

Bioelectrochemical upgrading of anaerobic digester biogas under thermophilic conditions

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Abstract. Bioelectrochemical systems (BESs) can be integrated *in situ* into anaerobic digesters for increasing methane (CH₄) content of biogas. Using BES *ex situ* for improving biogas quality has recently been gaining attention. However, information on the process under thermophilic conditions is very limited. In this study, we placed a BES cathode in-line at the exit gas from a thermophilic anaerobic digester to convert carbon dioxide (CO₂) in the biogas into CH₄. The performance of the *ex situ* BES reactor under thermophilic conditions was evaluated. When poisoning the cathode at −1.1 V versus Ag/AgCl in the *ex situ* BES reactor, CH₄ content increased from 50% to 85%. Of the incoming CO₂ 73% was biologically converted to CH₄ and 23% absorbed by alkalinity generated in the cathode. The energy output as additional CH₄ as a percentage of the energy input to operate the BES was calculated at 56%. The biocathode of the BES reactor was dominated by *Methanothermobacter* spp., which are thermophilic hydrogen consuming methanogens. This study confirms that thermophilic BES can be used as an *ex situ* treatment process for enriching the CH₄ content of biogas. However, energy efficiency of the process was found to be limited by the lack of an energetically efficient anodic reaction. For industrial applications, optimisation of energy efficiency is an area for further research.

Keywords: Anaerobic digestion / thermophilic / bioelectrochemical / biomethane / biogas upgrading

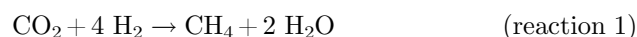
1 Introduction

Biogas is a product of anaerobic digestion that can be used in gas turbines to produce electricity. It typically contains 50–70% methane (CH₄), 30–50% carbon dioxide (CO₂) and trace amounts of hydrogen (H₂), hydrogen sulfide (H₂S) and ammonia (NH₃) [1]. Typically, the calorific value of biogas is approximately 22 MJ/m³, whereas that of natural gas is 36 MJ/m³. Because the energy content of biogas is directly proportional to its CH₄ content, removing the CO₂ would increase the calorific value of the biogas. Hence, to achieve its full potential the removal of CO₂ and other impurities from the biogas is necessary [2]. The purified methane-enriched biogas can, for example, be injected into a natural gas network for town gas supply.

Conventional methods for removing CO₂ from biogas are largely physical/ chemical based, including for example pressure swing adsorption, water scrubbing, organic physical scrubbing, and chemical scrubbing [3]. Despite having excellent performance in enriching the methane

content in biogas, these physical and chemical methods typically involve multiple and complicated steps with high energy input and corresponding operational costs [2]. On the other hand, biological gas treatment has been considered as a possible less reagent-intensive and energy-intensive biogas upgrading alternative. Ghosh and Klass were the first to suggest that biogas from anaerobic digestion could be passed through a secondary methanogenic digester to remove CO₂ and H₂S from biogas [4]. Following this idea, Strevett et al. studied the ability of a chemo-autotrophic archaea (*Methanobacterium thermoautotrophicum*) to upgrade biogas by reducing CO₂ to CH₄ using H₂ as an electron donor [5]. The biogas (50–60% CH₄, 40–50% CO₂ and 1–2% H₂S) was mixed with H₂ and passed through a hollow fibre membrane colonised by the microorganisms capable of catalysing the hydrogenotrophic methanogenesis reaction (reaction 1). The results showed that the anaerobic chemo-autotrophic process could effectively remove CO₂, increasing the CH₄ content from 50–60% to 96%.

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Recently, integrating bioelectrochemical systems (BES) with anaerobic digestion (BES-AD) has been considered a promising way to enhance biogas production [6–8]. We investigated and compared the effectiveness of two BES-AD configurations, single-chamber (membrane-less) and two-chamber (membrane-separated), on biogas production under thermophilic conditions [9]. However, the results showed that operating a BES directly in an AD reactor led to a suppression of organics conversion into biogas, which is understandable as increased H_2 partial pressures are known to interfere with organics conversion to biogas. Therefore, it would be worth retrofitting the process with the BES being deployed downstream of the anaerobic digester as a standalone unit process, such that it serves as a biogas converter (CO_2 to CH_4). Such an *ex situ* biogas upgrading approach has the potential to facilitate upgrading of biogas produced from multiple (small-scale) digesters. Hence, the aims of this study were: (1) to determine if the *ex situ* thermophilic BES reactor could increase the methane content of biogas; (2) to characterise the microbial community on the cathode surface and the bulk medium to gain insight into the biogas upgrading mechanisms of the BES reactor; (3) to evaluate the energy efficiency of the BES reactor for identifying areas of further improvement towards practical application. Investigations were conducted under thermophilic conditions as no previous studies had been carried out under these conditions and performance at thermophilic conditions is expected to be higher than at lower temperatures.

2 Materials and methods

2.1 Setup of *ex situ* BES reactor

The *ex situ* BES reactor was set up based on the two-chamber BES reactor described in our previous study [9]. The two-chamber reactor consisted of two identical acrylic half-cell cylindrical vessels (500 mL capacity in each vessel) with several sampling ports. The two half-cells were separated by a cation-exchange membrane (CEM) (30 cm², AS2S, A2-11, Membranes International Inc., US). The counter electrode (anode) chamber contained 350 mL of 150 mM $NaHCO_3$, and the counter graphite electrode (length $\times$ diameter: 15 cm $\times$ 2.5 mm, Progresso 8911/8B) was inserted at the middle of the counter chamber. The working volume of the cathodic chamber was 350 mL. A sheet of carbon felt (width $\times$ length: 6 cm $\times$ 22 cm) (MGM-Carbon Industrial, Ltd. Co., China) was used as the working electrode (WE), which was folded into a cylindrical form within the cathodic chamber. The distance between the working (the side that was closest to the CEM) and the counter electrodes was approximately 10 cm. Electrical connection between the carbon felt and the external circuit was made via a titanium wire, with one end tightly fastened to the felt. A silver silver chloride (Ag/AgCl) reference electrode (saturated KCl), pH and redox potential (ORP) probes were tightly mounted (sealed with epoxy glue) into the cathodic chamber to allow real-time monitoring. Instead of carrying out simultaneous AD and BES within the reactor as was the case in our previous paper, AD was conducted in a separate reactor. Biogas

from the AD reactor or synthetic biogas was then used to feed into the *ex situ* BES reactor for testing the conversion of CO_2 to CH_4 .

