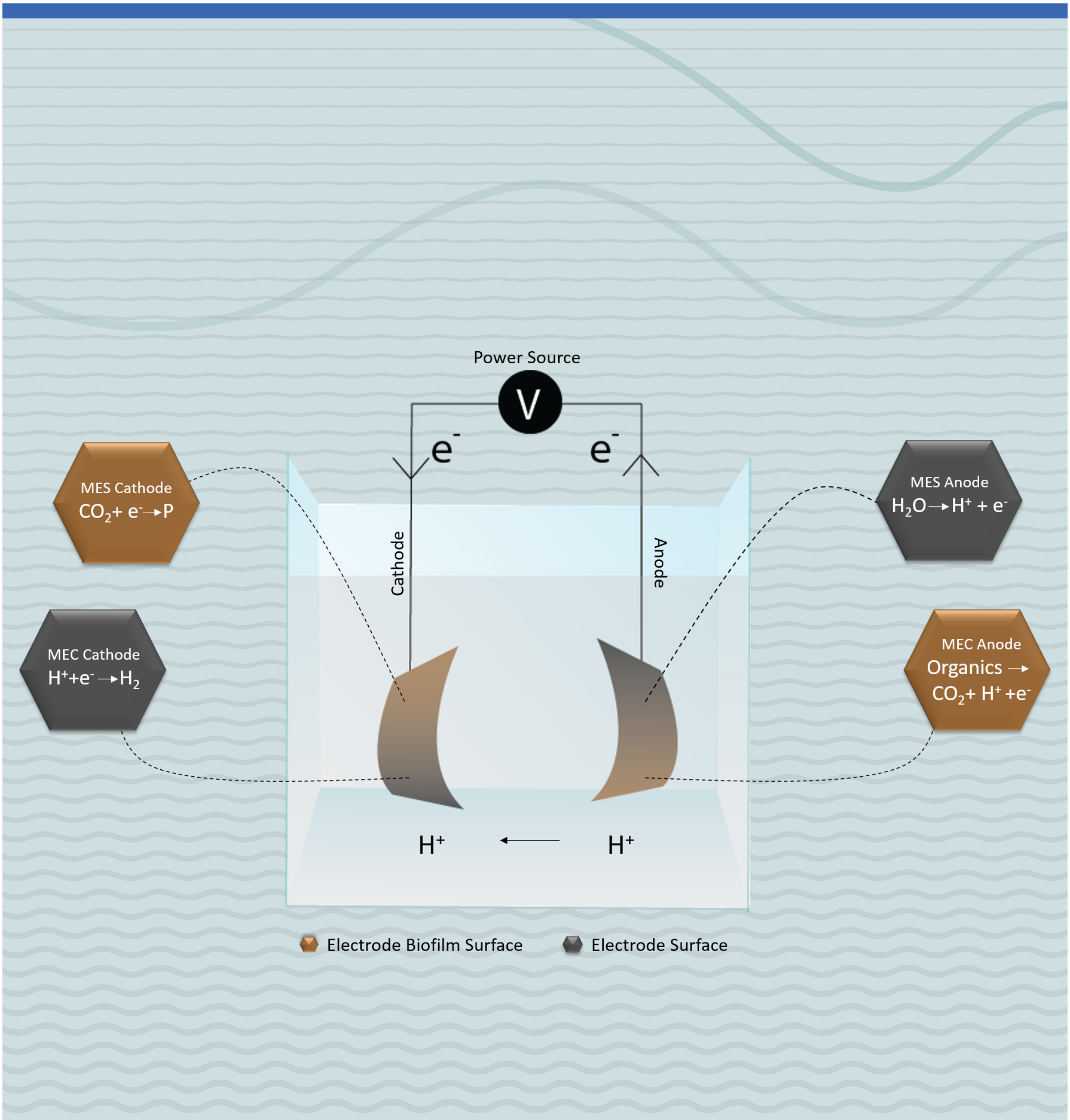
University of South-Eastern Norway
Faculty of Technology, Natural Sciences and Maritime Studies
—
Doctoral dissertation no. 62
2020

Anirudh Bhanu Teja Nelabhotla

Electrochemical Unit Integration with Biogas Production Processes



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A PhD dissertation in

Process, Energy and Automation Engineering

Faculty of Technology, Natural Sciences and Maritime Studies
University of South-Eastern Norway
Porsgrunn, 2020

Doctoral dissertations at the University of South-Eastern Norway no.62

ISSN: 2535-5244 (print)
ISSN: 2535-5252 (online)

ISBN: 978-82-7206-546-0 (print)
ISBN: 978-82-7206-547-7 (online)

Print: University of South-Eastern Norway

Preface

This thesis is submitted in partial fulfilment of the requirements for the degree of Philosophiae Doctor (PhD) at the University of South-Eastern Norway (USN). The thesis is based on the work carried out at the Department of Process Energy and Environmental Technology in the Faculty of Technology, Natural and Maritime Sciences from December 2016 to February 2020. This work is financed by the Norwegian Ministry of Education and Research through the PhD program -Process, Energy and Automation Engineering- at USN.

The dissertation contains two parts. In the first part, a literature review, a brief description of materials and methods followed by a summary of all the results and discussion and conclusions are given. The articles that the dissertation is based on are included in the second part. The reactor design, construction, and operation together with the chemical analyses were performed at USN.

Acknowledgements

First, I wish to express my deep gratitude to my advisors: Associate Professor Carlos Dinamarca and Professor Rune Bakke, thank you for the opportunity to pursue my Ph.D. at the University of South-Eastern Norway (USN). Thank you for your guidance and support.

I would like to thank Hildegunn Hegna Haugen, Kadja Bless and Frank Aarvak for help with laboratory and technical tasks. Thanks to Michal Sposob for getting me started with my reactor setup and experimental work. Thanks to Eshetu Janka Wakjera and Amund Heggholmen for their cooperation in acquiring reactor feeds from Knarrdalstrand. Special thanks to all my friends that distracted/helped me during my PhD studies. Among of them are Fasil Tassew, Samee Maharjan, Liubomyr Vytvytskyi, my master's student Mahdi Khoshbakhtian, research group mates, and fellow Ph.D. students. Thanks to all the Ph.D. students, for your company and I hope you enjoy your reading.

Finally, I am grateful to my wife Sruthi Subramanyam and my parents N T Sunil Babu and Anjani Kumari and my sister Alakananda for their love, help, and support. This would not be possible without them.

Abstract

Power to Gas (PtG) is being viewed as systemic innovation in terms of integrating renewable electricity systems and wastewater treatment systems to provide renewable transport fuel. The highly varied nature of the sun and wind does usually produce either less or more electricity than the required amount during certain period of the day or a year. The PtG technologies can be integrated with the renewable electricity systems that are able to utilize the excess electricity to produce renewable transport fuel. This helps not only save the electricity produced but also integrate the transportation sector in the renewable energy ecosystem.

The current thesis addresses a specific use of PtG with the help of microbial electrosynthesis (MES) to upgrade biogas in food waste/wastewater treatment systems. The thesis starts with an extensive state-of-art review of all the existing reactor configurations especially single chambered systems, cathode materials that support biofilm growth, electron transfer mechanism and finally the integration of MES with anaerobic digestion (AD) systems. It also identifies research gaps in terms of lack of analysis and optimisation experiments in terms of pH and cathode potentials in single chamber continuous flow reactor configuration. A major research gap is identified in terms of direct interspecies electron transfer (DIET) and using anaerobic reject water as feed for biogas upgrading. This thesis attempts to address the gaps identified and contributes to the literature on MES integrated AD systems.

Simple cyclic voltammetry tests were first used on artificial wastewater to compare the different electrode materials and it was identified that carbon felt performs relatively similar to platinum-coated titanium as an anode. The experiments also provided approximate optimised values of pH and temperature for MES operation. Carbon felt was subjected to MES operation at -0.80 V for over 2 months in fed batch mode to grow biofilm. Two of the biocathodes were selected and different optimisation experiments were conducted at different operational conditions.

It was observed that the pH directly affects the heterotrophic methanogenesis and the electrochemical methane production indirectly through the availability of CO_2/HCO_3^-. The reactor pH must be controlled below 8.0, which implied that the feed pH must be in the range of 7.0 to 7.2. The main reasons identified for the increase in pH is the consumption of protons and acetic acid through heterotrophic methane production with simultaneous conversion of CO_2 to bicarbonate/metane. The optimised cathode potential for methane formation was identified to be around -0.65 V vs Standard Hydrogen Electrode (SHE) whereas for acetic acid formation to be above -0.80 V vs SHE.

In order to study the electron transfer mechanisms, electrochemical experiments at both the above-mentioned cathode potentials were compared with each other. Blank and control experiments were also conducted to compare the methane production and acetic acid consumption rates. The baseline MES operation (19.5 mmol/$L_{(reactor)}$-d) showed 13 – 39% more methane than the control experiment (16.5 – 14.5 mmol/$L_{(reactor)}$-d) in terms of methane production rates. It was demonstrated that the effluent pH could be lowered by feeding low concentrations of acetic acid. This also showed a simultaneous increase in current production and decrease in alkalinity concentrations, denoting biocathode adaptation to electrochemical conditions.

Further adapting the biocathode to feed with no supplemented acetic acid (reject water from sludge AD at Knarrdalstrand wastewater treatment plant, Porsgrunn) increased the methane production rate by 50% from 4.0 mmol/$L_{(reactor)}$-d to approximately 6.0 mmol/$L_{(reactor)}$-d. All the continuous flow experiments were conducted at 24-h HRT and reactor pH (measured in the effluent) through the different operating conditions was brought down to 8.2 from 8.7. HRTs lower than 24 h were analysed for lowering the pH below 8.0 and other observations were made regarding biogas production rates and methane concentrations. The 18-h HRT operation showed 12.2 and 7.4 mmol/$L_{(feed)}$-d methane production yield respectively with approximately 90% methane concentration in the biogas. High COD removal of approximately 40.6 and 23.4% were observed in the 18-h HRT MES operations of feeds with and without supplemented acetic acid. Moreover, observations were made regarding electro-oxidation of COD at the anode.

As the HRT is lowered to 12 hrs and below, the current production shows an increase with a corresponding decrease in alkalinity concentrations. This denoted enhanced electrochemical activity. However, when HRT was reduced below 6-hrs the amount COD removal decreased along with decrease in CO_2 reduction rate resulting in higher CO_2 biogas content.

A total of 4 mechanisms for methane production are observed in the thesis and are discussed as part of unpublished work. It is concluded that 45% of total methane produced in feeds that do not contain acetic acid is via the direct interspecies electron transfer mechanism (DIET) by converting bicarbonate to methane. Finally, the thesis concludes with a proposed scale-up of MES-AD integration at the Knarrdalstrand WWTP from where the feed was sourced during the course of thesis. It is estimated that an MES reactor sized approximately $82m^3$ preferably in multi-train tubular configuration. The extrapolated values show 4% increase in methane production only through reject water treatment and doesn’t include CO_2 conversion. CO_2 conversion to methane is expected to increase in plug flow configuration as the electrode surface area to reactor volume ratio increases. However, the final COD is estimated to decrease by 15-20 % by extrapolating results obtained in thesis.

Keywords

Microbial electrosynthesis system, methane, CO_2 reduction, biogas upgradation and hydraulic retention time.

List of papers

Article 1

Nelabhotla, A. B. T., & Dinamarca, C. (2018). Electrochemically mediated CO_2 reduction for bio-methane production: a review. Reviews in Environmental Science and Biotechnology, 17(3), 531–551. https://doi.org/10.1007/s11157-018-9470-5

Article 2

Nelabhotla, A. B. T., & Dinamarca, C. (2018). Optimisation of Electrochemical Treatment of Artificial Wastewater using Cyclic Voltammetry. *International Journal of Environmental Science and Development*, *9*(8), 218–221. https://doi.org/10.18178/ijesd.2018.9.8.1104

Article 3

Nelabhotla, A. B. T., & Dinamarca, C. (2019). Bioelectrochemical CO_2 Reduction to Methane: MES Integration in Biogas Production Processes. *Applied Sciences*, *9*(1056), 16–18. https://doi.org/10.3390/app9061056

Article 4

Nelabhotla, A. B. T., Bakke, R. & Dinamarca, C. (2019). Performance Analysis of Biocathode in Bioelectrochemical CO_2 Reduction. Catalysts, 9, 683. https://doi.org/10.3390/catal9080683

Article 5 (Submitted, January 23, 2020; Revised February 20, 2020)

Nelabhotla, A. B. T., Khoshbakhtian, M., Chopra, N. & Dinamarca, C. (2020). Effect of Hydraulic Retention Time on MES Operation for Biomethane Production. Energy Research

Article 6 (Additional Contribution)

Samarakoon, G., Dinamarca, C., Nelabhotla, A. B. T., Winkler, D., and Bakke, R. (2019) Modelling Bio-electrochemical CO2 Reduction to Methane. In: Trondheim Carbon Capture and Storage. pp 55–61

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Abbreviations

AD – Anaerobic Digestion

COD – Chemical Oxygen Demand

DIET – Direct Interspecies Electron Transfer

DMEA – Dimethylethanolamine

HRT – Hydraulic Retention Time

MEA – Methylethanolamine

MEC – Microbial Electrolysis Cell

MES – Microbial Electrosynthesis System

MFC – Microbial Fuel Cell

MPR – Methane Production Rate

PEM – Proton Exchange Membrane

PSA – Pressure Swing Adsorption

PtG – Power to Gas

SHE – Standard Hydrogen Electrode

VFA – Volatile fatty acids

WWTP – Wastewater Treatment Plant

Part I

Part II

PART – I

1 Introduction

Anaerobic Digestion (AD) is the process of converting complex organic material into simple sugars, amino acids and fatty acids which are further converted to acetic acid and then to a mixture of methane and carbon dioxide called biogas (Fig. 1, Batstone et al., 2002). These processes are carried out by microorganisms that thrive in anaerobic conditions and are sensitive to many physicochemical parameters such as pH, temperature, total solids and conductivity of the organic waste being treated (Moset et al., 2015).

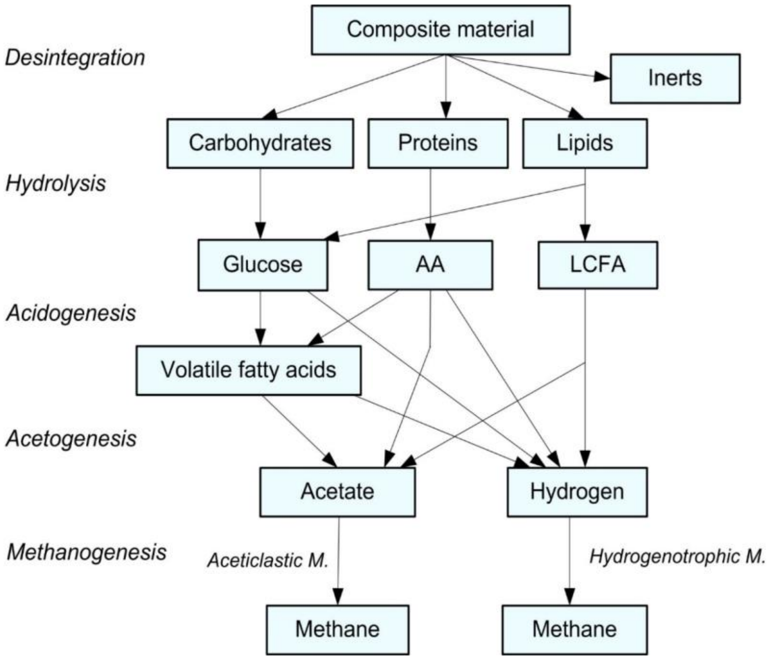


Figure 1.1: Schematic representation of anaerobic digestion process

1.1 Biogas Upgrading

Biogas is a useful source of energy and can be used for various purposes such as heat, cooking gas, generating electricity and transport fuel (Lausund, 2014). The application of biogas depends on the concentration of methane in the biogas. A higher concentration of methane implies higher calorific value and high-quality fuel gas (Esposito et al., 2019). A traditional AD process produces biogas with methane content between 60 – 80% and CO_2 of about 20 – 40% (Eq. 1 & 2) (Rasi et al., 2007). The methane concentration in biogas can be increased to improve the biogas quality, termed biogas upgrading. This can be done in two ways, either by removing carbon dioxide (carbon capture) or converting carbon dioxide to methane (carbon capture and conversion).

Acetoclastic (heterotrophic) methanogenesis (Metcalf and Eddy, 2014)

$$CH_3COOH \rightarrow CH_4 + CO_2 \qquad \Delta G = -33\ kJ/mol \qquad (1)$$

Autotrophic methanogenesis*

$$4\,H_2 + CO_2 \rightarrow CH_4 + 2\,H_2O \qquad \Delta G = -135\ kJ/mol \qquad (2)$$

*Depending on the type of catalysts the same reaction can be termed as hydrogenotrophic methanogenesis or biomethanation (catalysts: hydrogenotrophic methanogens), catalytic methanation (catalysts: metals).

1.2 Carbon Capture Technologies

There are currently many commercial methods available for capturing carbon dioxide present in the biogas. Popular methods are a) Absorption, b) Adsorption and c) Membrane separation (Ebner and Ritter, 2009; Meisen and Shuai, 1997; Mondal et al., 2012; Olajire, 2010; Sahota et al., 2018; Yang et al., 2008).

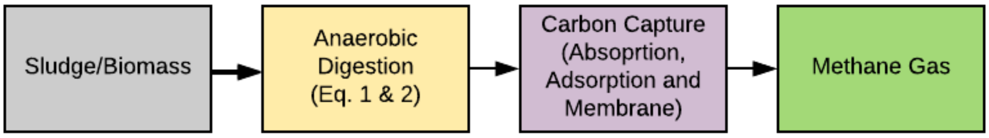


Figure 1.2: Schematic representation of use of carbon capture technologies for biogas upgradation.

1.2.1 Absorption

Absorption can be either physical or chemical where the gas diffuses into liquid phase crossing an interfacial region. Absorption largely depends on the type of solvent used, as it is the selectivity of the solvent that determines which gaseous component is absorbed (Mondal et al., 2012). In case of biogas upgradation, the solvent must be capable of solubilizing carbon dioxide and other impure gaseous matter such as hydrogen sulphide. Water scrubbing, physical absorption (e.g. Organic solvents, polyethylene glycol) and chemical absorption (e.g. Amines: MEA, DMEA, Alkali solutions) are the three popular absorption methods and are able to upgrade biogas to about 93 to 98% methane (Yang et al., 2008). However, these methods would require a capital investment of about 1 -2 million €/1000 m^3 and an operation and maintenance cost of about 15,000 – 59,000 €/y/1000 m^3 (Sahota et al., 2018). In addition, these methods are not considered highly sustainable, as they require large quantities of water or chemicals with a risk of contamination and methane loss to the atmosphere.

1.2.2 Adsorption

Unlike absorption, adsorption is a surface phenomenon and depends on the binding characteristics of both gas of interest and the micro-porous material used. Depending on the binding forces, adsorption can be either reversible or irreversible. Reversible adsorption or physisorption relies on the weak Van der Waal's forces and can be multi-layered (Sahota et al., 2018). The irreversible or chemisorption relies on the 'chemical bonding known as Langmuir adsorption between the gaseous component and the adsorbate material' and always exists as monolayer (Sahota et al., 2018).

Pressure swing adsorption (PSA) is the most popular and most commercialised form of biogas upgradation technology as there is no requirement of either water or harmful chemicals (Ebner and Ritter, 2009). As PSA is a physisorption technique, it can regenerate the adsorbate easily by releasing pure CO_2 at lower pressure levels and storing it separately. It can produce 96 – 98% methane containing biogas, but at very high capital, maintenance and operating (electricity) costs. It is also susceptible to breakdown as it is sensitive to the presence of hydrogen sulphide in the feed biogas (Sahota et al., 2018).

1.2.3 Membrane separation

Membrane separation technology involves penetration of the gaseous component through membrane that depends on the concentration gradient, chemical affinity and molecular size of the gases of interest (Olajire, 2010). Polymeric materials create a strong affinity towards small sized gas molecules such as H_2, H_2S and CO_2 than a larger molecule such as CH_4. Although the technology requires low maintenance, the operating costs are high as membrane processes require high energy supply (Sahota et al., 2018).

Moreover, membranes are not capable of achieving high degree of gas separation and therefore cannot be used for large scale separations. The technology itself is new and is in need of innovative solutions for improving transport properties of the membranes (Mondal et al., 2012).

1.3 Power-to-Gas (PtG) Technologies (Summary of Article 1)

The concept of Power-to-Gas technologies gained a huge traction with worldwide renewable electricity production showing a steep rise in the past decade. The contribution of wind and solar power to world electricity production has increased 700% from 130 GW in 2008 to 1052 GW in 2018 (BP, 2019). However, the fundamental issues of irregular production and the unreliable nature of these energy sources have remained the same. PtG emerged as a potential renewable electricity storage solution as an alternative to intermittent production. It also provides a potential opportunity to renewablise the transport sector by converting renewable electricity into fuel gases such as methane and hydrogen. There are mainly three ways to achieve this conversion:

a) Non-microbial electrolysis combined with methanation
b) Microbial electrolysis of wastewater for hydrogen production (MEC)
c) Microbial electrosynthetic methanation (MES)

1.3.1 Electrolysis combined Methanation

1.3.1.1 Electrolysis

Electrolysis here refers to the splitting of water into hydrogen and oxygen using electricity, which can be either, renewable or fossil fuel generated. Electrolysis is carried out in an electrochemical cell with a cathode where the hydrogen molecule and a charge carrier are produced via reduction of water and an anode where oxygen is produced via oxidation of the oxide ion. Depending on the technology, the charge carrier can be either OH^- (alkaline electrolysis), H_3O^+ (PEM electrolysis), or O^{2-} (solid oxide electrolysis) (Carmo et al., 2013).

Electrolysis Reactions (Rabaey and Rozendal, 2010)

$$4\,H_2O \rightarrow 2\,O_2 + 8\,H^+ + 8\,e^- \qquad E^\circ = +0.81\,V\ vs\ NHE \qquad (3)$$

$$2\,H^+ + 2\,e^- \rightarrow H_2 \qquad E^\circ = -0.414\,V\ vs\ NHE \qquad (4)$$

The alkaline and proton exchange membrane (PEM) electrolysis are currently available as commercial products in the market. The solid oxide electrolysis on the other hand is still under development. The alkaline and PEM systems are operated at lower temperatures (20 – 100 °C) and higher cell voltages (1.8 – 2.4 V) whereas the solid oxide electrolysis is operated at lower cell voltages (0.9 – 1.3 V) and higher temperatures of about 800 – 1000 °C (Götz et al., 2016). The end product of electrolysis i.e. hydrogen, is an efficient fuel with very high calorific value, but it is a huge challenge to store and transport hydrogen to be utilised as a fuel (Chalk and Miller, 2006; Mazloomi and Gomes, 2012; Mori and Hirose, 2009). Moreover, it needs to be converted to methane using an additional methanation step.

1.3.1.2 Catalytic methanation

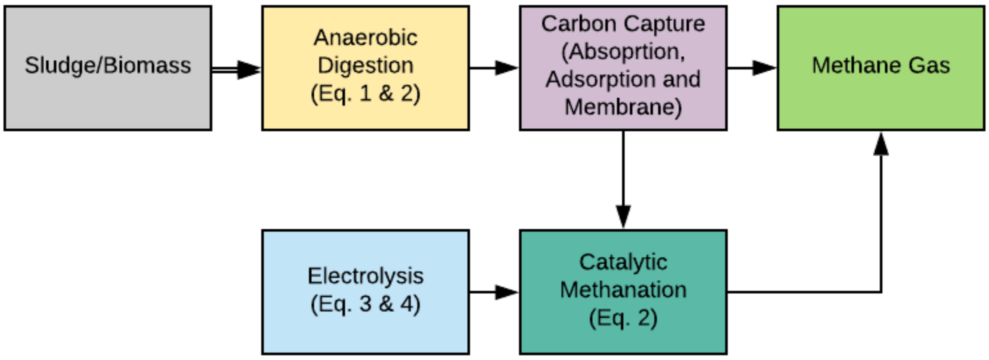


Figure 1.3: Schematic representation of use of catalytic methanation for biogas upgradation.

Catalytic methanation is the hydrogenation of carbon oxides to methane (Eq. 2) using metal catalysts such as nickel, cobalt, iron, ruthenium etc. Catalytic methanation takes place at high temperatures (250 -500 °C) and high pressures (1-100 bar) (Götz et al., 2016). There are different types of catalytic reactors such as a) fixed bed (Zhang et al., 2013), b) fluidized bed (Liu et al., 2012), c) three phase (Zhang et al., 2014) and d) structured (Liu and Ji, 2013). An important and necessary characteristic of a methanation reactor is for it to be flexible or dynamic in its operation (Bartholomew, 2001). As Power-to-Gas systems depend highly on renewable electricity, which by nature are intermittent in their production supplies, the reactors need to be stable over longer periods of no power supply but need to have short start-up period when the power supply is back on.

However, such dynamic operations significantly affect the metallic catalyst performance and the reactor conditions, which depend on high temperatures and pressures. Some catalysts have shown oxidation of CO_2 during down time that affects the reactor adversely. It was suggested that in order to maintain reactor stable during stand-by period and continuous supply of H_2 must be provided (Mutz et al., 2015), which again depends on the supply of renewable electricity. Although some recent studies have shown reduced catalytic instability, there is not enough research available for deducing or developing pilot plants with capability of dynamic operation.

1.3.1.3 Biological methanation

Biological methanation carry out power-to-gas reactions using microorganisms as catalysts by reducing CO_2 to CH_4 with help of hydrogen (or electron equivalents) provided through renewable electrolysis. These microorganisms are naturally part of the mixture of microbes already present in wastewater and are called hydrogenotrophic methanogens (Hu et al., 2008). Depending on the availability of nutrients and favourable physico-chemical parameters, these microbes can either remain dormant or become active in a matter of few minutes to hours. Biological methanation is carried out at relatively low temperatures (20 – 70 °C) and atmospheric pressures. In these ways, biomethanation reactors are more stable and flexible towards changes in external factors.

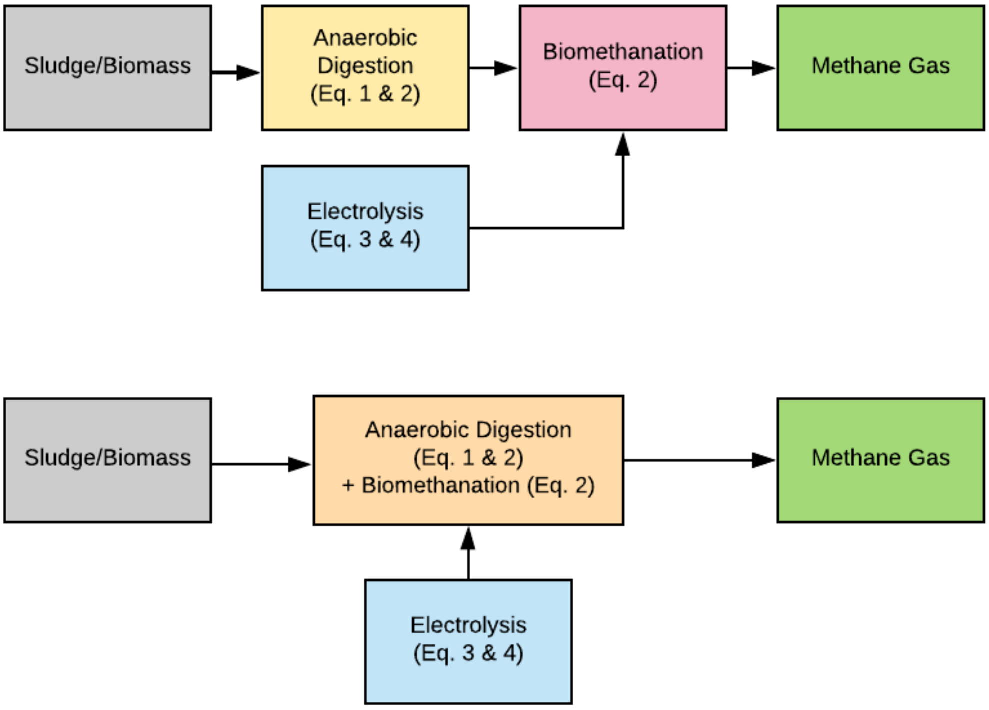


Figure 1.4: Schematic representation of use of biomethanation for biogas upgradation in a separate step or integrated in AD.

However, as biological methanation is carried out parallel to other anaerobic reactions such as acetoclastic methanogenesis, changes in physico-chemical parameters such as pH, temperature and ion concentrations can destabilise the reactor. This in turn affects the methane production rate and methane percentage in the biogas produced. On the other hand, since hydrogen is supplied as a gas from an external electrolysis reactor into the bulk liquid of either the digester or a methanation reactor, the gas liquid mass transfer resistance reduces the reduction reaction efficiency (Götz et al., 2016).

1.3.2 Microbial Electrolysis Cell (MEC)

1.3.2.1 Concept

An MEC is a modified form of microbial fuel cell (MFC), one of the first bioelectrochemical systems that demonstrated the use of microbes as catalysts to transport electrons (Potter, 1911). An MFC is capable of treating wastewater to produce electricity via the oxidation of organic matter by the bacteria (Logan et al., 2006). The electrons that are released by the bacteria are used for the production of current by connecting a resistor in the external circuit. However, this method of production of electricity is expensive and highly inefficient for a low value product such as electricity. The concept of MFC was then used to produce high value gases and chemicals with the development of MEC (electrolysis) and MES (electrosynthesis).

A microbial electrolysis cell (MEC) was developed for production of hydrogen gas through electrochemical treatment of wastewater. In an MEC, the positive electrode is a bioanode and is used to treat the organic matter to generate electrons and protons that are used to generate hydrogen gas at the cathode (Call and Logan, 2008; Guo et al., 2010). In many cases, the anodic and cathodic chambers of MEC are separated by a proton exchange membrane (PEM) in order to obtain pure hydrogen gas (Eq. 2) in the cathodic chamber (Cheng and Logan, 2008; Jeremiasse et al., 2010; Kiely et al., 2011; Logan et al., 2008). However, use of PEM results in higher overpotentials and reduced mass transfer coefficients (Sleutels et al., 2009). On the other hand, hydrogen production at cathode in an MEC is not biologically catalysed and requires precious metals such as platinum to obtain highly efficient results at a relatively higher standard potential.

Microbial electrolysis reaction (Rabaey and Rozendal, 2010)

$$C_2H_4O_2 + 2\,H_2O \rightarrow 2\,CO_2 + 8\,H^+ + 8\,e^- \qquad E^\circ = +0.280\,V\ vs\ NHE \qquad (5)$$

$$4\,H^+ + 4\,e^- \rightarrow 2H_2 \qquad E^\circ = -0.414\,V\ vs\ NHE \qquad (4)$$

1.3.2.2 Development

The concept of MEC was also evaluated for integration with anaerobic digestion mainly through indirect electron transfer (Eq. 2 + Eq. 4 + Eq. 5). This was mainly due to the realization that methane was an unavoidable by-product during targeted hydrogen production in an MEC (Clauwaert and Verstraete, 2008). The integration allowed MEC unit placed as a pre-treatment prior to main anaerobic digestion process or to be placed in together in one single reactor (Bo et al., 2014; Gao et al., 2017; Guo et al., 2013). This was further optimised to develop microbial electrosynthesis systems that allow direct interspecies electron transfer and can be more efficient without the membrane separating the anodic and cathodic chambers (Clauwaert and Verstraete, 2008).

1.3.3 Microbial Electrosynthesis System

1.3.3.1 Concept

A microbial electrosynthesis system (MES) is a type of biological methanation reactor that also carries out partial water electrolysis. In an MES, the cathodic half reaction of electrolysis is modified to biomethanation with the help of cathode potential and biofilm. The protons and electrons generated at anode are combined with CO_2 at cathode to produce methane, termed as direct interspecies electron transfer (Zhao et al., 2016). MES either can be part of AD as an integrated unit or as a pre or a post AD treatment attachment unit. In this thesis, the latter theme is explored, and various advantages and challenges involved in using MES as a post AD biogas upgradation system are discussed.

Microbial electrosynthesis reaction (Rabaey and Rozendal, 2010)

$$4\,H_2O \rightarrow 2\,O_2 + 8\,H^+ + 8\,e^- \qquad E^{\circ} = +0.810\,V\ vs\ NHE \qquad (3)$$

$$CO_2 + 8\,H^+ + 8\,e^- \rightarrow CH_4 + 2\,H_2O \qquad E^{\circ} = -0.244\,V\ vs\ NHE \qquad (6)$$

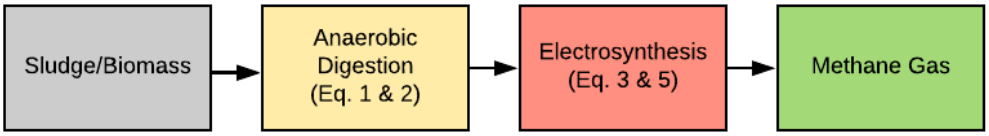


Figure 1.5: Schematic representation of use of electrosynthesis for biogas upgradation.

One of the main reasons for selecting MES is first to avoid the separation of hydrogen production step that has proven to be an economic barrier for the success of electrolysis combined methanation based biogas upgradation solutions. Secondly, to investigate the potential in electrochemical degradation of residual organic matter that is present in the effluent of an AD (Candido et al., 2013; Cho et al., 2014; Ghimire et al., 2019). Thirdly, it is a practical way to modify existing wastewater treatment plants without huge capital investment or operating costs. The fourth motivation, as explained earlier, is that biomethanation is more flexible for dynamic operation using renewable electricity (Bartholomew, 2001). The reactors use microbes as catalysts growing as biofilm on relatively cheap electrode materials. The internal stability, CO_2 reduction efficiency, residual COD degradation and electron transfer mechanisms are studied in this thesis.

