See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/327724210>

Membrane electrolysis-assisted CO₂ and H₂S extraction as innovative pretreatment method for biological biogas upgrading

Article · September 2018

DOI: 10.1016/j.ccej.2018.09.120

CITATIONS

0

READS

26

4 authors, including:

Kristof Verbeeck

Ghent University

7 PUBLICATIONS 62 CITATIONS

[SEE PROFILE](#)

Jo De Vrieze

Ghent University

54 PUBLICATIONS 870 CITATIONS

[SEE PROFILE](#)

Korneel Rabaey

Ghent University

297 PUBLICATIONS 18,940 CITATIONS

[SEE PROFILE](#)

Some of the authors of this publication are also working on these related projects:

REWATER [View project](#)

Steering medium chain fatty acids production from organic wastewater with electricity (Horizon 2020 Super-W Network) [View project](#)

Accepted Manuscript

Membrane electrolysis-assisted CO₂ and H₂S extraction as innovative pretreatment method for biological biogas upgrading

Kristof Verbeeck, Jo De Vrieze, Marie Biesemans, Korneel Rabaey

PII: S1385-8947(18)31837-0
DOI: <https://doi.org/10.1016/j.cej.2018.09.120>
Reference: CEJ 19959

To appear in: *Chemical Engineering Journal*

Received Date: 11 July 2018
Revised Date: 13 September 2018
Accepted Date: 17 September 2018

Please cite this article as: K. Verbeeck, J. De Vrieze, M. Biesemans, K. Rabaey, Membrane electrolysis-assisted CO₂ and H₂S extraction as innovative pretreatment method for biological biogas upgrading, *Chemical Engineering Journal* (2018), doi: <https://doi.org/10.1016/j.cej.2018.09.120>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Membrane electrolysis-assisted CO₂ and H₂S extraction as innovative pretreatment method for biological biogas upgrading

Kristof Verbeeck^[a], Jo De Vrieze^[a], Marie Biesemans^[a] and Korneel Rabaey^{*[a]}

^[a] Center for Microbial Ecology & Technology (CMET), Ghent University, Coupure Links 653, B-9000 Gent, Belgium

*Corresponding author: Korneel Rabaey; Ghent University; Faculty of Bioscience Engineering; Center for Microbial Ecology and Technology (CMET); Coupure Links 653; B-9000 Gent, Belgium; phone: +32 (0)9 264 59 76; fax: +32 (0)9 264 62 48; E-mail: Korneel.Rabaey@UGent.be; Webpage: www.cmet.UGent.be.

Kristof Verbeeck: Kristof.Verbeeck@UGent.be

Jo De Vrieze: Jo.DeVrieze@UGent.be

Korneel Rabaey: Korneel.Rabaey@UGent.be

Abstract

Turning raw biogas into biomethane as energy carrier requires the selective removal of CO₂ in a biogas upgrading process or a total conversion of CO₂ to CH₄ which is generally energy intensive. During membrane electrolysis, electrical energy can be used to simultaneously remove CO₂ (and H₂S) and produce H₂ as side product. Biogas is thus scrubbed with catholyte and the captured HCO₃⁻ and HS⁻ migrate towards the anode. Simultaneously, cathodic H₂ mixes with residual biogas in a ratio that can be fine-tuned. We obtained in one step an ideal 4:1 H₂:CO₂ ratio in the reactor off gas. Subsequently the gas could be further upgraded via chemoautotrophic microbial conversion of CO₂ to CH₄. Biomethanation delivered biomethane with 98.9 ± 0.9 % purity. The electrochemically-assisted scrubbing and stripping of CO₂ and H₂S resulted in high CO₂ removal efficiencies (up to 100%), without addition of chemicals. The system was flexible depending on temporarily available power. Electrochemical biogas upgrading (EBU) can be envisaged as a scalable and decentralized storage of excess or off-peak renewable power, making better use of the power input used to drive a biological CO₂ conversion.

Keywords

Biomethane; Anion exchange membrane; Power-to-gas; Hydrogenotrophic methanogenesis; Biogas desulfurization.

1. Introduction

Biogas is a mixture of mainly methane (CH_4) and carbon dioxide (CO_2), containing impurities, such as NH_3 , H_2S , water vapour and siloxanes. It is produced from organic substrates through anaerobic digestion, and represents a reliable and versatile renewable energy carrier that is mainly valorised as a fuel for on-site heat and power generation. Alternatively, biogas can be upgraded to natural gas quality, injected into the natural gas grid and used in all the downstream applications of fossil methane [1]. Raw biogas typically contains 40 - 75 % CH_4 and 25 - 60 % CO_2 , but to work as an efficient renewable energy carrier that can be stored and distributed within the existing natural gas grid, its CH_4 content typically needs to be increased to more than 97 % CH_4 , meeting the (local) quality standards for grid injection [2]. At industrial scale, the transformation of raw biogas into pipeline-quality 'biomethane' is nowadays performed by various physical-chemical techniques to separate CO_2 from CH_4 (e.g., water scrubbing, amine scrubbing, pressure swing adsorption, membrane technology or variants) [3, 4]. Recently, the chemoautotrophic microbial conversion of CO_2 to CH_4 was proposed as an innovative and sustainable method for biogas upgrading using renewable power [5, 6], particularly in the context of peak power shaving [7]. It is increasingly considered as a form of intermittent energy storage, whereby through electrolytic H_2 is used to convert CO_2 into additional CH_4 . The reduction of CO_2 to CH_4 relies on the action of hydrogenotrophic methanogens capable of using H_2 gas as sole electron donor for autotrophic CH_4 production ($\text{CO}_2 + 4 \text{H}_2 \rightarrow \text{CH}_4 + 2 \text{H}_2\text{O}$) [8]. For a complete (theoretical) removal of CO_2 from biogas, H_2 needs to be supplied at a stoichiometric ratio of 4:1 ($\text{H}_2:\text{CO}_2$), implying a demand of 8 moles of electrons for every mole of CO_2 that needs to be converted. The H_2 gas can be supplied either via bubbling through the anaerobic digester itself [9], in a separate biomethanation reactor [5, 10] or via in-situ electron or H_2 supply at a negatively poised electrode in a so-called bioelectrochemical system [11-13]. The low CH_4 production rates and efficiencies of this 'electromethanogenesis' route, compared to other CH_4 -producing technologies, currently hamper its feasibility as a high-rate biogas upgrading technology [14]. Furthermore, the low

conductivity of microbial growth media will limit the maximum current consumption (and thus the rate of upgrading), as cell potentials will increase rapidly due to high ohmic losses [15]. In this perspective, methanation of CO₂ and H₂ in a separate bioreactor seems to be the most straightforward way of scaling up biological biogas upgrading today. A challenge is the production of H₂ via water electrolysis, which makes methanation energy intensive (>7.2 kWh_e Nm⁻³_{raw biogas}) compared to conventional upgrading techniques (0.2 – 0.3 kWh_e Nm⁻³_{raw biogas}), but on the other hand it enables the use of renewable power to drive a biogas upgrading process without addition of chemicals, while storing renewable energy in a gaseous energy carrier [16].

