg m^{-3}. Anaerobic bacteria consortium obtained from an anaerobic digestor of Jungrang sewage treatment plant located in Seoul, Korea was used to inoculate the fixed bed reactor. 6.0 L of the anaerobic bacteria consortium (11 600 mg L^{-1} of volatile suspended solids) was transferred anaerobically to the reactor packed with 1.8 L of reticulated polyester urethane sponge. The sponge acted as a support for biofilm growth and to let gas bubbles stay longer in the reactor. The headspace of the reactor was filled with oxygen-free nitrogen at the initial operation time and then spontaneously replaced with the gas products generated from the mixed culture during the operation. Temperature of the reactor was maintained at 35 °C in a constant temperature chamber. A mixture of CO_2 and H_2 was provided to the bottom of the reactor through a gas sparger. Mole ratio of H_2 to CO_2 in the inlet gas line to the reactor was varied from 1 to 8 by changing the flow rate of H_2. Gas retention time was changed by varying the gas flow rate of gas mixture to find the optimum operating conditions and collect the data for reactor design including the volumetric CO_2 conversion rate and the volumetric methane production rate. At the beginning of reactor operation, acetate was added to the reactor to be 200 mg L^{-1} to check if methylotrophic and acetoclastic methanogens were active under the condition.

Analysis

250 µL of gas samples were taken from inlet and outlet of the reactor to analyze CO_2, H_2 and CH_4 and injected into gas chromatography (GC 6000 series, Younglin, Korea) equipped with TCD (thermal conductivity detector). Argon was used as the carrier gas at a flow rate of 30 mL min^{-1}. Gas chromatography was optimized for analytes and the following parameters were used: oven temperature 35–210 °C (20 °C min^{-1}), injection temperature 220 °C, detector temperature 220 °C). 1 µL of liquid samples was taken from the reactor to analyze acetate and injected into the gas chromatograph (GC 6000 series, Younglin, Korea) equipped with FID (Flame Ionization Detector). Helium was used as the carrier gas at a flow rate of 1 mL min^{-1}. Gas chromatography was optimized for analytes and the following parameters were used: oven temperature 45–220 °C (8 °C min^{-1}), injection temperature 220 °C, detector temperature 240 °C).

RESULTS AND DISCUSSIONS

Conversion of CO_2 to CH_4 by hydrogenotrophic methanogens

Methane formation commenced on the first day of reactor operation as shown in Fig. 2. As soon as the gas mixture of CO_2 and H_2 was provided to the bottom of the reactor, the mixed culture inoculated into the fixed bed reactor started reducing CO_2 with H_2 and producing CH_4. Due to the biological conversion, the volume percentage of H_2 and CO_2 in the outlet gas of the fixed bed reactor decreased and the volume percentage of CH_4 increased. However, the concentration of acetate was not changed in the reactor medium. In the anaerobic reaction,