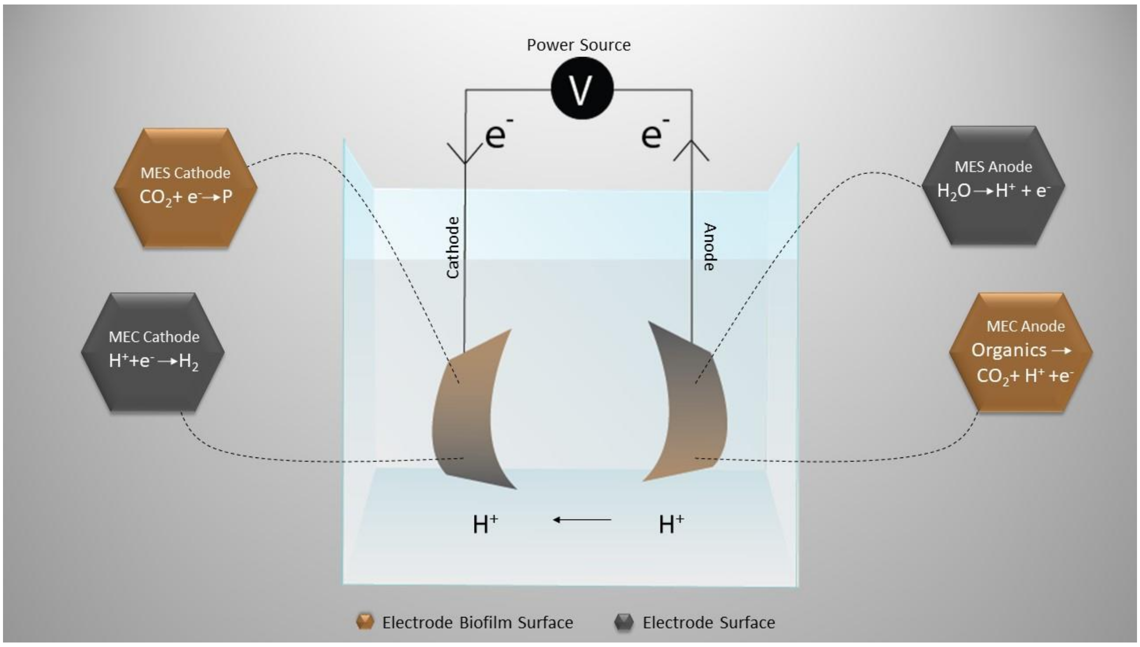


Figure 1.6: Schematic representation of the different reactions in MEC and MES

1.3.3.2 Biocathodes

Biocathodes play a major role in the functioning of MES and are the backbone for the microbial catalysts that carry out the electrosynthetic reactions. A MES cathodic material must possess the following characteristics: a) high conductivity b) large surface area c) cheap and d) long operational life. Many carbon-based materials have been explored previously such as carbon cloth, carbon fibre, graphite granules, rods, beds and plate, carbon nanotubes, and carbon felt (Siegert et al., 2014). All these materials support biofilm growth for either electrochemical methane or acetate production with coulombic efficiencies ranging from 55 – 100%. Cathodic biofilm is the lifeline of an MES, and the efficiency of the reactor is determined by mass and electron transfer through and within the biofilm network. Many factors contribute to a healthy biofilm such as electrode surface, pH of electrolyte, temperature of the reactor, cathode potential and the biofilm thickness itself. These conditions allow biofilm to change its physiology and metabolism towards the electrochemical product.

The advantages of using a biocatalyst are manifold: a) biofilms are native to the feed conditions and can be selectively enriched further by providing favourable physico-chemical conditions , b) biofilms are self-replicating and rejuvenating and thereby do not require to be replaced on a timely basis, c) In case the physico-chemical conditions are changed rapidly, the biofilms do not die or get eliminated, rather become inactive and are activated quickly as soon as favourable conditions are provided, d) Almost all biocatalysts are active at ambient temperatures and pressures unless they are thermophilic when the highest temperature required is around 65 °C. This implies that biocatalysts are less energy intensive than other methanation processes that require 250 - 500 °C. The biocatalysts are disadvantageous when one is starting up the reactor for the first time or after a long hiatus, as they require some time to regain primary functionality. Biofilms that are thick could be unhealthy and inefficient in their productivity as the upper layers of biofilm effect the mass and electron transfer to the roots of biofilm (Torres et al., 2008).

1.3.3.3 Extracellular Electron Transfer Mechanisms

Electron transfer efficiency is the key to electrochemical reaction and productivity. There are mainly two types of extracellular electron transfer (EET) mechanisms involved during CO_2 reduction to methane – a) indirect electron transfer (Eq 2 + Eq 4 + Eq 5) and b) direct electron transfer (Eq 3 + Eq 6). “EET is defined as a microbial metabolic process that enables electron transfer between microbial cells and extracellular solid materials” such as electrode materials and other microbes (Kato, 2015). In direct electron transfer, microbes attach themselves to solid materials such cathodes or anodes and transfer electron either to or from the electrode material. This is mainly done through conductive filamentous growth structure termed pili (Gorby et al., 2006). With the help of pili, a microbial cell is able to conduct electricity without being in direct contact with the electrode material. The efficiency of biofilm over its thickness increases due to these structures and direct EET.

Moreover, it has been identified that, such filamentous structures are able to establish syntrophic relations between microbes of different characteristics and metabolic functions. This syntrophy is termed as direct interspecies electron transfer (DIET). For microbial methane generation in anaerobic digestion through degradation of organic matter and volatile fatty acids, hydrogen is used as key electron carrier molecule. This constitutes indirect electron transfer or interspecies hydrogen transfer (IHT). The efficiency of such IHT is dependent on the physico-chemical characteristics and parameters of the process. Slight changes in pH or ion balances can impact hydrogen formation and hydrogen mass transfer. Therefore, DIET is considered more stable and efficient to carry out methanogenesis reactions. Presence of conductive materials such as carbon can further enhance DIET and accelerate electron transfer reactions. More recently, it was reported that DIET (44.9×10^3 e^-/cp/s) had much higher external electron transfer rates per cell pair (cp) than hydrogen-interspecies electron transfer (IET 5.24×10^3 e^-/cp/s) (Storck et al., 2016).

1.3.3.4 Current State

Microbial electrosynthesis systems have gained immense research interest in the past 5 years with the need for development of sustainable industries and reduced carbon emissions. Another motivation for increased research towards MES is that it presents a viable solution for utilising excess and/or intermittent electricity production through renewable resources (solar and wind). MES systems are capable of reducing carbon dioxide to many chemicals such ethanol, formate, acetate and butyrate (Bajracharya et al., 2015; Ganigue et al., 2015; Jiang et al., 2013; Katuri et al., 2018). However, they are stand-alone processes and are favourable only for continually operating large scale production in order to be financially viable (Christodoulou et al., 2017). MES for methane, on the other hand, can be used as a subsidiary process to anaerobic digestion and does not demand renewable electricity in a scale equivalent to large volume chemical production.

Although new, much research has been carried out on MES, mostly on batch and semi-continuous testing of reactors. Some continuous operations have been published with a maximum span of 72 days of operation (Cai et al., 2016; Yin et al., 2016). Many publications involve two chamber reactor systems that are not scalable for integrating with full scale AD systems. Moreover, two chamber systems reduce process efficiency and require continuous monitoring and regular maintenance work (Clauwaert et al., 2008; Guo et al., 2017). Single chamber systems have also been studied but majority of research involve microbial electrolysis cells where the main product is hydrogen that is used for integrating with anaerobic systems for enhanced methane production using indirect electron transfer. Some single chamber MES have been discussed in the past but no comprehensive results have been produced (Fu et al., 2015; Zhao et al., 2015). The current PhD study is comprehensive starting from electrode material selection, reactor design, parameter optimisation and integration of AD with food waste or wastewater treatment facilities.

2. Aims, Objectives and Approach

2.1 Objectives

1. An extensive review on bioelectrical systems. A “state of the art” to stablish a knowledge platform. The field of bioelectrical systems in water /wastewater could be divide in direct electricity generation (from wastewaters) and applications towards process intensification and optimization of organics synthesis. It is important to have a broad “database” from the literature as a platform for our approach.
2. A section is dedicated to the study of the electrochemical unit itself where a) Electrode material selection based on material conductivity, erosion resistance, compatibility with biofilms; b) Energy requirements; c) Design; and d) Cell effect related to the flow dynamics in the electrochemical units are studied.
3. The main study was on how the flow of electrons can be manipulated in a biologically mediated process and how this influences the several sub-processes co-coexisting in a biogas reactor. E.g. hydrolysis, acidogenesis, acetogenesis and methanogenesis may all be influenced by changes in the electron flow, perhaps even “bottleneck” sub-processes.
4. Study the electrochemical unit(s) integration in the overall biogas process: Evaluate the possibilities of “physical” installation of such units in typical process lines; look for the feasibility of such based to costs and energy balances to evaluate potential improvements in the process against costs of installation and operation.
5. The experimental work is supported by modelling and simulation both in planning and interpreting experiments. It is used to identify the most important parameters that can be affected by the change in the electron flow and for preliminary design of electrochemical units related to the flow dynamics and gas yield. ADM1 (anaerobic digestion model 1 implemented in AQUASIM) was applied.

2.2 Aims

The goal is to establish a new bio-electrochemical approach to the biogas research at USN to bring it to the international forefront of bioprocess research. The long-term aim is to make methane production by anaerobic digestion substantially more attractive and sustainable than what is achievable by biology alone. A shorter term and internal goal is to establish more interdisciplinary research at faculty of Technology, Natural Sciences and Maritime Sciences (TNM) at USN.

The biotechnology team cooperates extensively with the monitoring, control, modelling and simulation experts at TNM. The project seeks to strength this cooperation by studying and developing control and monitoring strategies (models) in biogas/water treatment technology. Building and operation of reactors with online data logging will give access to great amount of data for the participation of different specialists. There is also expertise in our region, outside HSN, the field of electrochemistry that we may establish cooperation with so that it can become part of our research portfolio at the TNM faculty.

2.3 Approach

The PhD study started with an extensive literature review of microbial electrosynthesis systems and other associated processes such as carbon capture and reduction mechanisms, chemical and microbial electrolysis systems and chemical and biological methanation methods. The study of MES involved state-of-art review regarding the developments in biocathodes, electron transfer mechanisms and reactor configurations.

This was followed by experimental studies dealing with electrode material selection using cyclic voltammetry on actual and artificial wastewater. Carbon felt was selected for biocathode development and reject water from sludge anaerobic digestion was electrochemically treated for 2 months in fed batch mode. Parallelly, a continuous flow stirred tank reactor (CSTR) was designed, setup and tested using clean water.

The main experiments were then run on the CSTR for 16 months starting with biomethane production experiment, pH and cathode potential optimisation, MES-AD integration (for food waste and wastewater sludge reject water), control and mass balance experiments, biocathode adaptation and hydraulic retention time optimisation (Figure 2.1).

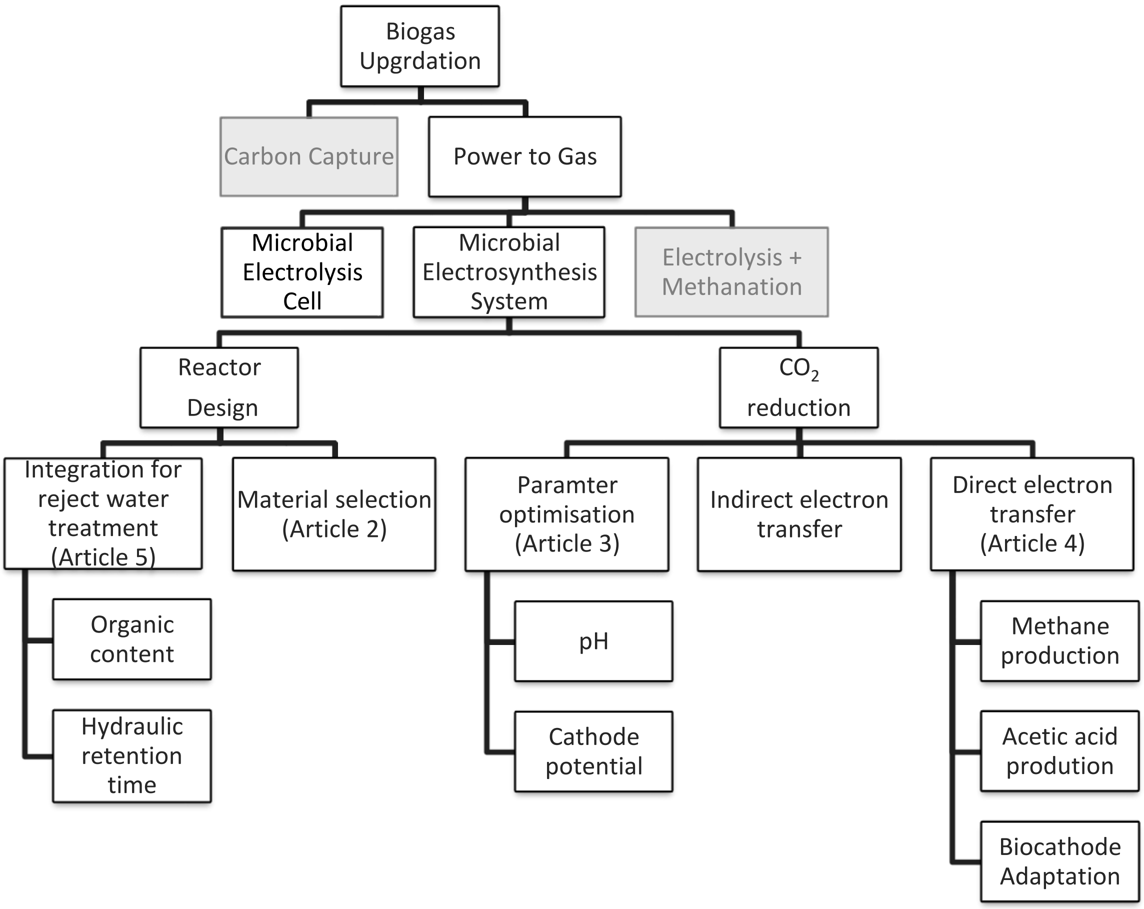


Figure 2.1: Flow chart of research plan and experimental approach

3 Materials and Methods

Series of laboratory experiments were conducted to investigate first electrode materials and temperature and secondly diverse process parameters affecting CO_2 conversion to methane in continuous flow experiments with different feed compositions. The parameters such as temperature, pH, cathode potential, acetic acid concentration and feed flow rate where analysed using routine chemical analysis of gas volume, methane percentage, CO_2 percentage, change chemical oxygen demand (COD), change volatile fatty acid (VFA) concentration, change in alkalinity and change in pH.

3.1 Materials

3.1.1 Electrodes

To select the most appropriate electrode materials for MES operation three electrode materials were purchased (Table 1). The main criteria behind obtaining these materials were literature study, cost and ease of repetition or replacement. In the beginning few of the carbon felt pieces and graphite rods were pre-treated by soaking them in 1 M HCl followed by 1N H_2SO_4 to remove all the organic impurities present in the pores of electrode material. However, the graphite rods showed degradation of material while operating potentiostatic experiments and thus such pre-treatment was not carried out again.

An Ag/AgCl reference electrode with a standard potential of +0.199 mV vs SHE (Amel S.r.l., Milano, Italy) was used for the cyclic voltammetry experiments. All the following potentiostatic experiments were carried out using an Ag/AgCl reference electrode with a standard potential of +0.209 mV vs SHE (3 M NaCl, QVMF2052, ProSense, BB Oosterhout, The Netherlands).

Table 3.1: Brief description of the electrode materials used in the thesis.

Material	Dimensions	Geometric Surface Area	Source
Platinum coated Titanium	2 cm x 2 cm x 0.3 cm	10.4 cm^2	Ti Shop, London, UK
Carbon felt	2 cm x 2 cm x 0.3 cm	10.4 cm^2	Alfa Aesar, Thermo Fisher GmbH, 76057, Karlsruhe, Germany)
Graphite rod	15.2 cm x 0.6 cm | 10 cm x 0.6 cm (under wastewater)	11.3 cm^2	Alfa Aesar, Thermo Fisher GmbH, 76057, Karlsruhe, Germany)

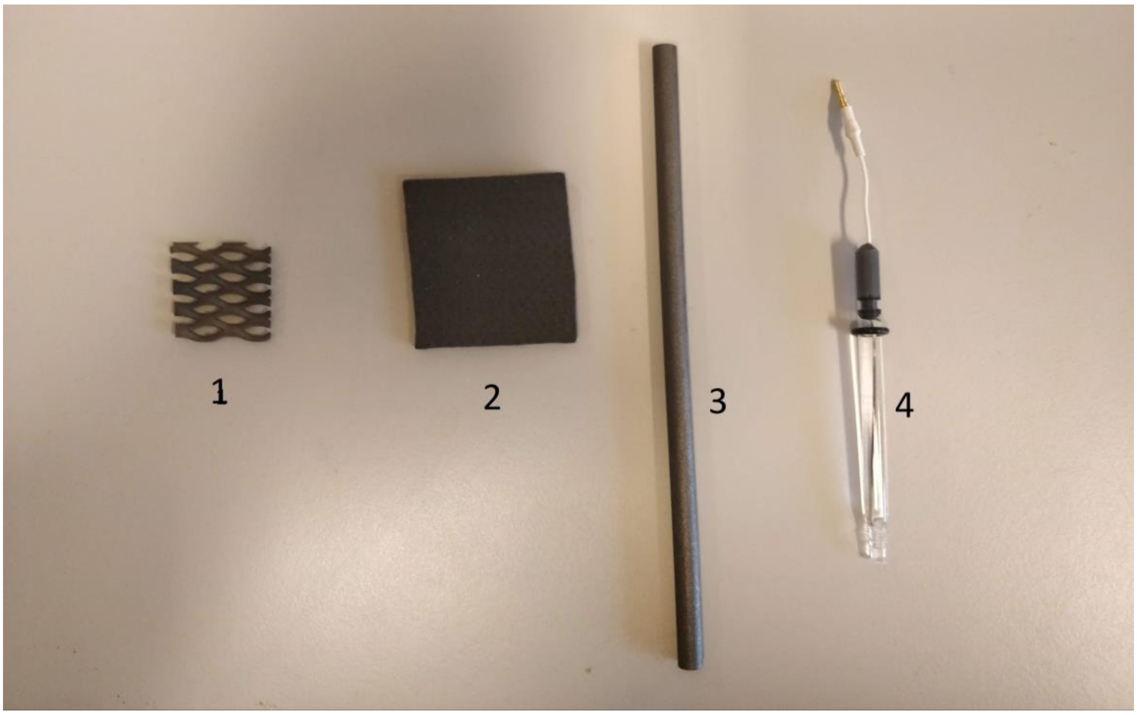


Figure 3.1: Electrode materials used in during PhD 1) platinum coated titanium mesh 2) carbon felt piece 3) graphite rod and 4) Ag/AgCl reference electrode.

3.1.2 Chemicals

The following chemicals were used to prepare artificial wastewater and supplementing the reject water feeds. Artificial wastewater made of $K_2HPO_4 \cdot 3H_2O$ 3.0 g/L, KH_2PO_4 11.8

g/L, $NaHCO_3$ 6.0 g/L, NaCl 1.0 g/L, NH_4Cl 1.0 g/L, $CaCl_2$ 0.2 g/L, $MgSO_4 \cdot 7H_2O$ 0.15 g/L (Jiang et al., 2013), 10 mL/L of trace metal solution (Muyzer et al., 1993), and 10 mL/L of vitamin solution (Nevin and Lovley, 2000). The reject water was obtained from Knarrdalstrand wastewater treatment plant in Porsgrunn, Norway. The reject water supplemented with acetic acid at a concentration of 17.3 mM and 85.0 mM $NaHCO_3$ to simulate reject water of food waste treatment plant. The reject water was supplemented with 85 mM sodium hydrogen carbonate to provide inorganic carbon source to the MES.

3.1.3 Reactor Setup

3.1.3.1 Batch studies (Article 2)

A batch reactor was prepared using 100 mL Duran glass bottle where the three electrodes (anode, cathode and reference) were immersed into artificial wastewater using 3-port Teflon cap. A magnetic stirrer was also placed in the reactor which was seated on a magnetic plate.

3.1.3.2 Continuous flow studies (Articles 3, 4 and 5)

A continuous flow stirred tank reactor was constructed using 100 mL Duran glass bottle modified by fabricating two glass ports extended on opposite sides of the bottle (one at neck and one at bottom of the bottle). A 3-port Teflon cap was used to insert the anode and reference electrode along with the effluent tube. The bottom side port was used for feed inlet and the cathode was inserted into the reactor using side port at the neck of the bottle. The electrode terminals were connected to the respective potentiostat terminals. A reject water tank was connected to the CSTR using a Tygon tube through a pump to control flow of the feed. The effluent tubing was also Tygon and a 1-inch Teflon tube was used to avoid gas/effluent leaks. The effluent tube also carried the gas produced in the reactor, it was then separated using a gas separator (a 15 mL bottle with two side ports at the bottom and an open mouth at the top).

The gas-effluent separator was placed upside down on a metallic clamp stand and one of the side ports was used as the inlet for the effluent-gas mixture. The other side port was connected with a tube that lead the gas into a water displacement tank. The open mouth of the separator was placed in the bottom and connected to Tygon tube through a Teflon tube and rubber cork to let to effluent collection bottle. The height of the separator and U-shaped effluent tube was used to collect the effluent in a drip system and avoid gas leakage from the mouth of the separator. The reactor was placed in an incubator which was maintained at a temperature of 35 ± 0.1 °C. All the electrode connection and tubing were passed through the side holes drilled through the walls of incubator. Cotton was used to fill the remaining gaps in the drilled holes to maintain minimum heat exchange between the room and incubator.

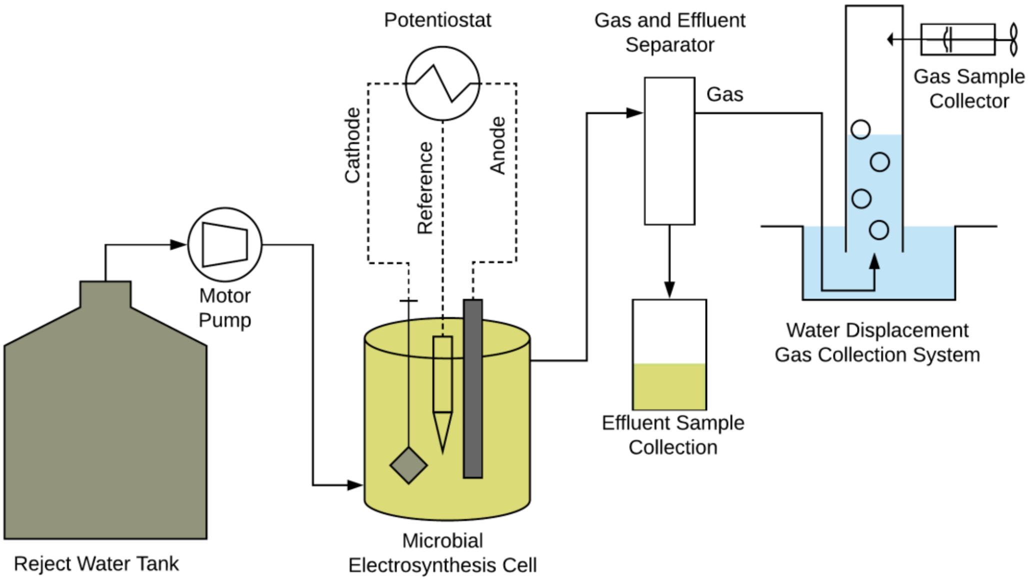


Figure 3.2: Schematic representation of reactor setup used for continuous-flow experiments

All the electrochemical experiments were carried out using Gamry 1010 B potentiostat purchased from Gamry Instruments, Warminster, PA, USA. The electric current and electron coulombs were measured using the software Gamry Framework v7.06. The tubing pump REGLO Analog MS-4/6 was purchased from ISMATEC, Cole-Parmer GmbH, Futtererstrasse 16, 97877 Wertheim, Germany.

3.2 Methods

3.2.1 Experimental Methods

The experiments were first setup for electrode material selection using cyclic voltammetry of artificial wastewater using platinum-coated titanium as cathode and evaluating the anode for comparing the electrode materials. Carbon felt was selected as the designated biocathode and was used to develop biofilm by running a potentiostatic fed-batch experiment on reject water supplemented with both acetic acid and sodium bicarbonate. This was followed by a biomethane potential experimental as a base for optimisation experiments.

The parameters of pH and cathode potential were studied and optimised by changing the feed conditions and cathode potentials for every potentiostatic mode of operation in a continuous flow system. Furthermore, biocathode performance was studied at different potentials in order to understand the mechanism of direct interspecies electron transfer. The biocathode was then adapted to feed containing no acetic acid by gradually decreasing feed acetic acid concentration for every potentiostatic operation. Finally, the effects of hydraulic retention time were evaluated on MES using both types of feeds (reject water with and without acetic acid). The HRT experiments further enhanced the results of the biocathode adaptation experiments where electro-oxidation of COD at the anode was also possible.

3.2.2 Feed Preparation

Raw feed was collected from the effluent of the centrifuge tank in wastewater treatment plant, post-anaerobic digestion process for every 2 months in 10 to 20 litre cans. The feed was brought to laboratory and stored in a cold room that is maintained at 6 to 7 °C. 500 mL to 3 L of the feed was taken out for every experiment and centrifuged at 10000 RPM for 15 min. Depending on the experiment, the centrifuged feed was then supplemented with acetic acid, sodium bicarbonate, 1M HCl solution or Phosphate buffer.

3.2.3 Analytical Methods

All the feed and effluent samples were subjected to a series of analytical tests: pH, chemical oxygen demand, alkalinity and volatile fatty acids. COD was analysed using Merck COD cell test kit 110047 which follows the standard method APHA SMWW 5220D. VFA was analysed using the standard method APHA SMWW 6200B and a Gas Chromatograph Hewlett-Packard 6890 where the carrier gas helium and hydrogen at 4 bar pressure are passed through the DB-FFAP GC column (30 m, 0.25 mm, 0.50 µm, 7 inch cage) and are detected using a Flame Ionisation Detector (FID). Alkalinity was measured using the Merck cell test kit 11009 following the standard method APHA SMWW 2320B [38]. The voltage and current were measured the Gamry Echem Analyst v7.06 (Gamry Instruments, Warminster, PA, USA) respectively. Biogas was analysed using the 8610C gas chromatograph (SRI Instruments, Torrance, CA, USA) equipped with a thermal conductivity detector and with a Haysep-D (HD) and MoleSieve (MS13X) column which separates oxygen, nitrogen, methane and carbon dioxide. The carrier gas was Helium at 4 bar pressure and the oven temperature was kept constant at 80 °C.

Table 3.2: Characteristics of reject water

Characteristic	Value	Remarks
Total solids	4250 mg/L	-
Volatile suspended solids	2640 mg/L	-
COD (soluble)	1600-1800 mg/L	Increased by supplementing acetic acid
VFA	100-200 mg/L	Increased by supplementing acetic acid
Alkalinity	1000-1500 mg/L	Increased by adding sodium bicarbonate
pH	7.2 – 7.4	Changed by adding acetic acid, sodium bicarbonate, phosphate buffer and HCl

4 Summary of Results

In this section, the research leading to the four papers, key findings, and some unpublished results are summarized.

4.1 Article 2: Optimisation of Electrochemical Treatment of Artificial Wastewater Using Cyclic Voltammetry

A cyclic voltammetry study reveals at which cathodic potential a particular reaction occurs when the potential is varied within a range at a constant rate (here at 100 mV/s). The peak electric current and the corresponding cathode potentials are compared to identify the optimal combination of parameters. This study was carried out in batch mode to identify suitable electrode materials for MES operation at six different temperatures (30, 35, 40, 45, 50 and 55 °C) and four different pH conditions (7.0, 7.5, 8.0 and 8.5) of the artificial wastewater feed. The carbon felt and graphite electrodes were used to compare the electrochemical activity with platinum-coated titanium mesh that is considered to be the ideal material for electrochemical hydrogen production reactions. The cathode for all the experiments was unchanged as platinum while the anodes were studied for platinum, carbon felt and graphite rod. The performance of carbon-felt electrode was very close to that of platinum coated titanium and the optimal pH and temperature were found to be approximately 7.0 to 7.5 and 35 to 40 °C that resulted in peak currents in the range of 30 to 32 mA corresponding to lower absolute potentials of -0.45 V.

4.2 Article 3: Bioelectrochemical CO_2 Reduction to Methane: MES Integration in Biogas Production Processes

The experiments involved study of carbon dioxide reduction to methane by treating actual reject water from the local municipal wastewater treatment plant supplemented with acetic acid at a concentration of 17 mM. The acetic acid supplementation was done to simulate integration of MES at the recycle loop of reject water line of the food waste AD reactor (F1). Biocathodes were developed in a fed-batch reactor over 2 months in a

3 litre reactor where 500 mL of feed was replaced with fresh feed every week. Two of the biocathodes were selected to carry out an initial biomethane production experiment for 6 weeks. The continuous flow experiment with 24-hr HRT was carried out at a cathode potential of -0.80 V and samples were collected during the last week of operation. This was followed by optimisation experiments of cathode potential (1 month) and pH (1 month) in a continuous flow stirred tank reactor.

The biomethane production experiment reveals that electrochemical CO_2 reduction is possible with carbon felt as a biocathode but requires optimisation of several parameters. The following experiments showed an optimal feed pH to be in the range of 7.0 to 7.5 and the optimal cathode potential in the range of -0.55 to -0.70 V. However, in the presence of acetic acid, heterotrophic methane production is dominant and makes it difficult to distinguish between the productivity of each of the pathways (heterotrophic or electrosynthesis). Methane concentrations of about 90% were consistently obtained but it was identified that due to dominant heterotrophic activity and high effluent pH the CO_2 released would dissolve into the effluent liquid. The study, therefore, concludes with the importance of separation of heterotrophic and electrochemical activities and proposes a novel method for integration of MES as a post treatment unit for the biogas production processes.

4.3 Article 4: Performance Analysis of Biocathode in Bioelectrochemical CO_2 Reduction

A set of blank (10 days) and control experiments (10 days) were carried out along with acetic acid production (34 days), baseline methane production (9 days) and biocathode adaptation (40 days). The open circuit operation (without electric supply) showed methane production rates of about 14.0 mmol/$L_{(reactor)}$-d whereas the COD consumption rate (acetic acid) was approximately 17.5 mmol/$L_{(reactor)}$-d. The blank (without acetic acid, without electric supply) operation showed negligible amount of methane production while the COD consumption rate was also negligible. These experiments established our control. The MES was able to produce acetic acid via CO_2 reduction at low rates when the applied cathode potential was -0.80 and -0.90 V vs SHE and feed pH of around 7.0. Both methane and acetic acid production rates were low when the feed pH was increased to 7.7.

The baseline MES operation was carried out with both acetic acid (17.0 mM) and sodium bicarbonate (85 mM) in the feed and operated at a cathode potential of -0.65 V vs SHE. The MPR for baseline operation (F1) was observed to be approximately 19.5 mmol/$L_{(reactor)}$-d compared to 14.0 mmol/$L_{(reactor)}$-d in open circuit operation. At the same time the COD consumption rate was also around 19.5 mmol/$L_{(reactor)}$-d which is higher than what was observed in the open circuit mode (17.5 mmol/$L_{(reactor)}$-d). Correspondingly, the COD consumption rate (19.5 mmol/$L_{(reactor)}$-d) was higher than the VFA (acetic acid; 17.5 mmol/$L_{(reactor)}$-d) consumption rate indicating oxidation or hydrolysis of additional COD in MES operation. However, the baseline operation showed no reduction in alkalinity owing to the dominance of heterotrophic methane production that also produces carbon dioxide (at equilibrium with bicarbonate in the effluent).

Biocathode adaptation experiments were then carried out to evaluate the efficiency of direct interspecies electron transfer by reducing the amount of acetic acid in the feed. The share of methane production via electrochemical pathway increased gradually from 7.5% (baseline operation) to approximately 45% when no additional acetic acid was supplied to the feed (F2: feed simulating wastewater treatment reject water). The average MPR was decreased by 80% whereas the acetic acid concentration was decreased by 90%. At the same time, the alkalinity in the reactor was reduced at a rate of 9.5 mmol/$L_{(reactor)}$-d showing the source of methane to be bicarbonate. The methane concentration in biogas was always maintained above 90% for all feed acetic acid concentrations. To obtain a mass balance the coulombic efficiency was assumed to be 100%, and the heterotrophic efficiency was observed to increase from 90.0% (baseline operation) to 99.5% (at feed acetic acid concentrations of about 8.3, 4.5 and 2.0 mM). This implies that COD required to support biomass growth and maintenance becomes limited at feed acetic acid concentration of approximately 8.3 mM. This also establishes that electron transfer mechanism in the MES operation to generate methane is via bicarbonate at high effluent pH.

4.4 Article 5: Effect of Hydraulic Retention Time on MES Operation for Biomethane Production

The pH during biocathode adaptation experiments (at 24 hours HRT) never decreased below 8.4 which implied overall low methane production rates and harmful effluent. Therefore, hydraulic retention time (HRT) was used as a tool to optimise the feed flow rates to increase MPRs and lower the effluent pH. The food waste treatment reject water (F1) experiment were carried out in a new reactor (after biofilm growth and biomethane experiments for over 2 months) and the wastewater treatment reject water (F2) experiments were carried out in the same reactor used to carry out biocathode adaptation experiment. The experiments start with an HRT of 24-hrs and are operated at 18, 12, 6, 3, 2, 1-hr HRTs after every 8 to 10 sampling points.

The methane production rate for the HRT experiments were analysed based on two parameters: a) reactor volume and b) feed volume. For the feed F1, the highest MPR of about 40.3 mmol/$L_{(reactor)}$-d was obtained at 6-hr HRT operation while the highest methane yield was obtained at 18-hr HRT that was 12.2 mmol/$L_{(feed)}$-d. The methane percentages at 24- to 12-hr HRT operation was around 90-92% which decreased thereafter due to unreacted CO_2 at higher flow rates. Moreover, 18-hr HRT operation showed a high share of COD consumption 40.6%. Similar results were obtained during HRT optimisation of MES of feed F2. The adaptation of biocathode further increased methane production rates by 50% (4.0 to 6.0 mmol/$L_{(reactor)}$-d at 24-hr HRT). Further, increasing feed flow rate increased MPRs to about 19.6 mmol/$L_{(reactor)}$-d at 3-hr HRT. However, 18-hr HRT was identified as optimum due to high COD removal of 23.4% and methane production yield of about 7.4 mmol/$L_{(feed)}$-d. The pH of the effluent decreased below 8.0 at 18-hr HRT and remain stable around 7.5 to 7.8 during all other lower HRT operations. The methane percentage in biogas is observed to be around 87to 90% during 24, 18, 12 and 6 -hr operations and decreased at a faster rate thereafter.

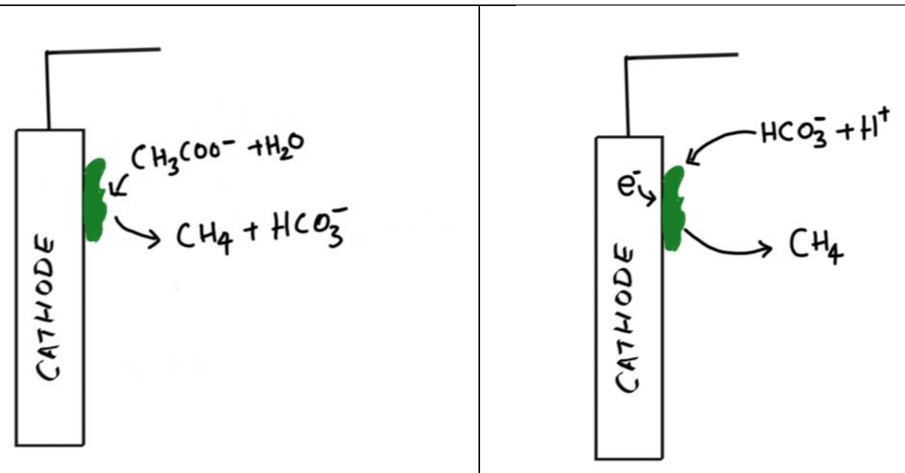
It can be concluded that the MES operation does not affect the electrochemical reaction efficiency as observed from the increasing ratio of heterotrophic and electrochemical methane. However, HRT affects the overall COD removal and methane production. The COD removal of around 20-25% was observed in experiments with feed F2. This was hypothesized to be due to direct electro-oxidation of organics at anode that is able to produce CO_2 and protons. Most of the CO_2 released via oxidation of organics remains unreacted and escapes as gas lowering the methane percentages. On the other hand, the protons seem to increase the current flow and reduce pH of the effluent as well.