2.2 Experimental conditions

2.2.1 Coupling of an anaerobic digester with the *ex situ* BES reactor

A semi-continuous anaerobic digester (400 mL) was fed with 3.5 mL of concentrated glucose solution (1 M) daily after withdrawing the same volume of bulk solution. The biogas produced was monitored. Once the biogas production pattern was established, the biogas from the AD was directly fed into the BES reactor via a Tygon tube (diameter 3.1 mm, Masterflex[®] 06409-16). The outflow gas from the BES reactor was collected in an inverted glass measuring cylinder (500 mL) to determine gas volume. A schematic diagram of the AD-*ex situ* BES reactor set-up is shown in Figure 1. Compositions of biogas from both AD and *ex situ* BES reactors were monitored daily. Working electrode (WE) potential in the *ex situ* BES reactor was applied at different levels (−0.9, −1.0, −1.1, −1.2 V vs. Ag/AgCl) to determine the optimum WE potential for CO_2 to CH_4 conversion.

All the reactors in this study were operated under thermophilic conditions in a thermostat water bath controlled at 55 °C. The WE potentials reported in this study refer to values against Ag/AgCl reference electrode (ca. +197 mV vs. standard hydrogen electrode). The current and pH in the BES reactor were recorded by a computer using a LabJack USC interface and National Instrument LabView software. pH in the BES reactor was maintained at around 8 by adding HCl (4 M).

2.2.2 Synthetic gas as feed to *ex situ* BES reactor

Two sets of experiments using synthetic biogas with known gas composition (50:50 (v/v) $CO_2:CH_4$, or 100% CO_2) were also used to evaluate the BES CO_2 reduction process. The synthetic gas was transferred from a gas-bag (3L, TEDLAR BAG, CEL Scientific Corp. USA) via pumping (MasterFlex[®], Peristaltic Pump, Cole-Parmer Instrument Company, USA) at a fixed volumetric loading rate (3.4 L/L/d). The set up was similar to Figure 1, except the gas bag with the peristaltic pump replaced the anaerobic digester. The CO_2 -converting electrode (i.e. the cathode) of the BES reactor was poised at a potential of −1.1 V versus Ag/AgCl. The outflow gas from the BES reactor was collected in another gasbag for gas composition analysis.

2.2.3 Role of cathodic biofilm on CH_4 enhancement

To determine the role of the biofilm attached to the carbon felt cathode (i.e. WE) in the bioelectrochemical conversion process ($CO_2 \rightarrow CH_4$), after the aforementioned experiments (Sect. 2.2.2) the bulk solution in the *ex situ* BES reactor was completely removed from the cathodic chamber and replaced with a cell-free bicarbonate buffer (150 mM $NaHCO_3$, which was the same as the anolyte). The WE potential was again maintained at −1.1 V versus Ag/AgCl in the BES reactor to determine to what extent,

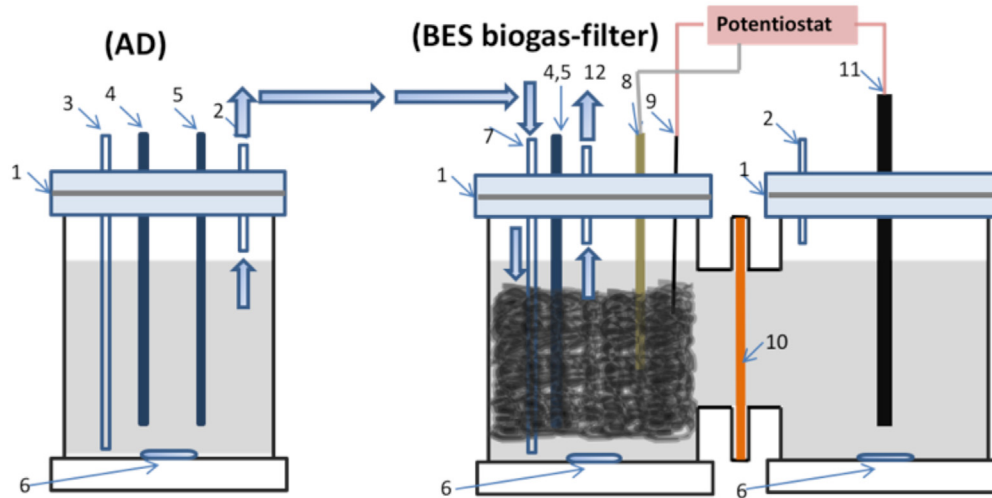


Fig. 1. Schematic diagram showing the coupling of the experimental anaerobic digester (AD) and a BES reactor. (1–Rubber gasket; 2–AD biogas output; 3–Influent/effluent port; 4–pH probe; 5–redox probe; 6–Magnetic stirrer; 7–Biogas inlet; 8–Ag/AgCl reference electrode; 9–Working electrode (graphite rod and carbon-felt); 10–Cation exchange membrane; 11–Counter electrode (graphite rod); 12–BES gas outlet).