Here we propose a combined electrochemical process, achieving simultaneous CO₂-H₂S scrubbing and H₂ production with the aim to lower the power input of biogas upgrading through a microbial conversion of CO₂ to CH₄. The Electrochemical Biogas Upgrading (EBU) process uses an electrochemical cell (EC) to achieve water electrolysis, leading to a high pH in the cathode (Figure 1). This enabled CO₂ and H₂S capture coupled to the active transport of (bi)carbonate and HS⁻ ions through an anion exchange membrane (AEM) towards an anode to maintain the cell electroneutrality (*i.e.*, the cell charge balance) (Eq.1). The gas leaving the cathode chamber is a mixture of H₂, CO₂ and CH₄, and can be further upgraded to biomethane in an external biomethanation reactor where the H₂ and CO₂ are converted into CH₄ (Eq.2). Additional H₂ could be supplied to this biomethanation reactor when power costs are low. From the anode, CO₂ will strip as a gas while it is expected that HS⁻ is oxidized to elemental sulphur or more oxidized S-species. This CO₂ removal strategy can be classified as a hybrid form of physical-chemical CO₂ scrubbing/stripping with H₂-mediated conversion of CO₂ to CH₄ as post-treatment to scavenge the produced H₂ and the residual CO₂, although other product outcomes based on CO₂-H₂ can also be envisaged.

We hypothesized that this approach makes better use of the power input as, theoretically, 9 moles of CO_2 can be removed per 8 moles of electrons supplied, while conventional biomethanation can only remove 1 mole CO_2 per 8 moles of electrons. This work presents a two-step pipeline for CO_2 -to- CH_4 based biogas upgrading, identifying the key operational parameters such as current density, pH and CO_2 loading rate on the electricity-driven extraction.

Figure 1 – Schematic reactor setup for electrochemical extraction of CO_2 (as HCO_3^- and/or CO_3^{2-}) and H_2S (as HS^- and/or S^{2-}) from a synthetic biogas stream ($\text{CH}_4:\text{CO}_2:\text{H}_2\text{S} - 60:39:1\%$). In the proposed pipeline, cathode off-gases could subsequently be upgraded further to biomethane in an external biomethanation reactor. Full black lines show liquid streams, dashed lines gas streams (---), and dotted lines electrical connections (.....). PS: power supply. AEM: anion exchange membrane. MFC: mass flow controller.

2. Experimental Procedures

2.1 Electrochemical reactor setup. The experimental setup comprised a two-chambered EC, constructed from two identical Perspex frames and plates, and separated by an AEM (Type II, Fujifilm Manufacturing, The Netherlands). The membrane was soaked in 5% NaCl for at least 24 hours prior to operation. Both electrode chambers had a working volume of 0.2 L (internal dimensions: $5 \times 20 \times 2 \text{ cm}^3$). The anode was a dimensionally stable iridium mixed metal oxide (Ir MMO) coated titanium-electrode mesh ($\text{TiO}_2/\text{IrO}_2$, 0.35/0.65, Magneto Special Anodes, The Netherlands). A stainless steel wire mesh of $5 \times 20 \text{ cm}^2$ exposed working area and $564 \mu\text{m}$ mesh width (Solana, Belgium) served as cathode. The membrane and electrodes had a projected surface area of 100 cm^2 (corresponding to $50 \text{ m}^2 \text{ m}_{\text{chamber}}^{-3}$). To limit the ohmic resistance, both electrodes were placed close to the membrane ($\pm 1 \text{ cm}$ between anode and cathode). Spacer material (turbulence promoter mesh, ElectroCell, Denmark) was used to prevent contact between the surface of the electrodes and the membrane.

2.2 Electrochemical reactor operation. Anolyte and catholyte were circulated from a 0.5 L Schott bottle to their respective compartment by a peristaltic pump at a recirculation rate of 4.8 L hr^{-1} . The recirculation bottles allowed compensation for water transport through the membrane, and ensured good gas-liquid separation. In both electrode chambers, the total working liquid volume was 0.5 L, including the liquid in the recirculation bottle, the electrochemical cell and tubing. The anolyte consisted initially of a 100 mM sodium sulphate solution, corrected to pH 2 with sulfuric acid. The absorption medium (referred to as catholyte) consisted of a 100 mM HEPES buffer solution with 100 mM sodium sulphate to ensure high electrolyte conductivity ($20.6 \pm 0.5 \text{ mS cm}^{-1}$). The solution was adjusted to pH 7 with NaOH. During experimental operation, the pH of both electrolytes was not controlled. All experiments were performed in a temperature controlled room of $20 \pm 1^\circ\text{C}$. A range of biogas flow rates to the cathode and applied current densities were tested to assess EC performance for CO_2 and H_2S removal. Synthetic biogas with

60 % CH₄ and 40 % CO₂ or 60% CH₄, 39 % CO₂ and 1 % H₂S (Linde Gas Benelux) was used to simulate real biogas. A mass flow controller (Bronkhorst, The Netherlands) was used to inject the desired biogas flow rate at the bottom of the cathode compartment. A ceramic sparger was used to produce fine biogas bubbles. Calibrated semi-open gas columns or in-house constructed gas meters with oil displacement were used to measure the flow rate of both cathode and anode off-gas.

2.3 Electrochemical experiments. The EC was controlled galvanostatically by a power source (DC Lab Power Supply, Velleman, Belgium). The cell was operated as a two-electrode setup in water electrolysis mode. The presumed anode and cathode reactions were the oxidation ($2 \text{ H}_2\text{O} \rightarrow 4 \text{ H}^+ + \text{O}_2 + 4 \text{ e}^-$) and reduction of water ($2 \text{ H}_2\text{O} + 2 \text{ e}^- \rightarrow \text{H}_2 + 2 \text{ OH}^-$), respectively. The applied current was reported as current density, and was defined as the set current divided by the exposed surface area of the membrane (100 cm²). Flux characterization was performed at eight different fixed current densities (20 - 400 A m_{membrane}⁻²), under three different volumetric biogas flow rates (25 ± 1 , 50 ± 2 and $100 \pm 2 \text{ L}_{\text{biogas}} \text{ d}^{-1}$). For each biogas flow rate, open circuit experiments were executed for 2 days to investigate diffusion-driven CO₂ transport through the membrane. Closed circuit extraction experiments were performed at least 3 hours in steady state conditions, and were executed in triplicate reactor runs. Gas samples were taken from the gas leaving the recirculation bottles. Liquid samples were taken from sampling ports in the recirculation loop of the reactor.

2.4 Biomethanation batch experiments. Batch biomethanation tests were set up to determine the potential of a pre-enriched anaerobic microbial inoculum to produce CH₄ from the cathode-off gas mixtures (H₂/CO₂/CH₄) originating from the EBU process. The original inoculum was obtained from anaerobic sludge harvested from a lab-scale mesophilic anaerobic digester that was fed for several months with waste activated sludge from a sewage treatment plant. The sludge was diluted 5 times in anaerobic modified *Methanobacterium* medium (1 L Scott bottle with 0.2 L medium), and the headspace

was repeatedly (at least 2 times per week) flushed with $\text{H}_2\text{:CO}_2$ (70:30 %, v/v) at 0.7 - 0.9 bar overpressure for 2 months.

The enrichment experiments were conducted in serum bottles (120 mL) filled with 30 mL anaerobic growth medium. The modified *Methanobacterium* medium did not contain any organic compounds to enrich for autotrophic methane formation. The composition of the growth medium is provided in Supporting Information (SI.1). Each serum flask was inoculated with 10 mL of the pre-enriched methanogenic culture. The inoculum biomass accounted for 2 g VS L⁻¹. All experiments were performed in triplicate. At day 0, the headspace was flushed for 15 min with the $\text{CH}_4/\text{CO}_2/\text{H}_2$ mixture coming from the EBU reactor. All incubations were done at 37°C on a rotary shaker maintained at 100 rpm. The upgrading tests were performed for two different gas compositions: 4:1 and 2:1 ratio of $\text{H}_2\text{:CO}_2$. The headspace gas composition and pressure were monitored on a daily basis for 4 days.