4.5 Additional Results

4.5.1 Distribution of Reaction Mechanisms

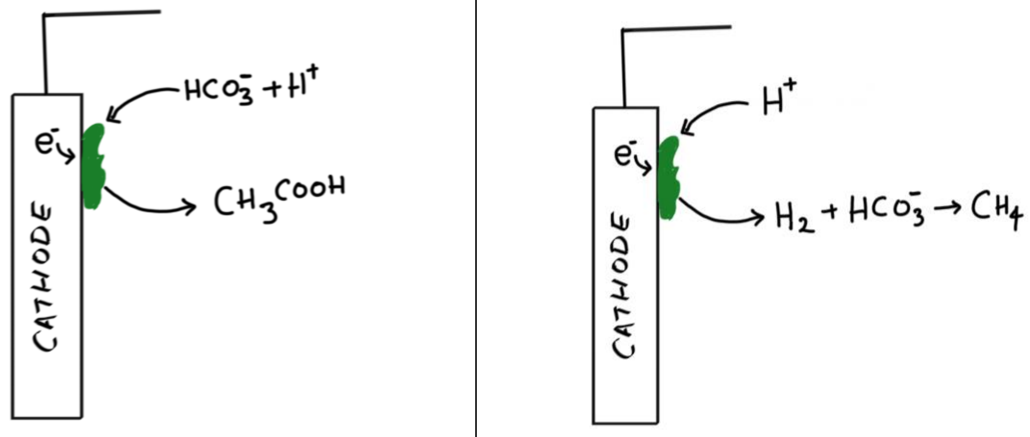
There are four possible reactions that can occur at the cathode to produce either of acetic acid or methane (Figure 4.1). Here it can be said that most of the methane was produced through via heterotrophic digestion of acetic acid by methanogens in the bulk (Fig 4.1 (a)). The methane contribution via heterotrophic pathway was around 90 to 95% v/v CH_4 with feed F1 and approximately 55% v/v CH_4 with feed F2. The methane share produced via electrochemical pathway (Fig 4.1 (b)) on the other hand, increased from about 7% to 45% when the feed was changed from F1 to F2. It is also important to consider that the CO_2/HCO_3^- required for electrochemical methane production can be obtained from four sources. 1) Heterotrophic conversion of acetic acid to methane and CO_2/HCO_3^- 2) CO_2/HCO_3^- dissolved in the feed 3) CO_2/HCO_3^- produced via electro-oxidation of COD and 4) CO_2 supplied as biogas for upgrading.

The third pathway involves COD consumption that may or may not be available for purely biological methane production via the heterotrophic methane production pathway. If the COD is easily degradable, such as acetate, the degradation and methane production in this case is not necessarily increased but just shifted to electrochemically stimulated autotrophic activity and thus contributes to electrochemical methane production pathway. If the COD degraded at the anode is a fraction that will other ways not be degraded, the electrochemically stimulated degradation and methane production will increase both methane yield and content. This residual COD degradation at anode will deliver protons required for the electrochemical cathode activity. Thus, the process avoids splitting of water to produce the required protons, thereby avoiding oxygen production that would hinder methanogenic activity.



(a) Heterotrophic methane
90-95% methane source with F1
~55% methane source with F2

(b) Direct interspecies electron transfer
5-10% methane source with F1
~45% methane source with F2



(c) Direct interspecies electron transfer at higher voltage (only with F2)

(d) Indirect electron transfer
No evidence

Figure 4.1: Reaction mechanisms that may have been contributing to methane and acetic acid production in this study where two feeds were applied (F1 – AD effluent with acetate suplement and F2 - AD effluent without acetate suplement). The source of bicarbonate in (b), (c) and (d) can be heterotrophic degradation of COD, externally supplied bicarbonate and anodic oxidation of COD.

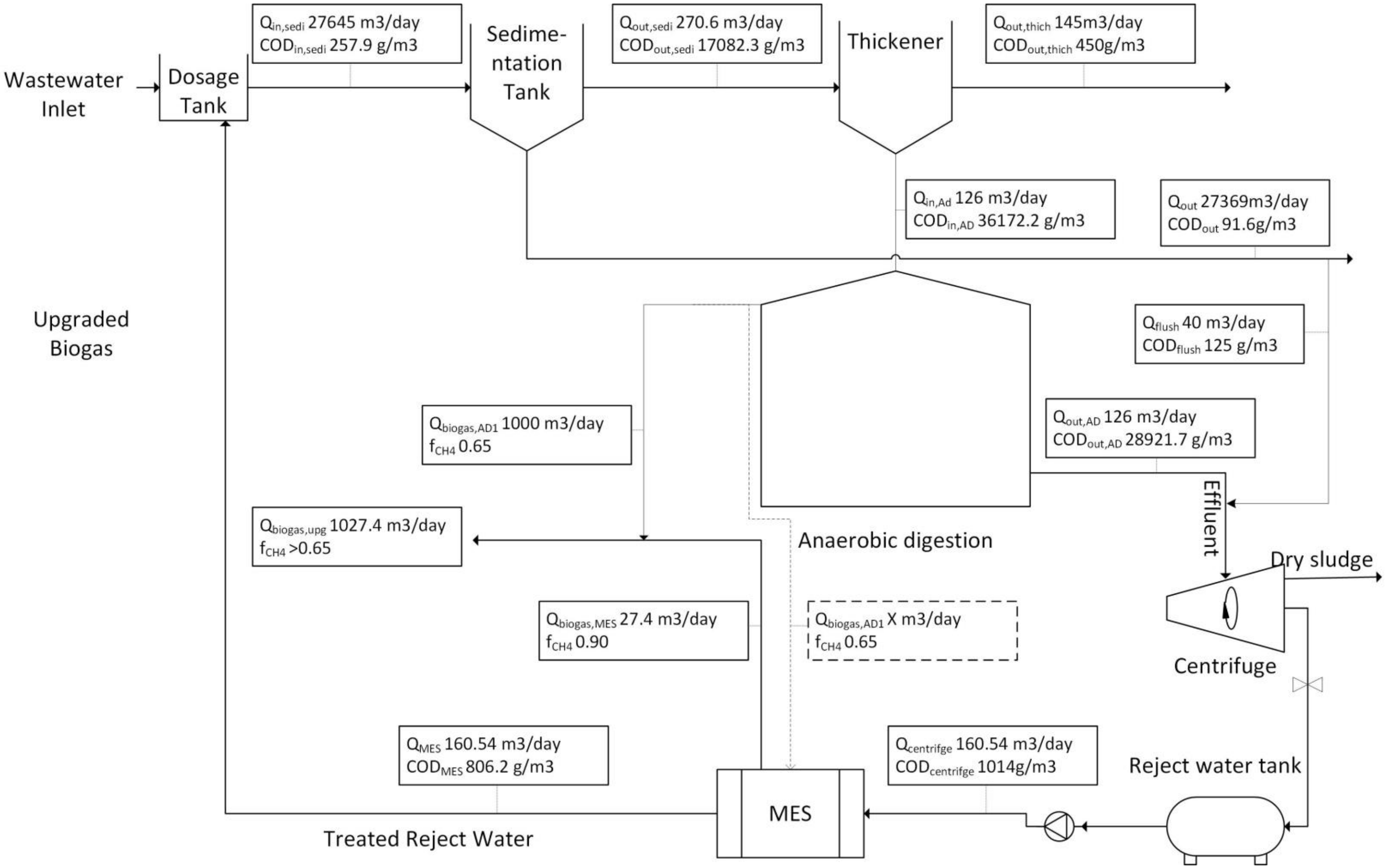


Figure 4.2: Schematic representation of flow balance of integrated MES and AD reactor in Knarrdalstrand WWTP.

The other recognized method to produce methane by bio-electrochemistry is by indirect electron transfer via protons to produce hydrogen gas (Fig. 4.1 (d)) but this is assumed less favourable as it requires higher voltage and is accompanied by oxygen generation at the anode. However, no evidence of hydrogen production was observed in the gas analysis. Hydrogen gas analysis was carried out by changing the carrier gas from Helium to Argon in reverse polarity in the Gas analyser. There was also no evidence of oxygen gas production in the gas analysis that would be recognised as Air under normal operation, so it is concluded that indirect electron transfer by hydrogen was avoided.

4.5.2 Integration Extrapolation

The current study is applied and extrapolated to the Knarrdalstrand wastewater treatment plant from where the reject water feed was obtained. The MES operation is scaled up to match the reject water flow rate and all the optimised parameters are used to estimate the result.

By scaling up the MES reactor for 12-hr HRT operation with a feed flow rate of 160 m^3/d that is observed as the effluent flow rate post centrifugation in the wastewater treatment plant (WWTP; Hashemi, 2018). This allows the reactor size to be around 80 to 82 m^3. Scaling up the methane production for such a reactor, it is calculated that 27 m^3/d biogas produced with 90 % methane concentration. The overall methane production at this WWTP thereby increases by 4 % from 650 m^3/d to 675 m^3/d with a methane percentage of about 66 % in biogas. It is possible to increase the methane concentration and production further by injecting some or all of the AD-biogas into the MES reactor, such that, CO_2 (35%) present in the biogas is also electrochemically reduced to produce methane. In such a case it is also estimated that the final output COD is decreased to 806 g/m^3 from 1014 g/m^3 which is currently the COD of the effluent, as a significant added benefit.

The electrode area to reactor volume ratio of the lab-scale reactor is approximately 2.8 m^2/m^3 which can and should be significantly increased in an industrial scale reactor, depending on the reactor design and electrode placement. Another factor that could impact in methane production positively is the current density that is propelled without changing the cathode potential. The current density for MES reactor at different HRTs with feed F2 is measured to be around 4-5 A/m^2 at -0.65 V cathode potential. This can be improved further by optimising reactor design at a larger scale. A plug flow tubular reactor would be able to maintain a healthy biofilm thickness with higher mass transfer efficiencies than a CSTR (Fassouane et al., 1990). Both these factors (area to volume ratio and current density) need to be evaluated firstly in pilot scale and can be applied to real-scale reactor upon optimisation. Such an optimised MES-AD integration solution appears capable to provide a cost-efficient biogas upgrading technology.

5 Conclusions

Carbon felt electrode material was chosen for its performance similar to that of platinum coated titanium electrode. It is highly conductive and an inexpensive material to purchase and/or replace as necessary. It is flexible in terms of electrode shape design and the large effective surface area is suitable to hold high biofilm density. Through the cyclic voltammetry experiment it was also concluded to maintain a feed pH of 7.0 to 7.5 and a temperature of 35 to 40 °C.

Single chamber microbial electrosynthesis system has many advantages over using a proton/cation exchange membrane separated two chamber bioelectrochemical cells. It increases current densities and due to the avoidance of hydrogen production it does not affect the purity of final product. It took approximately 2-3 months to achieve steady state current production when new biocathodes are prepared. These have been used for over 2 years under various operating conditions without interruptions. It was possible to produce biomethane at a cathode potential range of -0.55 to -0.70 V vs SHE while the optimum potential was observed at -0.65 V. Methane concentrations in biogas was observed to be always greater than 90% but it was identified that 90-95% of the methane was heterotrophic in nature and the CO_2 produced was dissolved within the reactor and came out as bicarbonate with the effluent. The main reason behind this was the acetic acid in the feed and pH within the reactor/effluent that was always in the range of 8.2 to 8.7. Evidence of electrochemical methane production was observed when the pH within the reactor was above 8.4 implying toxic heterotrophic environment. The control experiments showed only 13.6% improvement in methane through MES operation over open circuit mode of operation.

As the biocathodes were operated in baseline MES mode operation for over 2 months the methane productivity showed a significant increase, 39% more methane compared to open circuit operation in terms of MPR. It was then observed that the bioelectrochemical operation was not only reducing CO_2 to methane bust also oxidising COD to produce CO_2 and protons that are in turn converted to methane. The biocathode adaptation to lower feed acetic acid concentrations showed improvement in the electrochemical pathway for methane production from 7.5% to about 45% with and without additional acetic acid in the feed respectively. This showed the dominance of heterotrophic methane production over electrochemical methane. The electrochemical pathway contribution was made clear as it was observed the alkalinity was being consumed instead of being produced. The presence of acetic acid produces CO_2/HCO_3^- heterotrophically contributing to production of alkalinity. However, the adaptation experiments did not influence the effluent pH which were still in the range of 8.2 to 8.7.

It was also concluded that higher cathode potentials operations at -0.80 and -0.90 V vs SHE would contribute to the production acetic acid via electrochemically albeit al low production rates. However, such an evaluation would require change in the biota of the biofilm and requires rigorous adaptation to the new conditions, and thus was discontinued. Production of acetic acid by MES is also less relevant for biogas production since the turnover of CO_2 to methane trough acetate production is 50%.

Decreased hydraulic retention time to 18-hrs was able to bring down effluent pH below 8.1 while increasing the methane yield by approximately 7% compared to baseline experiment. However, the methane production was still dominated by acetic acid in the feed. HRT experiments without the acetic acid in the feed showed 50% higher MPRs compared to biocathode adaptation experiment at 24-hr HRT. 18-hr HRT experiment showed optimised performance of highest methane yield (7.4 mmol/$L_{(feed)}$-d) combined with anodic oxidation of organics (COD removal of 23.4%). The HRT did not affect the share of electrochemical methane production (via DIET) but improved COD degradation that can be utilised for methane production of lower recycling requirements.

Further advantages of using single chambered MES include low capital investment, operational and maintenance costs to be integrated with existing anaerobic digestion plants. The MES units can be an independent market, can be sold and serviced for the clients with minimal modification to the existing plant infrastructure. Moreover, MES systems are flexible that are not severely affected due to down time and can be used intermittently depending on the excess renewable electricity supply.

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Part II

Article 1

Electrochemically Mediated CO_2 Reduction for Bio-Methane Production: A Review

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Published in *Reviews in Environmental Science and Bio/Technology*. 17(3), 531–551. 2018.

Rev Environ Sci Biotechnol (2018) 17:531–551
https://doi.org/10.1007/s11157-018-9470-5

REVIEW PAPER

Electrochemically mediated CO_2 reduction for bio-methane production: a review

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Abstract A number of methods for carbon capture, more specifically, CO_2 capture have been researched in the past few years. One such method is electrochemical CO_2 reduction to biomethane which also serves the purpose of biogas upgradation using microbial electrosynthesis systems. This technology is also known as Power to Gas technology and the review starts with the importance and requirement of PtG in the modern world by studying energy production and consumption patterns in Europe, with a focus on Norway. The paper summarises the recent works and concepts in the field of bioelectrochemical systems with a focus on electron transfer mechanisms, biocatalysts and reactor designs. Works and gaps in the studies of direct interspecies electron transfer and biocathode developments are discussed in detail. This is followed by a discussion explaining various reactor designs, the advantages of single chambered microbial reactors and the importance of reactors that combine anaerobic digestion with microbial electrolysis cells.

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Keywords Bio-methane · CO_2 reduction · Microbial electrosynthesis systems · Power to gas · Anaerobic digestion · Microbial electrolysis cells

1 Introduction

Fossil fuels will play a major role as leading source of energy for a foreseeable future and their persistent use inherently result in production of greenhouse gases, particularly, carbon dioxide. Therefore, carbon capture, carbon sequestration and other carbon dioxide abatement techniques have gained major focus in the research and development sections of many industries and universities. At the same time, national and international governments of many countries especially in Europe have put forward strict regulations on greenhouse gas emissions and in improving renewable energy sources. There are many methods currently in research for carbon capture and one of them is the electrochemical reduction of carbon dioxide.

Electrochemical methods for biofuel/high value chemical production and waste treatment has attracted many researchers with a bulk of research articles published in the last 5 years on bioelectrochemical CO_2 reduction. A large part of the research focuses on bioelectrochemical systems (BES) where the microorganisms act as catalysts for the electrochemical reactions at the electrodes. Microbial fuel cells (MFC) are one of the most studied BES where bioanodes are used to treat wastewater and produce electricity. The microbial electrosynthesis system (MES) is a modified version of MFC, where an applied potential difference results in overcoming non-spontaneous reactions such as carbon dioxide reduction for the production of different chemical products including methane with a help of a biocathode (Guo et al. 2013b, 2017; Januszewska et al. 2014; van Eerten-Jansen et al. 2015; Bajracharya et al. 2016; Cai et al. 2016; Zhao et al. 2016; Aryal et al. 2017b; Bajracharya et al. 2017a). The microbial electrolysis cells (MECs) on the other hand use electricity to split water into hydrogen and oxygen using a bioanode. Although hydrogen is a direct product of electrolysis, due to the issues such as storage, stability and transport, it falls short to other biofuels such as methane (United States. Dept. of Energy 2004).

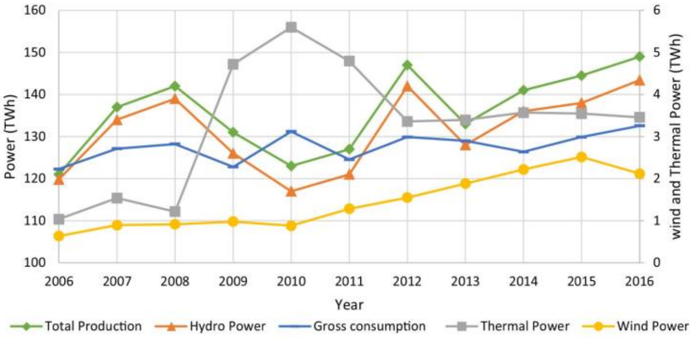
Microorganisms are able to generate a potential of about − 0.300 V by feeding on acetate present in the electrochemical cell. However, this voltage is not sufficient to generate hydrogen at the cathode, which requires a cathode potential of about − 0.414 V. With the help of the extra potential supplied through a potentiostat or main electric supply, hydrogen evolution is achieved at the cathode (Liu et al. 2005). An extension of this reaction with help of suitable microorganisms and optimised experimental conditions would lead to efficient carbon dioxide reduction with the formation of methane (Call and Logan 2008). This concept was developed as a cheaper option with the use of biocathodes and easier storage options compared to hydrogen production and storage (van Eerten-Jansen et al. 2015). Additionally, the volumetric energy density of hydrogen is very low (11 MJ/m^3), when compared to methane (36 MJ/m^3) making it a very impractical fuel to serve as an energy source. Methane therefore becomes an ideal fuel source that can be stored and transported inexpensively and used widely, especially for public transport (Balat et al. 2008).

Latest trends of energy statistics in some of the European nations such as Germany and Norway (Fig. 1) show that renewable electricity could be one of the major sources of energy. There is a need to create demand for this electricity and the best way for that is to find energy sectors that are able to replace fossil energy sources. The chief customer officer of the company SolarFuel in Germany, Stephan Rieke has reported that the excess renewable energy in Germany grew from 150 gigawatt-hours per year to 1000 gigawatt-hours per year in 2 years. The amount is expected to continue to grow as Germany pursues ambitious goals to cut greenhouse-gas emissions 80% by 2050 using largely renewable energy (Sterner 2009; Hoekman et al. 2010; Specht et al. 2010; Götz et al. 2011a, b; Graf et al. 2011). A similar situation is to arise in the Scandinavian nations and especially in Norway where already 96% of the electricity is sourced through hydroelectric power stations (SSB 2017a).

Figure 1 depicts the electric power production and consumption trends in Norway where different power generation sources such as hydro, thermal and wind have been included. It can be observed, except for 2010, that gross power consumption (blue) in Norway has always been lesser than total power production (green) every year except for 2010. For example in the year 2015, the total power production was around 145 TWh whereas the gross power consumption was only 130 TWh leading to almost 15 TWh of excess energy production. In the same year, the contribution from hydroelectric power (orange) to the total electricity production was 138 TWh, which in itself is more than the gross consumption. This leads to an excess electricity production of about 2.5 TWh through wind power (yellow) and 3.5 TWh through thermal power (grey).

Also, in the 5 year period of 2011–2015 it can be observed that wind power (orange) production has been more than doubled from 1.2 TWh in 2011–2.5 TWh in 2015 which indicate that Norwegian policies for renewable energy power are very encouraging (SSB 2017a). At present the excess electricity is being exported to the neighbouring countries and therefore Norway is rewarded financially. The capacity of these renewable sources for electricity would only increase in the coming years, an alternative to exporting the excess electricity is for it to replace fossil energy sources especially in the transport sector. This approach of carbon capture addresses the specific issue excess renewable energy that is going to be available in the coming years. This technology is otherwise coined as 'Power to Gas' (PtG) technology (Mohseni et al. 2017).

Fig. 1 Electric Power production and consumption trends in Norway for a period of 10 years between 2006 and 2016 (SSB 2017a)



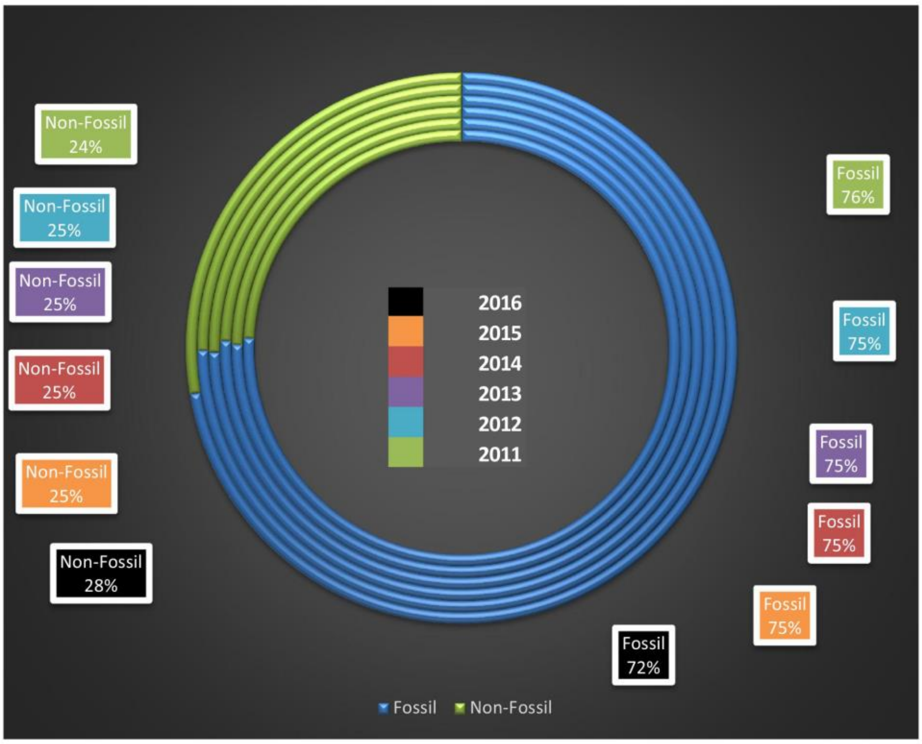


Fig. 2 Energy consumption share of fossil and non-fossil fuel sources in Norway. Data: (SSB 2017b)

2 Power-to-gas technology

The primary energy source in most countries of the world are fossil fuels such as coal, oil and natural gas, which also includes Norway, where electric power is sourced from non-fossil fuels (Fig. 2). However, the percent share of consumption of non-fossil versus fossil fuels is gradually increasing from about 24–28% from 2011 to 2016. A majority of the non-fossil energy is the electricity as it is produced through hydropower (96%), wind (1.7%) and thermal (2.3%) (SSB 2017a), other non-fossil energy sources being biomass and waste derived biofuels. Biofuels have a huge potential to be the primary transport fuel as waste treatment is a perennial activity which must be, which is currently dominated by oil industry followed by natural gas and electricity. Additionally, Norwegian government at present, provides various benefits to own an electric car such as tax exemptions and free parking.

The main advantage of PtG technology is that, it can reduce industrially produced carbon dioxide, which makes it an inexpensive carbon capture technique. This provides many industries with a motivating opportunity to reduce their carbon emissions which are currently highly warranted by government policies. Especially in the European nations, the requirement to reduce carbon emissions have become strict in order to encourage industries to be fully sustainable. Through the PtG technology not only do industries benefit from reducing CO_2 emission and waste generation but can also make themselves self-sustainable or generate some economy through the use or sale of high quality methane produced to the existing natural gas grid (ElMekawy et al. 2016). The European Renewable Energy Council has projected an energy mix of 21% of renewable energy in the EU's overall energy production by 2020 (EU Roadmap 2011). Hashimoto and team (1999) proposed a solar energy system equation to evaluate the desert area required for a solar plant to supply power to the whole world. In this hypothetical scenario, the authors explain the impracticalities involved in the transport of renewable electricity over long distances and suggest electrochemical reduction of industrial carbon dioxide to produce gas which can be efficiently transported by compression.

The main limiting factor for biogas to be a transport fuel is its purity (60% methane) as compared to natural gas which contains > 85% methane and other hydrocarbon fuels (Union Gas 2011). Therefore, the focus has shifted towards emerging technologies reduce carbon dioxide to methane using renewable electricity through electrochemical processing. Many reviews have discussed the importance of Power-to-Gas for handling high shares of renewable energies (Hashimoto et al. 1999, 2014; de Boer et al. 2014; Jentsch et al. 2014; Pleßmann et al. 2014). However, most of the literature available currently deals with the use of heterogeneous metal catalysts such as copper, nickel etc., (Hashimoto et al. 1999; Hoekman et al. 2010; Peterson et al. 2010; Zhan and Zhao 2010; Lim et al. 2014; Uhm and Kim 2014; Zhang et al. 2017).

Other method is to apply bio-electrochemical techniques where a syntrophic relation is established between various micro-organisms which act as catalysts for efficient electron transfer (Morita et al. 2011; Mueller 2012; Bo et al. 2014; Rotaru et al. 2014a; Zhao et al. 2015b; Biesemans 2016; Lin et al. 2016; Yin et al. 2016). Electron transfer can be of two types (a) direct electron transfer (DET) and (b) indirect electron transfer (IET). Both these mechanisms will be discussed in detail in further sections. Other applications of bioelectrochemical power-to- gas technology include sulphide reduction (Dutta 2009; Pikaar et al. 2014; Lin et al. 2016). In this review, we discuss the specific research on bioelectrochemical carbon dioxide reduction to methane using the excess renewable power. Focus will also be on single chambered electrolysis cells that can be combined with anaerobic digestion (AD) units and are able to convert CO_2 to CH_4 without the need of any separating membrane between anode and cathode (Guo et al. 2013b; Hirano et al. 2013; Bo et al. 2014).

3 Microbial electrosynthesis systems (MES)

Methane production was at first regarded as an unwanted by-product of electrolytic hydrogen production and efforts were made to eliminate or hamper methane production pathways (Hu et al. 2008; Wang et al. 2009). Methane was also an undesired product during the electrochemical synthesis of acetate and other chemicals (Bajracharya et al. 2017b). Prominently, two methods viz., heat shock and addition of sodium bromoethanesulfonate were used to inhibit methanogenic activity in such MES (Zinder et al. 1984; Patil et al. 2015). Bajracharya et al. (2017b) devised a method to avoid methanogenesis during long term operation of the MES through enrichment and acclimatisation of mixed culture repeatedly to produce acetate, hydrogen at a voltage of around − 1 V versus Ag/AgCl. The authors further processed the chemicals to produce ethanol and butyrate.

However, it was later realised to produce methane as the primary energy rich product (Hoekman et al. 2010; Villano et al. 2010). Combining the MECs with AD for efficient methane production was put forward by many scientists in the late 2000s as a practical alternative to biohydrogen production (Clauwaert et al. 2008b; Cheng et al. 2009). The other advantages to this shift were a) the ability to reduce carbon dioxide electrochemically to methane thereby increasing methane yield and biogas quality, b) the option of using non-precious electrodes such as graphite rod, carbon felt, carbon cloth etc., which are otherwise not useful for hydrogen gas production at lower potentials unlike the expensive platinum electrode (Graf et al. 2011; Van Eerten-Jansen et al. 2012).

There are two pathways to achieve electrochemical carbon dioxide reduction (Fig. 3):

Indirect electron transfer (MEC Cathode)

$$2H^+ + 2e^- \rightarrow H_2 E = -0.414 \text{ V vs NHE} \tag{1}$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{2}$$

Direct electron transfer (MES Cathode)

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2OE = -0.244 \text{ V vs NHE} \tag{3}$$

The theoretical potential for the reaction (3) that reduces CO_2 to CH_4 with a transfer of 8 electrons is below the theoretical potential for the electrolysis reaction of H_2 (1). Microorganisms involved in direct electron transfer would have a greater energy gain than organisms that use indirect electron transfer where hydrogen molecule acts as a shuttle for electron transfer. The methane producing MECs are able to carry out microbial reactions via interspecies hydrogen transfer (IHT) where hydrogen is not the final product but an electron mediator. The electrochemical principle states that a lower potential for the transfer of particular quantity of electrons is efficient against a use of higher potential for the transfer of same quantity of electrons (Mueller 2012). Hence, reaction (3) of MES, the direct electron transfer, which uses a lower potential is preferable over the MEC cathode reactions.

MEC Anode

$$CH_3COOH + 2H_2O \rightarrow 2CO_2 + 8H^+ + 8e^-E = -0.280 \text{ V vs SHE} \tag{4}$$

MES Anode

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-E = 0.820 \text{ V vs SHE} \tag{5}$$

The electrochemical potential and energy requirements of the two anode reactions 4 and 5 (Rabaey and Rozendal 2010), show that the theoretical anode potential required for acetate oxidation to bicarbonate

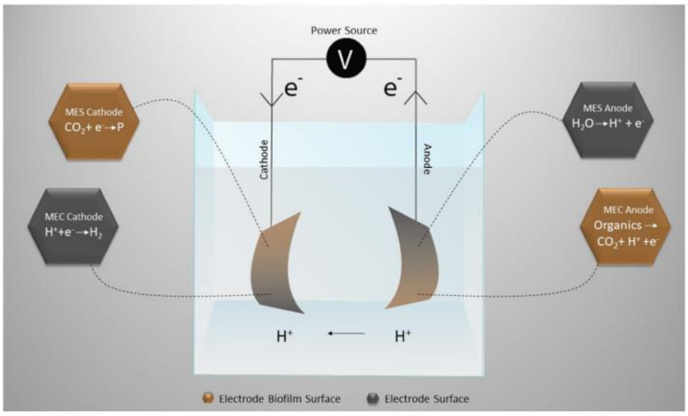


Fig. 3 A schematic representation of membraneless MES: microbial electrosynthesis system and MEC: microbial electrolysis cell for the treatment of wastewater and CO_2

is − 0.28 V while the oxidation of water to oxygen requires a theoretical anodic potential of 0.82 V. Hence, the bioelectrochemical acetate oxidation that happens in MEC will be preferred over the water oxidation (of MES) which is otherwise energy intensive. It can be observed that no one system generates the combination of reactions with lower potentials. Single chamber MECs (SCMEC) and combinations of AD and SCMECs, enable both the electrodes accessible to microbes and nutrients, have the potential to improve electron transfer and reduce voltages.

However, these potentials are only theoretical and when combined with losses that commonly occur, the absolute potentials required increase considerably which in turn increase the energy input. The losses that commonly occur are: (1) Overpotentials at the electrode surfaces that occur due to imperfect catalysis for the charge transfer to occur (Rabaey and Rozendal 2010); (2) Ohmic losses that occur due to the conductivity of the electrolyte to pass the electrons. This is considered to be one of the crucial parameters to be measured and optimised for the scale up of the system (Rozendal et al. 2008a); (3) Diffusion limitation that is occurred due to the double layer formation. This happens in the absence of proper mixing (to produce high current densities) of the electrolyte which reduces the movement of protons and hydroxyl ions towards the respective electrodes. These electrochemical losses hamper the electron transport and electron transfer rate thereby increasing the power input and decreasing the energy efficiency (Torres et al. 2008).

4 Electrocatalysis and electrocatalysts

4.1 Extracellular electron transfer (EET) mechanisms

There are mainly three mechanisms by which methane can be produced in an MES (Demirel and Scherer 2008)—(a) acetoclastic methanogenesis where methane is produced from acetate, (b) hydrogenotrophic methanogenesis where methane is produced from hydrogen that is produced at cathode (Clauwaert and Verstraete 2008; Villano et al. 2011) and (c) direct electron transfer at the cathode that produces methane by avoiding hydrogen gas as a mediator (Cheng et al. 2009; Villano et al. 2010; Lohner et al. 2014).

There are two steps in electron transfer: one involving electron transport into micro-organisms and the other involving extraction of electrons out of micro-organisms. A plethora of literature is available on electron transfer out of micro-organisms towards metals and electrodes (Habermann and Pommer 1991; Tender et al. 2002; Kim et al. 2004; Liu et al. 2004; Rismani-Yazdi et al. 2007). On the other hand, the studies on electrons transferring into the micro-organisms have gained interest only recently. However, a large part of this research is focused on bioremediation techniques such as perchlorate reduction (Thrash et al. 2007; Butler et al. 2010), denitrification (Gregory et al. 2004; Clauwaert et al. 2007; Virdis et al. 2008), reductive dechlorination (Aulenta et al. 2007, 2010; Strycharz et al. 2008) and uranium recovery (Wimalasena et al. 2014) and in bioproduction such as electro-fermentation (Hongo and Iwahara 1979) and more recently in electro-methanogenesis (Cheng et al. 2009). Studies on microbially assisted electrosynthesis (using whole micro-organisms as electrode catalysts) have been able to show production of hydrogen peroxide (Rozendal et al. 2009) depending on the type of metal cathode used but no practical applications have been suggested.

Both of the electron transfers can occur in two ways as described above i.e. direct and indirect electron transfer (IET). IET occurs through production and the subsequent use of electron shuttles and mediators. Examples of electron shuttles at anode that are produced by the microorganisms themselves are phenazines (Rabaey et al. 2004, 2005) and flavins (Marsili et al. 2008; Von Canstein et al. 2008). Additionally, some of the primary metabolites of the bacteria such as sulphur species (Nevin and Lovley 2000; Straub et al. 2004) and hydrogen (Berk and Canfield 1964; Schröder et al. 2003) are also capable of shuttling electrons. In case of EET at cathodes, hydrogen is one of the readily available electron shuttle molecule that is produced at cathode (Sakakibara and Kuroda 1993). It is a versatile agent as it is capable of providing various production pathways for many energy rich metabolic bioproducts such as acetate, methane (Clauwaert et al. 2008b). However, the low solubility, high overpotential and the requirement of expensive cathodic material make the process inefficient (Rabaey and Rozendal 2010). Therefore, alternative means of EET at cathode must be implemented in order to circumvent hydrogen production.

