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Bioelectrochemical Enhancement of Biogenic Methane Conversion of Coal

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Abstract: This study demonstrated the enhancement of biogenic coal conversion to methane in a bioelectrochemical anaerobic reactor with polarized electrodes. The electrode with 1.0 V polarization increased the methane yield of coal to 52.5 mL/g lignite, which is the highest value reported to the best of our knowledge. The electrode with 2.0 V polarization shortened the adaptation time for methane production from coal, although the methane yield was slightly less than that of the 1.0 V electrode. After the methane production from coal in the bioelectrochemical reactor, the hydrolysis product, soluble organic residue, was still above 3600 mg chemical oxygen demand (COD)/L. The hydrolysis product has a substrate inhibition effect and inhibited further conversion of coal to methane. The dilution of the hydrolysis product mitigates the substrate inhibition to methane production, and a 5.7-fold dilution inhibited the methane conversion rate by 50%. An additional methane yield of 55.3 mL/g lignite was obtained when the hydrolysis product was diluted 10-fold in the anaerobic toxicity test. The biogenic conversion of coal to methane was significantly improved by the polarization of the electrode in the bioelectrochemical anaerobic reactor, and the dilution of the hydrolysis product further improved the methane yield.

Keywords: coal; lignite; methane; biogenic conversion; bioelectrochemical reactor; inhibition

1. Introduction

Coal-bed methane (CBM) is an important source of natural gas that is formed in subsurface coal seams. The CBM is commonly extracted by wells, but the extraction rate is limited by the formation rate of CBM in the coal seam [1–3]. There are two types of CBMs in the coal seam, thermogenic and biogenic, that are converted from the organic matter contained in coal [3]. While the thermogenic CBM is formed as a side product of coalification at an elevated temperature and pressure, the biogenic formation of CBM is a continuous process that is carried out by a series of anaerobic microbial conversions of the organic matter in the coal. However, the rate of the microbial conversion of coal into methane is very low, and the methane yields are also too low to be economical [4,5]. The commercial availability of CBM requires improvements to the methane conversion rate and the yield from coal.

In the anaerobic conversion process of organic matter to methane, organic polymers are hydrolyzed and fermented by acidogens to intermediates, such as acetate and hydrogen. The intermediates are finally converted to methane by methanogens [6,7]. The physicochemical characteristics of the organic matter are key factors affecting the anaerobic conversion process. The organic matter contained in coal is mainly composed of hydrophobic substances, such as lignin, that are undergoing coalification, which are hydrolyzed very slowly. The hydrolysis products are composed of recalcitrant cyclic compounds, including long chain fatty acids, alkanes (C_{19}-C_{36}), and various aromatic hydrocarbons, and are difficult to for the acidogens to ferment [4,5,8]. The cyclic compounds can generally be degraded under aerobic conditions by oxidizing their rings or adding oxygen to their nuclei to open the rings [8,9]. When molecular oxygen is not available, some substances, including nitrate, iron, and sulfate, can be also used as the electron acceptor for ring opening of the cyclic compounds [8]. However, when there are no electron acceptors at a low redox potential, carbon dioxide can be reduced to methane, but the ring opening reaction is less thermodynamically favorable.

To date, the methane conversion of coal has been mainly improved by increasing the bioavailability of coal, biostimulation, and bioaugmentation. The bioavailability of coal can be increased to some extent by reducing the coal particle size, increasing the porosity, and adding surfactants [10,11]. Bioaugmentation and biostimulation, in which a microbial consortium or inorganic nutrients, such as nitrogen, phosphorus, trace elements, and vitamins, are supplied to the coal bed, have also been used effectively for promoting coal conversion to methane [2,3,12,13]. However, the methane yield obtainable from 1 g of coal is still only a few tens of μL to a few mL [2,5,11,14]. The organic content of coal varies depending on the coalification degree, and in the case of lignite, is 0.5–0.8 g COD (chemical oxygen demand) per g of coal. In anaerobic degradation of organic matter, theoretically, 1 g of COD can be converted to 350 mL of methane. This suggests that the conversion potential of coal to methane is fairly high.

The free energy change driving the redox reaction at the electrode surface depends on the polarized potential of the electrode. Recently, the principle of an electrochemical redox reaction on an electrode surface has been applied to improve the anaerobic degradation of organic matter [7,15]. An anaerobic reactor with a polarized electrode is called a bioelectrochemical anaerobic reactor. In a bioelectrochemical anaerobic reactor, the electroactive microorganisms, including exoelectrogenic fermentation bacteria (EFB) and electrotrophic methanogenic archaea (EMA), are enriched on the surfaces of the polarized electrode [15–17]. The electroactive microorganisms can donate or accept electrons to the outside of the cell through the cytochrome C or conductive pili that extend to the outer membrane of the cell [7,18]. EMA are microorganisms that produce methane by directly accepting the electrons from the EFB and then reduce carbon dioxide [15,16]. Recently, it has been revealed that EFB and EMA can be enriched not only on the electrode surface, but also in the bulk solution [15,18]. The electrons can be directly transferred between the interspecies of the EFB and EMA through the electrode, conductive materials, and direct contact [18–20]. In the anaerobic degradation of organic matter, the limitations of the kinetics and thermodynamics are considerably mitigated by methane production via direct interspecies electron transfer (DIET) [18,21]. This suggests that the bioelectrochemical approach has great potential to improve the methane conversion of coal. However, the bioelectrochemical methane conversion of coal has not yet been studied.