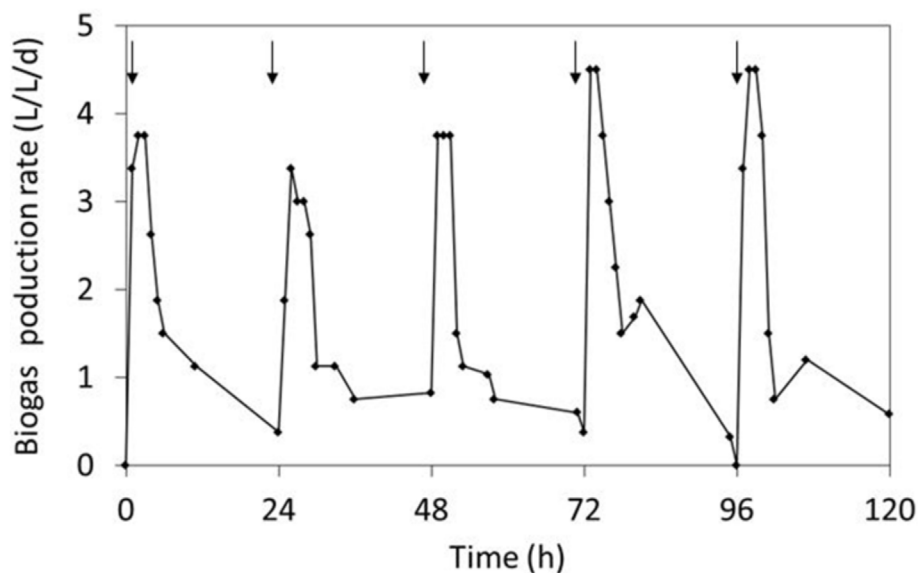


Fig. 2. Biogas production rate recorded for the AD reactor during steady-state operation. Glucose feeding events are indicated by the arrows.

in the absence of planktonic cells, the microbial communities in the cathodic biofilm could sustain the bioelectrochemical conversion.

2.3 Gas analyses

All biogas samples were taken using a glass syringe (100 μ L, GASTIGHT[®] #1710). Biogas compositions (methane, hydrogen and carbon dioxide concentrations) were immediately analyzed by a Varian Star 3400 gas chromatograph (GC) equipped with a thermal conductivity detector. The carrier gas was set at a flow rate of 30 mL/min. The headspace samples (100 μ L) were

manually injected into a GC column (2 m $\times$ 5 mm, Pora-PakQ) maintained at 40 °C. The temperatures of the detector and inlet were maintained at 40 and 120 °C respectively.

2.4 Microbial community analysis

To determine microbial community in the BES reactor, three samples were taken from the initial thermophilic anaerobic sludge inoculum, the biofilm on the cathode and the bulk solution in the BES cathodic reactor. DNA was extracted from these samples using the PowerSoil[®] DNA Isolation Kit as per the manufacturer's instruction. The

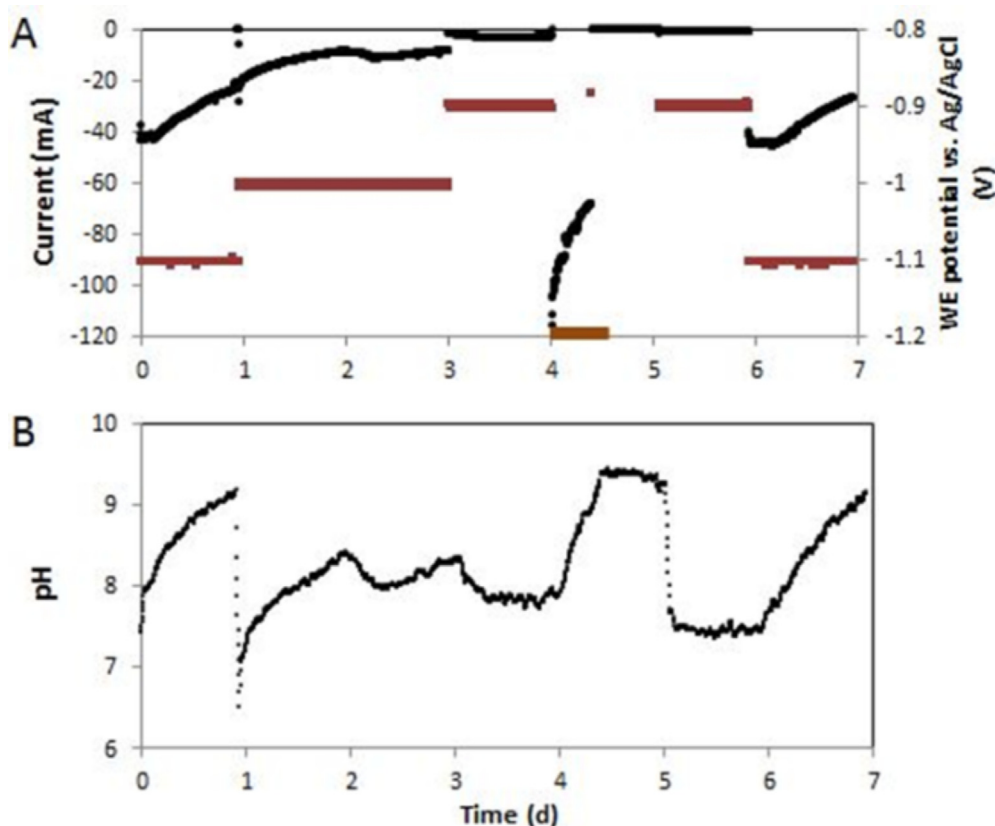


Fig. 3. Changes in (A) current of BES reactor and (B) cathodic chamber pH at different WE potential set points. (WE potential-red line and current-black line)

extracted DNA samples were then sent to Lister Lab (The University of Western Australia) for 16S Metabarcoding analysis.