Electron shuttles like neutral red, methyl viologen and thionin have been studied quite extensively as a part of fermentation processes of butanol and succinate (Stombaugh et al. 1976; Park and Zeikus 2000). Although these shuttle molecules are easily soluble their instability and the possible toxic effect on the microorganisms limit their usage (Peguin et al. 1994). The last and the most effective way of EET at cathode is by biofilms, where microorganisms are immobilised on the electrode surface. Direct electron transfer occurs between electrode and bacteria and they are in contact with each other for a prolonged period of time (Siegert et al. 2014a). The process efficiency is improved as it decreases electrode overpotentials and diffusional limitations that occur in both hydrogen based and shuttle based EET. Recent studies have revealed that a mixed population of microorganisms immobilised on cathode are able to limit hydrogen production entirely due to biofilm activity (Mueller 2012; Xu et al. 2014).

4.2 Direct interspecies electron transfer (DIET)

Anaerobic digestion is a complex system involving many redox reactions, and interspecies electron transfer process plays a key role in the proper functioning of AD systems (Boone et al. 1989; De Bok et al. 2002, 2004; Sieber et al. 2012). Methanogenesis and sulphur reduction reactions highly depend on syntrophic associations between bacteria and archaea. These syntrophic communities take advantage of the metabolic abilities of corresponding syntrophic partner to overcome thermodynamic barriers that help them breakdown compounds that are otherwise difficult to metabolise, especially when present in high concentrations (Stams and Plugge 2009). Until early 2000s it was believed that IET occurred only via electron shuttle components especially hydrogen and formate. The other potential alternative for electron transfer was suggested to be DIET (Reguera et al. 2005).

The process of DIET by methanogenic biofilm aggregates is important to discuss because it decreases a number of intermediary steps and intermediary products thereby decreasing process dependency and increasing process stability. This paradigm shift in the mechanisms of electron transfer significantly impact the “modelling and design of anaerobic wastewater reactors and the understanding of how methanogenic communities respond to environmental perturbations” (Morita et al. 2011). The first evidence of DIET through conductive pili which are otherwise called as nanowires, was provided by Reguera and collaborators (2005). Subsequently, Gorby et al. (2006) demonstrated that *Shewanella oneidensis* strain MR-1 developed electrically conductive pili when it was deprived of electron acceptor molecules. The study also confirmed that syntrophic methanogenic microorganisms, *P. thermopropionicum* and *M. thermoautotrophicus* are connected by flagellum like appendages to establish not only IET but also other energy exchange processes such as IHT.

Cheng and his team (2009) experimented several strategies (such as electrodes with and without biofilm and electrolyte with and without organic and inorganic carbon source) to verify whether the methane production was acetoclastic or hydrogenotrophic. Direct electron transfer was evident as current flow with an abiotic cathode reduced to 0 A at -0.95 V whereas for biocathode high currents were observed against a range of -1.00 to -0.70 V. The authors were able to generate methane when the sole source of carbon was CO_2 at a set potential of -1.0 V. Methane production rate of ~ 200 mmol-CH_4 d^{-1} - m^{-2} with a CO_2 consumption rate of ~ 210 mmol-CO_2 d^{-1} m^{-2} was achieved using a two-chamber methane producing MEC. Further strengthening the idea of DIET in anaerobic cultures, Rotaru et al. (2014b) showed carbon dioxide reduction through DIET between *Geobacter metallireducens* and *Methanosaeta harundinacea.* The same team of researchers explored the DIET capability of *Methanosarcina barkeri* when co-cultured with pilin-deficient *Geobacter metallireducens* (Rotaru et al. 2014a). The authors demonstrated that granular active carbon material can act as a conductive material replacing pili to transport electrons.

Following this discovery, a correlation was obtained between microbial community and granule conductivity by (Shrestha et al. 2014). A correlation of about $r = 0.67$ was observed between the abundance of *Geobacter* species and granule conductivity proving that the supplement of granular conductive material for the enhancement of DIET and thereby process efficiency. Another study was conducted to compare the DIET efficiencies with different conductive materials where carbon cloth demonstrated most effective syntrophic electron transfer in comparison to graphite and biochar (Zhao et al. 2015b). The above discovery was also remarkable in terms of electrochemical carbon dioxide reduction, as dispersed and high surface area cathodes such as granular activated carbon (Liu et al. 2012), carbon cloth (Chen et al. 2014a), biochar (Chen et al. 2014b) and magnetite (Liu et al. 2015) can, not only donate electrons to microbes, but also transport electrons between microorganisms. The microbes can just attach themselves to these conductive materials (biocathodes) and transport electron among them by saving the energy used in the generation of conductive pili (Zhao et al. 2015b).

This was immediately put into practice by (Zhao et al. 2015a) where an AD system was attached with an electric circuit containing graphite rod cathode and graphite brush anode. The authors observed 30% more electric conductivity in the electric-AD in comparison to the control AD system. It was also observed that rate of production of methane was higher with the electric-AD system by 3 times at the 33rd hour mark. In a study combining MEC-AD system for carbon dioxide reduction, the authors compared reactor performances with and without *Geobacter* species. It was observed that the carbon dioxide content in total gas generated from the AD reactor with *Geobacter* was only half of that generated from the same reactor without *Geobacter*, suggesting that *Methanosarcina* may obtain the electron transferred from *Geobacter* for the reduction of carbon dioxide to methane (Yin et al. 2016). One of the most recent studies on MEC-AD system it was observed that the conductive material, carbon cloth, apart from enhancing DIET among the microbes, it was able to stabilise the system for acid impacts and high hydrogen partial pressures (Zhao et al. 2017).

Although it is a proven theory that DIET improves AD process efficiency and in turn DIET can be enhanced with the supplement of conductive material, there is no clear explanation on the mechanism of these processes. Also, the details of interspecies connecting networks are not entirely clear, however, Malvankar et al. (2011), Morita et al. (2011) and Reguera et al. (2005) have reported metal like conductivity through the microbial nanowire network. Another possible mechanism suggested for electron transfer was through the c-type cytochromes present on the cell surface of microorganisms (Lovley et al. 2011).

4.3 Biocathodes

Biocathodes unlike bioanodes have gained research interest only recently, especially in the field for bioelectrochemical energy generation processes. These were developed as cheaper alternative to the expensive metal cathode catalysts such as Platinum. Although several ways have been implemented for the development of biocathodes: redox cycling of transition metals between the cathode and metal-oxidizing bacteria (Rhoads et al. 2005; ter Heijne et al. 2007) and enzyme based biocathodes (Pershad et al. 1999; Morozov et al. 2002), biofilm based biocathodes hold the highest position in terms process efficiency due to the possibility of direct electron transfer.

Rozendal et al. (2008b), for the first time, demonstrated hydrogen gas production using biofilms that were developed on graphite felt cathode. The authors were successfully able to convert a bioanode which was oxidising acetate and hydrogen into a hydrogen producing biocathode by through inversion of polarity and slowly adapting the microorganisms and the electrodes to reducing environments. However, it was in 2010 that for the first time direct CO_2 reduction was demonstrated using a graphite block cathode (Nevin et al. 2010). Several research papers have been published since then and a few have been summarised in Table 1. A recent review on all the cathode materials used for MES discusses the evolution of cathode materials from simple carbon rod to 3D-iron oxide carbon felt (Aryal et al. 2017a).

Modified graphite electrodes were used as cathodes (Villano et al. 2011; Mueller 2012) so as to increase the geometric surface area of the electrode where the biofilms can grow. Villano et al. (2011), were able to show that, when anode potential was maintained constant at + 0.50 V in a 2 chamber acetate supplied MEC inoculated with *G. sulfurreducens*, the acetate oxidation was linearly related to the biomass (microorganisms inoculated). These results indicated that electron transport is directly proportional to the biomass density on the biofilm. Biofilm development is the key area of research for biocathode development as it determines the bacterial community enriching over the electrode material and therefore the electron transfer efficiency via DIET.

There are several factors that allow a biofilm to form and attach firmly on the electrode surface such as hydrogen bonding, electrostatic attraction and van der

Table 1 List of biocathodes that reported biofilms formed on non-precious cathode material

Cathode material	Biofilm	Voltage (V) versus SHE	Main product (s)	Columbic efficiency (%)	Anode properties	References
Carbon cloth	*Methanobacterium palustre*	− 0.5 to − 0.8	Methane	96 (at − 0.8 V)	Graphite brush	Cheng et al. (2009)
Graphite granules	Mixed methanogenic cultures	− 0.85	Methane	74%	Graphite granules	Villano et al. (2011)
Graphite granules	Mixed methanogenic cultures	+ 0.5 (anode)	Methane	~ 100	Graphite granules with *G. sulfurreducens*	Villano et al. (2011)
Graphite rods with graphite beds	Mixed Methanogenic cultures	− 0.65, − 0.70, − 0.75 and − 0.80	Methane and hydrogen	0, 46, 56 and 59 respectively	Graphite rods with graphite beds	Mueller (2012)
Carbon felt	Mixed methanogenic cultures	− 0.953 to − 0.653	Methane and acetic acid	60–100	Carbon felt	Jiang et al. (2013)
Graphite granules	*Acetobacterium* spp.	− 0.59	Acetate	69	Graphite granules	Marshall et al. (2013)
Carbon fiber brushes, plain graphite blocks, graphite blocks coated with carbon black, platinum, stainless steel, nickel, ferrihydrite, magnetite, iron sulfide, molybdenum disulfide	Mixed methanogenic cultures	− 0.65, − 0.60 and − 0.55	Methane	Approximately 100 for all materials except platinum coated (~ 93). high variance in efficiency for carbon fiber brush	Carbon fiber brush	Siegert et al. (2014b)
Graphite plate	Methanobacterium	0.7 (cell voltage)	Methane	< 100 (bog) and > 100 (AD)	Graphite plate	Siegert et al. (2014a)
Graphite fiber brush, carbon cloth and stainless steel with Pt coating	Mixed methanogenic cultures	− 0.789. − 0.789 and − 0.589 respectively	Methane	75, 80 and 80 respectively	Graphite fiber brush, graphite fiber brush, platinum mesh respectively	Luo et al. (2014)
Graphite rod	Hydrogenotrophic methanogens	− 0.7	Methane	80–85	Graphite Rod	Xu et al. (2014)
Graphite rod	Hydrogenotrophic methanogens	− 0.19, − 0.14. − 0.09, − 0.04 (anode)	Methane	25–60 (anodic)	Graphite rod	Zhao et al. (2014)
Carbon felt	*Clostridiales* spp.	Constant current of $-5\ \mathrm{Am^{-2}}$	Acetate	55–65	–	Patil et al. (2015)

Table 1 continued

Cathode material	Biofilm	Voltage (V) versus SHE	Main product (s)	Columbic efficiency (%)	Anode properties	References
Carbon Cloth	*Methanothermobacter*-related methanogen and synergistetes- and thermotogae-related	− 0.8 to − 0.3	Methane	90–100 (0 for − 0.3 V)	Carbon cloth	Fu et al. (2015)
Multi-walled Carbon Nanotubes (electrophoretic deposit)	Mixed methanogenic cultures	−0.85	Acetic acid	100 ± 4	Multi-walled carbon nanoubes (electrophoretic deposit)	Jourdin et al. (2015)
Carbon felt	*Sporomusa ovata*	− 0.69	Acetate	76.6 ± 2.3	Graphite rod	Aryal et al. (2016)
3D-grpahene coated carbon felt	*Sporomusa ovata*	− 0.69	Acetate	86.5 ± 3.2	Graphite rod	Aryal et al. (2016)
Carbon cloth (Pt coated)	Mixed culture	0.8 (cell voltage)	Methane	–	Graphite brush	Liu et al. (2016)
Carbon cloth	Marine-derived non-photosynthetic electroactive inoculum	−0.4 and 0.0 (Switching)	Hydrogen and carbon monoxide	98	Platinum mesh	Yates et al. (2017)
Carbon felt	Mixed methanogenic (MM) and enriched hydrogenotrophic methanogenic (EHM)	− 0.8	Methane	62 and 98 respectively	Carbon felt	Dykstra and Pavlostathis (2017)

Waals interaction (Guo et al. 2013a; Zhang et al. 2013; Jourdin et al. 2016). Mixed cultures are generally considered to be more robust and efficient with regard to bio-electrosynthesis than pure cultures which are regarded to be intolerant towards environmental stress conditions and fluctuations (Ganigue et al. 2015; Jourdin et al. 2015; Bajracharya et al. 2015). The adaptability and strength of biofilm determine the biofilm thickness and biofilm cover over the electrode surface. Fu et al. 2015, showed that thermophilic microorganisms can be used as biocatalysts on a carbon cloth cathode for electromethanogenesis. At 55 °C and an applied voltage of 0.8 V high methane production rates of about 1103 mmol m^{-2} day^{-1} were obtained.

Although graphite electrode materials were popular and giving good results they were still 2 dimensional structures and limit the available surface area resulting in low electrocatalytic activity, high internal resistance, high activation overpotential and rapid creation of passivation layer. Other examples of 2D electrode materials used for MES were carbon plate and carbon cloth. Carbon felt was also explored as a cathode material for the first time in electromethanogenesis by Jiang et al. (2013). The authors showed how CO_2 is reduced to different products depending on the cathode potentials applied on carbon felt cathode. Methane and hydrogen were produced in the range − 0.65 to − 0.75 V (vs. SHE), methane, hydrogen and acetic acid were produced simultaneously at − 0.75 V (vs. SHE) and methane and acetic acid were produced at − 0.95 V (vs. SHE). Most recent work by Jourdin et al. (2018) revealed that unmodified carbon felt was able to develop a thick biofilm covering the whole thickness of the felt (1.2 cm) and was able to generate high current densities. Several high value products were targeted during the continuous operation of this MES ranging from acetate to n-caproate (Jourdin et al. 2018).

4.4 Nano-catalysts

Nanotechnology has gained huge traction in recent years especially in the last 5 years. They have large catalytic surface area and contain a large portion of edge or low-coordinated sites, which favour electron transfer mechanism as compared to fully coordinated sites on the flat surface of their bulk samples (Wang et al. 2016). Noble metals such as Au, Ag, and Pd have shown efficient reduction of CO_2 to CO at comparatively low overpotentials. Density functional theory (DFT) calculations suggested that edge sites on the Au nanoparticle surface favoured CO evolution, while corner sites favoured Hydrogen Evolution Reaction (HER). Faradaic Efficiencies of above 90% at potentials of less 1 V versus RHE were consistently obtained by various researches with the nanostructured precious metals Au, Ag and Pd electrocatalysts. (Chen et al. 2012; Kauffman et al. 2012; Monzó et al. 2013; Zhu et al. 2013, 2014; Kim et al. 2014; Lates et al. 2014; Manthiram et al. 2014; Mistry et al. 2014; Back et al. 2015; Feng et al. 2015; Hall et al. 2015; Koh et al. 2015).

Among the non-precious metals researchers explored many varieties of nanostructured copper such zero-dimensional (0D) nanoparticles, one-dimensional (1D) nanowires, two-dimensional (2D) overlayers, and three-dimensional (3D) foams to enhance its performance in these reactions. However, these various configurations on copper nanostructured catalytic materials were not able to generate as high faradaic efficiencies as the precious metals did (Gonçalves et al. 2013; Chi et al. 2014; Fan et al. 2014; Januszewska et al. 2014; Li et al. 2014; Qiao et al. 2014; Sen et al. 2014; Ma et al. 2015; Raciti et al. 2015; Verdaguer-Casadevall et al. 2015). On the other hand, nanostructured zinc was able to produce a Faradaic Efficiency of about 93% against an 18% efficiency of bulk zinc to produce CO from CO_2 (Quan et al. 2015). It can be observed that most of the metallic and nanostructured catalysts lead to the production CO which is not a hydrocarbon fuel in its solitude. However efficient the process of CO_2 reduction to CO might be, it leaves us with an additional step to convert into a potential fuel to be of practical use.

Biofilm development on nanostructured catalysts is required in order to generate methane from carbon dioxide. Among 3D nano-structured electrode materials, macro-porous carbon nanotube (CNT) textile material showed improved biofilm formation on both interior and exterior of the material as opposed to 2D nano structured materials that inhibit biofilm formation on the interior of the material (Xie et al. 2011). The 3D structures also greatly improved the MFC performance with efficient EET with the help of a complex nanowire network (Xie et al. 2014). Combining and doping the CNT electrode material with other compounds such as hematite, magnetite (Park et al. 2014), hydrogels (Liu et al. 2014) and manganese dioxide (Kalathil et al. 2013) also showed enhanced bioanode activity. More details on the mechanism of CNT, graphene and other nano- based anodes and their advantages have been detailed by Kalathil and Pant (2016).

Although a plethora of research is available on the relation between bacterial EET and nano-anode materials, a similar work on cathode materials has been dealt with some uncertainty (Kalathil and Pant 2016). Only acetate production was successfully implemented and improved by many researchers using nano based biocathodes in MESs (Nie et al. 2013; Zhang et al. 2013). *Sporomusa ovata* was the micro-organism of choice and carbon cloth was the base cathode of choice. The cathode was combined with polyanaline-polyacrylonitrile (PANI-PAN), Au, Pd and Ni nano materials to improve extracellular electron uptake and acetate production (Nie et al. 2013; Zhang et al. 2013). A nanoweb-RVC cathode was able to show enhanced microbe-electrode interaction by allowing thick biofilm formations on both exterior and interior sides, thereby improving acetate production by 2.6 fold (Jourdin et al. 2014).

One of the latest works carried out to screen a number of electrocatalysts for carbon dioxide reduction, which also included carbon nanostructures, concluded that only copper exhibits selectivity towards formation of hydrocarbons and multi-carbon oxygenates at fairly high efficiencies (Wu et al. 2016). Most others favour production of carbon monoxide or formate as previously discussed. Therefore, microbial catalysts that are able to reduce carbon dioxide directly to methane have been of great interest in recent times.

5 Single chambered MECs (SCMECs) and applications

Clauwaert and Verstraete (2008) showed that methane production can occur in a membraneless MEC and suggested that these SCMECs can be combined with AD systems for efficient methane production. The authors found that reduced ohmic resistance, minimized pH gradient and higher current density are advantages when membranes are removed from the MEC (Clauwaert et al. 2008a; Guo et al. 2017). An upflow SCMEC was used by Lee and Rittman (2010) to characterize energy losses in an SCMEC. The team observed a reduction in ohmic energy loss to about 0.005 V and pH energy loss to about 0.072 V at an applied voltage of ~ 1 V. However, due to the lack of metal catalysts on the electrodes, that authors observed large electrode losses, The authors also suggested that in order to generate energy-conversion efficiency (ECE) of more than 100%, the applied voltage must

Table 2 Various single chamber microbial electrolysis cells (SCMEC) for methane production

Substrate	Voltage (V)	Cathode	Anode	Products	Efficiency (%)	Reference
Buffer medium with sodium acetate	0.3, 0.4 and 0.6 cell voltage	Type B carbon cloth with 30% Pt wet-proofing	Type A carbon cloth	Hydrogen[a]	24, 32 and 75	(Hu et al. 2008)
50:50 mixture of medium and wastewater	0.3–0.9 versus Ag/AgCl at anode	Carbon cloth with 30% PTFE wet-proofing	Graphite brush	Hydrogen and methane[a]	~90	Wang et al. (2009)
Sodium acetate	0.2–1.0	Mipor titanium tube coated with platinum	Graphite granules	Hydrogen[a]	> 90	Guo et al. (2010)
Anaerobic digestion of sewage sludge	1.4 and 1.8 cell voltage	Ti/Ru	Ti/Ru	Hydrogen followed by methane[a]	–	Guo et al. (2013b)
Nutrient medium	0.4 and 1.0 cell voltage	Stainless steel	Carbon felt	Methane[b]	66.7 and 66.1	Bo et al. (2014)
Nutrient medium with sodium acetate	0.8 cell voltage	Carbon cloth	Carbon cloth	Methane[c]	> 90	Fu et al. (2015)
Waste activated sludge	0.6 cell voltage	Graphite rod	Graphite-brush	Methane[c]	–	Zhao et al. (2015a)
Domestic wastewater	1.0 cell voltage	Stainless steel	Carbon felt	Methane[b]	70–75	Moreno et al. (2016)
Nutrient medium with sodium acetate	1.0 cell voltage	Stainless steel	Carbon felt	Methane[b]	74.6	Yin et al. (2016)
Incineration leachate	0.7 cell voltage	Graphite rod	Graphite rod	Methane[b]	19–36	Gao et al. (2017)
Activated sludge	0.75, 1.5 and 2.0	Ni	RVC	Methane[a]	–	Sugnaux et al. (2017)
Cheese whey	–	Stainless steel mesh	Graphite rod	Hydrogen and methane[a]	92.7 and 31.8	Rivera et al. (2017)
Thermal alkaline pre-treated sludge	0.6, 0.8, 1.3, 1.8 and 2.3	Ti/Ru alloy mesh plates	Ti/Ru alloy mesh plates	Methane[b]	–	Xiao et al. (2018)

[a] Single chambered microbial electrolysis cells (SCMEC)

[b] SCMECs combined with AD or Wastewater treatment systems

[c] Single chambered microbial electrosynthesis systems

be less than 0.6 V with cathodic conversion efficiencies > 80% (Lee and Rittmann 2010).

Some researchers showed that membraneless MECs are able to combine anodically produced carbon dioxide with cathodically produced hydrogen gas with the help of hydrogenotrophic methanogens (Call and Logan 2008; Clauwaert et al. 2008b). These observations were further strengthened by Cheng et al. (2009) with the demonstration of methane production in a SCMEC using a biocathode at a potential of − 0.7 V versus Ag/AgCl (~ 0.491 V vs. SHE). Following these research results, the focus of production in MEC systems gradually changed from hydrogen to methane (Table 2).

With the developments in methane production many scientists approached electromethanogenesis as a biogas upgrading process (Biesemans 2016; Dykstra and Pavlostathis 2017). As a practical solution for scaling up, the developed electrochemical cell was combined with an existing anaerobic digestion system such that the CO_2 in biogas is reduced to methane and thereby improving the biogas quality. Another recent study has suggested that biogas could become important source of CO_2 for PtG as a practical solution for its financial viability (Götz et al. 2016). A recent review on electromethanogenesis has laid four possible mechanisms for combining AD and electrochemical systems (a) to boost hydrolysis by using the oxygen produced from electrolysis, (b) hydrogen produced at cathode to enhance methane production via hydrogenotrophic methanogenesis, (c) direct electron transfer to methanogens on the biofilm and (d) increasing the solid retention time (SRT) of AD using the electrodes. Of this, the third method is proposed to be the most efficient as it does not involve any intermediate products that decrease the energy efficiency (Blasco-Gómez et al. 2017).

Xu et al. (2014), compared two systems where the AD reactor was externally attached to the MEC cell and the other where a single reactor was used as both MEC and anaerobic digester. In the latter setup, the headspace of the digester was connected to the MEC such that the biogas is fed to the MEC that contained anaerobic granular sludge without any organic carbon source. The authors observed that columbic efficiency of the ex situ biogas upgrading system was more than the in situ system. Similar study was done by Zhao et al. (2014), and showed a 25% increase in methane production and 19% increase in acetate consumption in an AD-MEC combined reactor as compared to the performance of AD reactor without MEC.

Both the above studies used graphite rod cathodes and revealed that a large concentration of hydrogenotrophic methanogens were found on the electrode surface biofilm. Similarly, Siegert et al. (2014a) compared an acetoclastic culture rich AD sludge and hydrogenotrophic culture rich anaerobic bog sediment for electromethanogenesis. The results showed that bog samples as inoculum were most efficient attributing it to the high concentration of Methanobacterium spp. as they significantly reduced hydrogen gas recycling. Siegert et al., showed that *Methanobacterium* spp. was the most abundant species in the biofilms followed by *Methanosaeta* spp. (Acetoclastic methanogenesis).

In-situ CO_2 reduction to CH_4 was performed at an additional voltage of 1.0 V where a stainless steel barrel was used as the cathode material. The authors were able to increase the COD removal by 3 times, the efficiency by 56.2% and the biogas was produced with 98.1% methane (Bo et al. 2014). Moreno et al. (2016) studied the effect of HRT in a methane producing reactor that was combined with MEC. The authors suggested that the homoacetogenic activity which effect the efficiency of membraneless MECs was remediated by promoting hydrogenotrophic methanogenesis. The authors concluded that high HRTs (around 24 h) are favourable for the use of MEC combined methanogenic reactors as the anode respiring bacteria overcome the acetoclastic methanogens and thereby improving the energy recover (Moreno et al. 2016).

Moving away from mixed culture inoculums, a co-culture of *Geobacter and Methanosarcina* was used in an AD-MEC coupled system by Yin et al. (2016). The authors concluded that co-culture was highly efficient and enhanced the methane yield to 360.2 mL g^{-1}-COD, which is marginally more than theoretical methane yield from AD. *Geobacter* showed evidence of reducing system resistance and increasing the current density significantly which in turn lead to increased electron recovery by *Methanosarcina* via IHT and DIET (Yin et al. 2016). In a more recent study by Gao and collaborators (2017), *Methanosarcina* and *Methanospirillum* were enriched in AD-MECs by the authors to degrade the refractory organic matter present in the incineration leachate. It was observed that souring of the reactor was rapidly recovered with the introduction of electrochemical activity in the anaerobic digester. The AD-MECs were consistently producing 20–40% more methane compared to control reactors (without electrodes) during continuous operation for 60 days (Gao et al. 2017).

Further, it was suggested that Synergistetes- and Thermotogae-related bacteria established syntrophic associations with methanogens for efficient methanogens. In a novel approach for integrating MEC and AD Liu et al. (2016), were able to show that the MEC systems not only improved methane production rate by 3-fold but also enhance substrate degradation. Stressing the importance of hydrogenotrophic methanogens Dykstra and Pavlostathis (2017), laid out a direct comparison between mixed methanogenic (MM) and enriched hydrogenotrophic methanogenic (EHM) culture for methane production. The EHM based system produced 4 times more methane than MM based system (Dykstra and Pavlostathis 2017). Many new bacterial species such as *Propionivibrio, Thiomonas, Citrobacter, Actinomyces* etc., were identified at the biocathode due to their exoelectrogenic properties.

Apart from hydrogen and methane gas production, single chambered waste treatment systems have been applied for other applications. Electro-fermentation is one of the applications which was studies by Awate and collaborators (2017). In this study, an SCMEC with a bioanode was used for the bioprocessing of lignocellulosic substrates using a genetically engineered biofilm developed on the anodes. Ethanol was the target product of the electro-fermentation and the SCMEC was used for the removal of unwanted fermentation products such as lactate, formate, acetate etc., thereby improving ethanol product recoveries (Awate et al. 2017). Other application of SCMECs include phosphate recovery (Cusick and Logan 2012) and hydrogen sulphide removal (Lin et al. 2016). Phosphate was recovered in the form of struvite using stainless steel mesh cathodes with recoveries of about 40% phosphate at 1.05 V and at an overall energy efficiency of around 75% (Cusick and Logan 2012). Hydrogen sulphide removal is usually very expensive process, therefore, an effort to make it cheaper was explored by Lin and team with the help of cheap electrode materials such as carbon cloth and stainless steel in a SCMEC. The authors suggested that a voltage of about 3.0 V applied intermittently for 15 min a day would result in more than 90% removal of hydrogen sulphide from biogas in continuous operation (Lin et al. 2016).

6 Conclusion

In the last 5 years there has been a plethora of research on bioelectrochemical treatment of wastewater and biofuel production in the form of either hydrogen or methane. Although the earlier research focussed on biohydrogen production, gradually, it was shifted towards methane production as it was an unavoidable by-product and a better practical fuel to be used in the transport sector. Many non-precious cathode materials, for example, carbon cloth, carbon felt, graphite rod and graphite granules have been extensively researched for their capability to form biofilms and act as efficient biocathodes. The advantages of using SCMECs were described by many researchers. The single chamber systems are able to reduce the ohmic resistance and minimise the pH gradient due to the lack of membrane which make them highly efficient compared to 2 chamber systems.

The mechanism of direct interspecies electron transfer (DIET) in MESs and the role of hydrogenotrophic methanogens in DIET is currently identified as the gap in research in bioelectrochemical wastewater treatment. Many researchers have provided evidence for DIET but are yet to explain the process details that occur between electrode surface and microbial cell. The other research gap identified is at rather large scale, that is, how to combine the two processes of anaerobic digestion and MEC. There have been very few studies conducted on the combined processes of AD and MEC and there is lack of information on the effects of different feed conditions (scale and flow) and other important parameters for continuous operation. Currently, MECs are being considered as post processing step for the existing AD systems, however, there is a considerable lack of data on these aspects of the process.

Therefore, it can be concluded that the AD-MEC systems have the potential to be a practical and promising way of utilising the excess renewable electricity but is far from large scale implementation. It however, provides scientists with an ample amount of research to be carried out both at micro and macro levels.

Acknowledgements The authors would like to thank The Research Council of Norway for supporting this research project.

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Article 2

Optimisation of Electrochemical Treatment of Artificial Wastewater using Cyclic Voltammetry

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Published in *International Journal of Environmental Science and Development*, *9*(8), 218–221, 2018

International Journal of Environmental Science and Development, Vol. 9, No. 8, August 2018

Optimisation of Electrochemical Treatment of Artificial Wastewater using Cyclic Voltammetry

Anirudh B. T. Nelabhotla and Carlos Dinamarca

***Abstract*—Solar PV and wind turbine technologies are the prime sources of renewable energy and have rapidly increased their share in the total electricity production in the recent years. However, these technologies are highly dependent on nature and makes them an unreliable source of energy from an end-point perspective. Power to Gas (PtG) technology resolves this issue and provides an opportunity to convert these intermittent sources of energy into a more reliable one. With the processes of electrochemistry combined with methanogenesis PtG technology is able to provide a more reliable source of energy in the form gases (hydrogen or methane), that can be both stored and transported. This article discusses various electrochemical parameters such as voltage, current, electrode material, pH and temperature using cyclic voltammetry technique in order to select the best electrode material. Three electrode materials (platinized titanium mesh, carbon felt and graphite rod) are compared with each other for their electrochemical performances at 4 different pH and 6 different temperatures. The results show that carbon felt electrode material is the most efficient and inexpensive material for further research in the field of bioelectrochemical wastewater treatment.**

***Index Terms*—Cyclic voltammetry, hydrogen, microbial electrochemical cell, methane, wastewater.**

I. INTRODUCTION

There has been a rapid increase in the world renewable energy share, triggered in part by the staggering amount of research and engineering development in the field of sustainable energy supply. Especially in the renewable power sector, the non-hydro renewable electricity has increased by 17.3% in just 1 year (2015 to 2016). Solar PV and Wind power are the leaders in renewable power generation showing 32.9% and 12.7% increases in their respective capacities during the same year [1]. The increase in renewable electricity in some of the European countries have been such, that they have exceeded the demand of the electricity during certain days of the year. This is mainly due to the fluctuating nature of solar and wind power production systems as they are dependent on the dynamics of nature and remain irregular sources of renewable power [2]. In 2016, an estimated amount of about 30-60 GW of residual power was generated due to this intermittency in power production [3].

However, the world is still highly dependent on fossil fuels which have not seen any decline in their consumption over the years and thereby showing no decline in global CO_2 emissions. The IEA report states that approximately 32 Gt of CO_2 has been emitted for each of the 3 consecutive years from 2014 to 2016 [4]. Therefore, many researchers have shown interest in technologies which are able to harness the residual power to provide a more reliable and practical energy source and simultaneously be able to capture the industrial carbon emissions [5].

Power to Gas (PtG) technology is one such approach that has recently come into focus with the increase in available residual renewable power [3], [6]–[10]. PtG technology converts the excess renewable power into energy rich gases such as hydrogen and methane that can be integrated into the existing gas grids [2], [8], [11]–[13]. Electrochemical and bioelectrochemical treatment of wastewater are able to produce hydrogen [14], [15] and methane [16]–[18] respectively. Hydrogen can also be produced through bioelectrochemical methods but methane is often produced as a by-product and is preferred over hydrogen for other practical issues such as storage and transport [19]–[24].In this research article we explore non-precious and inexpensive electrode materials for the electrochemical treatment of artificial wastewater over various parameters in a single chamber electrochemical cell. The aim of the study was to optimise the working parameters and select the best electrode material combination for bioelectrochemical treatment of wastewater that is able to form biofilms and produce methane. The theoretical standard potentials required for electrolysis of water and bioelectrochemical treatment of wastewater can be defined with the following equations:

$$2H^+ + 2e^- \rightarrow H_2 \qquad E^{\circ\prime} = -0.414\ V$$

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \qquad E^{\circ\prime} = -0.244\ V$$

II. MATERIALS AND METHODS

A. Artificial Wastewater (AWW) Preparation

An 135 mL reactor bottle was used as the electrochemical cell and filled with 120 mL of artificial wastewater made of [25] $K_2HPO_4 \cdot 3H_2O$ 3.0 g/L, KH_2PO_4 11.8 g/L, $NaHCO_3$ 6.0 g/L, NaCl 1.0 g/L, NH_4Cl 1.0 g/L, $CaCl_2$ 0.2 g/L, $MgSO_4 \cdot 7H_2O$ 0.15 g/L, 10 mL/L of trace metal solution [26], and 10 mL/L of vitamin solution [27]. The pH of the solution was approximately 7 and the pH was changed using KOH pellets.

B. Electrode Preparation

Three different electrodes viz Platinum coated titanium mesh (Pt; 20 mm × 20 mm × 3 mm; Ti Shop, London, UK), Carbon felt (Fe; 20 mm × 20 mm × 3 mm; Alfa Aesar, Thermo

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Manuscript received March 5, 2018; June 23, 2018. This work was supported in part by the Norwegian Research Council and University College of Southeast Norway.

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doi: 10.18178/ijesd.2018.9.8.1104

Fisher GmbH, 76057, Karlsruhe, Germany) and Graphite rod (Gr; 152 mm × 6.15 mm; Alfa Aesar, Thermo Fisher GmbH, 76057, Karlsruhe, Germany) were soaked in 1 M HCl for 24 hours followed by 1 M NaOH for 24 hours so as to remove all the contaminants [28]. An Ag/AgCl reference electrode with a standard potential of +0.199 mV vs SHE (Amel S.r.l., Milano, Italy) was used for the cyclic voltammetry experiments. All the voltages mentioned in the article are vs Ag/AgCl reference electrode.

C. Cyclic Voltammetry (CV)

The electrochemical cell was fitted with two electrodes at a time as Cathode-Anode: Pt-Pt, Pt-Fe and Pt-Gr along with the reference electrode. The electrode connections were made using Gamry Interface 1000 B Potentiostat (Gamry Instruments, Warminster, PA, USA). The cyclic voltammetry was run on these electrode pairs at 6 different temperatures viz. 30, 35, 40, 45, 50 and 55°C and 4 different pH viz. 7, 7.5, 8 and 8.5. The CV ranges (the negative sign defines cathode and doesn't affect the magnitude of the voltage) for the different electrode combination were selected based on the electrochemical overload on the reactor and are tabulated (Table I). A scanning rate of 100 mV/s was applied for all CV experiments and were run in triplicates.