In this study, we first demonstrated that the polarized electrode remarkably improves the methane conversion of coal in a bioelectrochemical anaerobic reactor. The rate-limiting step controlling the overall methane conversion of coal was estimated and the inhibitory effects of the hydrolysis products of coal on the methane production were also evaluated.

2. Materials and Methods

2.1. Coal and Seed Sludge

Commercially available Canadian lignite as coal was purchased from a local distributor (Aquajiny Co., Daegu, Korea). The percentage of volatile solids in the lignite was 28.5%, and the organic and moisture contents were 0.52 g COD/g lignite and 18.4%, respectively. For the anaerobic batch experiment converting coal to methane, the lignite was powdered by crushing with a mortar and pestle, and screened with a 1 mm sieve, followed by drying at 105 °C for 12 h. The medium for the anaerobic batch experiment was prepared with the initial concentrations of 2.45 g/L $NaH_2PO_4.2H_2O$, 4.58 g/L $Na_2HPO_4.12H_2O$, 0.31 g/L NH_4Cl, and 0.31 g/L KCl. Small amounts of vitamins and trace metals were also added to the medium, following a previously reported method [22]. Anaerobic sludge collected from a sewage treatment plant (Busan, South Korea) was screened with a 1 mm sieve and then used as an inoculum by precipitating in a refrigerator at 4 °C for 24 h. The initial pH of the inoculum for the anaerobic batch experiment and the anaerobic toxicity test were 7.17 and 7.25, respectively, the VSS (volatile suspended solids) were 13.4 and 16.1 g/L, and the alkalinities were 2114 and 3702 mg/L as $CaCO_3$.

2.2. Experimental Apparatus for the Anaerobic Conversion of Coal to Methane

The bioelectrochemical anaerobic batch reactor (2 sets, effective volume 0.5 L, diameter 8.5 cm, and height 10 cm) was prepared using a cylindrical acrylic resin tube (Figure 1). The top of the anaerobic batch reactor was covered with acrylic plate and joined with a flange to seal the reactor. A blade for mixing was placed inside the reactor. The blade was connected to a DC motor over the acrylic cover plate using a steel shaft. The sampling ports for the gas and liquid and an off-gas valve were installed at the acrylic cover plate. The sampling ports for the gas and liquid were covered with n-butyl rubber stoppers. The liquid sampling port and the steel shaft hole of the acrylic cover plate were sealed with acrylic tubes extending into the liquid phase. The off-gas valve was connected to a floating-type gas collector by a rubber tube. The gas collector was filled with acidic saline water to prevent dissolution of the biogas. Copper foils (0.3 T, copper 99.9%, KDI Co., Seoul, Korea) with a large area (26 cm × 9 cm) and a small area (5.5 cm × 7 cm) were prepared. The surfaces of the foils were coated with a dielectric polymer (alkydenamel, VOC 470 g/L, Noroo paint Co., Busan, Korea) and used as a pair of electrodes. The electrodes were installed at the inner wall of the reactor and the outer wall of the sealing tube for the steel shaft. The interval between the inner and outer electrodes was 3.3 cm. The electrodes were connected to the terminals of an external voltage source (ODA Technologies, CO., Incheon, Korea) with titanium wires.

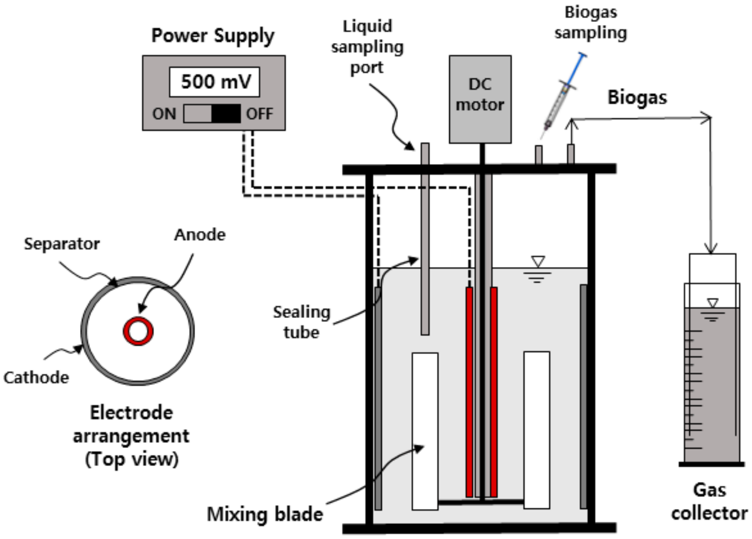

Figure 1. Schematic diagram of the bioelectrochemical anaerobic batch reactor.