2.5 Chemical analyses. Conductivity and pH were measured using a Consort EC and pH electrode respectively (Consort, Turnhout, Belgium). Gas samples were analyzed for the presence of O_2 , N_2 , CH_4 , H_2 and CO_2 by a Compact GC (Analyser Solutions, Breda, The Netherlands), as described in Supplemental Information (SI.2). Measurements of the bicarbonate concentration in anode and cathode were made by adding 1 mL of electrolyte to a vacuum tube containing 1 mL 1 M H_2SO_4 . After intensive mixing (200 rpm, 1 min), the headspace CO_2 was determined using the Compact GC. Using a standard curve, bicarbonate concentration could be determined from the vacuum tube CO_2 content. The total gas pressure in the serum bottles was measured using a UMS-Tensiometer (Infield 7). Liquid samples were immediately preserved in a Sulphide Antioxidant Buffer solution prior to analysis following Keller-Lehmann et al [17]. Sulphide, sulphite (SO_2^{-3}) and thiosulfate ($\text{S}_2\text{O}_2^{-3}$) concentrations were measured by ion chromatography (IC), using an IC930 compact Metrohm IC system (Metrohm, Switzerland). The eluent consists of 3.5 mM Na_2CO_3 and 3 mM NaHCO_3 at a flow rate of 0.8 mL min⁻¹. A 0.1 M NaOH solution is used to produce a pH

gradient needed for $\text{S}_2\text{O}_2^{-3}$ detection in the IC system. To measure the polysulfide and elemental sulphur (S^0) concentrations, all sulphur species were oxidized to SO_4^{2-} with excess H_2O_2 [18]. The difference in sulphur equivalent between the sulphate after H_2O_2 oxidation and other species measured before H_2O_2 oxidation (i.e. sulphide, sulphate, thiosulfate and sulphite) was regarded as the sum of polysulphides and elemental sulphur.

2.6 Calculations and data representation. The CO_2 and H_2S flux, CO_2 and H_2S removal efficiency, current efficiency for HCO_3^- and HS^- extraction, $\text{H}_2:\text{CO}_2$ ratio after EC treatment and power input were calculated to assess EBU performance. The methane production rate and gas composition were used to evaluate the biomethanation of the residual CO_2 in the EBU off-gas. Gas volumes are reported at standard temperature and pressure conditions (273 K; 101325 Pa). The CO_2 flux is defined as the volume of CO_2 that crosses the AEM as CO_2 , HCO_3^- or CO_3^{2-} per m^2 of membrane surface per day ($\text{L CO}_2 \text{ m}_{\text{membrane}}^{-2} \text{ d}^{-1}$). The membrane flux was calculated based on a CO_2 mass balance over the membrane and cathode chamber. The CO_2 removal efficiency ($\text{L CO}_2 \text{ removed L}^{-1} \text{ CO}_2 \text{ supplied}$) is measured comparing the cathode off-gas CO_2 concentration with the CO_2 content of the synthetic biogas (40 %). Current efficiency refers to the molar fraction of bicarbonate transferred across the membrane per mole of electrons supplied at the cathode (mole CO_2 extracted $\text{mole}^{-1} \text{ e}^-$ supplied). Off-gas composition (in particular the $\text{H}_2:\text{CO}_2$ ratio, v/v) is used to evaluate the ability of the electrolyzer to generate a stoichiometric 4:1 gas mixture. Power input is reported both as kWh per $\text{Nm}^3 \text{ CO}_2$ extracted and Nm^3 raw biogas treated, and reflects the electrical input to drive the extraction. Formulas used to calculate flux, efficiencies and power input are given in the Supplemental Information (SI.3).

3. Results and discussion

3.1 High CO₂ fluxes enable high-rate biogas upgrading

Synthetic biogas was injected into the cathode compartment of the EC to determine the operational parameters that drive the electricity-driven extraction of CO₂ across the membrane. The CO₂ flux characterisation was performed at various CO₂ loading rates (1000, 2000 and 4000 L CO₂ m⁻²_{membrane} d⁻¹), at current densities from 0 to 400 A m⁻² projected membrane surface. By direct injection of biogas in the cathode chamber of the EC, CO₂ is absorbed in the (slightly) alkaline catholyte, extracted across the AEM towards the anode and stripped in the low pH anolyte. Hydroxyl ions generated at the cathode prevent a pH decrease in this cathode compartment as a result of the dissolution of CO₂, while the anodic proton production is used to keep the anode acidic, resulting in a continuous driving force for membrane extraction. The added, high-molecular-weight buffer stabilizes the catholyte pH.

In open circuit conditions (no current), the diffusional (concentration-driven) flux of CO₂ across the membrane was 13 ± 2 L CO₂ m⁻² d⁻¹, accounting for only 5 ± 1 % of the flux at the lowest current density tested, 20 A m⁻² (Figure 2). No effect of the biogas flow rate on this diffusional CO₂ flux was observed. In the absence of current, only 0.3 – 1.5 % of the incoming CO₂ was removed from the biogas (Figure 3), indicating that passive transport of CO₂ gas, dissolved CO₂, carbonic acid and the deprotonated species (HCO₃⁻ and CO₃²⁻) through the membrane was limited, and that electromigration was the dominant process for CO₂ removal.

Figure 2 – Effect of the biogas loading rate and applied current density on the CO_2 flux across the anion exchange membrane (in $\text{L CO}_2 \text{ m}^{-2} \text{ d}^{-1}$). The dotted lines indicate 100% current efficiency for HCO_3^- transfer to the anode in function of the applied current density. Symbols: triangle, CO_2 loading rate of $1000 \text{ L CO}_2 \text{ m}^{-2} \text{ d}^{-1}$; diamond, $2000 \text{ L CO}_2 \text{ m}^{-2} \text{ d}^{-1}$ and circle, $4000 \text{ L CO}_2 \text{ m}^{-2} \text{ d}^{-1}$. The flux characterisation indicates that the extraction rate of CO_2 strongly correlated with both applied current and biogas flow rate, and that the non-linearity in the flux profile is caused by CO_2 limitations and CO_2 scrubbing/extraction losses. Averages of three samples over steady state are reported with standard deviation.

Figure 3 – The removal efficiency for CO_2 in function of the applied current density at different CO_2 loading rates (1000 , 2000 and $4000 \text{ L CO}_2 \text{ m}^{-2} \text{ d}^{-1}$). The dotted lines represent the removal at 100% current efficiency for HCO_3^- transfer to the anode for the different CO_2 loading rates (coded for each biogas flow rate). The CO_2 removal indicates that a complete removal of CO_2 from the biogas stream is possible, but

at much higher current densities than at maximum extraction rate. Averages of three samples over steady state are reported with standard deviation.