3 Results and discussion

3.1 Transferring biogas from the anaerobic digester to the BES

A steady biogas production was first established for the AD reactor prior to coupling the AD reactor with the BES reactor. Results showed that after approximately one month of operation, the AD reactor reproducibly and rapidly responded to glucose additions, allowing biogas production at a maximal rate of approximately 4 L/L/d (Fig. 2). The average biogas production rate recorded (~ 1.2 L/L/d) also matched the theoretical value (1.3 L/L/d) estimated based on the application rate of glucose. Thereafter, the cathodic half-cell of the two-chamber BES reactor was coupled via a Tygon tube to the headspace of the AD reactor.

The capability of the BES reactor in upgrading the AD biogas was evaluated by poisoning the carbon felt WE at different potentials, ranging between -0.9 V and -1.2 V (Fig. 3). Results showed that when the WE was operated at a more negative potential of -1.1 V and -1.2 V, a higher cathodic current was generated (Fig. 3A), which also coincided with a rapid pH rise of the catholyte (from 8 to 9) (Fig. 3B). The gas outflow from the BES reactor was found

to have a significantly higher CH_4 content than the biogas from the AD (Fig. 4). When the applied WE potential was at -1.1 V, the CH_4 content in the gas outflow from the BES reactor reached 90%, accounting for a 60% improvement. These results confirmed that the *ex situ* BES reactor was effective in augmenting the CH_4 content in the AD biogas. This could be due to two reasons, microbial conversion of CO_2 to CH_4 and/ or CO_2 adsorption by catholyte. As the varying gas production rate and CO_2 : CH_4 ratio in the AD biogas interfered with the investigation of the BES reactor, separate experiments using synthetic AD biogas streams were performed in subsequent tests.

3.2 Performance of the *ex situ* BES reactor with the use of synthetic biogas

Synthetic gas (CO_2 : CH_4 50:50) was continuously fed into the BES reactor at a rate of 3.4 L/L/d and the WE was poised at -1.1 V for 6 days (Fig. 5). As noted before, the catholyte pH increased soon after the onset of the cathodic current. To prevent the pH from becoming too alkaline for methanogens, it was controlled to approximately 8 using 4M HCl. The CH_4 content of the resulting outflow gas was determined and compared with that in the inflow gas stream. Results showed that the average CH_4 content (over the 6 days) in the outflow gas was significantly increased from 50% to approximately 85% (Fig. 5A). This suggested an effective CO_2 conversion and/or trapping had occurred in the BES reactor. When switching the BES to an open

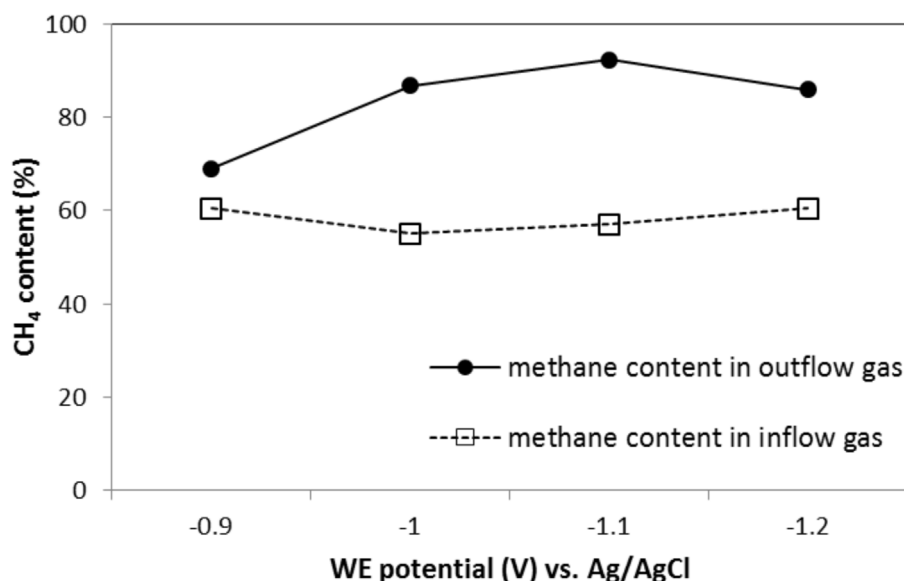


Fig. 4. Effect of WE potential on BES performance for CH₄ enhancement.

circuit mode operation, the CH₄ content in the outflow returned to approximately 50%, confirming that the cathodic current sustained by the bioelectrochemical reaction(s) within the BES was responsible for the CH₄ enrichment in the biogas.

To further determine if the increased CH₄ content was indeed generated from the cathodic bioconversion of CO₂, another synthetic gas experiment was conducted with pure CO₂ gas as the inlet feed. As in the previous experiment, the pure CO₂ gas was continuously fed into the BES reactor at a similar rate (3.4 L/L/d). The results showed that a notable concentration of methane (~20%) was recorded in the outflow gas of the BES reactor (Fig. S3), suggesting that the increase of CH₄ in the biogas was likely caused by a bioelectrochemical reduction of CO₂.