For the anaerobic batch experiments, seed sludge (250 mL), medium (250 mL), and lignite (2.5 g) were added to the reactor. The electrodes were polarized by applying voltage of 1 or 2 V using the external voltage source. The anaerobic batch reactor with an applied voltage of 1 V was called as BEF1 and the reactor with 2 V was called BEF2. The anaerobic batch reactor was placed in a temperature-controlled room (35 °C) and mixed with the rotating the blade at 120 rpm. An anaerobic batch reactor without an applied voltage was operated under the same conditions as a control. An anaerobic batch reactor without added lignite was prepared to examine the methane production from the inoculum alone.

2.3. Anaerobic Toxicity Test

The hydrolysis product of the lignite was collected from the anaerobic batch reactor after the experiment. The COD and pH of the hydrolysis product were 4.16 g/L and 8.25, respectively. In the anaerobic toxicity test of the hydrolysis product, serum bottles of 125 mL were prepared. The inoculum (40 mL) and the hydrolysis product solution, with volumes ranging from 8 to 32 mL, were added to the serum bottles, and the anaerobic medium was filled to a total liquid volume of 80 mL. As an easily degradable substrate, 0.2 g of glucose was also added to the serum bottle. The serum bottle was flushed with nitrogen gas and sealed with rubber and aluminum caps using a crimper. The sealed serum bottle was incubated in a rotary shaker (120 rpm) at 35 °C. A serum bottle without the hydrolysis product in the liquid was also incubated under the same conditions and used as the control. Another serum bottle with added inoculum and medium was used as a blank to correct for the methane production from the seed sludge. All the anaerobic toxicity tests in the serum bottles were performed in triplicate.

2.4. Analysis and Calculation

During the anaerobic batch experiments, small amounts of liquid sample was intermittently collected, and the physicochemical properties, such as TS, VS, TCOD, SCOD, and VSS, were analyzed according to the Standards Method. The pH was measured with a pH meter (YSI pH1200 laboratory pH meter 115–230 V (T1)). At the end of the anaerobic batch experiment, VFAs (volatile fatty acids) in the liquid sample were analyzed by HPLC (high-performance liquid chromatography, UltiMate 3000, Thermo Scientific, Sunnyvale, USA) equipped with a UV detector and a separation column (Amines HPX-87H). The biogas production was monitored using a floating-type gas collector, and the biogas composition (methane, hydrogen, and carbon dioxide) was analyzed using a GC (gas chromatograph Clarus 580, PerkinElmer Co., Ltd. Shelton, USA) equipped with a thermal conductivity detector and a separation column (Porapak-Q, 6 ft × 1/8″, SS). The cumulative production volumes of methane and hydrogen were estimated from the biogas production and the biogas composition using Equation (1).

$$V_{CH_4/H_2} = C_{CH_4/H_2} \times (V_{RH} + V_{GT} + V_{GC}) \tag{1}$$

where V_{CH_4/H_2} is the cumulative production volume of methane or hydrogen (mL) and C_{CH_4/H_2} is the percentage of methane or hydrogen in the biogas. V_{RH} is the head space of the batch reactor, V_{GT} is the volume of the rubber tube between the reactor and the gas collector, and V_{GC} is the gas phase volume in the gas collector. The methane and hydrogen production volumes were converted to the corresponding values at standard temperature and pressure (STP), following previous studies [15,22]. At the end of the anaerobic batch experiment, a cyclic voltammetry experiment for the bulk solution was performed using a potentiostat (ZIVE SP1, WonA Tech, Seoul, Korea) at the scan rate of 10 mV/s in the voltage range of −1.0 to 1.0 V. Small pieces of stainless steel mesh (1 cm × 1 cm) were used as the working and counter electrodes, and an Ag/AgCl electrode was used as the reference electrode. The redox peak potential and the current were determined from the cyclic voltammogram obtained using the SmartManager software (ZIVE BP2 Series, WonA Tech, Seoul, Korea).

In the anaerobic toxicity test, the biogas production was intermittently monitored using a lubricated glass syringe, and the mean methane production was obtained from the biogas volume and the composition, following a previous study [23], then it was converted to the corresponding value at STP. The cumulative methane production was fit with the Modified Gompertz equation, Equation (2), to estimate the lag phase time, the maximum methane production rate, and the ultimate methane production.

$$P = P_u \times \exp[-\exp(\mu_m \times \exp(1) \times (\lambda - t)/ P_u + 1)] \tag{2}$$

where P is the cumulative methane production (mL) at time t, P_u is the ultimate methane production (mL), μ_m is the maximum methane production rate (mL/day), and λ is the lag phase time (day). The nlstools package in R was used for the fitting the cumulative methane production.