At a loading rate of $2000 \text{ L CO}_2 \text{ m}^{-2} \text{ d}^{-1}$, the flux of CO_2 was $1387 \pm 67 \text{ L m}^{-2} \text{ d}^{-1}$ at 100 A m^{-2} (Figure 2), corresponding to a current efficiency (CE) of $64 \pm 3 \%$ (Figure 4). It is important to stress that current efficiency is not the key parameter: a low current efficiency can be beneficial to achieve optimal H_2/CO_2 ratios. At 400 A m^{-2} and a loading rate of $4000 \text{ L CO}_2 \text{ m}^{-2} \text{ d}^{-1}$, a maximum CO_2 flux of $3577 \pm 314 \text{ L m}^{-2} \text{ d}^{-1}$ was achieved, corresponding to a removal of $85 \pm 4 \%$ of the incoming CO_2 (Figure 3). The CO_2 flux was maximized at high applied current density and high CO_2 loading rate. For any set CO_2 loading rate, the CO_2 flux increased with increasing current density, with the applied CO_2 loading rate as the maximum flux rate. Since the maximum theoretical CO_2 flux across the membrane is limited by the electron flow rate from anode to cathode, the electromigrational flux of (bi)carbonate ions could only be increased by increasing the applied current, assuming that both the loading and dissolution rate of CO_2 are not limiting the extraction. For current densities of $20 - 100 \text{ A m}^{-2}$, the CO_2 flux increased linearly with the current density, whereas above 100 A m^{-2} fluxes levelled off to the respective maximum flux of CO_2 (Figure 3). The clear decrease in flux at lower CO_2 loading rates is mainly due to carbonate depletion in the catholyte at higher currents or lower biogas sparging rates. A high dissolved HCO_3^- concentration, thus, needs to be maintained in the catholyte. As full CO_2 removal from the biogas is typically not the aim, this situation should generally be the case.

Figure 4 – Influence of the applied current density on the current efficiency (CE) for HCO_3^- transfer to the anode chamber at different fixed CO_2 loading rates. The dotted line represent 100 % charge balancing by the HCO_3^- ion. At current densities under 100 A m^{-2} , CEs up to 80 % were observed. If no CO_2 limitation occurs, high CE can be achieved, even at high current densities. Averages of three samples over steady state are reported with standard deviation.

The removal efficiency for CO_2 increased with increasing current density, whereas higher biogas loading rates implied lower removal (Figure 3). The complete removal of CO_2 from the biogas ($\text{RE} = 100 \pm 2 \%$) was achieved at 200 A m^{-2} , $1000 \text{ L CO}_2 \text{ m}^{-2} \text{ d}^{-1}$ and 300 A m^{-2} , $2000 \text{ L CO}_2 \text{ m}^{-2} \text{ d}^{-1}$. For the highest loading rate tested, $4000 \text{ L CO}_2 \text{ m}^{-2} \text{ d}^{-1}$, complete removal of CO_2 could not be achieved for current densities of 20 - 400 A m^{-2} .

The CE for CO_2 extraction decreased with increasing applied current densities and decreasing biogas loading rates (Figure 4), with the highest CE, $81 \pm 5 \%$, observed at 20 A m^{-2} , $4000 \text{ L CO}_2 \text{ m}^{-2} \text{ d}^{-1}$, and the lowest CE, $23 \pm 1 \%$, observed at 400 A m^{-2} , $2000 \text{ L CO}_2 \text{ m}^{-2} \text{ d}^{-1}$. The CE increase at higher CO_2 feeding rates corresponds to higher molecular availability of the target anion (HCO_3^-) in the bulk, thereby avoiding CO_2 transport limitations. The higher molar concentration of HCO_3^- at higher CO_2 feeding rates is due to the combined effect of a lower cathode pH (neutral) and a higher gas-liquid CO_2 mass transfer. At high applied

currents, the current use for CO₂ extraction was limited by this CO₂ transfer, as confirmed experimentally by low concentrations of carbonate species in the catholyte (data not shown). It was demonstrated that by increasing the biogas flow and, thus, buffer load, the pH increase in the cathode due to the hydroxyl production could be lowered (Figure A.1), which eventually resulted in a higher relative contribution of HCO₃⁻ to the charge balance. The cathode pH increased from 7.0 ± 0.2 at open circuit conditions to 12.4 ± 0.1 and 10.5 ± 0.5 at 400 A m⁻² and 2000 and 4000 L CO₂ m⁻² d⁻¹, respectively, showing that the buffer capacity of HEPES is not able to stabilize pH. The pH increase results in a 10³ - 10⁵ fold increase in the concentration of hydroxyl ions that then compete with (bi)carbonate transport, thus reducing the CE of HCO₃⁻ (OH⁻ has a higher ion mobility than carbonate species: 20.64 × 10⁸ versus 7.18 × 10⁸ m² s⁻¹ V⁻¹). Furthermore, the proportion of bicarbonate ions in the total dissolved inorganic carbon decreases at higher pH. The distribution of carbonate species at a given pH can be derived from the Henderson-Hasselbach equation. At a cathode pH of 12.4, CO₃²⁻ accounts for 99 % of the total dissolved carbonate, whereas at pH 10.5 the degree of dissociation was only 60 % (40 % HCO₃⁻). As CO₃²⁻ is a bivalent anion, the theoretical CO₂ flux carried by CO₃²⁻ is only half of the maximum flux carried by HCO₃⁻ (assuming equal ion transport numbers for both species). The CE decrease at higher current density is an apparent effect of this, as it is mostly linked to the higher relative contribution of CO₃²⁻ in the charge balance. It should be recognized that at high pH the current carried by carbonate species was drastically underestimated when represented by the CE for HCO₃⁻ extraction. It is also likely that the participation of protons in balancing the electron flux (backflux over AEM) increased at higher current density, due to a decreasing pH of the anolyte [19]. Our observation that the membrane flux rate is closely linked with the relative molar concentration of the different species in the broth has been described in previous work involving membrane electrolysis [19, 20].

Considering only the membrane transport of carbonate species, a neutral cathode pH seems to be more favourable than a high pH, but since the extraction is highly dependent on the CO₂ mass transfer from

biogas to catholyte, the kinetics of CO₂ dissolution, hydration and dissociation are crucial to take into account as well. The CO₂ hydration reaction, yielding carbonic acid, is kinetically relatively slow (slower than the ionization of carbonic acid), and proceeds much faster at higher pH, as CO₂ reacts directly with OH⁻ to form bicarbonate (hydroxylation reaction: CO_{2,aq} + OH⁻ = HCO₃⁻) [21]. The absorption rate of CO₂ is strongly affected by the pH of the solution, since the Henry constant is a function of pH (affecting the solubility of CO₂ in solution) [22]. Additionally, the mass transfer coefficient plays a major role in the absorption rate of CO₂ [23], highlighting the need for the design of effective scrubbers (bubble column, sieve tray column, packed bed column) [24]. The mass transfer coefficient was not optimized in this study, but it is expected that significant improvements can be obtained by increasing the retention time and decreasing the bubble size of the biogas (higher gas–liquid interfacial area) [25]. Another way to enhance the CO₂ water absorption rate is to increase the CO₂ partial pressure and, hence, solubility in the water, by increasing the operating pressure in the electrochemical cell. There is no need to compress the biogas prior to injection in the cathode, since, theoretically, the auto-generative pressure of the electrolyzer can be used to pressurize the biogas. High-pressure electrolysis is already performed at full-scale up to a H₂ pressure of 700 bar [26]. To obtain a full understanding of the reactor performance at set conditions, and the influence of varying conditions (biogas composition, flow rate, current, pressure, cathode pH, anode pH, etc.) on the (non-linear) reactor behaviour, a mass transfer model including CO₂ chemistry and electrochemical reactions could give more insight in the process.