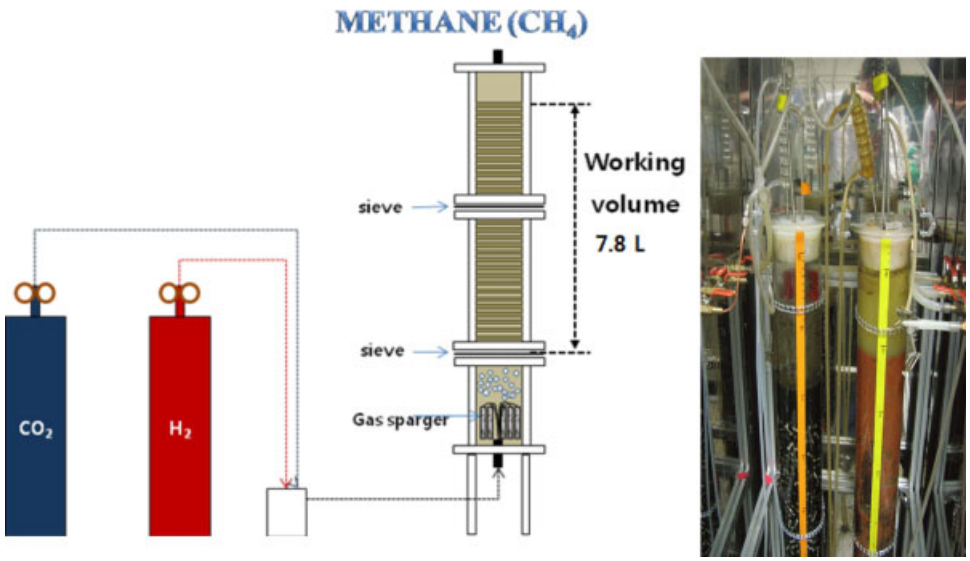

Figure 1. Experimental set-up for biological conversion of CO_2 to CH_4.

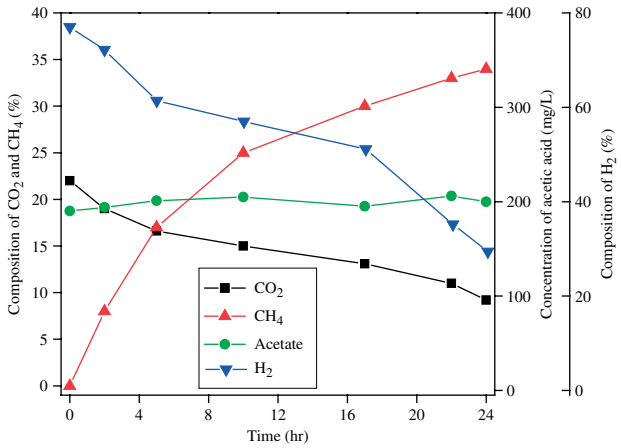

Figure 2. Monitoring of CO_2, H_2, CH_4 concentration in the outlet of the fixed bed reactor fed with a gas mixture of H_2 and CO_2 at 2 : 1 and acetate concentration in reactor operated with a gas retention time of 5.5 h.

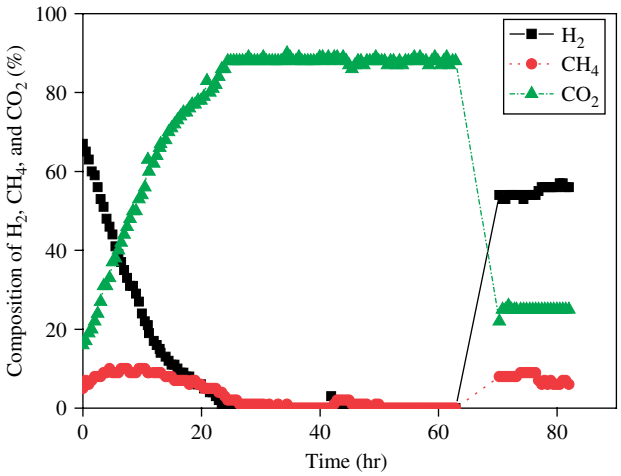

Figure 3. Change in composition of CO_2, H_2, and CH_4 after H_2 feed was stopped during operation of reactor with a gas retention time of 2 h.

acetate can be cleaved to form methane and carbon dioxide by methyltrophic methanogens and carbon dioxide from the carboxyl group by acetoclastic methanogens.[12] If acetate is not consumed, methylotrophic and acetoclastic methanogens are not active under the condition. The condition developed in the fixed bed reactor may make hydrogenotrophic methanogens dominant in the microbial community. Under high partial pressure of hydrogen anaerobic mixed culture may change the structure of methanogenic community. Leybo *et al*. used terminal restriction fragment length polymorphism (T-RFLP) analysis of 16S rRNA genes to monitor the changes in the composition of the population of methanogens in enrichment cultures under high and low hydrogen concentrations.[10] Hydrogen concentration was shown to determine the structure of a methanogenic community. High hydrogen concentration probably favors the hydrogen utilizing representatives of *Methanosarcinaceae,* while a more diverse methanogenic community is favored by low hydrogen concentrations. The high hydrogen concentration environment developed in the fixed bed reactor operated in this study may lead to the dominant role of hydrogenotrophic methanogens in anaerobic mixed consortium.