3. Results and Discussion

3.1. Bioelectrochemical Conversion of Coal to Methane under Electrostatic Field

In BEF1 with an applied voltage of 1 V, the methane production was delayed after start-up, but suddenly increased to 32.5 mL/g lignite on the 24th day. During the following several days, the cumulative methane production tended to decrease somewhat, but increased again to 52.5 mL/g lignite on the 31st day (Figure 2). To the best of our knowledge, this is the highest value of methane yield of coal reported to date. In previous studies, one of the highest methane yields of coal was 7.4 mL/g lignite, depending on the type of coal and degree of coalification [3,5]. This was mainly attributed to the organic matter in the coal, which was not a good substrate to be metabolized easily by microorganisms. The common organic constituents in coal are complex organic polymers, such as lignin, which are difficult to decompose [2]. There have been several attempts to improve the methane conversion of coal. The methane yield can be improved to 1.66–2.93 mL/g subbituminous coal by adding nutrients, such as yeast, algae, and cyanobacteria [3]. Aerobic pretreatment that promoted the bioavailability of coal improved the methane yield to 4.98 mL/g lignite [2]. However, the methane yield obtained in BEF1 was 10.5–31.6 times higher than those reported in previous studies [2,3]. Intriguingly, the methane production in BEF1 was discontinuous, resembling a pulse (Figure 3). In anaerobic digestion, the common intermediates are acetate and hydrogen, which are converted to methane by acetoclastic and hydrogenotrophic methanogens, respectively [6,21]. During the operation of BEF1, hydrogen was also observed in the biogas. The amount of hydrogen in the biogas increased and decreased repeatedly. However, the methane production in BEF1 did not exhibit the same behavior as that of hydrogen (Figure 3), indicating that there was little correlation between the hydrogen consumption and the methane production. This implies that the methane conversion mechanism of coal in BEF1 may be different from the known interspecies hydrogen transfer. It has been revealed that the homoacetogens oxidize carbon dioxide with hydrogen in a bioelectrochemical system to produce acetate, a substrate for exoelectrogens [24–26]. In BEF1, it seems that the acidogens fermented the hydrolysis product to produce hydrogen, and the homoacetogens produced acetate from the hydrogen and carbon dioxide. In a bioelectrochemical anaerobic reactor, the exoelectrogens on the electrode surface or in the bulk solution fermented the low molecular organic matter and released electrons to outside the cell [7,15]. The electrotrophic methanogens take the electrons directly to produce methane by reducing carbon dioxide [15,27]. In the cyclic voltammogram for the bulk solution in BEF1, two pair of redox peaks were observed at −0.014/−0.239 V vs. Ag/AgCl (E_f = −0.127 V) and 0.913/0.025 V vs. Ag/AgCl (E_f = 0.461 V) (Figure 4). The redox peaks in the voltammogram indicate the presence of electroactive substances, such as electroactive microorganisms or electron transfer mediators in the bulk solution [15]. In anaerobic digestion, when the redox potential is more negative than −0.44 V vs. Ag/AgCl, carbon dioxide can be thermodynamically reduced to methane at standard conditions. This suggests that the 2nd redox peaks are not likely to be involved in the methane conversion of coal. The formal potential (E_f) that is effective in the methane conversion reaction is varied from −0.23 V vs. Standard Hydrogen Electrode (SHE) to 0.7 V vs. SHE, depending on the type of electroactive substances [28]. In BEF1, the applied voltage between the electrodes was 1.0 V, and the electric field in the bulk solution is theoretically 0.3 V/cm. This indicates that the 1st redox peaks were the effective electroactive substances that could contribute to the methane production. It seems that the methane in BEF1 was produced from the acetate by syntrophic metabolisms between the exoelectrogens and the electrotrophic methanogens or by the acetoclastic methanogens.

In BEF2 with an applied voltage of 2 V, the methane production began on the 15th day and reached a maximum value of 43.7 mL/g lignite on the 19th day (Figure 2). Hydrogen production in BEF2 was observed on the 15th day only (Figure 3). The correlation between the hydrogen consumption and methane production was low, similar to BEF1. This indicates that the potential of the hydrogenotrophic methanogenesis in BEF2 was also low. In the cyclic voltammogram for the bulk solution in BEF2, pairs of redox peaks were observed at 0.055/−0.286 V vs. Ag/AgCl (E_f = −0.116 V) and 0.986/0.135 V vs. Ag/AgCl (E_f = +0.561 V). Although the formal potential of the 1st redox peaks shifted in the positive direction somewhat compared to that of BEF1, these peaks may have contributed to the electron transfer for methane production. This suggests that the DIET between the exoelectrogens and the electrotrophs potentially plays a role in the fermentation of the hydrolysis product and the methane production.