3.2 H₂:CO₂ ratio can be optimized by selection of an appropriate current density and CO₂ loading rate.

During fixed current operation, CO₂ is removed while H₂ is added to the biogas. The process described here is, thus, not relying on complete CO₂ removal, as it will downstream be converted to the product of interest, *i.e.* biomethane. The composition and flow rate of the biogas after electrolysis is highly dependent on the operational conditions. For experiments with a CE higher than 50 %, a net decrease in

the biogas flow rate (out versus in) was observed, since more than one mole of CO_2 is removed per mole of H_2 gas formed (requiring 2 moles electrons). At higher currents (often $\text{CE} < 50\%$), a net increase in the biogas flow rate was achieved, due to the high H_2 production rate. The relative composition of off-gas mixture for the different biogas flow rates is shown in Figure A.2. At 400 A m^{-2} and $4000 \text{ L CO}_2 \text{ m}^{-2} \text{ d}^{-1}$, the CO_2 content was reduced to 5.2% , while 33.8% of the gas mixture was H_2 , leading to a $\text{H}_2\text{:CO}_2$ ratio of $7\text{:}1$. Biomethanation of this $\text{H}_2\text{-CO}_2$ mixture will allow to convert all CO_2 into CH_4 , but as there is a stoichiometric excess of reducing equivalents, the final biomethane will still contain residual H_2 . Since H_2 concentrations in most European natural gas grids can vary between 0.1 and 6% , 100% conversion is not necessary [27], but evidently excess H_2 comes at a cost. Alternatively, additional CO_2 -rich biogas can be added to the biomethanation reactor. Theoretically, pure CH_4 can only be produced if the EC step generates a gas mixture with a $\text{H}_2\text{:CO}_2$ ratio close to $4\text{:}1$, the stoichiometric ratio needed to convert all CO_2 into CH_4 [8]. A ratio of $3.5\text{:}1$ was achieved at $1000 \text{ L CO}_2 \text{ m}^{-2} \text{ d}^{-1}$, 80 A m^{-2} and $4000 \text{ L CO}_2 \text{ m}^{-2} \text{ d}^{-1}$ and 300 A m^{-2} (Figure 5). At lower current densities the H_2 production and CO_2 removal rate were not high enough to obtain the ideal $\text{H}_2\text{:CO}_2$ ratio, as there was an excess of CO_2 relative to H_2 . At higher current densities more H_2 was available than needed to convert all CO_2 to CH_4 . In the EC system, biogas flow rate and current density can be adjusted to control the $\text{H}_2\text{:CO}_2$ ratio to optimize the overall upgrading capacity.

Figure 5 – The $\text{H}_2:\text{CO}_2$ ratio of the biogas leaving the electrochemical cell at different fixed current densities and CO_2 loading rates: an ideal 4:1 $\text{H}_2:\text{CO}_2$ ratio can be achieved by the appropriate selection of current density. The dotted line represent the stoichiometric ratio for biomethanation. Averages of three samples over steady state are reported with standard deviation.

3.3 CO_2 stripping at the anode results in stable operation.

The operational stability and reproducibility of the current-driven extraction of CO_2 was evaluated over an experimental period of 48 hr (100 A m^{-2} , $2000 \text{ L CO}_2 \text{ m}^{-2} \text{ d}^{-1}$). The experiment exhibited stable performance, since CO_2 was absorbed in the catholyte, extracted through the AEM and stripped from the anolyte proportionally with incoming CO_2 . The bulk pH in the cathode compartment was stable throughout the experimental run (10.0 ± 0.1), enabling constant hydroxyl ion and carbonate species distribution and concentration (Figure A.3). The extraction of a gaseous compound through the liquid phase has the advantage that its extraction does not suffer from end-product accumulation in the acid anode chamber, as described for extraction of carboxylates [19]. Anodic (bi)carbonate measurements showed that no (bi)carbonate accumulation was observed, thereby enabling extraction at a constant efficiency. The protonation of (bi)carbonate in the anolyte ($\text{pH } 1.5 \pm 0.5$) and the rapid dehydration of H_2CO_3 resulted in efficient stripping of CO_2 from the anolyte. The off gas had a $55.0 \pm 5.0 \%$ CO_2 content,

the remainder was 44.8 ± 5.0 % O_2 and 0.2 ± 0.1 % H_2 . Since only a small portion of the aqueous CO_2 exists as H_2CO_3 (< 0.3 %), little CO_2 is expected to pass back across the AEM. Both absorption and stripping processes are, thus, driven by pH, which is steered by the reduction and oxidation of water in the absorption and stripping solutions. The extraction drives the hydration and ionization of CO_2 by continuous removal of the dissociation products (Le Chatelier's principle).

This experimental run also served to check if mass was conserved in the system (Figure A.3). Therefore, the gas flow rate and composition of both anode and cathode off-gases were measured. No measurable CH_4 transfer across the membrane was detected, indicating no significant CH_4 slip towards the anode. A mass balance over the cathode chamber also confirmed that no CH_4 was lost through tubing, sampling ports and connectors. Taking all experiments with synthetic biogas into account, the average CO_2 mass balance under closed current conditions was 88 ± 3 %. The small gap in the balance was likely due to CO_2 loss in the anode chamber and measurement errors (flow rates, concentrations).

The transport of water due to electro-osmosis, the motion of water through a membrane as a consequence of current-driven ion transport, was observed and showed (linear) current dependency. At $400 A m^{-2}$, a water flux of $2.5 L m^{-2} d^{-1}$ was observed, indicating a considerable water loss from the cathode solution. For the purpose of the process, the excess anode effluent could just be sent to the cathode, balancing everything out without impacting the system in a major way (the cathode pH would benefit somewhat from a lowering in many cases).

The required cell potentials were stable over time. The cell potential was dependent on the applied current density, and varied from 2.51 to 6.47 V (Figure A.4). The power input needed to drive the CO_2 flux was determined by the voltage input together with the extraction efficiency, and ranged from 3.73 to 17.38 kWh per Nm^3 CO_2 removed from the biogas. The power input increased with increasing applied current (increasing voltage) and decreasing CO_2 loading (decreasing extraction efficiency). It has to be mentioned that both the flux and voltage input could be optimized to reduce the power input, which

relates more to the design and operation of the electrolysis cell, including selection of electrolytes, electrodes, membrane, mixing and biogas injection strategies. The cell potential can be reduced substantially when switching to highly conductive electrolytes [28]. The use of biocatalysed electrodes (so-called bio-anodes and bio-cathodes) has often been described as a way to reduce overpotentials of electrode reactions. The use of a bio-anode to provide the electrons for electrochemical bicarbonate extraction indeed showed a low operating cell voltage (1.2 V) [29], but in terms of biogas upgrading rates and scalability the pure electrochemical extraction as described here currently seems to be closer to practical implementation.

Optimizing the system requires a compromise between power input (operational cost) and CO₂ removal (upgrading). The ideal working point should be defined via an in-depth energy assessment and further process development. Our study already revealed that achieving low residual CO₂ concentrations in the off-gas requires a proportionally higher applied current, which in turn leads to an increase in the power input for upgrading. However, in the combined EC - biomethanation approach, no 100% removal of CO₂ is needed, thereby avoiding the high energy losses associated with removal of residual CO₂. It should be recognized that in a fully realized system higher current densities than achievable in the presently used setup are preferable. However, the cell potential (and thus the power input) is expected to increase further at these current densities, unless the aforementioned interventions can alleviate this.

