Bioelectrochemical systems serve anaerobic digestion process for process monitoring and biogas upgrading

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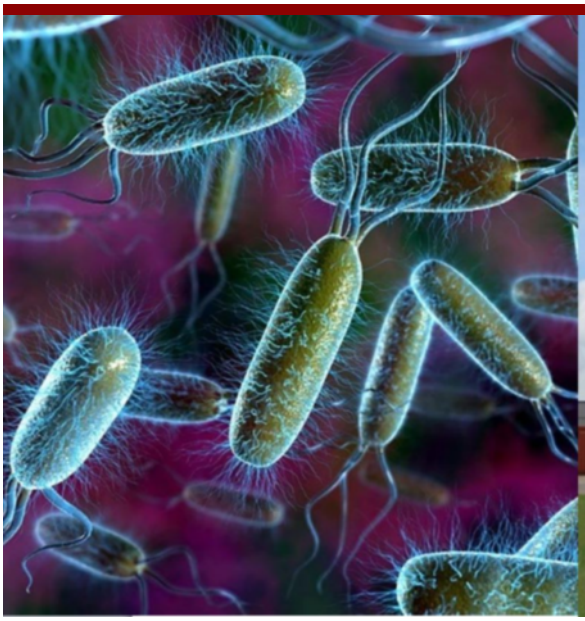

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PhD Thesis
October 2017

DTU Environment
Department of Environmental Engineering

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Preface

This PhD thesis, entitled "Bioelectrochemical systems serve anaerobic digestion process for process monitoring and biogas upgrading", comprises the research carried out at the Department of Environmental Engineering, Technical University of Denmark from October 13, 2014 to October 14, 2017. Professor Irini Angelidaki and Senior Researcher Yifeng Zhang were the supervisor and co-supervisor, respectively.

The thesis is organized in two parts: the first part puts into context the findings of the PhD project in an introductive review; the second part consists of the papers listed below. These will be referred to in the text by their paper number written with the Roman numerals **I- III**.

I Jin, X., Angelidaki, I., Zhang, Y. 2016. Microbial electrochemical monitoring of volatile fatty acids during anaerobic digestion. Environmental Science & Technology, 50(8), 4422-4429.

II Jin, X., Li, X., Zhao, N., Zhang, Y., Angelidaki, I. 2017. Bio-electrolytic sensor for rapid monitoring of volatile fatty acids in anaerobic digestion process. Water Research, 111, 74-80.

III Jin, X., Zhang, Y., Li, X., Zhao, N., Angelidaki, I. 2017. Microbial electrolytic capture, separation and regeneration of CO_2 for biogas upgrading. Environmental Science & Technology, 51(16), 9371-9378.

In addition, the following publications, not included in this thesis, were also concluded during this PhD study:

Li, X., Jin, X., Angelidaki, I., Zhang, Y. 2017. Efficient treatment of aniline containing wastewater in bipolar membrane microbial electrolysis cell-fenton system. Water Research, 119, 67-72.

Li, X., Jin, X., Zhao, N., Angelidaki, I., Zhang, Y. 2017. Novel bio-electro-Fenton technology for azo dye wastewater treatment using microbial reverse-electrodialysis electrolysis cell. Bioresource Technology, 228, 322-329.

In this online version of the thesis, paper **I-III** are not included but can be obtained from electronic article databases e.g. via www.orbit.dtu.dk or on request from DTU Environment, Technical University of Denmark, Miljoevej, Building 113, 2800 Kgs. Lyngby, Denmark, info@env.dtu.dk.

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Firstly, I would like to express my sincere appreciation and thanks to my supervisor Professor Irini Angelidaki and my co-supervisor Dr. Yifeng Zhang. I would like to thank my supervisor for her continuous support of my PhD study and related research and she is a tremendous mentor for me. The advice she gave me on both research as well as on other aspects have been valuable. I wish to thank Yifeng for his patience, motivation and immense knowledge. He gave me a lot of guidance in all the time of my research, paper writing as well as this thesis writing.

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I thank my fellow labmates who were working in the same lab. Those are Xinyu Zhu, Hailin Tian, Ilaria Bassani, Panagiotis Tsapekos, Martina D'Este, Adam Kovalszki, Enrico Mancini, Basma Omar, Davide De Francisci, Panagiotis Kougias, Laura Treu, Ioannis Fotidis, Merlin Alvarado-Morales. I have to say I had a great time in the bioenergy group.