3.3 Role of cathodic biofilm on methane enhancement

In order to eliminate any possible CH₄ produced from residual organics in the digester solution around the cathode of the BES, the bulk solution of the cathodic chamber was replaced by a fresh bicarbonate buffer (150 mM). The activity of hydrogenotrophic methanogens on the biocathode was evaluated by poisoning WE potential at -1.1 V. Gas inflow (CO₂:CH₄ = 50:50) to the BES reactor was maintained from a gas-bag and the resulting outflow gas content was monitored for three days. Analysis of the outflow gas in this experiment indicated a similar increase of CH₄ content (peaked at around 80% at the end of the third day) that was obtained from the BES reactor before the replacement of the bulk solution (Fig. 6).

Gas monitoring over a 24 h experiment showed that for the 636 mL of CO₂ removed, about 462 mL extra CH₄ was produced (Fig. S4). Of the CO₂ that was removed, 73% was biologically converted into CH₄, whereas the remaining 27% was trapped (absorbed) by the alkaline bicarbonate solution. This result confirmed that the bioelectrochemical reaction catalysed by the cathodophilic biofilm was the

main CO₂ removal mechanism, supporting the finding of Cheng et al. (2009) who first demonstrated that electro-methanogenesis can be catalysed by a biofilm in a MEC [10]. Nonetheless, it should be mentioned that without acid dosing for pH control, our system should facilitate an even greater proportion of CO₂ absorption by the alkaline catholyte.

3.4 Microbial community in the BES

To identify the major groups of microorganisms in the population on the cathode, the biofilm was scratched off from the carbon felt on the cathode (sample MG11) and investigated by 16S Metabarcoding analysis. For comparison, the initial inoculum (sample MG2: thermophilic anaerobic sludge) and the bulk solution in BES reactor (sample MG12) were also examined. The results suggested that the majority of the microbes in the samples were bacteria (see Supplementary Materials). Given that methanogenic microorganisms are largely under the domain of archaea, in this section, only the changes of archaea in different samples were discussed and shown in Table 1: (1) a small amount of *Methanosarcina* (0.2%) presented in the initial inoculum; (2) after one week anaerobic digestion and 7 weeks BES operation, the hydrogenotrophic methanogen *Methanothermobacter* developed in the solution and also on the cathode of the BES reactor; (3) the fraction of *Methanothermobacter* on the cathode population was remarkably higher than that in bulk solution.

The results suggest that the BES under the tested conditions facilitated the growth of hydrogenotrophic methanogens of the genus *Methanothermobacter*, whereas the start-up inoculum (anaerobic sludge) was dominated by *Methanosarcina*, a genus of methanogens specialised on acetate oxidation that can also use hydrogen. The abundance of *Methanothermobacter* in the bulk solution was very nominal (about 5% of that in the cathodic

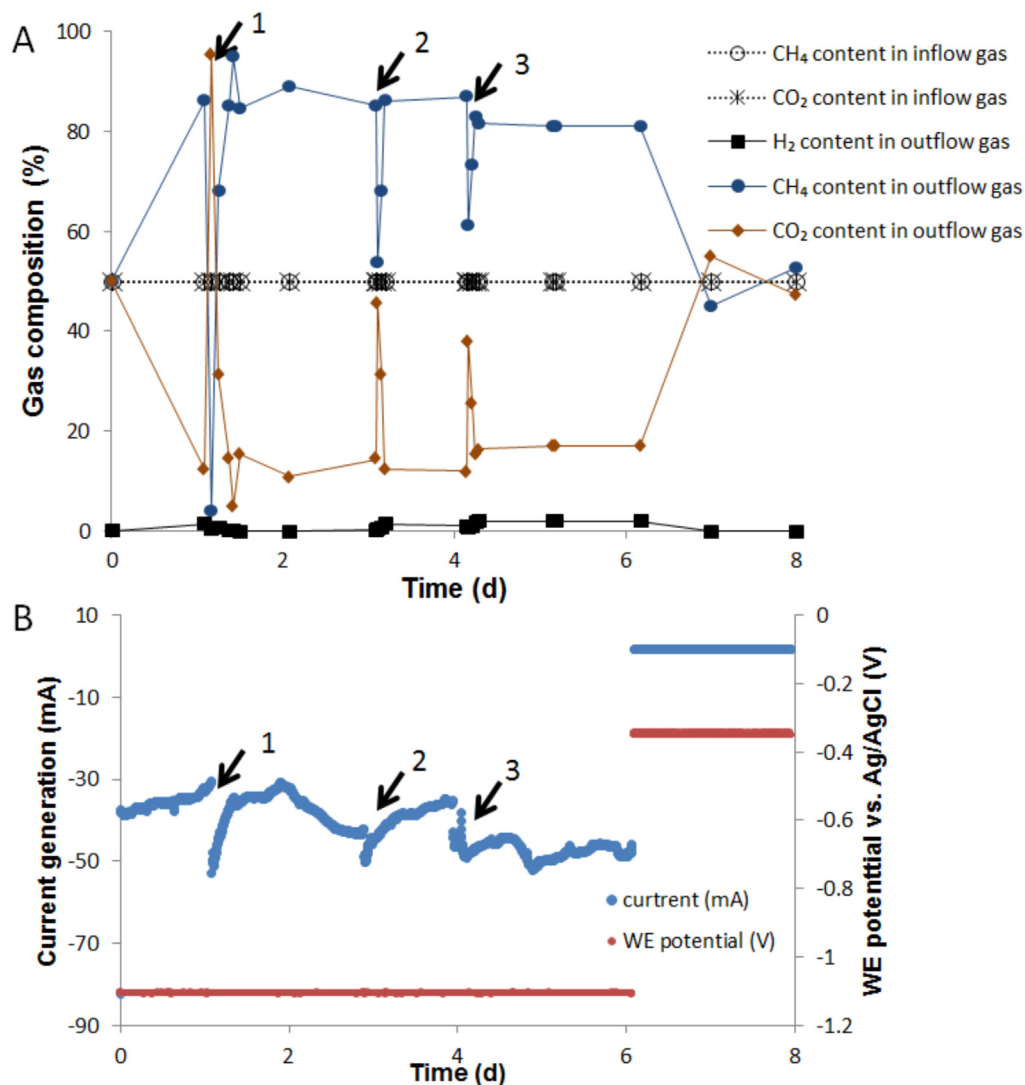


Fig. 5. Performance of BES reactor on CH₄ enhancement with constant flow and composition. (A) Gas composition in outflow gas; (B) Current generation (blue line) at a constant WE potential versus Ag/AgCl (red line). pH adjustment at arrows 1, 2, and 3.