3.4 Simultaneous H₂S removal from biogas

At a fixed current density of 100 A m⁻², 100 ± 1 % of the incoming H₂S was scrubbed from the biogas (at a biogas feeding of 25 L d⁻¹, corresponding to a H₂S loading rate of 25 L H₂S m⁻² d⁻¹). When the H₂S loading rate was increased to 100 L H₂S m⁻² d⁻¹, the H₂S removal efficiency was 98 ± 1 % at an applied current density of 300 A m⁻², corresponding to a residual H₂S content of 160 – 180 ppmv after EBU. To meet the

gas quality standards, the H_2S concentration must be limited to values $< 5 \text{ mg H}_2\text{S Nm}^{-3}$ (or 3.6 ppmv) [30].

It should however be recognized that typical concentrations of H_2S in biogas are of approximately 1000 ppmv rather than the 10000 ppmv tested [31], indicating that desulphurization via EBU (without post-treatment) should be feasible. Moreover, the passage through the biomethanation reactor should further decrease H_2S through scrubbing and consumption of H_2S by methanogens.

The HS^- concentration in the absorption solution remained stable and low during closed circuit operation ($0.4 - 3.2 \text{ mg HS}^- \text{ L}^{-1}$), indicating that the extraction is continuously removing sulphide from the scrubbing liquid. Current use for extraction of sulphide was in between 1.5 – 7 %. At 100 A m^{-2} and a H_2S loading of $25 \text{ L m}^{-2} \text{ d}^{-1}$, $100 \pm 1 \%$ of the sulphide that crossed the AEM was converted, indicating rapid oxidation of sulphide species in the acid anolyte. When the biogas flow rate was increased (to $100 \text{ L H}_2\text{S m}^{-2} \text{ d}^{-1}$), the sulphide conversion efficiency in the anode dropped to 70 %, while 30 % of the sulphide coming over the membrane was stripped off in the acid anolyte, leaving the anode chamber as H_2S ($\text{pH}_{\text{anolyte}} < \text{pK}_a (\text{H}_2\text{S}/\text{HS}^-) = 6.9$) (S-mass balance in SI, Figure A.5). Quantification of the sulphide oxidation products via IC showed that sulphate was the main oxidized sulphur specie and that no elemental sulphur or polysulphide was formed. The indirect oxygen mediated oxidation of sulphide appears to be the most plausible mechanism because the low pH of the anolyte results in a fast stripping of the extracted sulphide, obstructing the direct anodic oxidation. Overall, the H_2S removal rates showed that even in acid conditions sulphide can be converted. Residual H_2S in the gas could be catalytically reacted with the O_2 downstream to obtain a likely pure elemental sulphur.

3.5 Biomethanation of EBU off-gases

Abiotic (uninoculated but with $\text{CH}_4/\text{CO}_2/\text{H}_2$ headspace) and biotic (inoculated but no $\text{CH}_4/\text{CO}_2/\text{H}_2$ headspace) control experiments were conducted for one week, but did not result in production of methane or the removal of CO_2 from the headspace. The off-gas from two different EBU runs, one

delivering a gas mixture with a non-ideal ratio of 2:1 $\text{H}_2\text{:CO}_2$ (at 100 A m^{-2} and $2000 \text{ L m}^{-2} \text{ d}^{-1}$) and one with a stoichiometric ratio of 4:1 (at 60 A m^{-2} and $1000 \text{ L m}^{-2} \text{ d}^{-1}$) were added as headspace in inoculated serum flasks. In all flasks, the concentration of H_2 and CO_2 decreased, and additional CH_4 was produced (Figure 6). Starting with a 4:1 ratio resulted in an ultimate CH_4 content of $98.9 \pm 0.9 \%$, and all H_2 was consumed after 3 days. The residual amount of CO_2 accounted for $1.1 \pm 0.9 \%$, showing good removal properties. This gas quality complies with the tightest standards for grid injection without the need for additional CO_2 removal. If started from a 2:1 ratio, no complete CO_2 conversion took place (still $7.1 \pm 1.6 \%$ CO_2 after 3 days), as H_2 was the limiting reagent in the biomethanation process. These observations match with a reported optimum H_2/CO_2 ratio between 3.67 and 4.15 [8, 32].

The successful bioprocess development of biological methanation will largely depend on the (volumetric) H_2 conversion rate/ CH_4 productivity of a pure or enriched culture of hydrogenotrophs, since this will determine the biogas upgrading capacity of the bioreactor. As H_2 transfer from the gas to the liquid is known to be the rate limiting step in the biomethanation process [33], H_2 gas-liquid mass transfer is the most important criterion when selecting or designing the bioreactor. Different reactor types, including stirred tank, bubble column, packed bed, trickle bed and hollow fibre membrane bioreactors, were evaluated in lab scale set ups both in the mesophilic and thermophilic range [34]. At thermophilic conditions, volumetric methane productivities reached values in between 78 and $689 \text{ Nm}^3 \text{ CH}_4 \text{ m}^{-3} \text{ reactor d}^{-1}$ when a surplus of the gaseous substrates, H_2 and CO_2 , is provided (according to Monod kinetics). While aiming at high reactor conversion/production rates, the envisaged gas composition/quality is still the main criterion when operating a biogas upgrading technology, because grid injection standards (often $>97\%$) needs be achieved. Low final methane concentrations in the produced gas are intrinsically linked to high gas retention times and lower volumetric methane production, so biomethanation rates in biological biogas upgrading reactors will always be lower than under excess gas atmosphere. A biogas upgrading

capacity up to $3.7 \text{ Nm}^3_{\text{biogas}}$ per $\text{m}^3_{\text{reactor volume}}$ per day can be achieved in a trickle-bed bioreactor if a methane content higher than 96 % is targeted [32].

Figure 6 – Gas composition of the headspace over time for batch biomethanation tests with off-gases from EBU at 100 A m^{-2} and a biogas flow rate of $50 \text{ L}_{\text{biogas}} \text{ d}^{-1}$ (A) and at 60 A m^{-2} and $25 \text{ L}_{\text{biogas}} \text{ d}^{-1}$ (B) ($n=3$).

3.6 Energy requirements

In this study, H₂ was produced at an energy input of 6.5 to $15.5 \text{ kWh Nm}^{-3} \text{ H}_2$, which is higher than the energy requirement of the current best water electrolysis processes ($\sim 4.5 \text{ kWh Nm}^{-3} \text{ H}_2$) [35]. Considering that the produced H₂ has an energy content of 3.54 kWh Nm^{-3} (higher heating value) [36], our EBU process has an energy efficiency towards H₂ of 23 – 54 %. Assuming that all H₂ is used for conversion of residual CO₂ to CH₄ in the biomethanation step, $2.7 \text{ kWh Nm}^{-3} \text{ H}_2$ can be recovered in the form of CH₄ (assuming $10.8 \text{ kWh Nm}^{-3} \text{ CH}_4$), leading to a net electrical input for CO₂ removal and conversion in between 2.0 and $11.4 \text{ kWh Nm}^{-3} \text{ CO}_2$. The net energy requirement for biogas upgrading (from 60 % to 97 % CH₄) via the proposed approach is thus $0.8 - 4.6 \text{ kWh Nm}^{-3} \text{ raw biogas}$. With a specific power demand of $0.2 - 0.3 \text{ kWh Nm}^{-3} \text{ biogas}$ [3], water scrubbing and pressure swing adsorption require a lower electricity demand compared to the EBU process in combination with H₂-mediated conversion of residual CO₂. However,