Besides, many thanks to our technicians: Hector Hernan Caro Garcia, Hector Osvaldo Ampuero Diaz, Satomi Matsuura and Sinh Hy Nguyen for their support in experiment facility service and analytical measurements.

Last but not the least, I would like to thank my family: my parents and my brother for supporting me spiritually throughout my PhD study. Special thanks go to Changle for his support, understanding and encouragement in my daily life.

This PhD thesis is dedicated to everyone who has helped, supported and loved me.

Summary

Bioelectrochemical systems (BES), which employ microbes as catalysts to convert chemical energy stored in organic matter into sustainable electricity and high-value chemicals, is an emerging and promising technology. BES have broad applications including wastewater treatment, chemical production, resource recovery and waste remediation. Recently, new concepts of integrating BES with anaerobic digestion (AD) for process optimization have been proposed. The purpose of this work was to optimize the AD process using BES in two aspects: developing a new volatile fatty acid (VFA) monitoring system which can be used as the AD process indicator, and for improving biogas quality by removing CO_2.

In this thesis, a microbial desalination cell (MDC) was developed for measuring VFAs concentrations. The MDC was composed of three chambers, namely an anode, a cathode and a middle chamber. The samples were measured in the middle chamber, which was separated from the anode by an anion exchange membrane (AEM). Driven by concentration gradient, VFAs in their ionized form contained in the sample, diffused through AEM to the anode where they were microbially oxidized and produced current signals. The effect of operating parameters such as ionic strength and external resistance on the performance of the MDC-typed biosensor were assessed. High ionic strength and small external resistance were advantageous for current signal amplification. Two linear relationships between current outputs and VFA concentrations were observed. The response time was approx. 5 h and the detection range was 1 to 200 mM. The selectivity of the biosensor was demonstrated since organic matter such as protein and lipids were retained by the AEM and their interference was eliminated. The reliability was proved by real AD effluents.

In order to reduce the construction cost and simplify the VFA biosensor, a new configuration was developed. The number of chambers was reduced from three to two. The new configuration was a microbial electrolysis cell (MEC). The anode and cathode chambers were separated by an AEM and a small additional voltage was supplied to the cell. The samples were measured in the cathode. The effect of different parameters such as external voltage, ionic strength and VFA composition ratio on the MEC-typed biosensor performance was evaluated. Higher current signals were observed under larger external voltage and higher ionic strengths. The current output was mainly contributed by acetate which was always dominant in AD reactors.

The current density increased linearly along with VFAs concentrations ranging from 5 to 100 mM. The response of the biosensor was now only 1 h due to the faster transfer of VFAs supported by the external voltage. The interference from other non-ionic organic matter (glucose, cellulose, lipids and protein) could be eliminated since they were retained by the membrane. During the process, hydrogen (H_2) was generated from water hydrolysis. The produced H_2 could potentially contribute to the energy needs for operating the biosensor and thereby to a self-sustaining system. Moreover, the biosensor was successfully validated both with synthetic and real AD effluents.

To improve biogas quality, a microbial electrolytic capture, separation and regeneration cell (MESC) was developed. The effects of external voltage and inlet gas flow rate were elucidated. The current output increased along with the gas flow rate, while cathodic pH and upgrading performance showed opposite trends. The current output, cathodic pH and upgrading performance increased with the increasing external voltage supply. In MESC, acid and alkaline generation, CO_2 capture, biogas upgrading and COD removal were simultaneously achieved. Under the optimum condition at 1.2 V external voltage and 19.6 mL/h gas flow rate, pH in the regeneration and cathode chambers could reach 1.34±0.04 and 9.19±0.11, respectively; the maximum methane content was up to 97.0±0.2% and COD removal efficiency reached 98.2±2.6%. The energy consumption for biogas upgrading was around 0.17 kWh/m^3 raw biogas. Moreover, the generated H_2 from water hydrolysis could potentially compensate for 23.4% of the energy consumption.