TABLE I: CV RANGES FOR DIFFERENT ELECTRODE COMBINATIONS

Electrode Combinations	CV range (V)
Pt-Pt	-1.000 to 1.000
Pt-Fe	-0.700 to 1.000
Pt-Gr	-0.700 to 1.000

III. RESULTS

A Cyclic voltammetry experiment is carried over a range of voltages to determine the voltage at which a particular electrochemical reaction occurs. The peak current of the CV curve and the corresponding voltage represent hydrogen production from artificial wastewater. The peak current and the corresponding voltages for all the temperatures and pH have been represented in the following Fig. 1-4. By comparing all the curves at different pH, it can observed, as general trend, that the peak currents decrease and voltages increase in their magnitude with the increase in pH (with a few exceptions). This could be due to the decrease in proton concentration, which is the reactant for the electrochemical reaction. Similarly, a general trend can be drawn on the effects of changing temperature, where the peak currents show an incline in their graph with the increase in temperature. This could be mainly due to the increase in ion movement within the electrolyte that increases the diffusion towards electrode and thereby the rate of reaction corresponding to the current generated. On the other hand, the voltages do not show a visible trend in their changes with increase in temperature.

Comparing the individual graphs and the electrode combinations: In Figure 1, i.e. the AWW at pH 7, the highest peak current of about 36.6 mA is observed for Pt-Fe at a voltage of -0.453 V and 45°C, however, it can be observed that at 50°C a lesser peak current of about 35.9 mA occurs at a lesser voltage of -0.440 V. In Figure 2, even at a pH of 7.5 the Pt-Fe electrode combination was able to generate the highest peak current of about 36.3 mA at corresponding voltage of 0.514 V and a relatively high temperature of about 55°C. The effect of temperature on voltage is still to be investigated as there seems to be no particular pattern unlike current as mentioned previously. In figures 3 and 4 we can observe that the peak currents never cross 35 mA and the corresponding magnitudes of voltages are always above -0.450 V and -0.500 V respectively. These results suggest that the conditions set for the reactor are clearly unfavorable for the electrochemical reaction to be carried out.

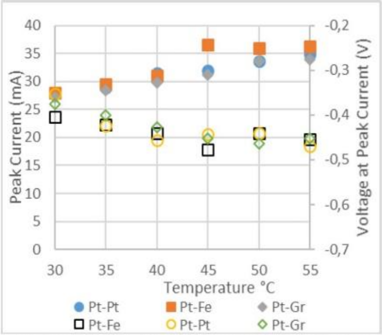

Fig. 1. Peak current (solid fills) and voltage (no fill and secondary axis) at peak current at different for CV of AWW at pH 7.

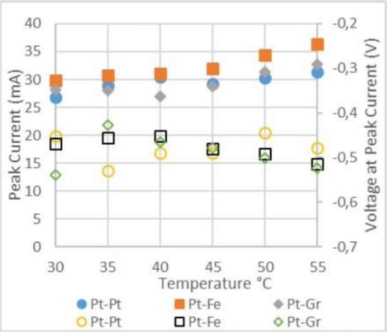

Fig. 2. Peak current (solid fills) and voltage (no fill and secondary axis) at peak current at different for CV of AWW at pH 7.5

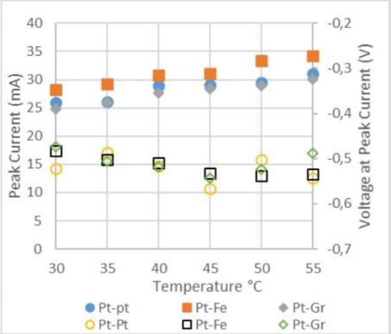

Fig. 3. Peak current (solid fills) and voltage (no fill and secondary axis) at peak current at different for CV of AWW at pH 8.

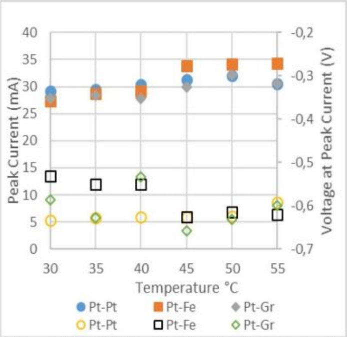

Fig. 4. Peak current (solid fills) and voltage (no fill and secondary axis) at peak current at different for CV of AWW at pH 8.5.

On observing all the figures it can stated that the electrode combination of Pt-Fe has been performing better than other electrode combinations in a consistent manner resulting in higher peak currents. Although the corresponding voltages do not reflect similar level of consistency they have been relatively low. Followed by the carbon felt electrode, the graphite electrode has performed comparable to the platinised platinum electrode. All the graphs evidently show most overlaps of peak current have occurred between Pt-Gr and Pt-Pt. Previous reports have suggested the use of carbon felt electrode as a bioanode and turned into biocathode for wastewater treatment in 2 chamber electrochemical cell [29]. Other researchers were able to use carbon felt as a biocathode for the production of acetate [30]. Similar reports on graphite rod have shown graphite as a cathode for methane production via electrochemical methanogenesis [31], [32].

IV. CONCLUSION

From the above results it can be said that the carbon felt electrode material at a temperature of 45°C and a pH of 7 make up an optimized electrochemical reaction. The carbon felt electrode has "high surface area and porosity that is able to provide abundant redox reactions sites, excellent electrolytic efficiency and mechanical stability" [33]. It is very commonly used electrode material as it provides good electrical conductivity at a relatively low cost. Due to the above mentioned properties the authors have now started developing biofilm on the carbon felt material to operate a Single Chambered Microbial Electrochemical Cell (SCMEC) for wastewater treatment that can be integrated with existing Anaerobic Digestion plants.

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Article 3

Bioelectrochemical CO_2 Reduction to Methane: MES Integration in Biogas Production Processes.

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Published in *Applied Sciences*, *9*(1056), 16–18. 2019.

applied sciences

MDPI

Article

Bioelectrochemical CO_2 Reduction to Methane: MES Integration in Biogas Production Processes

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Received: 31 January 2019; Accepted: 6 March 2019; Published: 13 March 2019

Abstract: Anaerobic digestion (AD) is a widely used technique to treat organic waste and produce biogas. This article presents a practical approach to increase biogas yield of an AD system using a microbial electrosynthesis system (MES). The biocathode in MES reduces carbon dioxide with the supplied electrons and protons (H^+) to form methane. We demonstrate that the MES is able to produce biogas with over 90% methane when fed with reject water obtained from a local wastewater treatment plant. The optimised cathode potential was observed in the range of −0.70 V to −0.60 V and optimised feed pH was around 7.0. With autoclaved feed, these conditions allowed methane yields of about 9.05 mmol/$L_{(reactor)}$-day. A control experiment was then carried out to make a comparison between open circuit and MES methanogenesis. The highest methane yield of about 22.1 mmol/$L_{(reactor)}$-day was obtained during MES operation that performed 10–15% better than the open circuit mode of operation. We suggest and describe an integrated AD-MES system, by installing MES in the reject water loop, as a novel approach to improve the efficiency and productivity of existing waste/wastewater treatment plants.

Keywords: MES; CO_2 reduction; methane production; reject water; biogas

1. Introduction

Electrochemical carbon dioxide reduction has garnered immense attention in recent times, given the interest in reducing carbon emissions from industries and transport fuels. Increasing government policies on carbon reduction targets have also made businesses on the lookout for cheaper carbon abatement technologies. The other aspect that has empowered electrochemical biogas upgradation is the utilisation of excess renewable electricity for transportation. The concept of electrochemical reduction involves the conversion of carbon dioxide which is the non-energy-rich component of the biogas produced in the anaerobic digester to the energy-rich component of methane. This reduction is possible through the chemical reaction between carbon dioxide, protons and electrons (from electricity) in a microbial electrosynthesis system (MES) [1]. This is otherwise known as Power-to-Gas (PtG) technology, which allows electrochemical units to act as carbon sinks for industrial waste and more importantly industrial CO_2 emissions [2]. With PtG, it is possible to generate biogas of natural gas grade without the need to remove CO_2 using expensive techniques such as amine scrubbing or pressure swing adsorption [3]. This allows biogas (biomethane) generated from waste treatment plants to be directly connected to existing gas grids or to be used as a transport fuel.

Many studies have described the concept of electrochemical CO_2 reduction under various conditions such as short-term experiments [4–9], batch studies [6,10–12] two-chambered systems [13–15], and with buffered nutrient medium [13,16–18]. Electrochemical studies combining anaerobic digestion (AD) units have been demonstrated with both processes taking place in a single reactor [19]. A few researchers have suggested combining AD and microbial electrolysis cells (MECs)

Appl. Sci. 2019, 9, 1056; doi:10.3390/app9061056

as two separate units where the MECs were used for in-situ hydrogen gas injection into AD reactors for biogas enrichment [20–23]. Several studies on biogas upgrading technologies using in situ and/or ex situ hydrogen gas injection have been discussed by Aryal et al., 2018 [24]. Bioelectrochemical upgrading has also been reviewed in detail by the authors where small scale batch and continuous setups have been discussed. The authors suggest further research in the areas of long-term electrode stability, high current densities, electron transfer mechanism and reactor design and configuration [24] and some of these issues are addressed in the present article.

Direct Electron Transfer:

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \qquad E = -0.244 \text{ V vs. NHE} \tag{1}$$

Indirect Electron Transfer:

$$2H^+ + 2e^- \rightarrow H_2 \qquad E = -0.414 \text{ V vs. NHE} \tag{2}$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{3}$$

From the above-mentioned research studies and chemical reactions, the concept of electrochemical CO_2 reduction has been successfully established in theory and in practice albeit in short-term and laboratory scale experiments. The process stability with long-term experiments carried out on actual wastewater, as a post processing step for AD, is one of the least explored. Here, we describe a method to treat reject water from a local wastewater treatment plant using an MES, specifically as a biogas upgrading technology by placing it in the recycling loop of an AD system. This system allows efficient direct interspecies electron transfer (DIET; Reaction (1)) that is much more efficient than electrolysis (Reactions (2) and (3)) and is able to produce biogas with less than 10% carbon dioxide. The article also analyses process stability in terms of cathode potentials and pH in continuous flow MES systems over 1-month operation periods.

2. Materials and Methods

2.1. Electrode Materials and Preparation

Two electrode materials were chosen for these experiments—the cathode was a Carbon felt (20 mm × 20 mm × 3 mm; Alfa Aesar, Thermo Fisher GmbH, Karlsruhe, Germany) while the anode was a Graphite rod (L: 152 mm × D: 6.15 mm; Alfa Aesar, Thermo Fisher GmbH, Karlsruhe, Germany). To remove organic impurities, both materials were prepared by soaking them in 1 M HCl for 24 h followed by 1 M NaOH for a further 24 h [25]. These materials were selected based on a cyclic voltammetry study [26] showing comparable performance with a platinum-coated titanium electrode (which had the same geometrical dimensions as the carbon felt electrode). Additionally, these carbon-based electrodes are the most inexpensive-efficient materials available that make electrochemical processes scalable and practical [27].

2.2. Reactor Setup and Operation

2.2.1. Biofilm Growth

Biofilm was cultured in fed batch mode in a 3.0-L large glass vessel (R1) with 6 side ports and a multiport glass top cover. Raw reject wastewater (W) was obtained from Knarrdalstrand wastewater treatment plant (WWTP), Porsgrunn, Norway. The plant treats municipal wastewater collected from the counties of Porsgrunn and Skien serving a total population of approximately 80,000. Reject water was centrifuged at 10,000 rpm for 15 min and was analysed for total solids (TS), volatile solids (VS), chemical oxygen demand (COD) and acetic acid concentration. W was then spiked with 1 mL/L acetic acid (17.5 mM) to provide easily digestible COD for biofilm growth (W_a). Seven g/L of sodium bicarbonate (83.3 mM) was then added to provide a carbonate source that can be reduced to methane (W_a). Reject water pH changed from 7.8 (W) to 7.0 (W_a) and was used for carrying out the biofilm growth and biomethane production experiments.

The carbon felt cathode pieces were arranged as an elliptical chain by stringing them on a titanium wire. They were separated from each other by 1 cm Tygon tubes of 0.5 mm inner diameter and were strung on the titanium wire after each electrode piece. The graphite rod electrode was used as the anode and an Ag/AgCl electrode (+0.209 V vs. SHE; 3 M NaCl, QVMF2052, ProSense, BB Oosterhout, The Netherlands) was used as the reference electrode. All the potentials mentioned in this article are presented as vs Standard Hydrogen Electrode (SHE).

R1 was fitted with a carbon felt cathode chain, graphite rod anode and the reference electrode through the multiport top cover. The reactor was then filled with 2.5 L of the prepared reject water (W_a) leaving 500 mL of headspace. The reactor was inoculated with a total 5 mL digested anaerobic sludge obtained from various treatment plants. The reactor was bubbled with nitrogen gas for 20 min while the magnetic stirrer mixed the prepared reject water. The electrodes were then connected to their respective terminals and the reactor was operated at potentials of −1.00, −0.95, −0.90 and −0.85 V vs. SHE each for 1 week during the 1st month of operation. The reactor was then operated for another 1-month period at a constant potential of -0.80 V. During the 2-month biofilm growth period, 500 mL of wastewater was removed every week and was replaced with freshly prepared W_a of the same volume.

2.2.2. Biomethane Production Experiment

Biofilm growth was observed on most electrodes after the 2-month operation (not documented). Two of the 2×2 cm^2 cathodes which showed maximum biofilm cover were selected for the biomethane production experiment. This experiment was performed in a 135 mL reactor (R2), a modified version of standard 135 mL Duran glass bottle with a 3-port Teflon screw cap, used as a continuous-flow stirred tank reactor (CSTR; Figure 1). The two biocathodes were tied together using a titanium wire, which also acted as the electrode terminal and was connected to the potentiostat. W_a was fed to R2 continuously at 1-day hydraulic retention time (HRT) and was operated potentiostatically at −0.80 V vs SHE at 35 °C. It was operated for 1 month to regrow the biofilm lost during the transfer from R1 to R2 achieving steady state conditions (constant current). The experiment was then measured for various parameters during a 1-week operation of the biomethane production process.

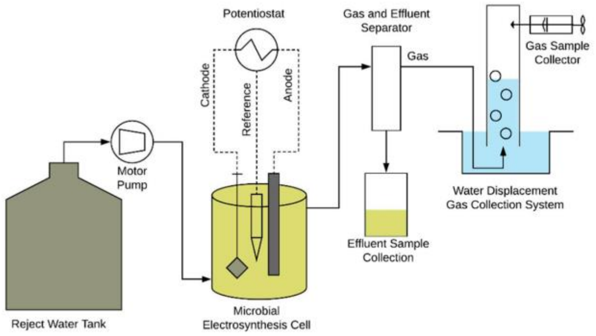

Figure 1. Biomethane production experimental setup for both optimisation and control experiments.

2.2.3. Optimisation of Cathode Potential

Reactor R2 was used in these experiments with a modified feed (W_{aA}); it was prepared in the same way as W_a with an additional step of autoclaving prior to the addition of acetic acid and sodium bicarbonate. It had an initial pH of 7.8. This was done to ensure all the biomethane produced is from the biofilm present on the carbon felt cathodes and not from suspended biomass. The aim of the experiment was to identify the activity of biofilm, optimum voltage and to ensure consistent performance in long term operation. The experiment was carried out for a total of 34 days in continuous flow with an HRT of 24 h at 35 °C. The initial cathode potential was set at −0.80 V vs. SHE and was reduced gradually, when the electrochemical methane yield (EMY; $\text{Methane}_{(\text{actual})}/\text{Methane}_{(\text{electro-conversion})} \times 100$) either remained unchanged or reduced. The EMY reduced drastically when the applied potential was −0.55 V and the experiment was terminated. Parameters such as pH, average current, biogas production and methane content were measured for all the experiments.

2.2.4. Optimisation of pH

A 25-day continuous flow electrochemical treatment of reject water at 24-h HRT was carried out to investigate the effect of pH on biogas production and coulombic efficiency. The experiment started with an initial feed pH of 7.8 (W_{aA}) at −0.70 V cathode potential. After 13 days, W_{aA} was modified with the addition of phosphate buffer to maintain the feed pH between 6.8–7.0 (W_{aB}). This was done to control the effluent pH below 8.5, and the effects of pH were observed over the final 12 days.

2.2.5. Verification of Optimised MES Performance

Following the optimisation experiments, a set of open circuit and electrochemical experiments were carried out. These experiments help to differentiate between heterotrophic and electrochemical methane production. The experimental setup used was the same as all the experiments described previously (Figure 1). W_a feed was used for both open circuit and MES operations. All the parameters such as COD, alkalinity and gas measurements were recorded at regular intervals. The open circuit operation was carried out over 10 days followed by MES operation for 9 days.

2.3. Analytical Methods and Calculations

The voltage and current were both set and measured using Gamry 1000B potentiostat and the Gamry Framework v7.06 (Gamry Instruments, Warminster, PA, USA) respectively. Chemical oxygen demand and alkalinity of wastewater samples were analysed using COD and Acid capacity Cell Test kits, respectively (Merck, Darmstadt, Germany). Biogas was analysed using the 8610C gas chromatograph (SRI Instruments, Torrance, CA, USA) equipped with a thermal conductivity detector and with a Haysep-D (HD) and MoleSieve (MS13X) column which separates oxygen, nitrogen, methane and carbon dioxide. The carrier gas was Helium at 4 bar pressure and the oven temperature was kept constant at 80 °C.

The electrochemical methane yield (EMY) was calculated according to Equation (4). Eight electrons are required to reduce 1 mole CO_2 to produce 1 mole of CH_4. The heterotrophic methane yield (HMY) was calculated according to Equation (5). One mole of acetic acid requires 64 g of oxygen for complete oxidation (COD) and 1 mole of COD produces 1 mole of methane gas.

$$EMY = \frac{\left[\frac{X\ (mL)}{24{,}450\ mL}\right]}{\left[\frac{n_e\ (\mathrm{C})}{8*F\ (\mathrm{C})}\right]} \times 100 \tag{4}$$

$$HMY = \frac{\left[\frac{X\ (mL)}{24{,}450\ mL}\right]}{\left[\frac{(COD_{feed} - COD_{effluent})*volume\ of\ feed}{64}\right]} \times 100 \tag{5}$$

where X is the volume of methane produced, and one mole gas at 25 °C at 1 atm occupies a volume of 24,450 mL. n_e is the number of electrons consumed, which can be calculated as an integral of current over time (obtained from Gamry Echem Analyst v7.06) and F is Faradaic constant (96,485 C/mol e^-).

3. Results and Discussion

3.1. Biofilm Growth

The total solids and volatile solids of centrifuged reject wastewater (W) were 6915 mg/L and 5185 mg/L, respectively. COD of W was 1600 mg/L and the acetic acid concentration was 66.7 mg/L. Biofilm growth was visibly significant on the electrodes that were positioned in the middle and bottom of reactor R1. The current corresponding to −1.00 V vs. SHE was measured at 0.20 mA initially and gradually increased to around 7.50 mA where it attained steady state. As the potential was decreased by 0.05 V every week, the current decreased immediately (around 1–2 mA) and increased gradually over the week to a steady current by the end of the week. The biofilm growth was determined to be stable when current remained constant over a period of one week in continuous operation.

3.2. Biomethane Production Experiment

The biomethane production experiment was carried out under potentiostatic conditions at −0.80 V vs. SHE and was able to produce 550 mL of biogas during the 1-week evaluation period (Table 1). The methane content was approximately 91%. The methane production rate was recorded as approximately 21.7 mmol/$L_{(reactor)}$-day. The COD was reduced from 3160 mg/L to 1422 mg/L and the pH of the effluent changed to around 7.8–7.9 from the feed pH of around 7.0 (W_a). The overall efficiency was 80.5% with methane conversion rate of 304.1 mL/mg-COD (87% of max. theoretical conversion). The simultaneous occurrence of electrochemical and heterotrophic methanogenesis results in such high COD to methane conversion rates. The EMY was measured to be 467.8% and suggests that a large portion of methane was produced via heterotrophic methanogenesis.

Table 1. Results of 1-week biomethane production experiment.

Parameter	Result
Biogas production	550 mL (22.5 mmol)
Methane	500 mL (20.5 mmol)
Carbon dioxide	34 mL (1.4 mmol)
COD Consumption	1644.3 mg (52%)
Voltage	−0.8 V vs. SHE
Methane Concentration	90.9%
Mass Balance Efficiency	80.5%
Electrochemical Methane Yield	467.8%

However, low concentrations of CO_2 in the biogas (i.e., 7%; CO_2 concentrations of around 35–45% are found in biogas produced via traditional anaerobic digestion reaction [28]) suggests electrochemical reduction of CO_2. With an aim to determine the electrochemical activity, the next set of experiments were performed by autoclaving the reject water before the addition of acetic acid and sodium bicarbonate (W_{aA}) effectively reducing heterotrophic methanogenesis.

3.3. Optimisation of Cathode Potential

The total methane production in the 34 days of continuous flow operation was about 541 mL (22.1 mmol) with an average methane percentage of about 85% (432 mL or 17.7 mmol). It has been previously reported that when the applied cathode potentials are more negative than −0.75 V vs. SHE electrochemical CO_2 reduction reactions result in simultaneous production of acetic acid (electrochemical) and methane rather than methane alone [5]. Therefore, to identify the optimal cathode potential for methane production, we begin the experiment at −0.80 V and reduce it step by step to −0.55 V.

The methane production rates (MPR; Figure 2) in these experiments ranged from 0.94 to 6.10 mmol/$L_{(reactor)}$-day. The lower production rates during first two days of the experiment could be due to the use of autoclaved feed and the total dependence on biocathode for methane production.

However, the MPRs increase and stabilize around 1.5 to 3 mmol/$L_{(reactor)}$-day over the next few days, suggesting biofilm acclimatization to the experimental conditions. The production rates increased as the cathode potentials were changed from −0.80 to −0.65 V and decreased thereafter. High MPRs of about 5.75 to 6.10 mmol/$L_{(reactor)}$-day occurred when the cathode potential was maintained at −0.65 V, which was double the production rate obtained in Section 3.2. MPRs were also low when the cathode potentials were more negative than −0.65 V which could be due to CO_2 conversion to acetic acid rather than methane [4]. The electrochemical reduction of CO_2 to acetic acid contributes to the increase in COD concentration of the effluent and thereby results in a low COD to methane conversion rate. The methane concentration in biogas was found to be around 83–87% during the first 23 days of operation that correspond to cathode potentials of −0.8 to −0.65 V. High concentrations of methane (90–93%) were obtained when the applied potential was −0.60 V. Therefore, the optimum cathode potential for electrochemical CO_2 reduction to methane with relatively high MPRs was found to be between −0.70 V and −0.60 V.

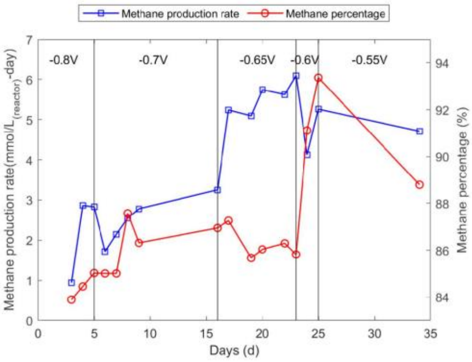

Figure 2. Methane production and methane percentage at different cathode potentials.

This is also reflected in the EMY plot (Figure 3) where the yield gradually increased from 45% to 110% when the potentials were changed from −0.80 V to −0.55 V. The slight dips in the EMY plot correspond to the changes in applied cathode potentials. However, the EMY recovers and surpasses its previous value at every cathode potential. Unlike EMY, the current generated increased gradually from the applied potentials of −0.80 V to −0.65 V and decreased abruptly at a potential of −0.60. The current remained constant and never recovered even after 9 days of potentiostatic operation at −0.55 V.

It can also be observed that at cathode potentials of −0.60, and −0.55 V, the EMY is consistently maintained above 100% even with decreasing current from 6.43 mA to 5.40 mA, respectively (Figure 3). This can be attributed to favourable heterotrophic methane production. In other words, cathode potentials more positive than −0.65 V limit the electrochemical activity of CO_2 reduction to either acetic acid or methane, and cathode potentials more negative than −0.65 V support simultaneous electrochemical acetic acid and methane production. An optimised cathode potential or voltage provides an opportunity to decrease the input cost of the electrochemical technology.

EMYs above 100% denote simultaneous electrochemical and heterotrophic methanogenic activities, albeit at a low rate due to the high pH. The pH of the effluent in the beginning of the experiment was about 8.1, but it gradually increased to about 8.7 (not represented graphically). This can be attributed to the consumption of protons through electrochemical activity, thereby affecting heterotrophic methanogenesis. This is also reflected in the overall methane production rate that was lower than when the effluent pH was 7.8 (Section 3.2). These preliminary observations on the effect of pH form the basis for the next set of experiments.

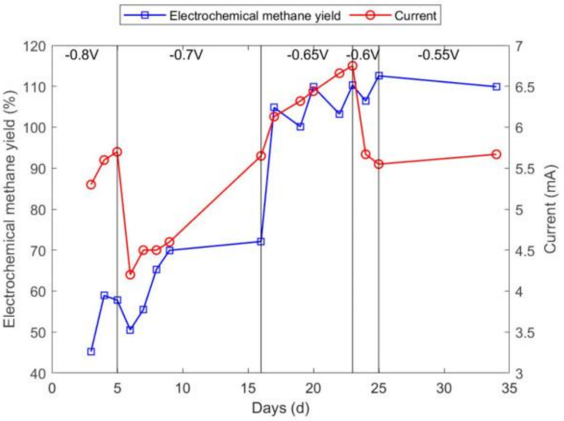

Figure 3. Electrochemical methane yield and current production with respect to cathode potential.

3.4. Optimisation of pH

The overall methane production in the 25 days of this −0.70 V potentiostatically operated experiment was around 432 mL (17.7 mmol) with an average methane concentration of about 91.4% (395 mL or 16.1 mmol; Figure 4). While the reaction was continuously fed with W_{aA} (feed pH ~7.8) and operated potentiostatically at −0.70 V, the effluent pH can be seen increasing from 8.2 to 8.7. Correspondingly, a fall in methane production rates (MPRs) from about 5.28 mmol/$L_{(reactor)}$-day to its lowest value of 2.62 mmol/$L_{(reactor)}$-day is observed (Figure 5). Thereafter, a change of feed to W_{aB} (pH of ~7.0) generated a significant impact on the effluent pH and thereby the MPRs. The effluent pH was gradually brought down to 8.1 and this in turn improved the MPR significantly to 9.05 mmol/$L_{(reactor)}$-day (Figure 5).

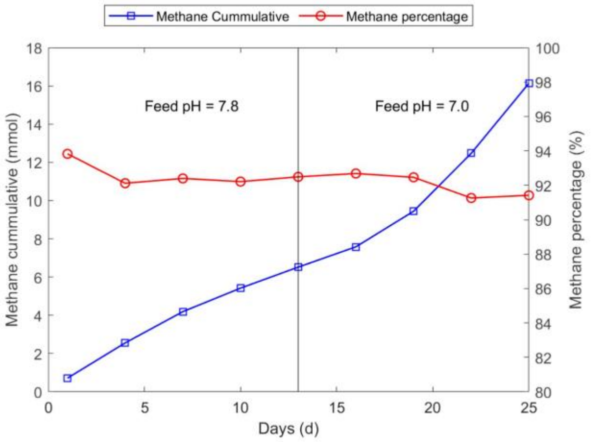

Figure 4. Cumulative methane production and methane percentage during optimisation of the pH experiment.

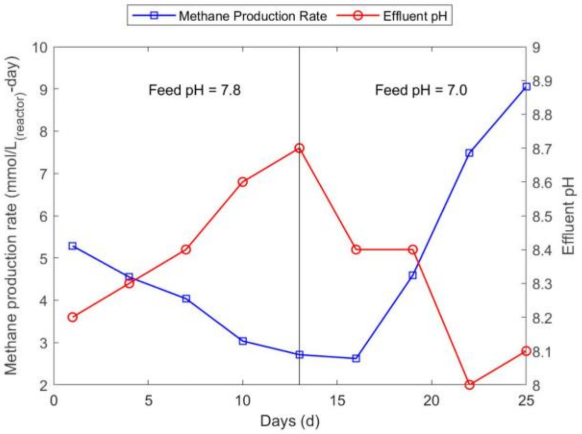

Figure 5. Methane production rate and effluent variation with feed pH.

EMY during the first half of the experiment starts at 87.7%, reaches the lowest value of 70% and stabilises at around 77% (Figure 6). However, during the second half of the experiment, it rises to 225% at an exponential rate. This clearly shows the impact of pH on methane production. High ranges of pH ~8.7 have been reported to eliminate or reduce the heterotrophic methanogenesis activity [29]. This means that during the first half of the experiment, a majority of methane production was autotrophic and during the second half, a large portion of methane production was heterotrophic. This suggests that the pH directly affects only heterotrophic methanogenesis. This can also be confirmed from the values of current generated (or electrons supplied) in the last week of the experiment that have remained constant, while the MPR and EMY have increased significantly. This emphasizes that the impact of pH was not significant on the electrochemical CO_2 reduction to methane.

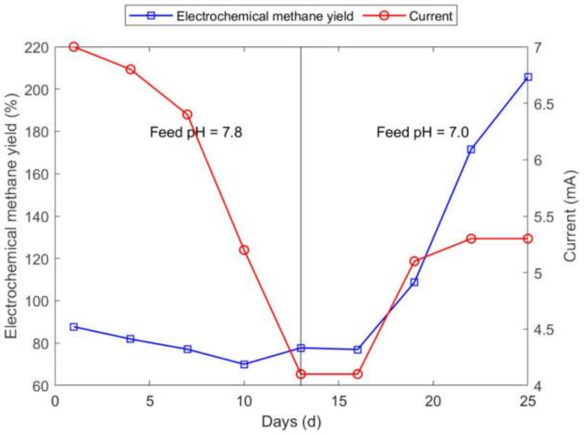

Figure 6. Electrochemical methane yield and currents production with respect to feed pH.

Another observation that contributes to this hypothesis is the methane concentration in biogas. It can be observed in Figure 4 that the methane percentage is continually maintained around 92–93% for the first 20 days. As the feed pH is decreased, the increased heterotrophic activity leads to a slight decrease in the methane concentration to about 91%. This can be attributed to the production of heterotrophic biogas that contains relatively higher concentrations of CO_2 [28]. These observations provide a new argument that electrochemical CO_2 reduction does depend on pH indirectly, as it reduces the heterotrophically generated CO_2. Moreover, it can be concluded that electrochemical methane production is not directly dependent on the pH but more dependent on the biofilm cover and the applied potential. An open circuit experiment is carried out to determine the share of methane production through each of the two production pathways.

3.5. Verification of Optimised MES Performance

The open circuit experiment was carried out at feed pH 7.0 with the potentiostat turned off and for the MES experiment, a cathode potential of −0.65 V was provided keeping the same feed. The average MPR (Figure 7) during open circuit operation (10 days) was measured to be 18.4 ± 1.3 mmol/$L_{(reactor)}$-day and for the MES mode operation was around 20.9 ± 0.9 mmol/$L_{(reactor)}$-day. This is an increase of approximately 13.6% in MPR due to the supply of electricity. Highest MPR of about 19.1 mmol/$L_{(reactor)}$-day was obtained during open circuit operation whereas during MES mode, the peak MPR was about 22.1 mmol/$L_{(reactor)}$-day. Further, COD analysis (Figure 7) during open circuit operation reveals HMY to be approximately 93.5% of COD consumed (607 mL/649.3 mL) whereas for MES mode, HMY was around 107.7% (623.6 mL/578.7 mL). The extra methane produced represents electrochemical CO_2 reduction to methane, which is 98.9% (44.9 mL/45.4 mL) efficiency in supplied electrons to methane conversion. At the same time, the methane concentration (Figure 7) in biogas for open circuit operation is consistently below 90% whereas for MES operation it has been consistently above 90%. High methane percentages in open circuit operation indicate CO_2 solubilisation within the reactor and therefore, require alkalinity analysis.

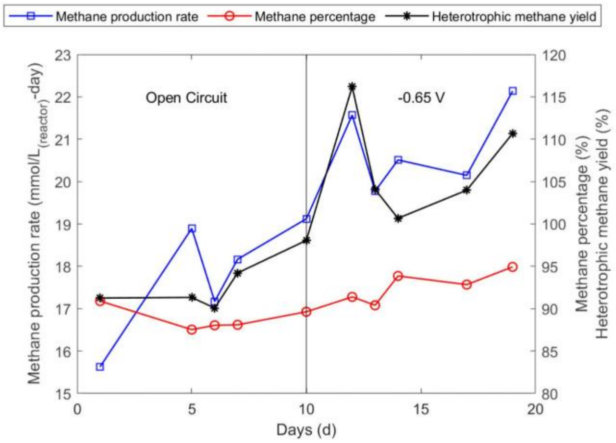

Figure 7. Comparison of methane production and efficiency in open circuit and MES mode operations.

Alkalinity of the reactor effluent denotes the acid capacity of the liquid in terms of dissolved hydroxide, bicarbonate or carbonate and is measured as mmol/L acid neutralizing capacity (ANC). When the pH is in the range of 8 to 8.4, alkalinity is mainly found in the form of bicarbonate [30] and as pH decreases, bicarbonate is transformed into CO_2. The red circles in Figure 8 represent the 'increase in alkalinity' or the change in amount of dissolved carbon dioxide within the reactor compared to the feed W_a. It can be observed that during open circuit operation the increase in alkalinity was more than the increase during the MES mode of operation. A similar trend can be seen with effluent pH (Figure 8) which also decreased as the experiment progressed towards electrochemical operation. These trends denote a decrease in CO_2 solubility within the reactor. Combined with high methane percentages in produced biogas, these results indicate electrochemical CO_2 conversion to methane. However, during the MES operation, the average current production remained very low at approximately 2 mA. Further attempts are being made to divert more microorganisms towards electrochemical methane production and increase current density. More importantly, new strategies must be developed to extract more energy-rich compounds from the carbon dioxide fed or produced within the reactor. This could mainly be done by controlling the pH within the reactor and keeping it less than 8.0 while maintaining the feed pH at 7.0. It will also be interesting to look at the effects of decreasing HRT on MES performance, as increased flow rate could control pH effectively.