compared with the net power demand of 3.6 kWh Nm^{-3} raw biogas for upgrading via methanation of all CO_2 into CH_4 , our electrochemical extraction can reduce the energy input related to complete biological upgrading up to a factor 4.5 [14]. Moreover, techniques such as scrubbing only partially remove CO_2 , still requiring additional technology for further biogas polishing. The approach also removed H_2S . It could be considered to use water scrubbing as first line bulk CO_2 removal process, followed by EBU based fine-tuning of the concentration and further production of CH_4 through biomethanation. Considering the ability of electrochemistry to compress a gas [37], the energy consumption related to biomethane compression can be (partially) omitted. The energy demand of high-pressure compression (60 - 200 bar) accounts for 30 to 50 % of the total energy input of a biomethane plant ($0.25 - 0.50 \text{ kWh Nm}^{-3}$ biogas) [38]. Next to CO_2 removal, H_2 production and biogas compression, electrolysis generates an O_2 - CO_2 gas mixture at the anode. The O_2 can be used, for example, as a highly concentrated O_2 source (20 – 60 %) for on-site biological waste water treatment of the liquid fraction of the digestate, while the CO_2 can be sold to local greenhouses.

The economics of this approach is briefly demonstrated for a digester generating 1000 Nm^3 raw biogas hr^{-1} (60 vol. % CH_4) and a natural gas grid accepting biomethane with a CH_4 content of 97 %. Biogas upgrading, thus, needs to remove $370 \text{ Nm}^3 \text{ CO}_2 \text{ hr}^{-1}$. Assuming a CO_2 removal rate of $20 \text{ Nm}^3 \text{ m}^{-2} \text{ d}^{-1}$ at 1000 A m^{-2} current density, 444 m^2 membrane surface area and a reactor of 11 m^3 (assuming 40 m^2 membrane electrode assembly per cubic meter reactor [39]) will be needed. If the EC can be operated at 3 V, upgrading via EBU + biomethanation can be realized at an electricity cost of $0.13 \text{ € Nm}^{-3}_{\text{raw biogas}}$ (assuming $0.10 \text{ € kWh}_e^{-1}$), not including the produced methane *via* methanation. With an upgrading cost for water scrubbing of $0.08 - 0.14 \text{ € Nm}^{-3}_{\text{raw biogas}}$ [40] and an electricity cost for methanation with electrolytic H_2 of at least $0.72 \text{ € Nm}^{-3}_{\text{raw biogas}}$, the EBU process is in between.

Further process optimization and testing with real biogas is required before a detailed process cost calculation can be made, including investment and operational cost. Nonetheless, EBU appears to be a

promising technology for biogas upgrading via sequential electrochemical and biological CO₂ removal. The advantage of the two-step upgrading pipeline considered here over biological upgrading of the full CO₂ load is largely due to the lower power consumption, since electrons are used for both (bi)carbonate flux and CO₂ removal *via* H₂-mediated biomethanation. The injection of biomethane produced with electrolytic H₂ as sole energy source can be put forward as a scalable and decentralized upgrading strategy while storing excess or off-peak renewable power in methane molecules using CO₂ as carbon source.

4. Conclusion

In this work, we have proposed and demonstrated a two-step processing pipeline for upgrading biogas into pipeline-quality biomethane: (i) Membrane Electrolysis, the removal of CO₂ and H₂S via (alkaline) water scrubbing and the electrolytic extraction of (bi)carbonate and (bi)sulphide ions across an anion exchange membrane, and (ii) Biomethanation: a microbial conversion of CO₂ to CH₄ using electrolytic hydrogen gas as electron source and hydrogenotrophic methanogens as biocatalyst. The electrochemical extraction of (bi)carbonate ions across an anion exchange membrane was evaluated under a range of biogas flow rates and applied currents. This study has shown that membrane electrolysis can be used to remove 100% of the incoming CO₂, but has much more potential when coupled to a methanation reactor. Electrochemical biogas upgrading has been used to generate the ideal 4:1 H₂:CO₂ ratio for further biological upgrading into a high-purity biomethane (>97% CH₄), significantly reducing the power associated with upgrading *via* reduction of CO₂ into CH₄. Electrochemical extraction appears to be a promising pre-treatment process for biogas upgrading through biological methanation and should be further investigated for application in the power-to-gas context. With increased removal rates and decreased energy input this technology has the potential to become a sustainable alternative for biogas upgrading that is fully electricity driven and moves away from chemical and heat intensive upgrading processes.

Acknowledgements

K.V. is supported by FWO-Vlaanderen through a Ph.D. scholarship. J.D.V. is supported as postdoctoral fellow by the Research Foundation Flanders (FWO-Vlaanderen). K.R. acknowledges support by the European Research Council grant ELECTROTALK. Equipment used was supported *via* “BOF Basisinfrastructuur 01B05912”.

The authors have no competing interests to declare.