In order to confirm that hydrogen is used as the only electron donor, feeding of hydrogen to the reactor was stopped for 40 h as shown in Fig. 3. Without hydrogen, CO_2 could not be reduced by hydrogenotrophic methanogens or other anaerobic mixed populations. After the feeding of hydrogen was stopped, the volume percentage of CO_2 increased in the outlet gas from the reactor. Methane production was subsequently stopped as CO_2 was not biologically reduced. This indicates that hydrogen is the only electron donor and CO_2 conversion is done by hydrogenotrophic methanogens. When the feeding of hydrogen was resumed, the volume percentage of CO_2 in the outlet gas started to decrease due to reduction reaction with hydrogen.

Effect of ratio of CO_2 to H_2 in feed gas on the conversion rate of CO_2

Considering the stoichiometry, 1 mol of CO_2 needs 4 mol of H_2 to produce 1 mol of CH_4. To find the optimum ratio of H_2 to CO_2 in the feed gas, it was varied from 1 to 8 by changing the flow rate of H_2. Flow rate of CO_2 was maintained at 8 mL min^{-1}. In Fig. 4, as the flow rate of H_2 increased to 40 mL min^{-1} (the corresponding ratio of H_2 to CO_2 is 5), methane production was increased. When H_2 flow rate was 4 times that of CO_2, methane was produced at about 8 mL min^{-1}. This indicates that methane is produced from CO_2 and H_2 according to the stoichiometry of the chemical equation. When the ratio increased to 5, methane production rate increased further. Methane production was observed to be higher than the quantity of CO_2 applied (8 mL min^{-1}). The reason for this may be that hydrogenotrophic methanogens utilized excess hydrogen with the residual CO_2. The residual CO_2 remained during feeding of insufficient hydrogen. The solubility of hydrogen in water is limited. To maximize methane production and minimize use of hydrogen, the ratio of H_2 to CO_2 can be maintained at 4.

After H_2 feed rate was increased to 7 times that of CO_2 feed rate, methane production rate started to decrease. When the ratio of H_2 to CO_2 increased further to 8, methane production rate decreased to less than 2 mL min^{-1}. It seems that high partial pressure and concentration of H_2 developed in the fixed bed reactor inhibited the activity of hydrogenotrophic methanogens. The hydrogen partial pressure is known to be an important parameter, which defines process stability or upsets in the anaerobic process.[12] In their review,[11] the activity of the hydrogenotrophic methanogens is crucial for a stable and efficient process performance. In contrast, their role and activity in the anaerobic process has not been discussed and relatively little literature about this topic exists. The results obtained from this study indicate that high partial pressure of hydrogen may suppress the activity of hydrogenotrophic methanogens.

CO_2 conversion efficiency in the fixed bed reactor using hydrogenotrophic methanogen

To find the CO_2 conversion efficiency in the fixed bed reactor with respect to the engineering parameters, the gas retention time was varied by changing the flow rate of gas mixture of CO_2 and H_2 at the ratio of 4. As shown in Table 1, when the retention time of the mixed gas in the fixed bed was 3.8 h or longer, CO_2 conversion rate was 100%. Due to an increase in volumetric gas loading rate, the volumetric CO_2 conversion rate was increased from 0.884 to 1.434 m^3 m^{-3} day^{-1} as the gas retention time was decreased from 6.5 to 3.8 h. Methane was produced according to the stoichiometry and its volumetric production rate was close to the volumetric CO_2 conversion rate. However, when retention