biofilm), likely due to the lower availability of the key substrate hydrogen in the solution compared to the proximity of the cathode (where hydrogen was evolved). The overall results show that under thermophilic conditions, the growth of *Methanothermobacter* was favourable, leading to their high abundance recorded in the cathodic biofilm. So far only a few AD-BES integration studies have been carried out under thermophilic conditions, and the same finding was reported by Fu et al. (2015) that *Methanothermobacter* was the major group of archaea on the cathode that involved in CO₂ reduction to CH₄ [11].

3.5 Calculation of electron balance

To further investigate the relative CO₂ removal by bioelectrochemical conversion and catholyte trapping, an electron balance of the BES reactor was calculated. The data on day 6 from the experiment shown in Figure 5 was taken as an example for this calculation (Tab. 2). The total electron

(e⁻) flow was calculated from the current, and the theoretical CH₄ generated based on the e⁻ flow was estimated by considering that one CH₄ molecule accepts 8 electrons.

A second example from the experiment shown in Figure 3 shows the electron balance for different WE potentials by the same calculation (Tab. 3). When applying WE potentials at -0.9, -1.0 and -1.1 V, the actual CH₄ content in the outflow gas was higher than the theoretical contents. This may be attributed to CO₂ trapping in the BES reactor. However, when applying WE potential at -1.2 V, the actual methane content was less than the theoretical content. Upon inspection it was found that there was erosion on the anode that interfered with the BES reactor operation. Therefore, this condition was not considered technically feasible.

The results above show that CO₂ was both absorbed and bioelectrochemically converted to CH₄. In some cases, absorption was more predominant than conversion (Tabs. 2 and 3) and in other cases conversion was more predominant (Fig. S4). Based on the stoichiometry of the