References

- [1] E. Ryckebosch, M. Drouillon, H. Vervaeren, Techniques for transformation of biogas to biomethane, *Biomass Bioenerg* 35 (2011) 1633-1645.
- [2] M. Pöschl, S. Ward, P. Owende, Evaluation of energy efficiency of various biogas production and utilization pathways, *Applied Energy* 87 (2010) 3305-3321.
- [3] F. Bauer, T. Persson, C. Hulteberg, D. Tamm, Biogas upgrading – technology overview, comparison and perspectives for the future, *Biofuels, Bioproducts and Biorefining* 7 (2013) 499-511.
- [4] J. Niesner, D. Jecha, P. Stehlík, Biogas upgrading technologies: state of art review in European region, *Chem Eng Trans* 35 (2013) 517-522.
- [5] M.R. Martin, J.J. Fornero, R. Stark, L. Mets, L.T. Angenent, A Single-Culture Bioprocess of *Methanothermobacter thermautotrophicus* to Upgrade Digester Biogas by CO₂-to-CH₄ Conversion with H₂, *Archaea* 2013 (2013) 157529.
- [6] G. Luo, I. Angelidaki, Integrated biogas upgrading and hydrogen utilization in an anaerobic reactor containing enriched hydrogenotrophic methanogenic culture, *Biotechnology and Bioengineering* 109 (2012) 2729-2736.
- [7] M. Götz, J. Lefebvre, F. Mörs, A. McDaniel Koch, F. Graf, S. Bajohr, R. Reimert, T. Kolb, Renewable Power-to-Gas: A technological and economic review, *Renewable Energy* 85 (2016) 1371-1390.
- [8] L.M. Agneessens, L.D.M. Ottosen, N.V. Voigt, J.L. Nielsen, N. de Jonge, C.H. Fischer, M.V.W. Kofoed, In-situ biogas upgrading with pulse H₂ additions: The relevance of methanogen adaption and inorganic carbon level, *Bioresource Technology* 233 (2017) 256-263.
- [9] G. Luo, S. Johansson, K. Boe, L. Xie, Q. Zhou, I. Angelidaki, Simultaneous hydrogen utilization and in situ biogas upgrading in an anaerobic reactor, *Biotechnology and bioengineering* 109 (2012) 1088-1094.
- [10] K.A. Strevett, R.F. Vieth, D. Grasso, Chemo-autotrophic biogas purification for methane enrichment: mechanism and kinetics, *The Chemical Engineering Journal and the Biochemical Engineering Journal* 58 (1995) 71-79.
- [11] H. Xu, K. Wang, D.E. Holmes, Bioelectrochemical removal of carbon dioxide (CO₂): An innovative method for biogas upgrading, *Bioresource Technology* 173 (2014) 392-398.
- [12] S. Cheng, D. Xing, D.F. Call, B.E. Logan, Direct Biological Conversion of Electrical Current into Methane by Electromethanogenesis, *Environmental Science & Technology* 43 (2009) 3953-3958.
- [13] M. Villano, F. Aulenta, C. Ciucci, T. Ferri, A. Giuliano, M. Majone, Bioelectrochemical reduction of CO₂ to CH₄ via direct and indirect extracellular electron transfer by a hydrogenophilic methanogenic culture, *Bioresource Technology* 101 (2010) 3085-3090.
- [14] F. Geppert, D. Liu, M. van Eerten-Jansen, E. Weidner, C. Buisman, A. ter Heijne, Bioelectrochemical Power-to-Gas: State of the Art and Future Perspectives, *Trends in Biotechnology* 34 (2016) 879-894.
- [15] P. Clauwaert, P. Aelterman, T.H. Pham, L. De Schampelaire, M. Carballa, K. Rabaey, W. Verstraete, Minimizing losses in bio-electrochemical systems: the road to applications, *Appl Microbiol Biotechnol* 79 (2008) 901-913.
- [16] R. Muñoz, L. Meier, I. Diaz, D. Jeison, A review on the state-of-the-art of physical/chemical and biological technologies for biogas upgrading, *Reviews in Environmental Science and Bio/Technology* 14 (2015) 727-759.
- [17] B. Keller-Lehmann, S. Corrie, R. Ravn, Z. Yuan, J. Keller, Preservation and simultaneous analysis of relevant soluble sulfur species in sewage samples, *Proceedings of the Second International IWA Conference on Sewer Operation and Maintenance*, 2006, pp. 28.
- [18] P.K. Dutta, K. Rabaey, Z. Yuan, R.A. Rozendal, J. Keller, Electrochemical sulfide removal and recovery from paper mill anaerobic treatment effluent, *Water Research* 44 (2010) 2563-2571.
- [19] S.J. Andersen, T. Hennebel, S. Gildemyn, M. Coma, J. Desloover, J. Berton, J. Tsukamoto, C. Stevens, K. Rabaey, Electrolytic Membrane Extraction Enables Production of Fine Chemicals from Biorefinery Sidestreams, *Environmental Science & Technology* 48 (2014) 7135-7142.

- [20] A.K. Luther, J. Desloover, D.E. Fennell, K. Rabaey, Electrochemically driven extraction and recovery of ammonia from human urine, *Water research* 87 (2015) 367-377.
- [21] A.L. Soli, R.H. Byrne, CO₂ system hydration and dehydration kinetics and the equilibrium CO₂/H₂CO₃ ratio in aqueous NaCl solution, *Marine Chemistry* 78 (2002) 65-73.
- [22] P.-C. Chen, Absorption of carbon dioxide in a bubble-column scrubber, INTECH Open Access Publisher 2012.
- [23] M. Eckert, G. Fleischmann, R. Jira, H.M. Bolt, K. Golka, Acetaldehyde, *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA 2006.
- [24] W.M. Budzianowski, C.E. Wylock, P.A. Marciniak, Power requirements of biogas upgrading by water scrubbing and biomethane compression: comparative analysis of various plant configurations, *Energy conversion and management* 141 (2017) 2-19.
- [25] G. Vázquez, M.A. Cancela, C. Riverol, E. Alvarez, J.M. Navaza, Application of the Danckwerts method in a bubble column: Effects of surfactants on mass transfer coefficient and interfacial area, *Chemical Engineering Journal* 78 (2000) 13-19.
- [26] J.C. Ganley, High temperature and pressure alkaline electrolysis, *international journal of hydrogen energy* 34 (2009) 3604-3611.
- [27] M. Persson, O. Jönsson, A. Wellinger, Biogas upgrading to vehicle fuel standards and grid injection, IEA Bioenergy task, 2006, pp. 1-34.
- [28] U. Schröder, F. Harnisch, Electrochemical losses, in: K. Rabaey, L.T. Angenent, U. Schröder, J. Keller (Eds.) *Bioelectrochemical Systems: from extracellular electron transfer to biotechnological application*, IWA Publishing, London, 2010.
- [29] X. Jin, Y. Zhang, X. Li, N. Zhao, I. Angelidaki, Microbial Electrolytic Capture, Separation and Regeneration of CO₂ for Biogas Upgrading, *Environmental Science & Technology* 51 (2017) 9371-9378.
- [30] I. Díaz, S.I. Pérez, E.M. Ferrero, M. Fdz-Polanco, Effect of oxygen dosing point and mixing on the microaerobic removal of hydrogen sulphide in sludge digesters, *Bioresource Technology* 102 (2011) 3768-3775.
- [31] S. Rasi, J. Lantelä, J. Rintala, Trace compounds affecting biogas energy utilisation – A review, *Energy Conversion and Management* 52 (2011) 3369-3375.
- [32] L. Rachbauer, G. Voith, G. Bochmann, W. Fuchs, Biological biogas upgrading capacity of a hydrogenotrophic community in a trickle-bed reactor, *Applied Energy* 180 (2016) 483-490.
- [33] G. Jud, K. Schneider, R. Bachofen, The role of hydrogen mass transfer for the growth kinetics of *Methanobacterium thermoautotrophicum* in batch and chemostat cultures, *Journal of Industrial Microbiology and Biotechnology* 19 (1997) 246-251.
- [34] S. Rittmann, A. Seifert, C. Herwig, Essential prerequisites for successful bioprocess development of biological CH₄ production from CO₂ and H₂, *Critical Reviews in Biotechnology* 35 (2015) 141-151.
- [35] S.P.S. Badwal, S.S. Giddey, C. Munnings, A.I. Bhatt, A.F. Hollenkamp, Emerging electrochemical energy conversion and storage technologies, *Frontiers in Chemistry* 2 (2014).
- [36] A. Midilli, M. Ay, I. Dincer, M.A. Rosen, On hydrogen and hydrogen energy strategies, *Renewable and Sustainable Energy Reviews* 9 (2005) 255-271.
- [37] B. Rohland, K. Eberle, R. Ströbel, J. Scholta, J. Garche, Electrochemical hydrogen compressor, *Electrochimica acta* 43 (1998) 3841-3846.
- [38] P. Weiland, Biogas production: current state and perspectives, *Appl Microbiol Biotechnol* 85 (2010) 849-860.
- [39] J. Desloover, A. Abate Woldeyohannis, W. Verstraete, N. Boon, K. Rabaey, Electrochemical Resource Recovery from Digestate to Prevent Ammonia Toxicity during Anaerobic Digestion, *Environmental Science & Technology* 46 (2012) 12209-12216.
- [40] A. Petersson, A. Wellinger, Biogas upgrading technologies – developments and innovations, IEA Bioenergy, 2009.

Highlights

- Membrane electrolysis allows to simultaneously remove CO_2 and add H_2 to the biogas
- H_2S absorption in the alkaline catholyte removes up to 98% of the incoming H_2S
- Electrochemical Biogas Upgrading can generate an optimal $\text{H}_2:\text{CO}_2$ ratio for biomethanation
- The two-step approach can generate biomethane with > 98 % CH_4