Interestingly, the cumulative methane production in BEF1 and BEF2 gradually decreased after increasing to maximum values (Figure 2). It seems that the methane was consumed by methanotrophs. In general, methanotrophs metabolize methane in aerobic conditions and have a unique ability to oxidize a wide range of alkanes, aromatics, and halogenated alkenes [29–31]. However, when the available molecular oxygen is limited, the methanotrophs use sulfate, nitrite, and nitrate as the electron acceptor [31,32]. Recently, it was revealed that the methanotrophs can also use the anode as an electron acceptor to oxidize methane in bioelectrochemical anaerobic systems and can outcompete the methanogens when the available substrate is deficient [32,33]. The anaerobic batch reactors of BEF1 and BEF2 are substrate limited bioelectrochemical reactors with applied voltages, and the hydrolysis product of coal is composed of cyclic compounds. These are conditions under which the methanotrophs could be enriched. It seems that methanotrophs play an important role in the methane conversion of coal, but further studies are needed in the future.

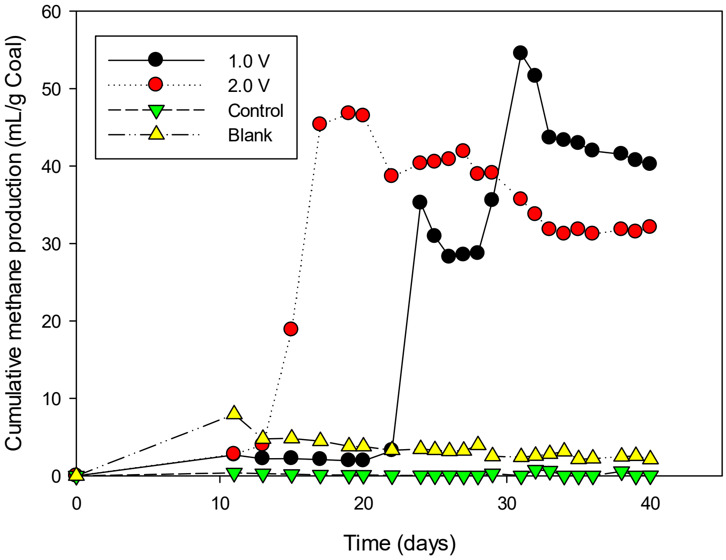

Figure 2. Cumulative methane production in bioelectrochemical anaerobic reactor.

The methane production was very small in the control without an applied voltage and was less than the blank (Figure 2). In the blank, methane was produced from the anaerobic degradation of organic matter contained in the inoculum. It seems that the hydrolysis products of coal had an inhibitory effect on the methane production in the control. Under anaerobic conditions, the hydrolysis products of coal include long chain fatty acids, polycyclic aromatic hydrocarbons, and heterocyclic compounds [2,4]. It is known that the fermentation of the hydrolysis products into precursors, such as acetate and hydrogen, is the rate-limiting step in the entire methane conversion process of coal [2].