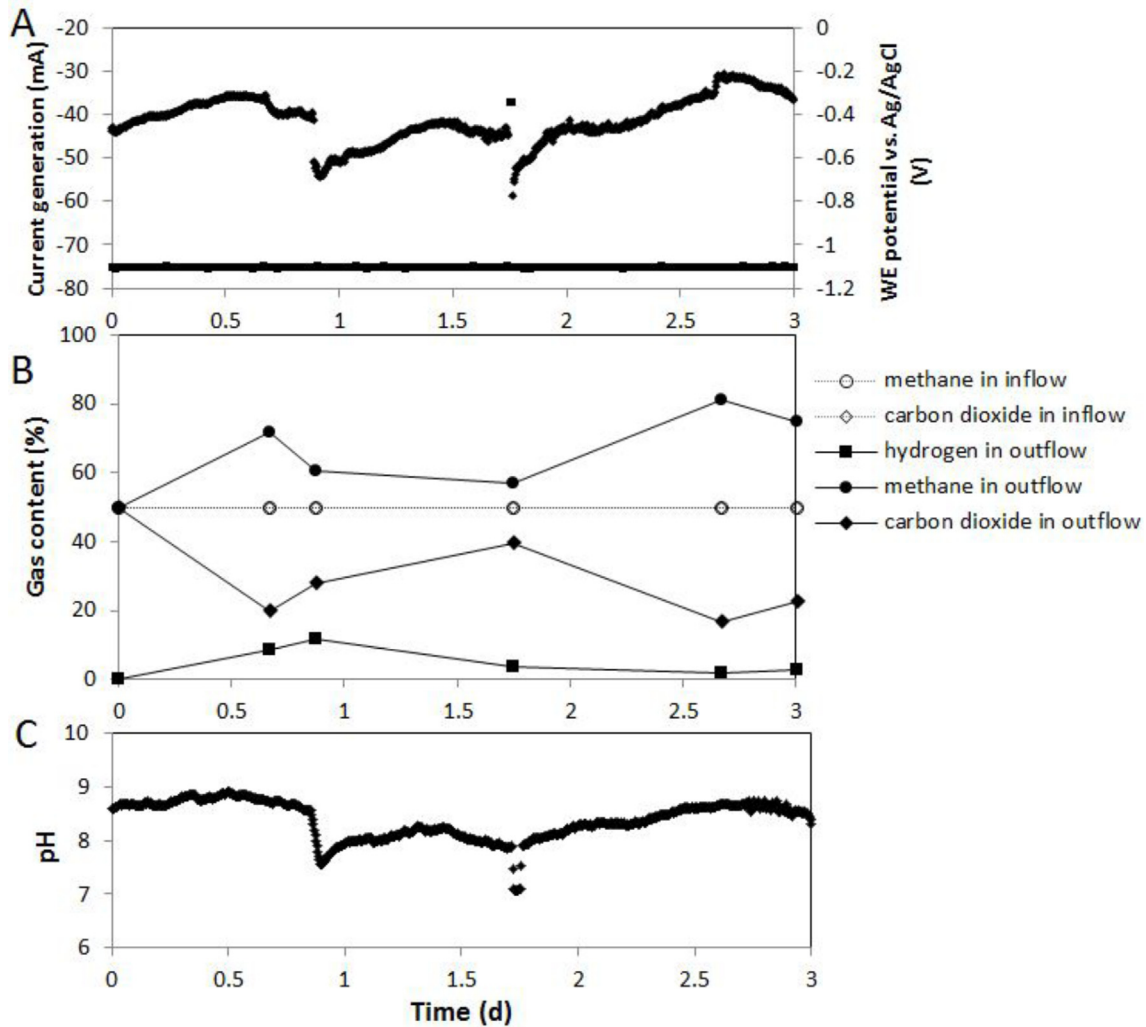


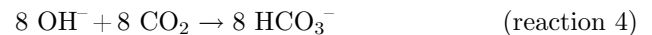
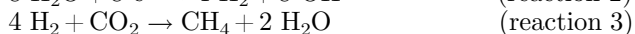
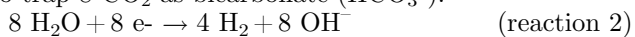
Fig. 6. Performance of cathodic biofilm on CH_4 enhancement. (A) Current generation at a constant WE potential (depicted as the horizontal straight line) of -1.1 V versus Ag/AgCl; (B) Gas composition after BES; (C) catholyte pH.

Table 1. The proportion of archaea with more than 0.1% abundance detected by the 16S Metabarcoding analysis in the microbial community.

Family	Genus	MG2 (%)	MG11 (%)	MG12 (%)	Substrate
Mathanobacteriaceae	Unidentified	0	0.3	0	NA
Mathanobacteriaceae	<i>Methanobacterium</i>	0	0.1	0.9	H_2 , CO_2 , formate
Mathanobacteriaceae	<i>Methanothermobacter</i>	0	10.3	0.2	H_2 , CO_2
Mathanomicrobiaceae	<i>Methanoculleus</i>	0	0	0.1	H_2 , CO_2 , formate
Mathanosarcinaceae	<i>Methanosarcina</i>	0.2	0.1	0	H_2 , CO_2 , acetate, methanol

Sample MG2: initial inoculum (thermophilic anaerobic sludge); MG11: carbon felt (cathode) in the BES reactor after 1-week of anaerobic digestion and 7 weeks of BES operation, and MG12 bulk solution in cathodic chamber after 1-week anaerobic digestion; NA = not applicable.

BES reactions (reactions 2, 3 and 4), 8 electrons are required for the conversion of 1 CO_2 into CH_4 , but it can also trap 8 CO_2 as bicarbonate (HCO_3^-).



According to this stoichiometry, CO_2 absorption can contribute up to 8 times more than the CO_2 conversion in methane upgrading (Fig. S5). The likely reasons why our experiments showed lower CO_2 absorption contribution

Table 2. Electron balance of the BES process (data derived from the day 6 operation as shown in Fig. 5).

	Unit	
Working volume	L	0.35
Gas inflow per reactor volume	L/L/d	3.4
Actual gas inflow	L/d	1.19
CH ₄ content	%	50
CH ₄ inflow	L/d	0.595
CH ₄ inflow	mmol/d	24.3
Current	mC/s	47.2
Electrons (e ⁻)	mmol/d	42.3
Extra CH ₄ from e ⁻	mmol/d	5.3
Extra CH ₄ from e ⁻	L/d	0.13
Theoretical CH₄ content ⁽¹⁾	%	61
Actual CH₄ content ⁽²⁾	%	80

(1) Theoretical CH₄ content calculated from reduction of CO₂ by electrons assuming no CO₂ was absorbed in the process; (2) Actual CH₄ content in the outflow gas.

Table 3. Electron balance at various cathodic (WE) potentials.

WE Potential	Actual CH ₄ inflow	Current	Extra CH ₄ from e ⁻	Theoretical CH ₄ content ⁽¹⁾	Actual CH ₄ content ⁽²⁾
V versus Ag/AgCl	L/d	mC/s	L/d	%	%
-0.9	0.44	2.1	0.005	61.1	69.0
-1.0	0.4	15	0.043 ⁻	63.8	88.6
-1.1	0.42	35.3	0.12	73.9	92.4
-1.2	0.44	81.2	0.22	90	85.9

(1) Theoretical CH₄ content calculated from reduction of CO₂ by electron assuming no CO₂ absorbed in the process; (2) Actual CH₄ content in the off-gas.

was due to the pH control carried out which neutralised the cathodic hydroxide (reaction 2) and minimised CO₂ trapping by absorption.

3.6 Analysis of energy balance

To determine the feasibility of our system for industrial application, we evaluated the net energy balance of the system. The data from the experiment shown in Figure 5 was used as an example for the evaluation. The energy efficiency of the system was evaluated by comparing the energy input (as invested electricity through the potentiostat) with energy output as the CH₄ produced from CO₂. The heating energy for maintaining thermophilic conditions (55 °C) and energy input for chemicals such as acid dosing was not considered in this calculation, as an insulated thermophilic BES would not need to be heated for treating the gas coming from a thermophilic AD. The results show that the energy input to operate the BES for 6 days was 102.3 kJ, and the final energy output as extra CH₄ was 57.1 kJ (Tab. 4). This suggests a 56% energy efficiency or a 44% energy loss during the energy conversion (i.e. from electrical to thermal combustion energy of CH₄).