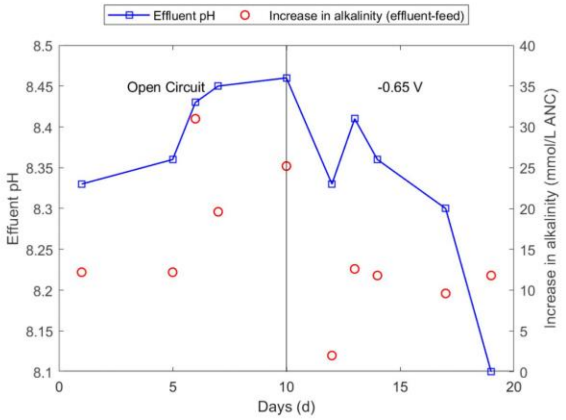

Figure 8. Comparison of pH and alkalinity in open circuit and MES mode operations.

3.6. Proposed AD-MES Integrated System

Results indicate that the electrochemical treatment of reject water can be used as a biogas upgradation technology. The optimised cathode potentials and pH provide proof-of-concept for electrochemical CO_2 reduction. Figure 9 describes the assembly of a food waste (solid lines) and/or wastewater treatment plant (dashed lines) and suggests implementation of an integrated MES unit. The inlets follow through a series of processing steps until the slurry is pumped into a biogas tank. The biogas generated is collected from the top and is sent either for upgrade or low value usage. Digested sludge is then centrifuged to separate the solids and liquid fraction otherwise called reject water. Reject water can contain a COD concentration ranging from 1000 to 8000 mg/L [31] depending on the type of feed and efficiency of biogas tank.

In food waste treatment plants, reject water is generally recycled for reducing total solids (TS) in the inlet feed, such that the mixture can be pumped without hindrance. It is also a common practice to use fresh water (make-up water) to achieve the desired TS and control inlet ammonium concentration. While in a WWTP, reject water goes back to the main wastewater inlet, that could be in the order of 1/100 of the total inlet flow and can, in many cases, causes instabilities in the main treatment train (coagulation-sedimentation); it therefore necessitates a reject water treatment system in existing WWTPs [32].

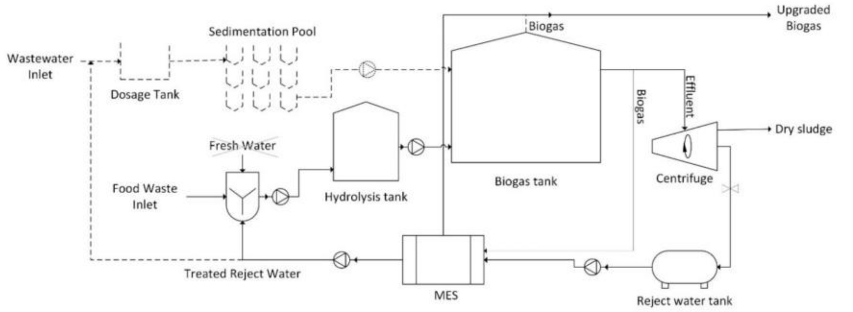

Figure 9. Proposed (generalized and simplified) AD-MES integrated treatment plant setup.

The proposed MES unit integration in a generalized biogas process as shown in Figure 9 has several advantages in addition to the benefit of biogas upgradation, such as the potential to reduce COD, ammonium and sulphide concentrations of reject water. An improved quality of the reject water will result in overall process optimization. It could completely eliminate the use of fresh water for food waste treatment plants and avoid variations in the main treatment train of typical WWTPs. Furthermore, there is a possibility of feeding biogas generated from the anaerobic digester to be upgraded to methane via electrochemical reduction of CO_2 already present in the biogas. This can be achieved by reducing the pH of reject water such that the CO_2 in biogas is made to dissolve in the feed. At the same time, the design of the MES reactor should allow the dissolved CO_2 to react with the electrons from the cathode.

Existing food waste or wastewater treatment plants could be refitted with the MES process as it neither interferes with the infrastructure present in the treatment plant nor is it a limiting capital investment. The system does not require extra feed as it generates more (methane, less pollution) from what is already available in the process and in this way, it is able to generate much more value than the investment it demands. However, research at this stage lacks information on mass balance, control experiments, hydraulic retention time and other waste feeds. Also, an economic analysis of integrated anaerobic digesters and microbial electrosynthesis systems is required to completely understand the scalability of such an integrated system.

4. Conclusions

From these experiments, it can be said that electrochemical methane production has huge potential to be one of the alternate fuel solutions. The cathode potential analysis revealed that electrochemical methane production is possible even at potentials as low as −0.55 V vs. SHE. The optimum cathode potential remains between −0.70 V and −0.60 V. Methane concentrations above 90% were consistently achieved. The carbon dioxide concentrations in biogas were kept below 15% in all the cases, achieving 50–60% reduction in CO_2 emissions in biogas production processes. We could also observe that when the feed/effluent pHs were kept high (i.e., >7.0/8.4 respectively), most of the methane is produced via the electrochemical pathway. As the pH moves closer towards neutral, coulombic efficiencies of over 200% were achieved, which is evidence of simultaneous electrochemical and heterotrophic methane production. The control experiments provide evidence of electrochemical CO_2 reduction showing an improvement of about 13.6% in terms of the average methane production rate. These experiments also show a decrease in the amount of CO_2 dissolving within the reactor when the electrodes are supplied with electricity. Further investigations are required to distinguish the mechanism of electron transfer during electrosynthesis of methane and/or acetic acid and how they depend on the applied cathode potential.

Author Contributions: Conceptualization, A.B.T.N. and C.D.; Methodology, A.B.T.N.; Validation, C.D.; Investigation, A.B.T.N.; Resources, C.D.; Data curation, A.B.T.N.; Writing—original draft preparation, A.B.T.N.; Writing—review and editing A.B.T.N. and C.D.

Funding: This research was funded by the Norwegian Ministry of Education and Research through the Ph.D. program in Process, Energy and Automation Engineering at University of South-Eastern Norway. The APC was funded by University of South-Eastern Norway.

Acknowledgments: Authors acknowledge Mrs. Sruthi Subramanyam for helping with the schematic diagram (Figure 1) in the article.

Conflicts of Interest: The authors declare no conflict of interest.

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Article 4

Performance Analysis of Biocathode in Bioelectrochemical CO_2 Reduction

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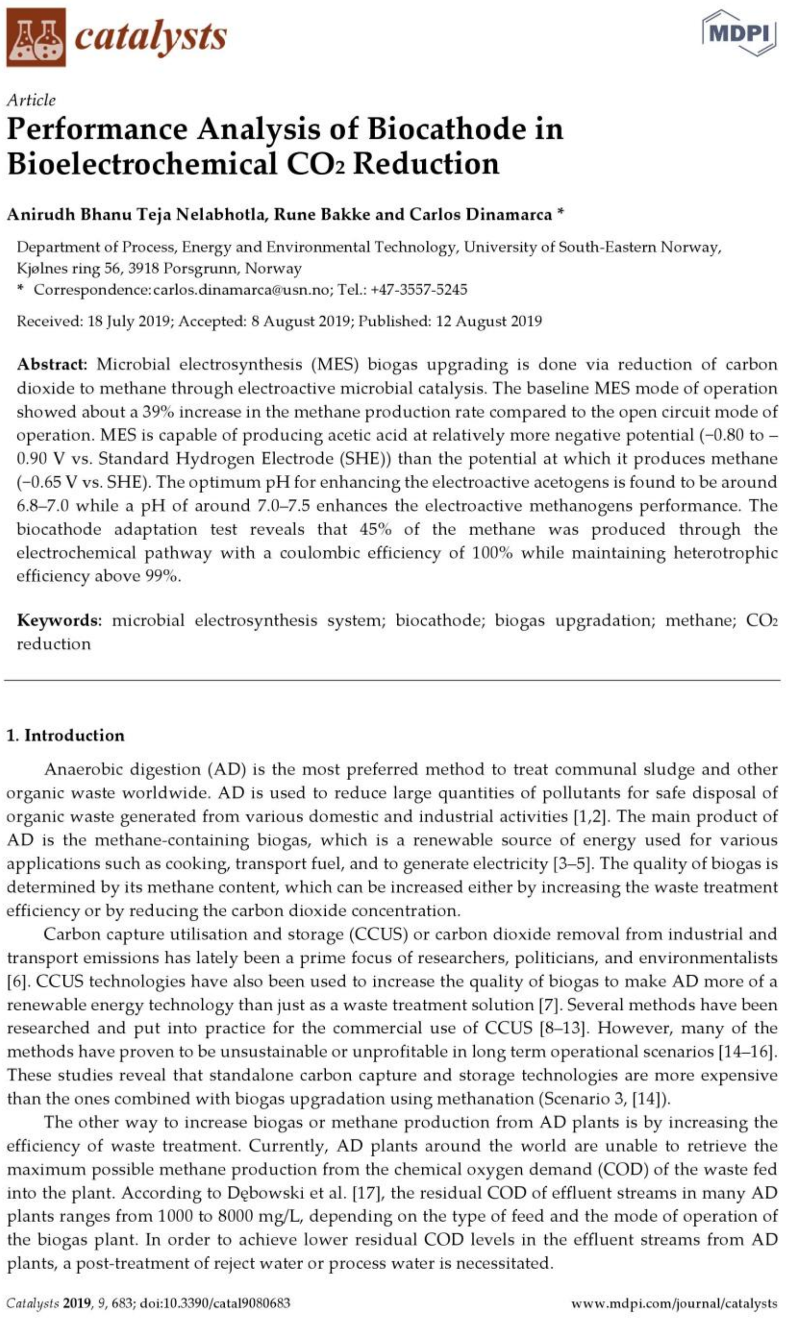
Published in *Catalysts* 2019, 9(8), 683



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Performance Analysis of Biocathode in Bioelectrochemical CO_2 Reduction

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Received: 18 July 2019; Accepted: 8 August 2019; Published: 12 August 2019

Abstract: Microbial electrosynthesis (MES) biogas upgrading is done via reduction of carbon dioxide to methane through electroactive microbial catalysis. The baseline MES mode of operation showed about a 39% increase in the methane production rate compared to the open circuit mode of operation. MES is capable of producing acetic acid at relatively more negative potential (−0.80 to −0.90 V vs. Standard Hydrogen Electrode (SHE)) than the potential at which it produces methane (−0.65 V vs. SHE). The optimum pH for enhancing the electroactive acetogens is found to be around 6.8–7.0 while a pH of around 7.0–7.5 enhances the electroactive methanogens performance. The biocathode adaptation test reveals that 45% of the methane was produced through the electrochemical pathway with a coulombic efficiency of 100% while maintaining heterotrophic efficiency above 99%.

Keywords: microbial electrosynthesis system; biocathode; biogas upgradation; methane; CO_2 reduction

1. Introduction

Anaerobic digestion (AD) is the most preferred method to treat communal sludge and other organic waste worldwide. AD is used to reduce large quantities of pollutants for safe disposal of organic waste generated from various domestic and industrial activities [1,2]. The main product of AD is the methane-containing biogas, which is a renewable source of energy used for various applications such as cooking, transport fuel, and to generate electricity [3–5]. The quality of biogas is determined by its methane content, which can be increased either by increasing the waste treatment efficiency or by reducing the carbon dioxide concentration.

Carbon capture utilisation and storage (CCUS) or carbon dioxide removal from industrial and transport emissions has lately been a prime focus of researchers, politicians, and environmentalists [6]. CCUS technologies have also been used to increase the quality of biogas to make AD more of a renewable energy technology than just as a waste treatment solution [7]. Several methods have been researched and put into practice for the commercial use of CCUS [8–13]. However, many of the methods have proven to be unsustainable or unprofitable in long term operational scenarios [14–16]. These studies reveal that standalone carbon capture and storage technologies are more expensive than the ones combined with biogas upgradation using methanation (Scenario 3, [14]).

The other way to increase biogas or methane production from AD plants is by increasing the efficiency of waste treatment. Currently, AD plants around the world are unable to retrieve the maximum possible methane production from the chemical oxygen demand (COD) of the waste fed into the plant. According to Dębowski et al. [17], the residual COD of effluent streams in many AD plants ranges from 1000 to 8000 mg/L, depending on the type of feed and the mode of operation of the biogas plant. In order to achieve lower residual COD levels in the effluent streams from AD plants, a post-treatment of reject water or process water is necessitated.

Catalysts **2019**, *9*, 683; doi:10.3390/catal9080683 www.mdpi.com/journal/catalysts

A microbial electrosynthesis system (MES), is one such technology that is able to act both as a post-treatment system for AD plants and as a CCU for the biogas produced. MES are capable of reducing carbon dioxide to various biochemicals (acetic acid, methane, etc.) of high industrial value, depending the operating conditions [18]. Different methods of reducing carbon dioxide to methane and the optimisation of such electrochemical operations has been previously discussed in Reference [19,20]. In this article, we study different pathways involved in bioelectrochemical CO_2 reduction to methane and dissect the operating conditions and activities involved in these pathways. Additionally, the article presents a novel method to observe the transition in biocathode performance from the heterotrophic dominant to the electrochemical dominant pathway. Listed below are the different paths to methane production.

Acetoclastic (heterotrophic) methanogenesis;

$$\mathrm{CH_3COOH} \rightarrow \mathrm{CH_4} + \mathrm{CO_2} \quad \Delta G = -33\ \mathrm{kJ/mol} \tag{1}$$

Hydrogenotrophic (autotrophic) methanogenesis;

$$4\ \mathrm{H_2} + \mathrm{CO_2} \rightarrow \mathrm{CH_4} + 2\ \mathrm{H_2O} \quad \Delta G = -135\ \mathrm{kJ/mol.} \tag{2}$$

Direct electron transfer (electrosynthesis reaction-bioelectrochemical methane);

$$4\ \mathrm{H_2O} \rightarrow 2\ \mathrm{O_2} + 8\ \mathrm{H^+} + 8\ \mathrm{e^-} \quad E^{\circ} = +0.81\ \mathrm{V\ vs\ NHE,} \tag{3}$$

$$\mathrm{CO_2} + 8\ \mathrm{H^+} + 8\ \mathrm{e^-} \rightarrow \mathrm{CH_4} + 2\ \mathrm{H_2O} \quad E^{\circ} = -0.244\ \mathrm{V\ vs\ NHE} \tag{4}$$

(Electroactive hydrogenotrophic methanogens as biocatalysts)

Indirect electron transfer (electrolysis-methanation reaction);

$$4\ \mathrm{H_2O} \rightarrow 2\ \mathrm{O_2} + 8\ \mathrm{H^+} + 8\ \mathrm{e^-} \quad E^{\circ} = +0.81\ \mathrm{V\ vs\ NHE} \tag{3}$$

$$2\ \mathrm{H^+} + 2\ \mathrm{e^-} \rightarrow \mathrm{H_2} \quad E^{\circ} = -0.414\ \mathrm{V\ vs\ NHE} \tag{5}$$

$$4\ \mathrm{H_2} + \mathrm{CO_2} \rightarrow \mathrm{CH_4} + 2\ \mathrm{H_2O} \quad \Delta G = -135\ \mathrm{kJ/mol} \tag{2}$$

(Hydrogenotrophic bacteria as biocatalysts)

Direct electron transfer (electrochemical acetate production);

$$4\ \mathrm{H_2O} \rightarrow 2\ \mathrm{O_2} + 8\ \mathrm{H^+} + 8\ \mathrm{e^-} \quad E^{\circ} = +0.81\ \mathrm{V\ vs\ NHE} \tag{3}$$

$$2\mathrm{CO_2} + 8\ \mathrm{H^+} + 8\ \mathrm{e^-} \rightarrow \mathrm{CH_3COOH} + 2\ \mathrm{H_2O} \quad E^{\circ} = -0.280\ \mathrm{V\ vs\ NHE} \tag{6}$$

(Electroactive acetogens as biocatalysts.)

Methane that is produced by acetoclastic methanogens (Reaction (1)) is called heterotrophic methane as the electron donor (acetate) is organic [21]. Methane that is produced from CO_2 reduction with the help of hydrogen as an electron donor (Reaction (2)) is called hydrogenotrophic methane [21]. The aforementioned pathways of methane production have been extensively studied for decades [22–24]. Methane that is produced through CO_2 reduction directly via electron and proton transfer with the help of hydrogenotrophic bacteria as biocatalysts is here called bioelectrochemical methane (Reactions (2), (3), and (4)). Methane production pathways in electrochemical reactors have been theoretically established and are termed indirect and direct (interspecies) electron transfer (DIET: Reactions (3) and (6)) [25].

In DIET methane production, the electrons are transferred through methanogenic archaea with the help of electrically conductive pili (hair-like appendage found on the surface of many bacteria and archaea) [26]. DIET is an efficient electron transfer mechanism that occurs at lower standard reduction potentials as compared to indirect electron transfer (Reactions (2), (3), and (5)). DIET can lead to product diversity that depends on both applied cathode potential and the microbial species in the electrode-attached biofilm. However, the margin for applied cathode potential is quite small and the biofilm selectivity is sensitive to physicochemical characteristics such as pH, temperature, and ion concentrations. Indirect electron transfer occurs when the electrons from an external power source are transferred indirectly via hydrogen gas or other mediator molecules, followed by hydrogenotrophic methanogenesis, to produce methane (Reactions (2), (3), and (5)).

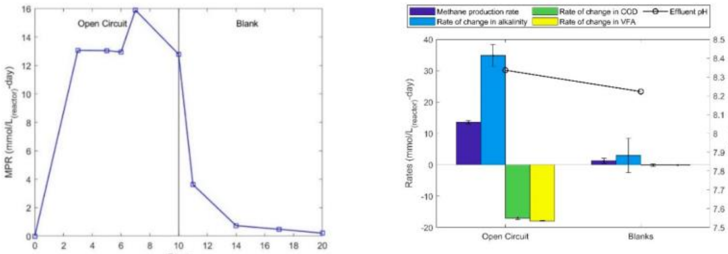
Research on DIET is at its initial stages and it is important to conduct a number of different studies that are able to provide deeper insight into the electron transfer mechanism. This article is one such work that lays out different pathways and parameters that influence DIET and, thereby, electrochemical CO_2 reduction. The study involves electrochemical treatment of reject water under different cathode potentials and feed conditions and parameters such as pH, COD, volatile fatty acids, (VFA), alkalinity, biogas production, and biogas quality are evaluated.

2. Results and Discussion

The reactor studied has been used continuously before [19] and after the tests presented here for more than a year, showing stability of such biological catalysts as it is self-replicating and rejuvenating.

2.1. Open Circuit and Blank Operation

Figure 1a shows the methane production rate (MPR) during open circuit and blank experiments, which were operated for 10 days each. It is observed that MPR was in the range of 13.0 to 16.0 mmol/L-d in open circuit and quickly came down to 0 in the absence of acetic acid. The effluent pH during open circuit (OC) operation was around 8.35, suggesting that CO_2 produced via acetate fermentation is in the form of bicarbonate (since pKa of $[CO_2]/[HCO_3^-] = 6.35$ [29,30]). CO_2 can exist in three different forms depending on the pH of the electrolyte. At a pH range of 8.00 to 8.53 (which is commonly found in the effluent of the experiments described in the present article) the equilibrium between CO_2 and HCO_3^- tends to be towards HCO_3^-. The changes in alkalinity can be represented as equivalent (not absolute) changes in HCO_3^- concentration, since the alkalinity of wastewater comprises of many other dissolved mineral salts that do not necessarily contribute to methane production. These experiments form the basis for the following experiments as control experiments.



(**a**) (**b**)

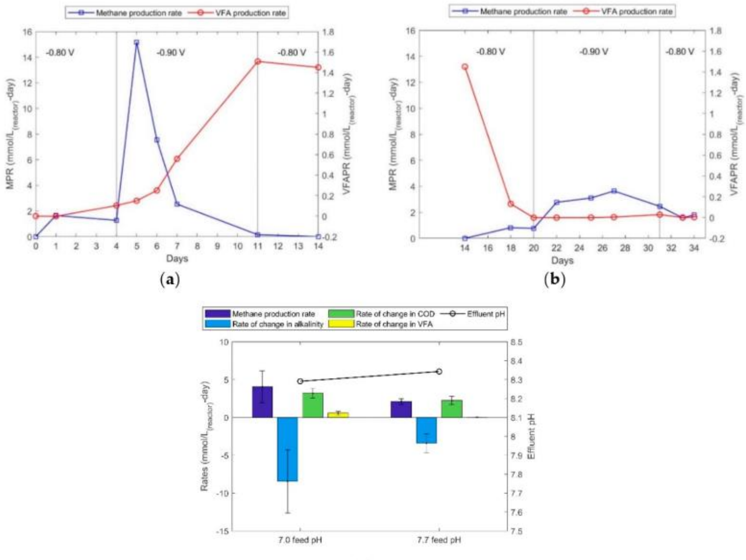
Figure 1: (**a**) Methane production rates in open circuit and blank operating modes. (**b**) Rate of different parameters and pH in open circuit and blank operating modes.

It can be observed in Figure 1b that both COD and VFA were consumed at a similar rate in the open circuit experiment corresponding to the production of methane. Since the initial VFA concentration was about 50% of the total initial COD concentration, the similar consumption rates imply that the biocathodes were not able to oxidize any extra COD in the absence of current. The COD consumed during the 10 day open circuit experiment produced methane with a heterotrophic efficiency of approximately 77%. The blank experiments show negligible VFA and COD consumption and work as a negative control. The low MPR and alkalinity values observed could be the residual methane and alkalinity from the open circuit experiments (MPR dropping with time (Figure 1a). The effluent pH, in both OC and blank experiments, remained between 8.20 and 8.35, increased from the feed pH of about 7.00. This pH in the OC mode supports solubilisation of bicarbonate, which is released heterotrophically, within the reactor and is represented through the increased value in alkalinity (Open Circuit, Figure 1b).

2.2. MES at High Cathode Potentials

The open circuit and blank experiments were followed by an MES operation to observe methane and acetic acid production at higher potentials. In Nelabhotla and Dinamarca [19], it was suggested that the optimum potential for methane production is around −0.65 V and at potentials more negative than −0.65 V the MES system supports simultaneous acetic acid and methane production. In Figure 2a and 2b the MPR and volatile fatty acid production rates (VFAPR) are presented in a time series plot at two different feed pH values. It can be observed that at a cathode potential of −0.80 V both MPR and VFAPR remained at low levels. This could be due to the need for incubation period after 10 days of blank operation. The cathode potential was then increased to −0.90 V and a sudden surge was observed in the methane production rate within 1 day, but it dropped gradually to ca. zero in 5 d, navigating the reaction towards acetic acid production.

The MPR increased to approximately 15.2 mmol/L-d and decreased to 7.6 mmol/L-d in one day, to 2.5 mmol/L-d in three days, and to 0.0 within a week (Figure 2a). On a molar basis, the methane production was approximately completely replaced by the acetic acid production (VFAPR). This VFAPR was also sustained at −0.80 V SHE cathode potentials. The transformation of MES from producing methane to producing acetic acid could be due to inhibition of methane-forming hydrogenotrophic bacteria (due to 'electro-shock'). A more likely reason could be that the applied potential favours acetic acid production under the given conditions. Reaction (6) shows that electrochemical acetic acid production theoretically occurs at a standard potential of −0.280 V vs. Normal Hydrogen Electrode (NHE), which is slightly higher than the standard potential for methane production, which occurs at −0.244 V vs. NHE (Reaction 4).



(**a**) (**b**)

(**c**)

Figure 2: (**a**) Methane and VFA production rates at low feed pH. (**b**) Methane VFA production rates at high feed pH. (**c**) Yields of different parameters at different feed conditions.

When the feed pH is changed to 7.7 keeping the cathode potential constant at -0.80 V an immediate drop in acetic acid production is observed with a slight increase in methane production. This could be due to the effect of pH on the electroactive acetogens (acetate producing bacteria) that are known to be efficient at lower pH ranges. Electroactive acetogen, *Clostridium ljungdahlii* produces volatile fatty acids in a range of pH from about 6.0 to 7.0 [27]. Many other studies show feed pH in the range of 6.8 to 7.0 for electrochemical acetic acid production using *Clostridium ljungdahlii* [28] and *Sporumusa spp.* [29,30]. The methanogens on the other hand seem to be more resilient to the higher pH conditions, as increased methane production rates (low level MPRs of about 2.0-4.0 mmol/L-d, from days 18 to 27) are observed (Figure 2b). This methane may partly be from the consumption of acetic acid previously produced and via the electrochemical pathway, leading to a decline in the MPRs from days 28 to 33 as the acetic acid was depleted. The optimum value of pH for methanogens is observed to be around 7.2 [31] while its range can be 6.5 – 8.0 [32] which supports tolerance for higher pH observed in the experiment.

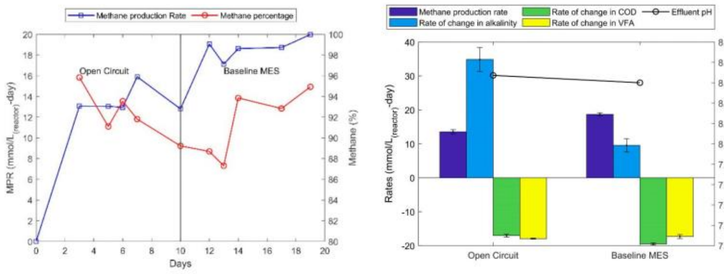
The negative impact of higher feed pH is reflected even on the source, as consumption of bicarbonate (alkalinity) is less than half of what was consumed at the lower feed pH (Figure 2c). It is also interesting to compare the rates of CODs and VFA as COD is produced at a rate of 4.0 mmol/L-d, which is significantly more than the production rate of VFA (0.5 mmol/L-d). At the higher feed pH, the VFA production rate is approximately 0.0 mmol/L-d, whereas the rate of increase in COD is approximately 3.0 mmol/L-d (Figure 2b). These higher COD concentrations in the effluent, that are not VFA, appear to belong to biomass and were probably caused by biofilm detachment, implying a reduced electrode biofilm biomass. This may explain the lower MPRs during the second half of the experiments. The biofilm may contain less electroactive hydrogenotrophic methanogens. It is not obvious what may have caused such biofilm deterioration but microorganisms can be sensitive to abrupt environmental changes, such as in pH, perhaps enhanced by cathode potential changes in this case.

Analysing the reactants, it is clear that the source of both acetic acid and methane in this experiment was bicarbonate (decrease in alkalinity; Figure 2c). It was also observed that the average reduction in alkalinity is more significant when the pH of feed was maintained at 7.0 than at 7.7, reinforcing the low electrocatalytic activity at higher feed pH. With these experiments it is concluded that a sudden change in either pH or in cathode potential could significantly affect the biofilm structure and function. The next set of experiments were carried out to establish baseline parameters for bioelectrochemical methane production and how a biocathode can be adapted to methane production via CO_2 reduction.

2.3. Open Circuit and Baseline MES Operation

The average MPR during open circuit mode was measured to be around 14.0 mmol/L-d whereas for MES mode it was around 19.5 mmol/L-d (Figure 3), which is an increase of 39% in terms of MPR. Further observations made regarding the change in alkalinity from feed to effluent, wherein the MES mode shows only one-third of what the increase in alkalinity was for the open circuit mode. This denotes the consumption of bicarbonate as it is being released in the reactor via heterotrophic methanogenesis through the consumption of VFAs.

In the open circuit mode, the COD and VFA reduction rates were very similar to each other whereas in the MES mode the COD reduction rate is approximately 15% more than VFA reduction rate. This implies that the oxygen produced via electrochemical activity (Eq. 5) may include oxidation at the anode of some part of soluble COD that is not VFA. Some studies have reported electrochemical processes capable of utilising chloride and hypochlorite ions for oxidising ammonia-nitrogen and COD present in wastewater [33–35]. Therefore, it can be said that the 39% increase in MPR could be due to a combination of electrochemical CO_2 reduction and electrochemical oxidation of COD followed by heterotrophic methane production. Further investigations are required to establish the latter. Such oxidation of organic matter present in the effluent of a wastewater treatment plant would be beneficial by reduced organic output to the environment and enhanced methane production.



(**a**) (**b**)

Figure 3. (**a**) Methane production rates in open circuit and baseline MES operations. (**b**) Yields of different parameters in open circuit and MES operating mode.

2.4. Biocathode Adaptation

To further explore the shares of heterotrophic methane and electrochemical methane, a series of biocathode adaptation experiments were carried out, targeted on the reject water feed that was supplemented with sodium bicarbonate (85 mM) and decreasing concentrations of acetic acid, designed to adapt the biocathode towards CO_2 reduction to methane as a primary product.

In Figure 4a, it can be observed that the methane production rates dropped with feed concentrations of acetic acid. The average methane percentage remained about 92% over the course of 49 days. It is important to note that the methane percentages were around 90% during days 22 through 49 when the acetic acid concentrations in the feed were low, indicating reduced heterotrophic methane and a reduced amount of heterotrophic bicarbonate being released. During the same time, it was observed that the alkalinity within the reactor suddenly stopped increasing and was followed by a significant reduction (Figure 4b). This suggests that the biocatalysts switch to utilize bicarbonate to produce methane when acetic acid becomes limited. The gas analysis during days 40 to 49 revealed 4.0 mmol/L-d and 0.3 mmol/L-d of methane and CO_2 production rates respectively. Correspondingly, the alkalinity reduction rate was about 9.8 mmol/L-d, whereas the COD and VFA reduction rates were only 2.0 mmol/L-d (Figure 4a). It implies that most of the methane was produced via electrochemical reduction/consumption of bicarbonate for methane production.

It was also observed that when the feed acetic acid concentration was decreased by about 90% (19.5 to 2.0 mM), the methane production rate was decreased by only 79% (19.0 mmol/L-d to 4.0 mmol/L-d). The additional methane production can be accounted to have produced via the bicarbonate based electrochemical pathway. Figure 4c shows the contribution of methane through two available pathways, heterotrophic (COD) and electrochemical (HCO_3^-/CO_2 and electrons), based on such mass balance analysis. The blue bars represent methane produced through degradation of COD and the orange bars represent the methane produced via bicarbonate. To distinguish bio-electrochemical and heterotrophic methane production it is assumed that the electrochemical pathway is 100% efficient in terms of electrons converting to methane and heterotrophic methane is calculated by subtracting the electrochemical methane from total methane measured. At 19.5 mM acetic acid conc. (Figure 4c) 92.5% of methane was by heterotrophic production and 7.5% was produced via the bio-electrochemical pathway. A gradual increase in the contribution of the bio-electrochemical pathway is observed with reduction feed acetate (45% at 2.0 mM acetic acid conc.).

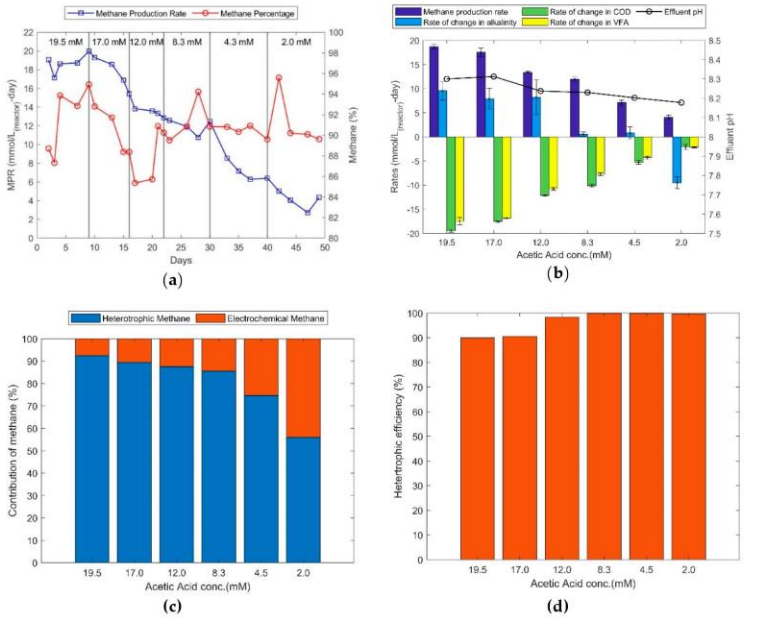


Figure 4: (**a**) Methane production rate (blue) and biogas methane percentage (red) at decreasing feed concentrations of acetic acid. (**b**) pH, methane production and rates of change in COD, VFA and alkalinity at tested acetic acid feed concentrations. (**c**) Methane source distribution between heterotrophic (blue) and electrochemical (red) methane. (**d**) Heterotrophic efficiency to methane considering 100% electrochemical efficiency.

In Figure 4d, it can be observed that the heterotrophic methane efficiency at 19.5 and 17.0 mM acetic acid feeds was approximately 90%. This implies that not all the COD consumed was utilised for methane production and that 10% of the consumed COD was utilised for biofilm growth and maintenance instead of methane production. The heterotrophic methane efficiency was > 98% for the lower feed acetic acid concentrations tested. This would imply that the concentration of COD required to support biomass growth and maintenance became limited at feed acetic acid concentration of approximately 8.3 mM. Correspondingly, the electrochemical pathway contributions increased from 7.5, to 45.0% of the total methane production with the step drops in feed acetate (Figure 4d). On the other hand, acetic acid feed concentration of about 17.0 mM and above would not only support biofilm growth and maintenance, but also promote heterotrophic methane production over electrochemical activity. This shows the sensitivity of the biofilm in utilising carbon dioxide for methane production when acetic acid is freely available and the importance of biocathode adaptation. Further improvements can be made to the electrochemical activity when the pH within the reactor can be brought down to less than 8.0, increasing the activity of electroactive hydrogenotrophic methanogens. This can be done, probably most easily, by increasing the feed flowrate, in other words, decreasing the hydraulic retention time (HRT) to maintain a higher level of un-reacted reactants in the MES.

3. Materials and Methods

3.1. Reactor and Feed Preparation

The experiments were performed in a 135 mL reactor, a modified version of a standard 135 mL Duran glass bottle with a 3-port Teflon screw cap, used as a continuous-flow stirred tank reactor, with ports for feed inlet, outlet, and electrodes. The cathode was a Carbon felt (20 mm × 20 mm × 3 mm; Alfa Aesar, Thermo Fisher GmbH, Karlsruhe, Germany) while the anode was a Graphite rod (L: 152 mm × D: 6.15 mm; Alfa Aesar, Thermo Fisher GmbH, Karlsruhe, Germany). The two biocathodes were tied together using a titanium wire, which also acted as the electrode terminal and was connected to the potentiostat. The graphite rod electrode was used as the anode and an Ag/AgCl electrode (+0.209 V vs. SHE; 3 M NaCl, QVMF2052, ProSense, BB Oosterhout, The Netherlands) was used as the reference electrode. All the potentials mentioned in this article are presented as vs Standard Hydrogen Electrode (SHE). The electrode selection criteria has been carried out using a cyclic voltammetry study previously published in Nelabhotla and Dinamarca [36].

The continuous flow stirred tank reactor was operated for a total of 150 days at 1-day hydraulic retention time (HRT) and at 35 °C. The feed was prepared using reject water from AD treated sewage sludge (separated by centrifugation) obtained from the Knarrdalstrand wastewater treatment plant, Porsgrunn, Norway. The basic reactor setup was used to carry out tests of different experimental conditions, such as open circuit, blank, high, and low cathode potential operations (Table 1). The MES feed was prepared by supplementing the reject water with 17 mM acetic acid (most of the time) and 85 mM sodium bicarbonate (all the time). 1M HCl solution was used to adjust the pH of the feed to 7.0 wherever mentioned.