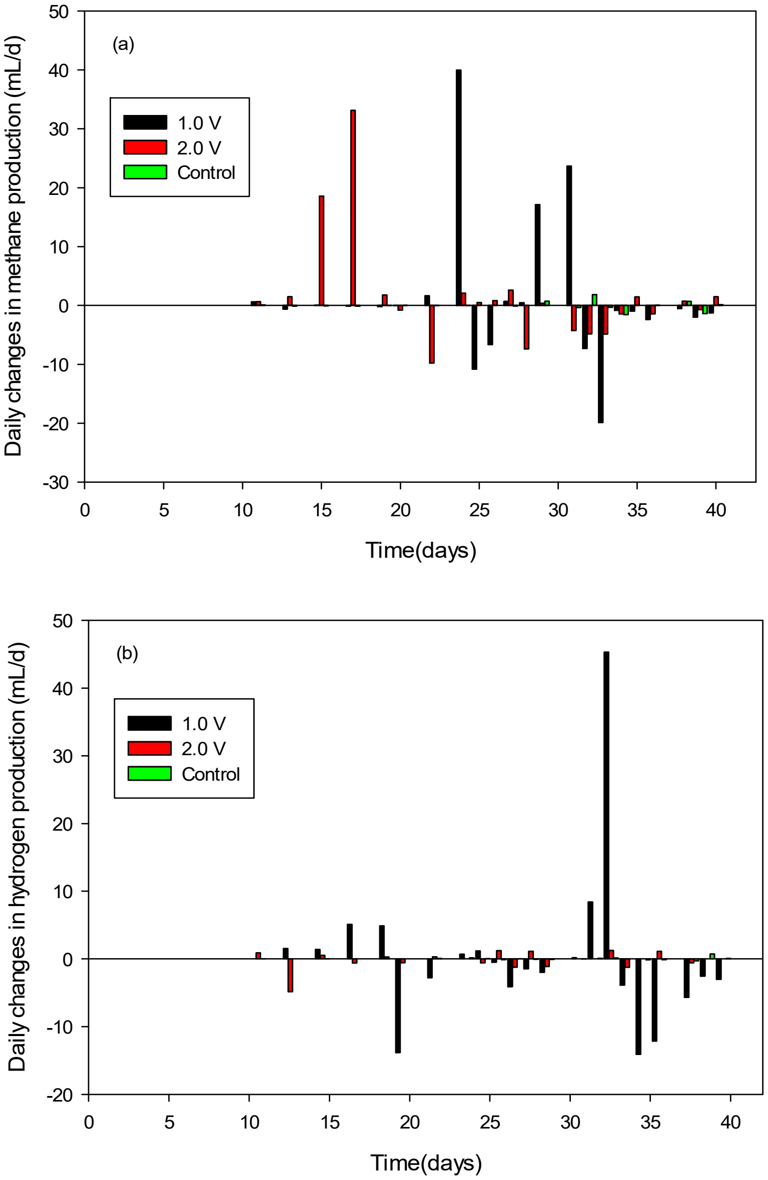

Figure 3. Daily changes in (**a**) methane production and (**b**) hydrogen production.

In previous studies, methane conversion of coal in the anaerobic reactor was observed between 30 and 60 days [3,4]. There is a possibility that the anaerobic microorganisms adapted to the anaerobic reactor for the methane conversion of coal. However, the expected methane production was still less than a few mL/g of coal.

The correlation between hydrogen consumption and methane production in the control was somewhat higher than those in BEF1 and BEF2. This suggests that the methane was produced in the control by indirect interspecies electron transfer via methane precursors, such as acetate or hydrogen. In the bulk solution of the control, redox peaks in the cyclic voltammogram were also observed at 0.08/–0.24 V vs. Ag/AgCl ($E_f = -0.08$ V) and 1.03/0.15 V vs. Ag/AgCl ($E_f = 0.59$ V). However, the small amount of methane production indicates that the redox species in the control did not contribute to the electron transfer for methane production.

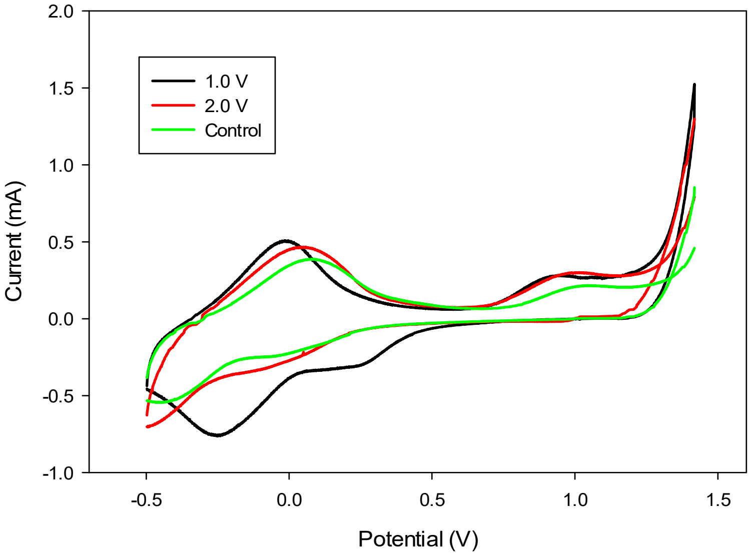

Figure 4. Cyclic voltammogram in the bulk solution for different applied voltages.

3.2. Methane Conversion Potential of Hydrolyzed Product from Coal

The methane conversion of coal experiments was stopped when no further methane production was observed in the reactors. However, the soluble organic matter in BEF1 and BEF2 were still 3.62 and 4.09 g SCOD/L, respectively, and was as high as 4.66 g SCOD/L in the control (Table 1). It is interesting that there was enough organic matter in the anaerobic batch reactors, but the methane production stopped. It is speculated that the residual organic matter was composed of recalcitrant compounds that were difficult to degrade or that the anaerobic microorganisms had lost activity for methane conversion by the toxicity of the compounds. During the anaerobic batch experiments, the pH values were initially 7.36, but increased to 7.79–8.06 (Table 1). In the anaerobic reactors, the accumulation of VFAs reduced the pH, but the alkalinity increased the pH [22,27]. The alkalinities in the anaerobic batch reactors increased from 3824 mg/L as $CaCO_3$ to about 4500 mg/L as $CaCO_3$, but the levels of VFA residuals were very low (Table 1). The alkalinity was generated by the methane production, sulfate reduction, and the ammonia produced from the degradation of nitrogenous compounds [22,27]. In BEF1 and BEF2, the methane production amounts were 116.92–136.27 mL, indicating that the alkalinities were not significantly increased by the methane production. However, the VSSs were reduced from the initial values of 9.25 g/L to 6–8 g/L. This indicates that the alkalinities mainly increased due to the ammonia released from microbial cell lysis due to the limited substrate. In the blank, the residual organic matter was 1.24 g SCOD/L. The hydrolysis products of coal were 2.38–3.42 g SCOD/L in the total organic residue in the anaerobic batch reactors.