To understand how the energetic performance of the tested process can be optimised, we attempted to determine the applied cell voltage at which the energy input (as electricity invested via the potentiostat) and the energy output (as the extra CH₄ produced via the bioelectrochemical conversion) can be balanced (i.e. 100% efficiency). When the cathode potential was poised at -1.1 V versus Ag/AgCl, and the current was 0.047 A (i.e. the settings reported in Sect. 3.7, Tab. 4), such a threshold cell voltage and the corresponding anode potential are 1.15 V and +54 mV versus Ag/AgCl, respectively (Fig. 7). Figure 7 also reveals that over 100% of energy efficiency may be achieved if the anodic potential of the BES could be maintained at below +54 mV versus Ag/AgCl. This suggests that effective strategies should be devised to lower the anodic potential. One such strategy could be to operate the anode as a bio-anode, whereby a suitable microbial culture is used for catalysing the anodic oxidation reaction. Suitable electron donors for the bio-anode would ideally be low value substrates contained in waste streams (e.g. wastewater or anaerobic digestate). This approach should be considered in future studies.

Table 4. Energy efficiency of the BES reactor.

Process parameter	Unit	Value
Time (t)	h	144
Average current (I)	A=C/s	0.047
Cell voltage (V)	V	4.2
Electrical energy ($V \cdot I \cdot t$)	Wh	28.4
Electrical energy input ($U \cdot I \cdot t$)	kJ	102.3
Gas inflow rate	L/h	0.050
Gas input	L	7.14
Methane input	L	3.57
Methane output	L	5.14
Extra methane produced	L	1.57
Heat of combustion of methane	kJ/L	36.4
Energy from extra methane	kJ	57.1
Energy efficiency	%	55.8

* Data from the first 6 days of experiment (Fig. 5) that WE potential was applied at -1.1 V; inflow gas – 50% methane and 50% CO_2 ; 1 mole of methane = 24.5 L; heat of combustion of methane = 891 kJ/mol.

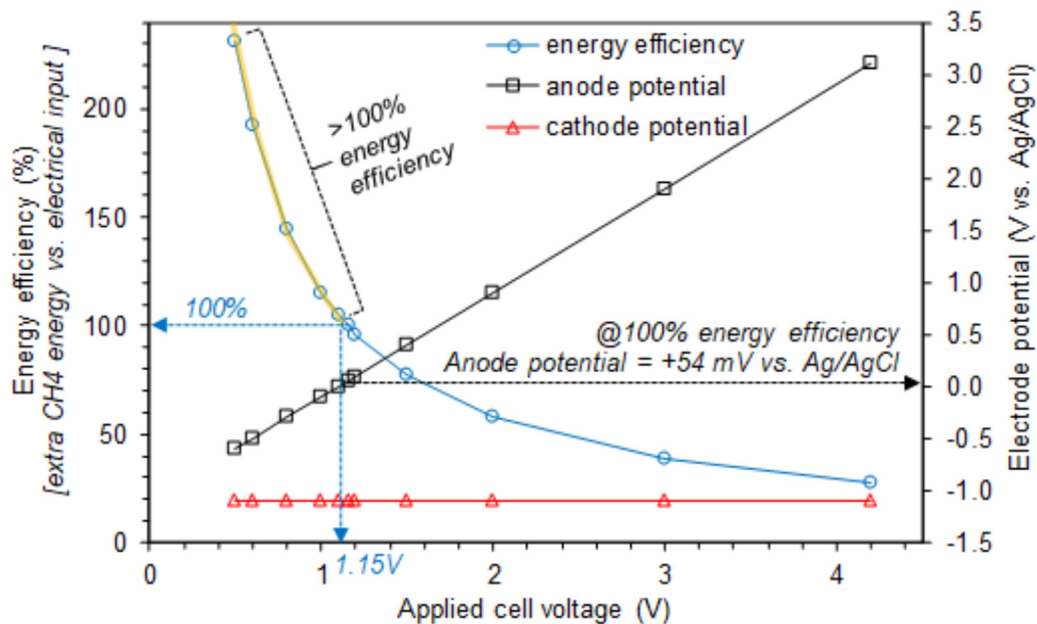


Fig. 7. Dependencies of the energy efficiency (primary y-axis) and anode potential (secondary y-axis) on the applied cell voltage of the BES process. The values were calculated using the set cathode potential of -1.1 V vs Ag/AgCl, and a current of 0.047 A (i.e. the settings used in Sect. 3.7, Tab. 4).

It should also be noted that the BES technology for biogas upgrading has only been explored in lab-scale, and no study has been conducted to optimise the energy efficiency of an *ex situ* BES reactor for biogas upgrading [12]. Hence, it would be meaningful to investigate how energy efficiency can be improved and to develop strategies for minimising energy losses (such as ionic losses) in this emerging biogas upgrading process.

4 Conclusions

Based on the results, the following conclusions are made: (1) biogas to biomethane conversion by using *ex situ* thermophilic BES reactor is theoretically and technically possible; (2) the operation of an *ex situ* BES CO_2 reduction system selectively enriched *Methanothermobacter* (95.4%) which was not detectable in the initial inoculum. Further

testing and optimisation of the BES reactor needs to be conducted, in particular with respect to replacing acid dosing by improved CO₂ absorption, as well as minimising the energy requirement of the process.

Supplementary Material

Figure S1: Microbial community analysis in the BES reactor at Phylum level. Only phylum comprising at least 0.1% relative abundances is shown, others are included in the “other” category.

Figure S2: Microbial community analysis in the BES reactor at Genus level. Only genus comprising at least 0.1% relative abundances is shown, others are included in the “other” category.

Figure S3: Comparison of outflow gas composition for the ex-situ BES reactor loaded with two different synthetic biogas compositions: (A) 50%/50% CO₂/CH₄; and (B) 100% CO₂.

Figure S4: Difference in the gas composition between the inflow and outflow of the BES reactor. (The values were determined from a 24-h period of continuous operation of the BES reactor).

Figure S5: Speculative mechanisms of CO₂ removal at the cathodic compartment of the ex-situ biogas conversion BES reactor.

The Supplementary Material is available at <https://www.rees-journal.org/10.1051/rees/2023009/olm>.

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