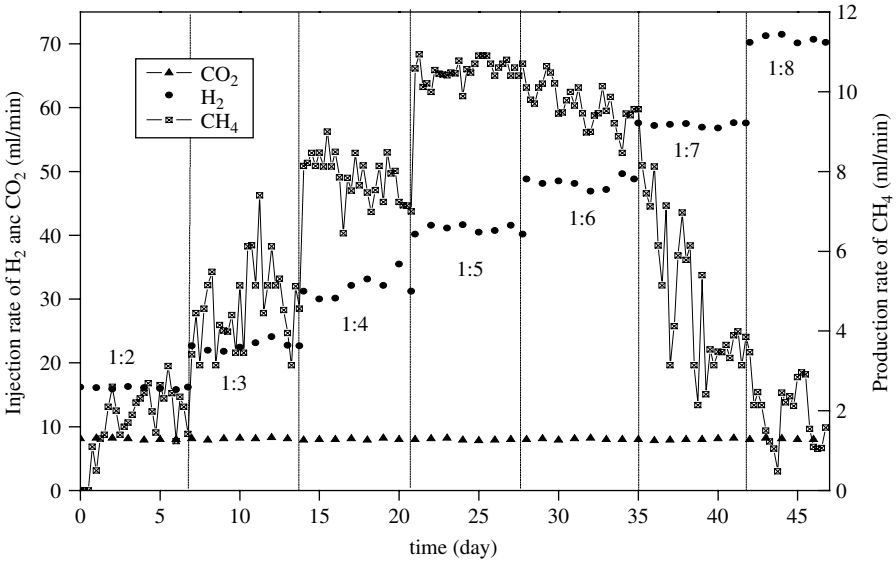

Figure 4. Continuous operation of the fixed bed reactor by feeding a gas mixture of H_2 and CO_2 with mixing ratios of 2 to 8 (gas retention time was also varied from 1.8 to 5.5 h depending on total flow rate of H_2 and CO_2).

Table 1. Biological CO_2 conversion efficiency using hydrogenotrophic methanogen in the fixed bed reactor fed with a gas mixture of H_2 and CO_2 at the ratio of 4

Gas retention time (h)	CO_2 conversion rate (%)	Volumetric CO_2 conversion rate ($m^3\ m^{-3}\ day^{-1}$)	Volumetric CH_4 production rate ($m^3\ m^{-3}\ day^{-1}$)
6.5	100	0.884 ± 0.05	1.047 ± 0.03
3.8	100	1.434 ± 0.028	1.337 ± 0.12
2.0	71	1.688 ± 0.05	1.789 ± 0.20
1.5	68	2.434 ± 0.21	3.225 ± 0.20

time was decreased from 3.8 to 2.0 h, CO_2 conversion rate was reduced to 71%. Methane production also occurred according to the stoichiometry even though the gas retention time was reduced from 3.8 to 2.0 h. When the gas retention time was decreased further from 2 to 1.5 h, methane production did not occur according to the stoichiometry. At the gas retention time of 1.5 h, the volumetric CH_4 production rate was higher than the volumetric CO_2 conversion rate.

CONCLUSIONS

Biological conversion of CO_2 to CH_4 by hydrogenotrophic methanogens was examined in a fixed bed reactor inoculated with anaerobic mixed culture from an anaerobic digester of the Junryang sewage treatment plant. Hydrogenotrophic methanogens were enriched in the fixed bed reactor by feeding a gas mixture of CO_2 and H_2. Methane formation commenced on the first day of reactor operation. CO_2 fed to the reactor was reduced with H_2 by hydrogenotrophic methanogens. This was confirmed by showing that CO_2 was not reduced in the reactor without hydrogen. Biological conversion of CO_2 to CH_4 by hydrogentrophic methanogens occurred according to the stoichiometry of the chemical equation: 1 mol of CO_2 was biologically reduced and 1 mol of CH_4 was produced. The ratio of H_2 to CO_2 is an important factor in determining methane production rate. When the ratio was 4, methane was produced at the expected rate according to the stoichiometry. CO_2 conversion rate was 100% when gas retention time was 3.8 h or longer.

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