In previous studies, the hydrolysis product of coal was composed of several complex cyclic compounds [2,3,13]. These compounds can be converted to the methane precursors by carboxylation, hydroxylation, and methylation for ring opening [8]. The initial value of particulate COD was 11.28 g/L in all anaerobic reactors and decreased to 0.51–1.01 g/L during the methane conversion experiment of coal, indicating that the particulate organic matter containing the coal was at least 91–96% hydrolyzed. However, the VFA residues in BEF1 and BEF2 were only 0.15 g COD/L and 0.19 g COD/L, respectively. This means that the fermentation of the hydrolysis products of coal into the methane precursors is a rate-limiting step in the overall methane conversion of coal [2,4].

In the anaerobic toxicity test, the methane production was severely affected by the content of the coal hydrolysis product in the anaerobic medium (Figure 5a). In the control without the hydrolysis product, the maximum methane production rate was 6.36 mL/day. When the hydrolysis product was added to the anaerobic medium up to 10%, the maximum methane production increased slightly to 6.49 mL/day. However, as the hydrolysis products increased to 20% and 40% in the anaerobic medium, the maximum methane production rates decreased to 2.36 and 1.86 mL/day, respectively. These indicate that the maximum methane production rates were inhibited by 62.9% and 70.8%, respectively. This suggests that the hydrolysis product has a substrate inhibition effect on methane production, and that the maximum methane production rate was 50% inhibited when the hydrolysis product was diluted 5.7-fold (Figure 5b). However, when the hydrolysis product was 10%, the ultimate methane production was 47.4 mL, which was higher than 38.6 mL of the control. The ultimate methane production increased to 52.4 and 49.5 mL with the increase in the hydrolysis products to 20% and 40%, respectively. Although the ultimate methane production depended on the amount of the hydrolysis product added to the anaerobic medium, the increase in the methane production compared to that of the control indicates that the hydrolysis product was metabolized by the anaerobic microorganisms. The methane yield was 175.2 mL/g COD_r in the control, but it decreased from 156.4 mL/g COD_r to 142.3 mL/g COD_r as the hydrolysis product content increased from 10% to 40% (Table 2). This indicates that the hydrolysis products were toxic to the anaerobic microorganisms. The methane yield from the hydrolysis product based on the coal ranged from 106.3 mL/g COD_{rCHP} (55.3 mL/g lignite) to 85.4 mL/g COD_{rCHP} (44.4 mL/g lignite) when the hydrolysis product increased from 10% to 40% in the anaerobic medium, respectively. The dependence of the methane yield on the hydrolysis product content indicates that the hydrolysis product of coal can be converted into methane if it is diluted. However, the substrate inhibition of the hydrolysis product to methane production could be mitigated through additional in-depth studies.

Table 1. Summary of biogenic conversion of coal to methane in bioelectrochemical anaerobic reactor.

Contents		Control	BEF1	BEF2
CH_4 yield (mL/g lignite)		0.75	52.5	43.7
SCOD residual (g/L)		4.66	3.62	4.09
VFAs residual (g COD/L)		0.57	0.18	0.15
Redox peaks in CV	$E_{p,ox}/E_{p,red}$ (V vs. Ag/AgCl)	0.083/−0.241; 1.031/0.154	−0.014/−0.239; 0.913/0.025	0.055/−0.286; 0.986/0.135
	E_f (V vs. Ag/AgCl)	−0.079; +0.593	−0.127; +0.469	−0.116; +0.561
	$I_{p,ox}/I_{p,red}$ (mA)	0.331/0.238; 0.113/0.148	0.473/0.356; 0.217/0.253	0.407/0.244; 0.146/0.011
Alkalinity (mg/L as $CaCO_3$)	Initial	3824	3824	3824
	Final	4026	4182	4462
pH	Initial	7.36	7.36	7.36
	Final	7.79	8.06	7.92
VSS (g/L)	Initial	9.25	9.25	9.25
	Final	5.05	6.10	7.95

Table 2. Summary of the anaerobic toxicity of the hydrolysis product of coal to methane conversion.

Parameter	Control	10%	20%	40%
P_u (mL)	38.6	47.4	52.4	49.5
μ_m (mL/day)	6.36	6.49	2.36	1.86
λ (day)	0	0	0	4.65
Total CH_4 yield (mL/g COD_r)	175.2	156.4	146.2	142.3
CH_4 from CHP (mL/g COD_r CHP)	0.00	106.3	100.0	85.4

(CHP: coal hydrolysis product, g COD).