Table 1. Experimental and feed conditions used in the current study.

Experiments	Duration (days)	Bicarbonate (mM)	AA(mM)	Inlet COD (mg/L)	Inlet AA (mg/L)	Feed pH	Cathode Potential (V vs. SHE)
Open Circuit	10	85	17	2700–2800	1200–1300	7.0	-
Blank	10	85	0	1400–1500	3–5	7.2	-
MES for Acetic Acid	34	85	0	1300–1600	2–8.5	7.0 (HCl) &7.7 (No HCl)	−0.8 to −0.9
Baseline Methane Production	9	85	17	2500–2700	1150–1200	7.0	−0.65
Biocathode Adaptation	49 *	85	17 to 0 (gradual)	2700–1500	1200–110	7.0 (AA and HCl)	−0.65

AA= acetic acid; * includes 9 days of baseline operation used as baseline for the adaptation experiments.

3.2. Open Circuit and Blank Operations

A series of open circuit (OC) and blank (B) experiments were run in a continuous flow stirred tank reactor at 1-day HRT, at 35 °C, and with no applied potential. Prior to this experiment, the reactor was operated electrochemically at a cathode potential of −0.65 V vs. SHE for 120 days until a stable biofilm was established. The OC was carried out with reject water feed that was supplemented with 17 mM acetic acid and 85 mM sodium bicarbonate, whereas the blank experiment used a feed with only 85 mM sodium bicarbonate. A total of 1M HCl was used to adjust the feed pH to the same level as open circuit feed pH, i.e., 7.0.

3.3. MES at High Cathode Potentials

The experiments were carried out at cathode potentials of −0.8 and −0.9 V vs. SHE, both at two different feed pH levels (feed pH was adjusted to 7.0 with addition of 1M HCl, while 7.7 was the pH of the feed without adding HCl). The feed was supplemented with 85 mM $NaHCO_3$ but was not provided with any acetic acid to avoid endogenous heterotrophic methane production and to identify electrochemical acetic acid production.

3.4. Open Circuit and Baseline Operation

The baseline MES mode of operation in this article is defined as an electrosynthesis operation of the feed supplemented with both acetic acid (17 mM) and sodium bicarbonate (85 mM) at a cathode potential of −0.65 V vs. SHE, 1-day HRT, and at 35 °C. The reactor was operated in baseline mode for 35 days prior to recording the data for 9 days. This data was compared to the open circuit mode of operation, discussed in Section 2.2 and 3.1.

3.5. Biocathode Adaptation

This test followed the baseline experiment that contained a similar concentration of HCO_3^- and, initially, with 80% of the previously supplemented concentration of acetic acid. The reactor was continually operated for a week and similar sets of experiments were continued every week with 60%, 40%, 20%, and 0% acetic acid supplemented to the reject water as feed. The unmodified reject water had a native concentration of about 2.0–2.5 mM of acetic acid (included as part of the VFA concentrations in all mass balances of all the experiments). All the experiments were carried out at −0.65 V vs. SHE, 1-day HRT, and at 35 °C. The feed pH was maintained at 7.0 by replacing acetic acid with 1M HCl.

3.6. Analytical Methods and Calculations

COD was analysed using Merck COD cell test kit 110047 which follows the standard method APHA SMWW 5220. VFA was analysed using the standard method APHA SMWW 6200B [37] and a Gas Chromatograph Hewlett-Packard 6890 where the carrier gas helium and hydrogen at 4 KPa pressure are passed through the DB-FFAP GC column (30 m, 0.25 mm, 0.50 µm, 7 inch cage) and are detected using a Flame Ionisation Detector (FID). Alkalinity was measured using the Merck cell test kit 11009 following the standard method APHA SMWW 2320 [37]. The voltage and current were both set and measured using Gamry 1000B potentiostat and the Gamry Framework v7.06 (Gamry Instruments, Warminster, PA, USA) respectively. Biogas was analysed using the 8610C gas chromatograph (SRI Instruments, Torrance, CA, USA) equipped with a thermal conductivity detector and with a Haysep-D (HD) and MoleSieve (MS13X) column which separates oxygen, nitrogen, methane and carbon dioxide. The carrier gas was Helium at 4 bar pressure and the oven temperature was kept constant at 80 ◦C.

Several parameters were analysed and compared amongst to achieve material balance and conversion efficiency. These are defined as follows:

$$\text{Methane production rate}\left(\text{MPR}, \frac{\text{mmol}}{\text{L}-\text{d}}\right) = \frac{\text{Measured methane (mL)}}{(24450\ \text{mL} \times \text{Volume of feed fed (L} - \text{d)}}$$

$$\text{Rate of change in alkalinity}\left(\frac{\text{mmol}}{\text{L}-\text{d}}\right) = \frac{[\text{Alkalinity}_{\text{eff}}(\text{mmol}) - \text{Alkalinity}_{\text{feed}}\ (\text{mmol})]}{\text{Volume of feed fed (L} - \text{d)}}$$

$$\text{Rate of COD to methane conversion}^{*}\left(\frac{\text{mmol}}{\text{L}-\text{day}}\right) = \frac{\left[\text{COD}_{\text{eff}}\left(\frac{\text{mg}}{\text{L}}\right) - \text{COD}_{\text{feed}}\left(\frac{\text{mg}}{\text{L}}\right)\right]}{64\left(\frac{\text{mg}}{\text{mmol}}\right) \times \text{duration (day)}}$$

$$\text{Rate of change in VFA}\left(\frac{\text{mmol}}{\text{L}-\text{d}}\right) = \frac{\left[\frac{\text{AA}_{\text{eff}}\left(\frac{\text{mg}}{\text{L}}\right) - \text{AA}_{\text{feed}}\left(\frac{\text{mg}}{\text{L}}\right)}{60\left(\frac{\text{mg}}{\text{L}}\right)} + \frac{\text{PA}_{\text{eff}}\left(\frac{\text{mg}}{\text{L}}\right) - \text{PA}_{\text{feed}}\left(\frac{\text{mg}}{\text{L}}\right)}{74\left(\frac{\text{mg}}{\text{L}}\right)}\right]}{\text{Volume of feed fed (L} - \text{d)}}$$

$$\text{Heterotrophic methane efficiency}\ (\%) = \frac{[\text{Methane}_{\text{Measured}}(\text{mL}) - \text{Methane}_{\text{Electrochem}}(\text{mL})]}{\text{Methane}_{\text{COD}}} \times 100$$

Where $\text{Methane}_{\text{Measured}}$ the actual amount of methane is produced and $\text{Methane}_{\text{COD}}$ is the amount of methane calculated by converting 100% of the COD consumed and $\text{Methane}_{\text{Electrochem}}$ is the amount methane calculated by converting 8 electrons transferred to 1 mole of methane.

$$\text{Methane}_{\text{COD}}\ (\text{mL}) = \frac{\text{COD consumed(mg)} * 24450(\text{mL})}{64\ \left(\frac{\text{mg}}{\text{mmol}}\right)}$$

$$\text{Methane}_{\text{Electrochem}}\ (\text{mL}) = \frac{\text{n}_\text{e}\ (\text{C}) \times 24450(\text{mL})}{8 \times \text{F}\ (\text{C})}$$

Where, 24450 mL = standard volume of a gas at RT; 64 mg/L = maximum theoretical conversion of COD to methane; AA = Acetic acid; PA = Propionic acid; eff = effluent; n_e is the amount electrons consumed; F is the Faradaic constant 96845 C/mol e^-; * Ignoring COD expenses for biomass growth and inorganic COD contributions.

The current article addresses a multitude of aspects of bioelectrochemical CO_2 reduction, discussed previously. This study started with a set of blank and open circuit operations carried out for 10 days each. This was followed by a set of experiments differentiating between two different ranges of feed pH and its effect on bioelectrochemical acetate production, which occurs at a higher cathode potential than required by bioelectrochemical methane production. A second run of open circuit and a baseline MES operation at −0.65 V were used as control experiments for the biocathode adaptation experiment that followed. These experiments were designed to differentiate how the heterotrophic activity dominates electrochemical activity to evaluate methods of improving electrochemical CO_2 reduction efficiency.

4. Conclusions

The current article analyses the performance of MES at different cathode potentials and feed conditions and evaluates how the biocatalysts perform under excess and limited acetic acid availability, with the help of control and blank experiments. An increased amount of methane production rate (39%) was observed in the baseline electrochemical operation when compared to the open circuit and blank operations. The performance analysis also showed how multiple parameters, such as pH and cathode potential, strongly influence the MES end product distribution. It is concluded that the optimum pH for electrochemical acetic acid production is around 6.8–7.0 and the optimum cathode potential is between -0.8 and -0.9 V vs. SHE. The optimum pH range for electroactive methanogens is wider and the optimum cathode potential is -0.65 V vs. SHE. Both heterotrophic and autotrophic methane production can be enhanced and their relative contributions depend on the feed composition. The biocathode adaptation experiments showed about 99%–99.5% heterotrophic methane efficiency when the acetic acid concentrations were lower than or equal to 12.0 mM in the feed assuming coulombic efficiency to be 100%. 45% of methane production was obtained via the electrochemical pathway when feed acetic acid concentration was brought down to 2.0 mM.

Author Contributions: Conceptualization, A.B.T.N. and C.D.; Methodology, A.B.T.N., C.D.; Validation, C.D.; Investigation, A.B.T.N.; Resources, C.D.; Data curation, A.B.T.N.; Writing—original draft preparation, A.B.T.N.; Writing—review and editing A.B.T.N., R.B., and C.D.

Funding: This research was funded by the Norwegian Ministry of Education and Research through core funding of the Ph.D. program in Process, Energy and Automation Engineering at University of South-Eastern Norway. The APC was funded by University of South-Eastern Norway.

Conflicts of Interest: The authors declare no conflict of interest.

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Article 5

Effect of Hydraulic Retention Time on MES Operation for Biomethane Production

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Submitted to Frontiers Energy Research on 23rd January 2020
Revised on 20th February 2020

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Submitted to Journal:
Frontiers in Energy Research

Specialty Section:
Electrochemical Energy Conversion and Storage

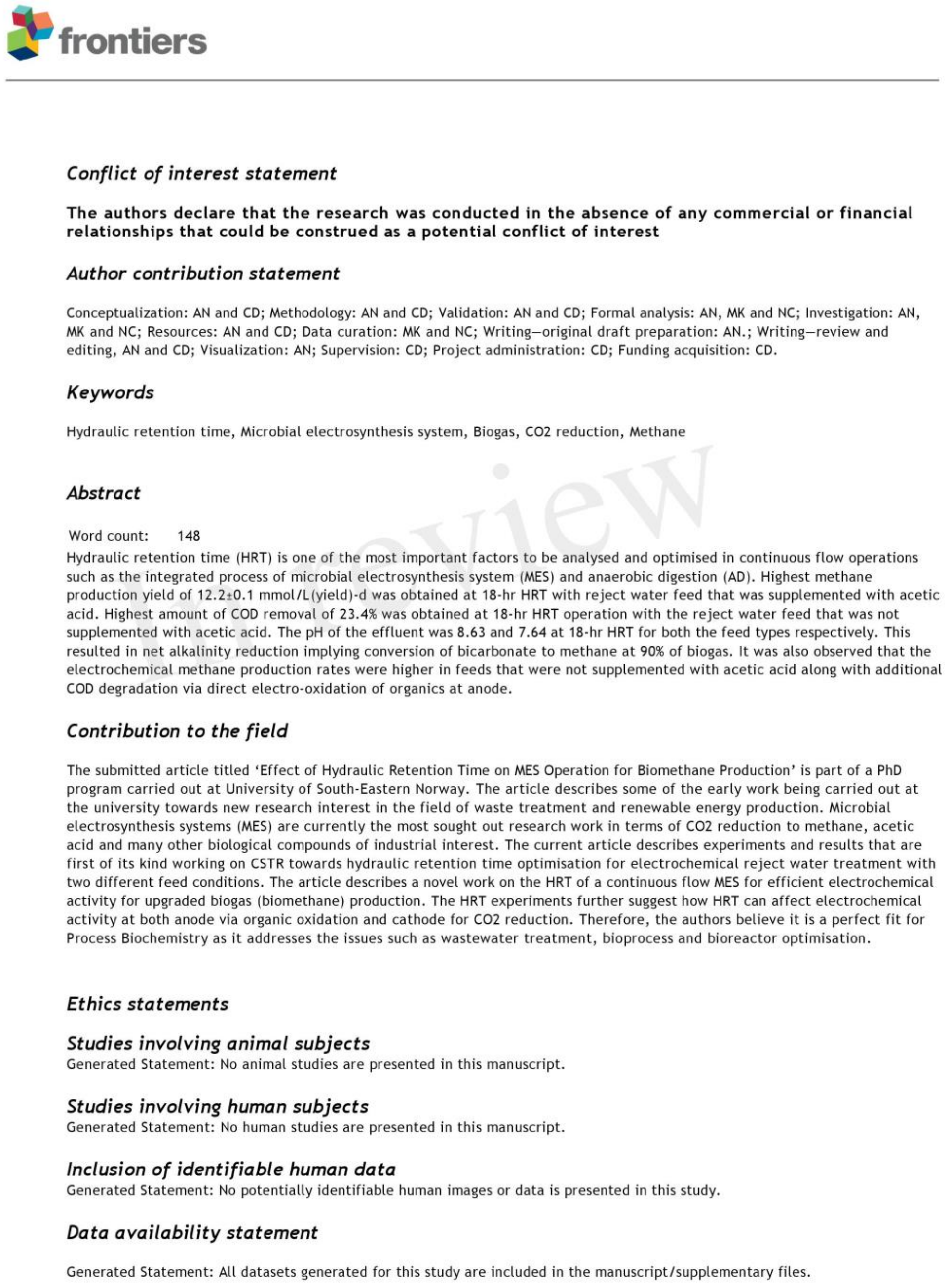
Article type:
Original Research Article

Manuscript ID:
529190

Received on:
23 Jan 2020

Revised on:
20 Feb 2020

Frontiers website link:
www.frontiersin.org



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Conflict of interest statement

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest

Author contribution statement

Conceptualization: AN and CD; Methodology: AN and CD; Validation: AN and CD; Formal analysis: AN, MK and NC; Investigation: AN, MK and NC; Resources: AN and CD; Data curation: MK and NC; Writing—original draft preparation: AN.; Writing—review and editing, AN and CD; Visualization: AN; Supervision: CD; Project administration: CD; Funding acquisition: CD.

Keywords

Hydraulic retention time, Microbial electrosynthesis system, Biogas, CO2 reduction, Methane

Abstract

Word count: 148

Hydraulic retention time (HRT) is one of the most important factors to be analysed and optimised in continuous flow operations such as the integrated process of microbial electrosynthesis system (MES) and anaerobic digestion (AD). Highest methane production yield of 12.2±0.1 mmol/L(yield)-d was obtained at 18-hr HRT with reject water feed that was supplemented with acetic acid. Highest amount of COD removal of 23.4% was obtained at 18-hr HRT operation with the reject water feed that was not supplemented with acetic acid. The pH of the effluent was 8.63 and 7.64 at 18-hr HRT for both the feed types respectively. This resulted in net alkalinity reduction implying conversion of bicarbonate to methane at 90% of biogas. It was also observed that the electrochemical methane production rates were higher in feeds that were not supplemented with acetic acid along with additional COD degradation via direct electro-oxidation of organics at anode.

Contribution to the field

The submitted article titled 'Effect of Hydraulic Retention Time on MES Operation for Biomethane Production' is part of a PhD program carried out at University of South-Eastern Norway. The article describes some of the early work being carried out at the university towards new research interest in the field of waste treatment and renewable energy production. Microbial electrosynthesis systems (MES) are currently the most sought out research work in terms of CO2 reduction to methane, acetic acid and many other biological compounds of industrial interest. The current article describes experiments and results that are first of its kind working on CSTR towards hydraulic retention time optimisation for electrochemical reject water treatment with two different feed conditions. The article describes a novel work on the HRT of a continuous flow MES for efficient electrochemical activity for upgraded biogas (biomethane) production. The HRT experiments further suggest how HRT can affect electrochemical activity at both anode via organic oxidation and cathode for CO2 reduction. Therefore, the authors believe it is a perfect fit for Process Biochemistry as it addresses the issues such as wastewater treatment, bioprocess and bioreactor optimisation.

Ethics statements

Studies involving animal subjects

Generated Statement: No animal studies are presented in this manuscript.

Studies involving human subjects

Generated Statement: No human studies are presented in this manuscript.

Inclusion of identifiable human data

Generated Statement: No potentially identifiable human images or data is presented in this study.

Data availability statement

Generated Statement: All datasets generated for this study are included in the manuscript/supplementary files.

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Effect of Hydraulic Retention Time on MES Operation for Biomethane Production

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Keywords: Hydraulic retention time; microbial electrosynthesis system; biogas; CO_2 reduction; methane

Abstract

Hydraulic retention time (HRT) is one of the most important factors to be analysed and optimised in continuous flow operations such as the integrated process of microbial electrosynthesis system (MES) and anaerobic digestion (AD). Highest methane production yield of 12.2±0.1 mmol/$L_{(yield)}$-d was obtained at 18-hr HRT with reject water feed that was supplemented with acetic acid. Highest amount of COD removal of 23.4% was obtained at 18-hr HRT operation with the reject water feed that was not supplemented with acetic acid. The pH of the effluent was 8.63 and 7.64 at 18-hr HRT for both the feed types respectively. This resulted in net alkalinity reduction implying conversion of bicarbonate to methane at 90% of biogas. It was also observed that the electrochemical methane production rates were higher in feeds that were not supplemented with acetic acid along with additional COD degradation via direct electro-oxidation of organics at anode.

1 Introduction

Microbial electrosynthesis systems (MES) have long been discussed as a tool for sustainable biochemical and biofuel production. One such application is to integrate MES with anaerobic digestion (AD) systems as a post-treatment unit for enhanced biomethane production and organic degradation (Nelabhotla and Dinamarca 2019). One of most important aspects of a continuous flow reactors is the organic loading rate (OLR) which increases with shorter hydraulic retention time (HRT). These parameters have never been explored in the context of biomethane production via MES and integration of MES with AD.

It is important to differentiate between hydraulic retention time and solid retention time (SRT) in biochemical reactors when biofilm activity is an integral part of reactor design. HRT is defined as the average length of time that a soluble compound remains in a constructed bioreactor which in case of MES is the feed wastewater and its components. SRT on the other hand is defined as the average time the activated-sludge solids are in the system which mainly implies the micro-organisms that carry out the metabolic activities in the bioreactor. In a normal CSTR the SRT is equal to HRT whereas the presence of a surface within the bioreactor that is able to support biofilm growth the value of SRT can dramatically increase compared to HRT (Metcalf and Eddy 2014).

HRT influences the flow of nutrients, products and unreacted chemicals through reactor, whereas the SRT influences the rate of nutrients converting into products. The biocathodes present in the MES can maintain a constant and indefinite SRT. Therefore, there is a need to optimise the HRT/OLR to exploit optimal and favourable productivity. HRT is a major factor to evaluate not only technical viability but most importantly economic viability. HRT can also influence biofilm thickness and biofilm efficiency in case of MES when strategized together with reactor design. The feed flow pattern and shear force exerted on the biofilm surface can impact biofilm structure and activity (Chang et al. 1991)

Previous articles have discussed other electrode material selection, parameters optimisation, biocathode adaptation using control and mass balance experiments and suggested a novel method to integrate MES with existing AD plants. In this article, two scenarios for optimising HRT in MES are studied: a) feed simulating food waste reject water (high acetic acid in feed) and b) reject water from wastewater treatment plant (low acetic acid in feed). This study shows how HRT influences the two main pathways of methane production in MES i.e. the electrochemical and the acetoclastic pathways.

2 Materials and Methods

2.1 Reactor and Feed Preparation

The experiments were performed in a 135 mL electrochemical reactor designed according to materials and methods described in Nelabhotla et. al., 2019 (Nelabhotla, Bakke, and Dinamarca 2019). The cathodic surface area was 8 cm^2 in the 135 mL reactor that gives an electrode surface area to reactor volume ratio of 6 m^2/m^3. The current density measured during the experiment was at an average 2 A/m^2. The continuous flow stirred tank reactor was operated in various conditions at 1-day hydraulic retention time (HRT) prior to the current study and discussed in previous publications (Nelabhotla and Dinamarca 2019; Nelabhotla, Bakke, and Dinamarca 2019). The same reactor setup was duplicated and were used to carry out HRT experiments with two different feed streams. The feed was prepared using reject water from AD treated sewage sludge and was obtained from Knarrdalstrand wastewater treatment plant, Porsgrunn, Norway. The reject water has a total solid concentration of 4250 mg/L and volatile suspended solid concentration of approximately 2640 mg/L.

The first MES, R1 was fed with reject water containing 17 mM acetic acid and 85 mM sodium bicarbonate. The second reactor setup, R2 was fed with reject water without any added acetic acid but was supplemented with 85 mM bicarbonate. 1M HCl was used to adjust the pH of the feed to 7.0. Both R1 and R2 were adapted to the electrochemical operation using the respective feed conditions for 2 months at 24-hr HRT before recording data. All the other conditions such as temperature 35 °C, cathode potential -0.65 V vs Standard Hydrogen Electrode (SHE) was kept same for both R1 and R2. The hydraulic retention time was changed in steps of 24, 18, 12, 6, 3, 2 and 1 hour as soon as 8 to 10 samples were obtained during each experimental period. The samples were collected at intervals of at least their respective hydraulic retention times.

2.2 Analytical Methods and Calculations

All the analytical methods used to measure chemical oxygen demand (COD), cathode potential, current, biogas composition including the calculations for several parameters have been previously described in Nelabhotla et. al. 2019 (Nelabhotla, Bakke, and Dinamarca 2019). Additionally, the below mentioned parameters were also calculated:

Effect of HRT of Bioelectrochemical Methane Production

$$\textbf{Electrochemical MPR}\left(\textbf{ECMPR},\frac{\textbf{mmol}}{\textbf{L}-\textbf{d}}\right)=\frac{\textbf{Methane}_{\textbf{Electrochem}}\ (\textbf{mL})}{(\textbf{24450 mL}\times\textbf{Volume of the reactor}\ (\textbf{L}-\textbf{d})}$$

$$\textbf{COD consumption}\ \%=\frac{\left[\textbf{COD}_{\textbf{feed}}\left(\frac{\textbf{mg}}{\textbf{L}}\right)-\textbf{COD}_{\textbf{eff}}\left(\frac{\textbf{mg}}{\textbf{L}}\right)\right]}{\textbf{COD}_{\textbf{feed}}\left(\frac{\textbf{mg}}{\textbf{L}}\right)}\times\textbf{100}$$

Where, $\text{Methane}_{\text{electrochem}}$ is the amount methane calculated by converting 8 electrons transferred to 1 mole of methane.

$$\textbf{Methane}_{\textbf{Electrochem}}\ (\textbf{mL})=\frac{\textbf{n}_{\textbf{e}}\ (\textbf{C})\times\textbf{24450}(\textbf{mL})}{\textbf{8}\times\textbf{F}\ (\textbf{C})}$$

24450 mL = standard volume of a gas at room temperature; eff = effluent; n_e is the amount electrons consumed; F is the Faradaic constant 96845 C/mol e^-

3 Results and Discussion

3.1 HRT experiments with acetic acid in feed

Methane production in Figure 1a is measured in terms of methane produced per day and per litre of reactor volume. The HRT operations of 6 and 3 hours produce methane at the highest rate of 40.3±0.4 and 40.2±1.7 (mmol/$L_{(\text{reactor})}$-d) respectively. This is equivalent to a productivity of approximately 1.0 L/$L_{(\text{reactor})}$-d. However, it is important to note that the methane yield in terms of feed reduces by 50% (10.1 to 5.0 mmol/$L_{(\text{feed})}$-d: Table 1, Supplementary file) when the feed rate is doubled from 6-hr to 3-hr HRT. Optimum methane production is obtained at 18-hr HRT with highest feed based MPR of about 12.2 ±0.1 mmol/$L_{(\text{feed})}$-d at 90% methane concentration (Fig 1a and 1b). Other characteristics obtained at 18-hr HRT operation that suggest optimum performance is the amount of COD consumed that is approximately 40.6% of the fed COD (Fig. 1c). Other feed rate operations (at 24-, 12- and 6-hr HRT) show COD consumption of (38.7, 41.7 and 36.5%) of the fed quantity. Considering approximately 36-40% of fed COD is equivalent to the amount of supplemented acetic acid, it can be said that the lower HRT operations viz., 3-, 2- and 1- hr (25.6%, 18.6% and 8.6% of COD consumed) are limited to produce methane from the available acetic acid. On the other hand, the higher HRT operations can consume maximum of the available acetic acid and produce methane at heterotrophic efficiencies of more than 90%. The 12-hr HRT operation shows consumption of about 41.7% of fed COD which is marginally more than the COD equivalent of supplemented acetic acid. This suggests that electrochemical treatment of reject water could degrade COD that was not acetic acid and that was not digested in the AD reactor.

One of the primary reasons behind the HRT optimisation experiments is the effect on effluent pH and on the concentration of alkalinity. It is clearly observed in Fig 1a that as HRT is decreased the pH decreases gradually. Most importantly, it is observed that when pH is close to and below 8.0 the concentration of alkalinity in the reactor/effluent is negatively affected. This implies that a lower pH in the reactor positively affects bicarbonate consumption. The negative signs in Fig 1a and 2a sign represents 'consumption' and positive sign represents 'production'. It was not possible to obtain 100% COD to methane conversion efficiencies for many HRT operations except 18 and 6-hr, which implies incomplete conversion of degraded COD to methane at other HRT operations.

3.2 HRT experiments without acetic acid in feed

The MPR depicted in Fig 2a shows that highest rate of methane production of about 19.6±0.2 mmol/L$_{(reactor)}$-d occurs at 3-hr HRT operation. However, at 3-hr HRT methane yield is as low as 2.5 mmol/L$_{(feed)}$-d. 12- and 6-hr HRT operations show MPRs of about 12.6±0.2 and 14.7±0.1 mmol/L$_{(reactor)}$-d respectively but produce methane yields of about 6.3±0.1 and 3.7±0.0 mmol/L$_{(feed)}$-d respectively. However, the methane percentages obtained are 90% and 87% for 12 and 6-hr HRT operations respectively (Fig 2b). Therefore, it can be said that the 18-hr HRT operation that produces highest feed based MPR of about 7.4 ±0.1 mmol/L$_{(feed)}$-d at methane concentration of 90% shows optimum HRT for MES operation (Fig 2a and 2b). Further observing the amount of COD consumed i.e. 23.4% of fed COD shows highest COD degradation at 18-hr HRT operation (Fig 2c). It is important to note that the feed in these experiments was not supplemented with additional acetic acid, which implies that a large portion of 23.4% of COD consumed belongs to undigested COD from the AD. It can be speculated that this non-acetic COD was degraded via anodic oxidation of organics. It can also be observed that a mass balance is achieved between COD and electrons consumed with total methane production at 18-hr HRT operation. This implies that the additional degraded COD was also converted to methane. However, this was not the case at lower HRTs where the flow rate was too high to convert degraded COD to methane. The multiple pathways involved in COD degradation and methane production is explained in the following section.

The pH of effluent in these experiments reduced below 8.00 at 18-hr and all lower HRT operations. At 6-hr HRT operation the effluent pH was around 7.74 and the alkalinity was reduced at a rate of -22.1±3.3 mmol/L$_{(reactor)}$-d implying high bicarbonate conversion to methane and CO_2. Even higher reductions in alkalinity were observed at lower HRT operations but resulted in unreacted CO_2 gas and lower methane percentages in biogas (Fig. 2b; 12 hrs=87%, 6 hrs = 85%, 3 hrs = 80%, 2 hrs = 70% and 1 hr = 60%). While, higher methane production rates imply that bicarbonate was converted to methane, the lower COD to methane conversion efficiencies imply that anodic oxidation of organics lead to release of unreacted CO_2 gas and is explained in the Section 3.3. It is speculated that the high flow rates at lower HRT operations could damage the cathodic biofilm resulting in decreased CO_2 reduction rates. This can be avoided by adapting the biofilms for higher flow rates and by designing a reactor with high cathodic surface area to reactor volume ratio.

3.3 Electro-oxidation of Organics

Typically, two pathways are described for anodic oxidation of organics: a) direct and b) indirect. The direct anodic oxidation depends on direct contact between the organics and electrode surface and the final product released is CO_2 and protons (Ghimire et al. 2019). The indirect organic anodic-oxidation is possible in the presence of large concentrations of chloride ions (> 3g/L) (Chen 2004). Both the methods for anodic oxidation are possible in the MES experiments discussed in the current article. A recent publication states that direct oxidation of COD is characterized by the generation hydroxide radical (OH*) that is capable destroying wide range of pollutants (Ghanim and Hamza 2018). The authors demonstrated 86-87% of COD removal with two different electrode materials high temperatures of 50-55 °C. The current article demonstrates 23.5% COD removal at 18-hr HRT combined with methane percentage of 90% albeit at low production rates of 10.0 mmol/L$_{(reactor)}$-d.

Higher feed flow rates during the lower HRT might wash away weaker biofilm networks on the anode that bring direct contact between the feed and the electrode allowing direct electro-oxidation. Since, the pH of the feed in R2 was adjusted using diluted 1M HCl solution, indirect electro-oxidation is also a possibility. These pathways have not been quantified in this study. However, the results show increase in CO_2 percentage (Fig 2a; decrease in methane percentage from 87% to 52%)

in the biogas against decreasing HRT suggests the dominance of direct electro-oxidation of organics in MES. Although HRT does not directly improve methane production, it is revealed that HRT can affect COD degradation, which can also be beneficial in terms of lower discharge concentrations.

It is important to consider that the CO_2/HCO_3^- required for electrochemical methane production can be obtained from four sources. 1) Heterotrophic conversion of residual acetic acid to methane and CO_2/HCO_3^- 2) CO_2/HCO_3^- dissolved in the feed 3) CO_2/HCO_3^- produced via electro-oxidation of COD and 4) CO_2 supplied as biogas for upgrading. The third pathway although results in COD consumption for methane production, cannot be accounted for heterotrophic methane production pathway. The COD degradation in this case is as a result of electrochemical activity and thus contributes to electrochemical methane production pathway. This residual COD degradation at anode would also account for proton source required for electrochemical activity. Thus, the process avoids splitting of water that produces oxygen along with protons which would hinder methanogenic activity.

4 Conclusion

The article studies the impact of hydraulic retention time (HRT) on MES operation as a post AD treatment integration with anaerobic digestion systems. It can be concluded that HRT can be used as a tool to affect the final outcome of an integrated AD-MES system. An HRT of 18-hr operation offers optimised methane production rates (12.2±0.1, 7.4±0.1 mmol/$L_{(feed)}$-d) and COD reductions (40.6 %, 23.4 %) with both feed types that mimic reject water from food waste and wastewater treatments respectively. pH of the effluent was 8.63 and 7.64 for feed with and without acetic acid, implying low reductions in alkalinity, which in turn could be due to conversion of autotrophic CO2 to bicarbonate. HRTs lower than 6 hours decrease in both COD removal and methane production efficiencies. The MES is able to degrade an additional 20-25% of COD when there is no freely available acetic acid in the feed at HRTs maintained above 3-hrs. It was identified that the additional COD degradation was possible via direct electro-oxidation of organics at anode and contributed indirectly to electrochemical methane production. It is also to be noted that placement of cathode with respect to the inlet feed flow will influence methane/biogas generation. This is due to difference in electron transfer via diffusion with change in flow profile across cathode. Although, conclusive evidence could not be drawn in these set of experiments; still, future experimental studies can also focus on this aspect of reactor configuration and electrode design.

Conflict of Interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Author Contributions

Conceptualization: AN and CD; Methodology: AN and CD; Validation: AN and CD; Formal analysis: AN, MK and NC; Investigation: AN, MK and NC; Resources: AN and CD; Data curation: MK and NC; Writing—original draft preparation: AN.; Writing—review and editing, AN and CD; Visualization: AN; Supervision: CD; Project administration: CD; Funding acquisition: CD.

Funding

The research carried out in this article was funded by Norwegian Ministry of Education and Research through the University of South-Eastern Norway Ph.D. Programme.

Acknowledgments

The acknowledge the Norwegian Ministry of Education and Research for funding the Ph.D. program in Process, Energy and Automation Engineering at University of South-Eastern Norway.

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Table 1: Characteristics of the feed for the reactors R1 and R2

Reactor	Initial COD (mg/L)	Initial Alkalinity (mg/L)	Initial pH
R1	2500-2800*	5000-6000	7.0
R2	1600-1800	4500-5500	7.0

*1000 mg/L equivalent COD (36-40%) is supplemented as acetic acid

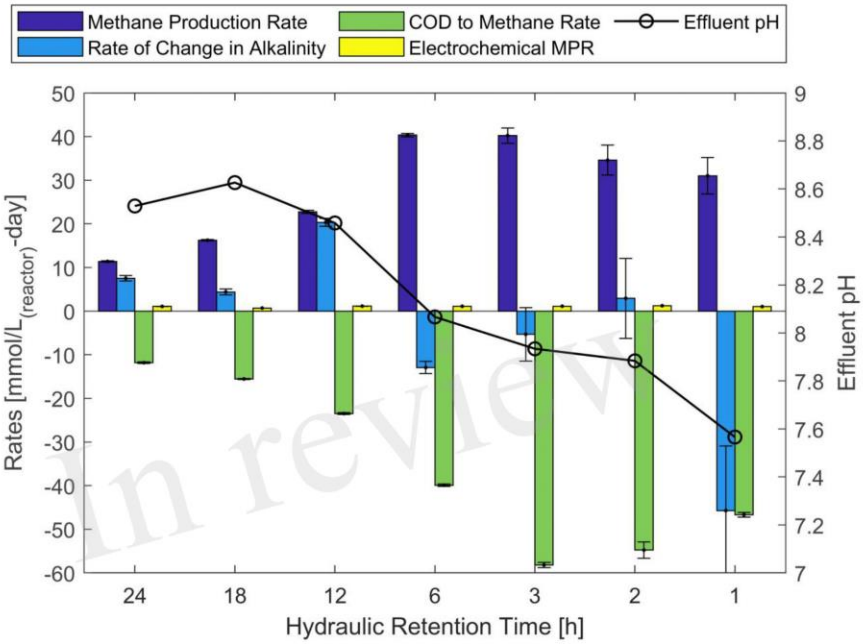
Figure 1: HRT experiments conducted with feed containing supplemented acetic acid (a) Overall and electrochemical methane production rates, methane percentage in the biogas and current measured. (b) Average overall and electrochemical methane production rates, rates of changes in COD and alkalinity. (c) Amount COD consumed and the heterotrophic efficiency to produce methane.

Figure 2: HRT experiments conducted with feed containing no acetic acid (a) Overall and electrochemical methane production rates, methane percentage in the biogas and current measured.