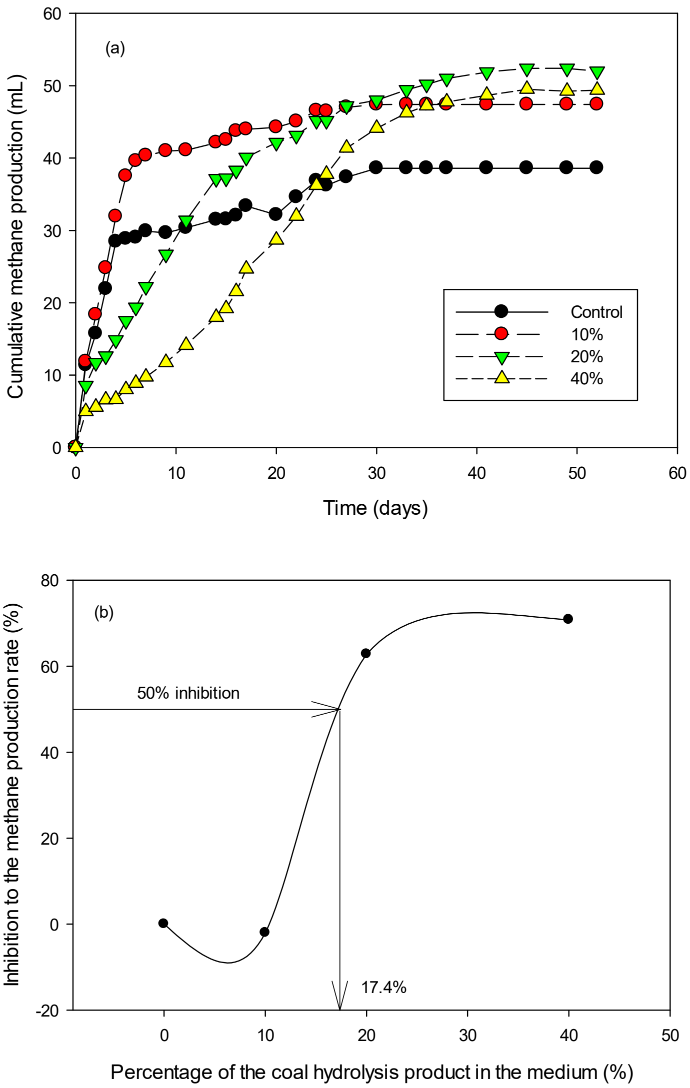

Figure 5. (**a**) Cumulative methane production and (**b**) the inhibition to the methane production depending on the amount of the coal hydrolysis product added in the anaerobic toxicity test.

3.3. Implications

Coal is the most buried fossil fuel on the planet and accounts for around 30% of the global energy use [10,11,34]. However, coal releases several pollutants, such as dust, sulfur oxides, nitrogen oxides, and carbon dioxide during use [10,35,36]. Methane is a major component of natural gas, a clean energy resource. The biological conversion of coal to methane is crucial for securing stable energy resources and sustainable development. Therefore, there have been several physicochemical and biological attempts to improve the coal conversion to methane [10,36]. Nevertheless, the methane yield was less than a few mL/g of lignite and required 30 to 85 days [5,37]. The coal conversion process to methane is significantly affected by the physicochemical characteristics of the organic matter contained in the coal. The organic matter in the coal is generally composed of recalcitrant lignified materials that are hydrolyzed into long chain fatty acids, polycyclic aromatic hydrocarbons, and heterocyclic compounds [2,4,5]. In bioelectrochemical anaerobic reactors, the coal conversion to methane was significantly improved by applying 1 V. The methane yield reached 52.5 mL/g lignite (Table 1), which is the highest reported value to the best of our knowledge. However, when the applied voltage increased to 2 V, although the methane yield was slightly reduced to 43.7 mL/g lignite, the methane production from coal was observed after a shorter lag phase time of 13 days. Interestingly, the organic residues of the coal hydrolysis product were still high, with values around 3620–4090 mg COD/L in the bioelectrochemical anaerobic reactor after methane production. In the anaerobic toxicity tests, the hydrolysis products had produced a substrate inhibition effect for methane production, which was 50% inhibited when the organic hydrolysis product was diluted approximately 5.7 times. However, the organic hydrolysis products were further converted to methane (106.3 mL/g COD_r CHP) by a 10-fold dilution (Table 2). This suggests that the methane production from the hydrolysis product after the bioelectrochemical conversion of coal to methane increases the methane potential of coal to 107.8 mL/g lignite (207.3 mL/g COD in lignite). The methane potential of coal is lower than 350 mL/g COD in glucose, but high enough to be commercially viable. However, additional in-depth studies are necessary to mitigate the inhibition of the coal hydrolysis products on the methane conversion in the field.

4. Conclusions

The polarization of the electrodes in the bioelectrochemical anaerobic reactors greatly improved the coal conversion to methane. The electrode polarized with 1.0 V in the bioelectrochemical anaerobic reactor increased the methane yield of coal to 52.5 mL/g lignite. The electrode polarized with 2 V shortened the time required to produce methane and improved the coal conversion rate. The organic residue of the hydrolysis products had a substrate inhibition effect for methane conversion, and the methane conversion rate was 50% inhibited when the hydrolysis products were diluted 5.7-fold. A 10-fold dilution of the hydrolysis products produced additional methane of 106.3 mL per g COD_r, which amounts to 55.3 mL/g lignite. The total methane potential of coal was improved to 107.8 mL/g lignite by the electrode polarization and the dilution of the hydrolysis products. However, the inhibition of the hydrolysis products to the methane conversion could be mitigated by additional in-depth studies.

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