Effect of HRT of Bioelectrochemical Methane Production

(b) Average overall and electrochemical methane production rates, rates of changes in COD and alkalinity. (c) Amount COD consumed and the heterotrophic efficiency to produce methane.

236 Figure 1A



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Effect of HRT of Bioelectrochemical Methane Production

Figure 1B

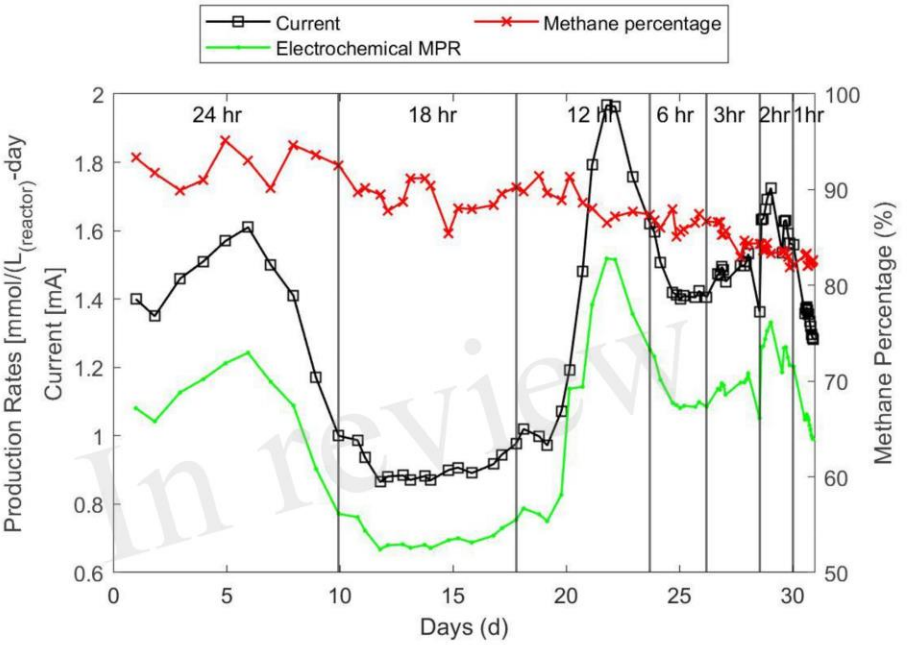
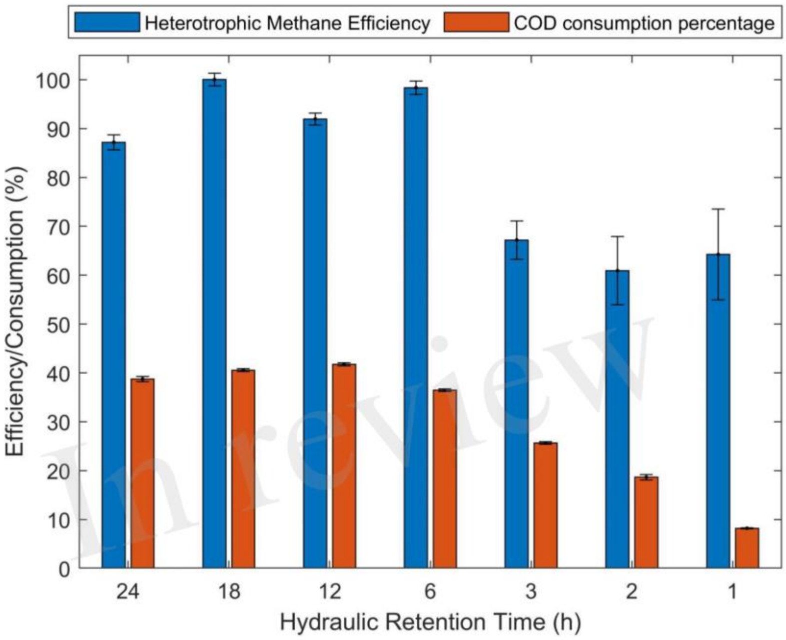
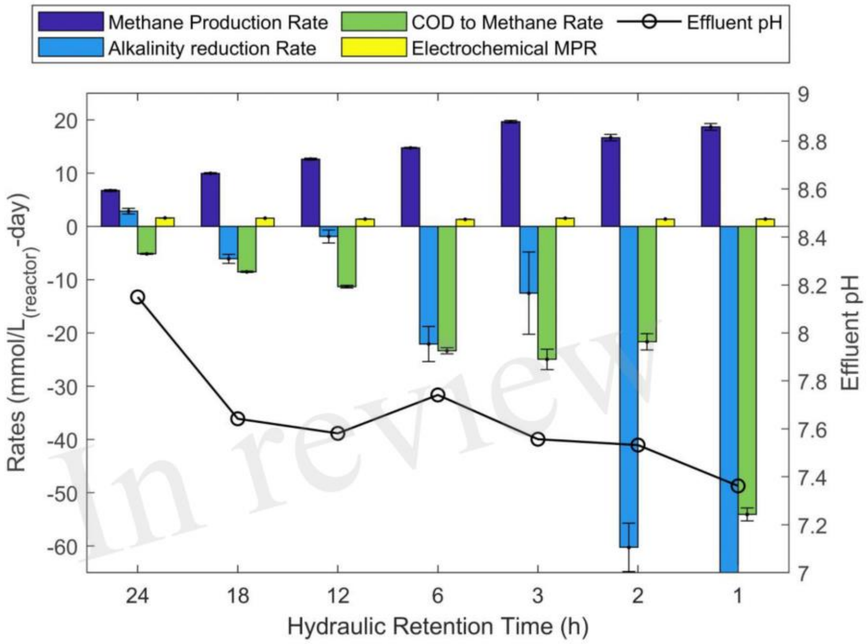


Figure 1C

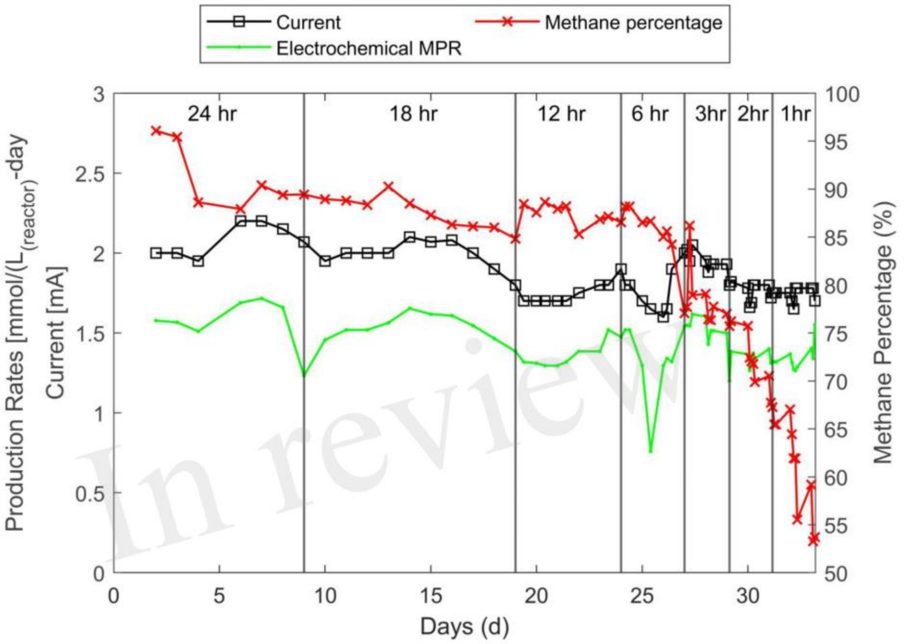

Heterotrophic Methane Efficiency
COD consumption percentage
Efficiency/Consumption (%)
100
90
80
70
60
50
40
30
20
10
0
24
18
12
6
3
2
1
Hydraulic Retention Time (h)

Effect of HRT of Bioelectrochemical Methane Production

Figure 2A



248 Figure 2B



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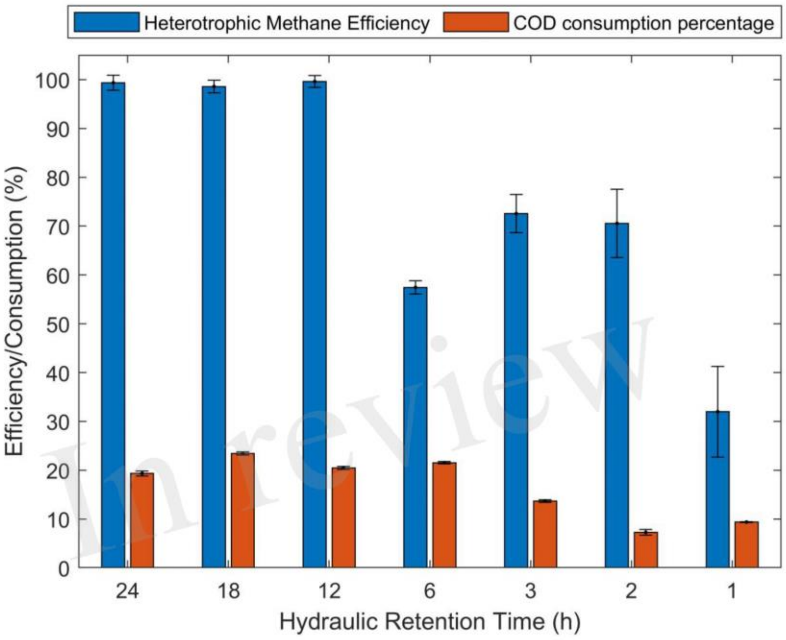
Effect of HRT of Bioelectrochemical Methane Production

Figure 2C



Additional Article

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In Conference Proceedings of 10th Trondheim Conference on CO_2 Capture and Storage

TCCS-10 2019
Trondheim, Norway

10th Trondheim Conference on CO2 Capture, Transport and Storage
June 18-19. 2019

MODELLING BIO-ELECTROCHEMICAL CO_2 REDUCTION TO METHANE

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Abstract

The most common platform for biogas process modelling, ADM-1, was extended adding the bio-electrochemical active CO_2 reduction to CH_4 reaction. The Nernst expression was incorporated as Monod-type kinetic expression to formulate the reaction rate, which is controlled by the electrical potential. The proposed model is applied to a complete mixed separate cathode compartment running in a continuous flow mode of operation. The model modification is relatively simple, mainly as a learning tool focused on the differences between an AD process with and without a Bio electrochemical system (BES). The simulation demonstrates the basic concepts of BES for biogas upgrade and its limitations. The simulation shows that biogas methane content can be increased up to ca. 85 % under the reactor settings selected for the simulation. The rate of the reduction reaction can be constrained by the local potential of the cathode and the substrate concertation. The necessity of maintaining some buffering from CO_2 partial pressure to prevent the inhibition due to rise in pH is also pointed out. The simulations suggest that simultaneous bio methanation of CO_2 from endogenous and external sources can be achieved using an AD with BES.

Keywords: *CO_2 negative solutions, CCUS, CO_2 utilisation, BES, bio-methane*

1. Introduction

Anaerobic digestion (AD) process is a highly economical and efficient method to produce methane (CH_4). It consists of series of biochemical conversions that uses a variety of organic wastes in a controlled environment. AD produces biogas containing 50 -70 % CH_4 and 50-30 % CO_2, meaning that the typical biogas has low calorific value, which limits its use [1]. Therefore, the biogas is upgraded by removing CO_2 before selling as transport fuel. Water scrubbing, physical absorption using organic solvents, chemical absorption using amines solutions are the some of the technique commonly used for CO_2 separation from biogas. This study is focused on the alternative to convert CO_2 to CH_4. The conversion can be done with anaerobic digestion integrated with bio-electrochemical systems (BES) and can be extended to also utilise CO_2 captured from other sources [2].

The bio-electrochemical system (BES) refers to processes that involve electrode reactions catalysed by microorganisms. CO_2 reduction to CH_4 (reaction 1) directly at the cathode using electricity as energy source and microorganisms as the catalyst has been demonstrated [3]. Electricity for BES should be from renewable source, as a way of storing renewable surplus electricity as methane [4].

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \qquad (1)$$

Conversion of CO_2 to CH_4 with intermediate production of hydrogen (H_2) is also possible. It follows two steps. First step is protons reduction to H_2 (reaction 2) and then the produced H_2 react with CO_2 (reaction 3). The later step is completely biological conversion.

$$8H^+ + 8e^- \rightarrow 4H_2 \qquad (2)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad (3)$$

The protons (H^+) and electrons (e) needed for the reduction reaction at the cathode are produced by oxidizing water or acetate (or easily degradable organics) at the anode. However, oxidation of acetate (or easily degradable organics) results produces CO_2.

Thermodynamic potential of CO_2 reduction to CH_4 and potential of water oxidation are reported to be -0.24 V vs NHE (Normal hydrogen electrode) [5] and 0.81 V vs NHE [6] respectively. All reported potentials are standard potentials under biological relevant conditions at pH 7 and 25 ^{0}C. Additional cathode potential over the theoretical thermodynamic potential should be always applied, to drive the reaction interested (activation losses), and to overcome other potential losses (e.g. ohmic losses as a result of resistance to the flow of charges, the concentration losses as a result of mass transfer limitation, bacterial metabolic losses[7]).

Electrode "respiring" bacterium involve this bio electroactive process via extra-cellular electron transfer (EET), the process by which microorganisms can transport electrons into and out of the cell from or towards an insoluble electron donor or acceptor (in this case, solid cathode). The current understanding on interactions of the microorganism with solid electron donors and their importance in nature and for bio-sustainable technologies has been explored by Tremblay et al. [8]. Conductive based and diffusion based are the main two routes that the electrons are transferred. The conduction-based EET relies on the transmission of electrons through a conductive biofilm matrix composed of extracellular polymeric substances, acquiring electrons directly from a solid donor at a given redox potential (In the biofilm matrix, the microorganisms are known to produce conductive pili to electronically connect the solid electrode.). The diffusion-based EET relies on the migration, diffusion, and/or advection of soluble electrochemically active molecules (mediators) to carry electrons from cells to the electron-accepting surface [8].

Although several studies have verified the applicability of this technology in lab scale, many limitations still need to be addressed to optimize the technology and make it economically feasible. Constraints regarding side reactions, mass transfer, inoculum type, electrode material, anode-cathode separation, operation parameters, system design or scaling-up are some of the bottlenecks [2]. In this scenario, process modelling is instrumental to understand the extensive experimental work to eventually commercialize the technology.

Recio-Garrido et al. [9] have reviewed several BES modelling approaches. The models reviewed were classified based on their complexity of the mass balances, transport phenomena and microbial populations. However, the complexity or the level of details of a model depends on the specified modelling objectives. Simple models are more accommodating to understand basics in this process which is demanding multidisciplinary knowledge (from microbiology, electrochemistry, material science, electrical engineering, etc.).

In this work, the generally accepted anaerobic digestion model no.1 (ADM1) [10] as a common platform was modified by taking into account the bio-electrochemical reaction (1): This integration of BES-AD to study CO_2 capture and utilization as methane is a first-of-kind (to the best of our knowledge) and the main objective is "model for learning". The level of the details of the model can be expanded later, based on the initial model simulations and as more experimental results are generated. The simulations will also give essential directions in planning experiments.

The extended model was used to evaluate the change in the biogas composition and other operation parameters when the electrochemical reaction was employed and controlled by electrical potential, and to identify the process limitations. The focus was given to observe the differences between AD process with and without BES. The possibility of using externally-produced CO_2 to produce methane biologically (biomethanation) was also used as a simulation case.

2. Method of model development approach

The ADM-1 was extended adding an electrochemical active biological reaction (1) controlled by the electrical potential. The ADM-1 model is the common platform of modelling and simulations AD process developed by IWA (International Water Association, 2002). The model was implemented in the simulation tool AQUASIM 2.1.

The following assumption were made:

1. Hydrogenotrophic methanogens catalyse methane production from CO_2 in BES via direct extracellular electron transfer (i.e. this microbial group can acquire electrons directly from the solid cathode).
2. Only hydrogenotrophic methanogens active on the cathode surface (any other parallel biochemical and bio-electrochemical reactions on the cathode surface are neglected.)
3. The model scenario is a complete mixed separate cathode compartment. The transport of the CO_2 and the electroactive microorganism to the solid cathode is so fast compared to the biochemical reduction reaction.
4. Non - limiting flow of proton, and electron current are supplied with separate anode compartment.

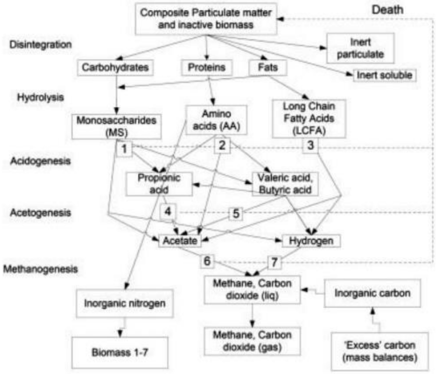


Figure 1: The reaction paths described in ADM-1 [10], with the following microbial groups: (1) sugar degraders, (2) amino acid degraders, (3) LCFA degraders, (4) propionic acid degraders, (5) butyric and valeric acid (VFA) degraders, (6) acetoclastic methanogens, and (7) hydrogenotrophic methanogens, taken from [11].

2.1 ADM-1 model

The ADM-1 is structured on anaerobic biochemical reactions catalysed by intra or extracellular enzymes and act on the pool of biologically available organic material (Figure 1). The complex organic materials are decomposed to the final product biogas (mainly CH_4 and CO_2) through a number of decomposition steps. The first step is the disintegration complex organic material (sludge or organic waste) into particulate constituents (carbohydrates, proteins, and lipids). The next step is hydrolysis of those constituents into sugars, amino acids and long-chain fatty acids (LCFAs). The hydrolysis products are then fermented into volatile fatty acids (Acedogenesis). These acids are broken down to acetate and hydrogen (Acetogenesis). The final step is the Acetoclastic methanogenesis, which converts acetate to methane, and hydrogenotrophic methanogenesis to convert carbon dioxide and hydrogen to methane.

The biological rate expressions and coefficients are given in a Peterson matrix [12] which incorporates the biological processes as rate equations, components and stoichiometric coefficients of relevant processes. the substrate uptake rates are described using Monod saturation type [13] kinetic equations. The stoichiometric coefficients for inorganic carbon and nitrogen are determined by balance equations. There are two types of physico-chemical reactions are also included: 1. Acid-base reactions implemented as equilibrium processes in an implicit algebraic equation set and 2. Liquid-gas transfer, implemented as non-equilibrium diffusive processes [10].

2.2. Kinetic equation for bio-electrochemical reaction

To account for the BES effect, the bio-electro active reactions associated with extracellular electron transfer (EET) are incorporated into ADM-1. Hydrogenotrophic methane production may occur either directly (reaction 1) or indirectly via H_2 (reactions 2 and 3). H_2 gas produced at the cathode will be rapidly utilized by hydrogenotrophic methanogens. Therefore, to simplify the model, only the reaction 1 (the electrons are directly taken up from the electrode and used to reduce the CO_2 to methane) was considered.

The Monod equation is used to describe the microbial growth kinetic on all substrates in ADM-1. In this case, the specific bacterial group is hydrogenotrophic methanogens assumed to grow at the cathode surface. The bacteria receive electrons form the cathode and deliver them to CO_2 as the final acceptor and use CO_2 as the carbon source to produce biomass. Thus, the rate of the reaction can be restricted by the availability of both the electron donor and the electron acceptor. When both substrates (the donor and the acceptor) are soluble, the rate can be defined as rate equation (r1) [14]:

$$\rho \quad = k_{\mathrm{m}}^{0} X \frac{S_a}{K_a+S_a} \frac{S_d}{K_d+S_d} \qquad \text{(r1)}$$

Where: ρ- kinetic rate, k_m^0 - maximum uptake rate, X – microorganisms' concentration, S_a and S_d – two "limiting-substrate" concentrations, K_a and K_d – half-maximum rate concentrations for substrates S_a and S_d.

The acceptor part (S_a/ K_a+S_a) of the Monod expression account the CO_2 which is soluble. However, the donor part (S_d /K_d + S_d) has no concentration and is solid cathode which allows electrons to pass in response to the electrical-potential gradient. The soluble concertation of donor part (S_d) is instead related to the cathodic potential using the Nernst equation [15]. Based on this, overall rate equation can be defined as rate equation (r2):

$$\rho_{c1} = k_{\mathrm{m\_eet}}^{0} X_{eet} \left(\frac{S_{co2}}{K_{s\_co2}+S_{co2}}\right)\left(\frac{1}{1+exp\left[-\frac{F}{RT}\eta\right]}\right) \qquad \text{(r2)}$$

The last term in the parenthesis (r2) which is derived from Monod equation is referred as the Nernst-Monod term. The main assumption for its' use is that microbial kinetics control the electron consumption. The Nernst-Monod term shows that the rate of substrate uptake increases as the local potential increases until a plateau is reached (Figure 2). X_{eet} is concentration of electrically active microorganisms, R ideal gas constant, T: absolute temperature, F: Faraday constant. η: local potential in reference to E_{KA}. E_{KA} is the potential in which the substrate consumption rate will reach half of the maximum substrate consumption (analogous to K_d) and can be determined experimentally. η is defined as $\eta = E_{KA} - E_{\text{cathode}}$. Since, E_{KA} is used as reference potential ($E \equiv 0$), η becomes $- E_{\text{cathode}}$.

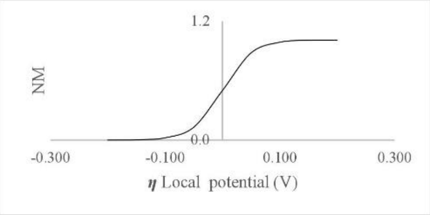


Figure 2: Plot of the Nernst-Monod (NM) term for $E_{KA} = 0$ V and T = 308 K and the local potential (η) from -0.2 to 0.2 V.

Further, two inhibitions effects are incorporated to the substrate utilization rate as given in the rate equation (r3); for describing microbial growth inhibition due to 1. Extreme pH conditions (I_{ph}) and 2. Limitation of soluble inorganic nitrogen (I_NH_limit).

$$\rho_{c1} = k_{\mathrm{m\_eet}}^{0} X_{eet} \left(\frac{S_{co2}}{K_{s\_co2}+S_{co2}}\right)\left(\frac{1}{1+exp\left[-\frac{F}{RT}\eta\right]}\right) I_{ph} I\_NH\_limit \qquad \text{(r3)}$$

2.2.1 Kinetic and stoichiometric parameters

The developed ADM-1 modification is relatively simple, and the main objective is to use it as learning tool and study the BES effects qualitatively. Therefore, attempts were not taken to precisely estimate the values for the kinetic and stoichiometric parameters. The values were either taken based on the parameter used in original ADM-1 or assumed roughly.

Table 1: Parameters used for the bio electrochemical process

Parameters	Description	Unit	value
$k_{\mathrm{m\_eet}}^{0}$	Maximum electrons uptake rate	Kmol-e.kg COD X.d^{-1}	4.5
X_eet	Con. Of electron up taking organism	kg COD.m^{-3}	
S_{co2}	Con. of CO_2 in bulk liquid	M	
Ks_co2	Half saturation constant for CO_2 reduction	M	0.06
F	Faraday's constant	C mol-e^{-1}	96485
R	Ideal gas constant	J mol^{-1} K^{-1}	8.3145
η	Local potential	V	
T	Temperature	K	308
I_{ph}	Microbial growth inhibition due to pH	-	
I_NH_limit	Microbial growth inhibition due to limitation of soluble inorganic nitrogen	-	
Y_eet	Yield of bio-electro active biomass uptake of electron	kg COD-X/ kmol -e	0.48

2.3 Simulation outline

Below is outlined how the simulation process was carried out to study BES effects on AD, and AD-BES for using CO_2 (Externally-produced) for biomethanation.

1. First, simulation was run for a conventional AD reactor for baseline data (The reactor settings were those used for ADM -1[10].). A reactor of V = 28 m^3, continuous flow and completely mixed (CSTR) is fed sludge from a wastewater treatment plant for 50 days (Figure 3). The feed step increases at day 16 and 37 [16] and the composition of the feed is given in Table 2. AD reactors are in general started with low organic loading and then gradually increased so that stable reactor operation is achieved.
2. The bio-electrochemical process was activated at day 50 (end of published experiment [10]), while maintaining a constant feed rate (5.31 m^3/d). The local cathode potential (η) was increased from -0.200 to +0.200 V stepwise every 50 days, to evaluate how the rate of the bio-electrochemical reaction varied and to identify its constrains.
3. The soluble CO_2 in the reactor compartment as an input from an "external CO_2 source" was altered to find out the possibility of using additional CO_2 for bio methanation. The total volumetric biogas production rate is always limited to the rate in which organic matter is converted to biogas. The volume of CO_2 produced that can be converted to methane by BES thus constrained by the applied carbon source (organic load) and rate of its conversion to biogas. It could be hypnotized that the overall methane production capacity might be increased by increasing the input of gaseous carbon from external sources. There by, a source of soluble CO_2 was added to the digester with BES activated when run at the highest local potential simulated (η = 0.200 V). The CO_2 loading rate simulated were 0.01, 0.015 and 0.02 M d^{-1}. However, the gas-liquid mass transfer (which was not accounted in detail in this simulation) may limit CO_2 gas solubility in the liquid phase.

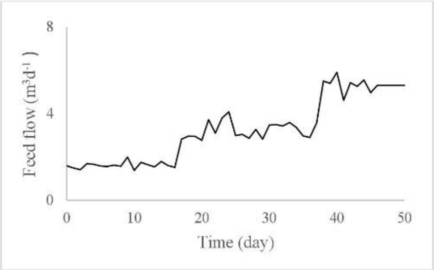


Figure 3: The sludge feed flow to the AD reactor [16].

Table 2: Input feed composition to the reactor.

Components in the reactor feed	Concentrations kg COD/m^3
Amino acids	4.2
Fatty acids	6.3
Monosaccharides	2.8
Complex particulates	10.0
Total	23.3

3. Simulation results and discussion

Figure 4 shows the biogas production rate and the composition of the biogas from the reactor (which is chosen for this study) running under conventional condition. As the feed rate is increased, biogas production rate increases. The reactor produces biogas with around 65 % methane (CH_4) content.

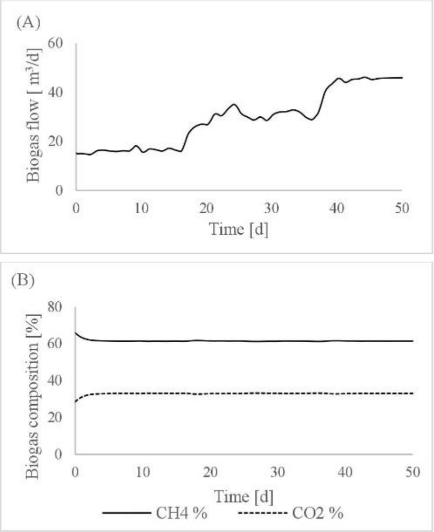


Figure 4: Biogas production rate (A) and the composition of the biogas (B) for the conventional biogas reactor (selected to simulate for baseline data). The feed rate changes at day 16 and 37.

The bio-electrochemical process was activated at day 50 and the local potential (η) was increased from -0.2 to + 0.2 V (with the step size = 0.05 V). The simulation was run for 50 days for each step.

As the local potential increases, the methane content of the biogas increases up to 85% as show in Figure 5. Increasing η further does not rise the biogas methane content further. The simulation demonstrates that around 30 % methane increase could be expected by employing BES in this reactor settings chosen for the study.

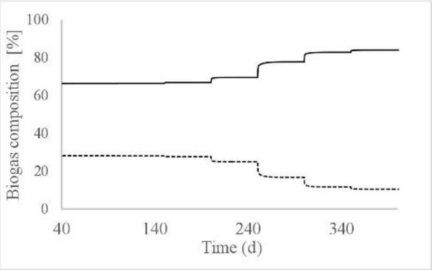


Figure 5: Response of biogas composition (— CH_4%, ··· CO_2%) to step increases of the local potential (η) from -0.2 to 0.2 V (step size =0,05). The bio-electrochemical process is activated at day 50.

When the local potential is sufficiently high, the cathodic donor saturates, and acceptor, in this case available dissolved CO_2 limits the rate. Figure 6 shows how the value of acceptor part which accounts for the rate expression decreases as the local potential increases. However, it should be noted that the effect shown here are qualitative and the exact values depends on the value assumed for the constant parameters (e.g. Ks_co2). Since the concentration of CO_2 decreases, the overall reaction rate decreases, thus it could result the reaction (1) to cease completely. Applying this finding to a practical setting; the cathodic compartment would be biofilm (not a completely mixed reactor as assumed here), thus the mass transfer in the biofilm can limit the reaction rate.

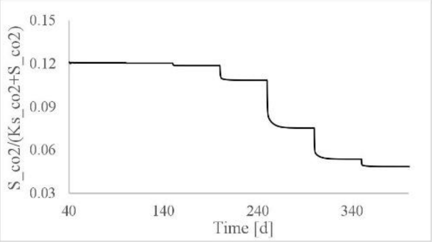


Figure 6: The Monod-type kinetic expressions (r3) due to available electron acceptor (soluble substrate, CO_2) after the bioelectrochemical process is activated at day 50, and the local potential (η) from -0.2 to 0.2 is increased stepwise (step size =0.05).

pH is one of the main parameters that can affect the performance of AD. Figure 7 shows the variation of pH in the digestor as local potential increases. The conventional AD has pH at 7.2. As local potential increases, pH increases. pH of the digester rises because of a fall in the bicarbonate strength due to depletion of headspace CO_2 as it being converted to methane. A large pH inhibits AD. The elevated pH can lead to deprotonation of ammonium ion, releasing free ammonia. Free ammonia is strictly inhibition for acetoclastic methanogens, the bacterial group which is responsible for decomposition of acetate into methane (Figure 1). In the conventional AD, a major portion of the methane is produced via this acetate path way. The simulation result showed an increased acetate concentration and slight reduction in total biogas production (The results are not presented here). Here, the pH reduction is not so significant to inhibit the process. The upper limit of pH at which anaerobic digestion is not inhibited is reported to be around pH 8.5[17].

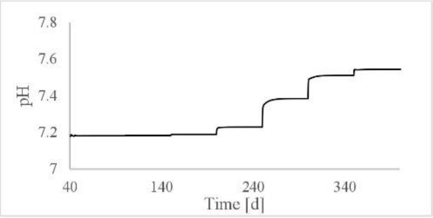
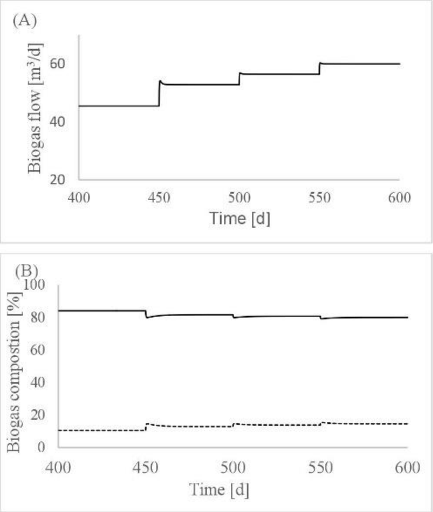


Figure 7: Response of pH in the digester to stepwise increases of the local potential (η) from -0.2 to 0.2 (step size =0.05). The bio-electrochemical process is activated at day 50.

This finding suggests that importance of controlling pH increase, when employing BES in AD.

3.1 Biomethanation of CO_2 from external source

The simulation result shows that CO_2 addition from external sources increase the overall biogas production (Figure 8, A). However, it reduces the biogas methane content, compared to the methane production without external CO_2 (Figure 8, B). Yet, the methane content is higher than that from the conventional AD (i.e. without BES). Therefore, the methane yield (m^3 CH_4/ kg COD organic loading to the digester) also increase (Figure 8, C). For a proper convention (i.e. keeping biogas methane content remained stable ca. 85%), the rate of CO_2 input to the digester, should be controlled according to the rate of the reduction reaction (3). However, the Carbon element balance showed that around 80 % of CO_2 moles added from the external source have been converted to CH_4, in the all three cases.



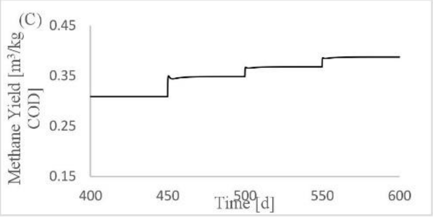


Figure 8: Biogas production rate (A), biogas composition (B) — CH_4 %, ··· CO_2 %, methane yield (C); after CO_2 addition form external source to the digester (AD with BES) at day 450. (η=0.200 V). The CO_2 loading rate simulated were 0.01, 0.015; and 0.02 M d^{-1}.

It can be anticipated that the reduction of CO_2 from external source could be possible because the AD with BES was adapted gradually, by increasing EET hydrogenotrophic methanogens population by increasing local potential (η), before the CO_2 addition. In general, every AD has a maximum level of handling organic loading beyond which complete reactor failure may occur. Simultaneous biomethanation from reduction of CO_2 from both endogenous and external sources demonstrate the biogas production can be increased beyond the organic loading limitation and it does not interfere with substrate degradation.

Further, pH inhibition effect can be avoided when CO_2 is added from external sources to AD with BES Figure 9. With increased CO_2 concentration in the liquid phase the substrate limitation, which affects the kinetics of the bio electrochemical reaction (r3), is overcome.

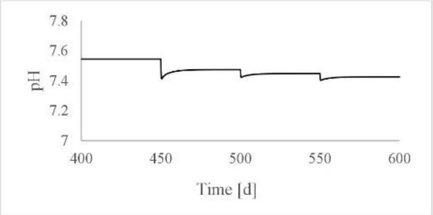


Figure 9: pH variation in the digester (AD with BES) after CO_2 addition form external source to the digester at day 450. (η=0.200 V). The CO_2 loading rate simulated were 0.01, 0.015, and 0.02 M·d^{-1}.

3. Conclusion

- The proposed model shows the basic concept of BES integrated with AD for biogas upgrade by converting CO_2 to CH_4 bio-electrochemically and limitations of such.
- The model shows that by employing BES in AD. the methane content in biogas can be increased (up to ca. 85 % under the reactor conditions simulated and further if substrate limitations are avoided).
- The rate of the reduction reaction can be constrained by the local potential of the cathode and the substrate concertation.
- The rise in pH (because of decreasing CO_2 that is being converted to CH_4) inhibits the digestion process. Therefore, it is essential to maintain some buffering from CO_2 partial pressure to prevent the inhibition.
- Simultaneous biomethanation of CO_2 from endogenous and external sources can be achieved.
- The study also shows the capacity of an AD with BES for CO_2 reduction to CH_4, beyond the constrains of the applied organic load.

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Errata

(Text)

Doctoral dissertation no. 62
2020

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Electrochemical Unit Integration with Biogas Production Processes

Dissertation for the degree of Ph.D

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Anirudh Bhanu Teja Nelabhotla

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ISBN: 978-82-7206-546-0 (print)
ISBN: 978-82-7206-547-7 (online)

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