It has been proved that the development of efficient, cheap, fast and reliable VFA monitoring with a wide detection range can be realized in BES which is sustainable and environmental friendly. The development technology could easily be installed as online monitoring system for optimizing the AD process. Moreover, BES could be a sustainable economic technology to upgrade biogas to biomethane and thereby increase the value of biogas. The proof-of-concept study in lab-scale offers ideas for expanding BES application.

Dansk sammenfatning

Bioelektrokemiske systemer (BES) der benytter mikrober som katalysator for at konvertere kemisk energi, oplagret i organisk materiale, til bæredygtig elektricitet og værdifulde kemikalier, er en spirende og lovende teknologi. BES har brede anvendelsesmuligheder, herunder spildevandsrensning, kemisk produktion, resourcegenanvendelse og affaldsbehandling. Senest er nye koncepter, der integrerer BES med anaerob omsætning (AD) til procesoptimering blevet foreslået. Formålet med dette arbejde har været at optimere AD processen ved brug af BES på to områder: Udvikling af et nyt overvågningssystem til flygtige fedtholdige syrer (VFA) der kan bruges som AD procesindikator, og forbedring af biogaskvaliteten ved at fjerne CO_2.

I dette projektarbejde blev en mikrobiel afsaltningscelle (MDC) med tre kamre udviklet for at måle VFA koncentrationer. MDC'en bestod af tre kamre: et anodekammer, et katodekammer og et mellemkammer. Prøverne blev målt i det midterste kammer, som var separeret fra anoden med en anionisk udvekslingsmembran (AEM). Drevet af en koncentrationsgradient, diffunderede prøvens indhold af VFA'er i deres ioniserede form igennem AEM til anoden, hvor de blev mikrobielt oxideret, hvilket resulterede i strømsignaler. Effekten af operationsparametrene såsom ionisk styrke og ekstern modstand på ydeevnen af den MDC-baserede biosensor blev målt. Høj ionisk styrke og lille ekstern modstand var gunstig for forstærkning af strømsignalet. To lineære relationer mellem strømoutput og VFA koncentrationer blev observeret. Responstiden var cirka 5 timer, og detektionsområdet var 1 til 200 mM. Selektiviteten af biosensoren blev demonstreret ved at organisk materiale såsom protein og lipider blev tilbageholdt af AEM og deres forstyrrelse undgået. Pålideligheden blev påvist ved brug af rigtige AD effluenter.

For at reducere produktionsomkostningerne og simplificere VFA biosensoren, blev en ny konfiguration udviklet. Den nye konfiguration reducerede antallet af kamre fra tre til to. Den nye konfiguration var en mikrobiel elektrolysecelle (MEC). Anode- og katodekamrene blev separeret af en AEM og en lille ekstra spænding blev tilført til cellen. Prøverne blev målt i katodekammeret. Effekten af de forskellige parametre såsom ekstern spænding, ionisk styrke og VFA sammensætning på den MEC-baserede biosensors ydeevne blev evalueret.

Højere strømsignaler blev observeret under højere ekstern spænding og højere ionisk styrke. Strømoutput blev primært genereret af acetat, som altid var

dominerende VFA type i AD-reaktorerne. Strømsignal øgedes lineært med VFA koncentrationer i området 5 til 100 mM. Responstiden fra biosensoren var nu kun 1 time grundet den hurtigere overførsel af VFA'erne, båret af den eksterne spænding.

Interferensen fra andre ikke-ioniseret organisk materiale (glukose, lipider og proteiner) kunne elimineres da de blev tilbageholdt af membranen. Under processen blev hydrogen (H_2) genereret ved vandhydrolyse. Den producerede H_2 kunne potentielt bidrage til energibehovet ved at drive biosensoren, og dermed gøre den til et selvforsynende system. Herudover blev biosensoren valideret både med syntetisk og ægte AD effluenter med succes

For at øge kvaliteten afbiogas, blev en mikrobiel elektrolyse bindings-, separations- og regeneratorcelle (MESC) udviklet. Effekten af ekstern spænding og gastilstrømningsflow blev undersøgt. Strømoutput steg i takt med gasflow, mens katodisk pH og opgraderingseffektivitet udviste modsatte tendenser. Strømoutput, katodisk pH og opgraderingseffektivitet steg ved øgning af den eksterne spænding. I MESC, blev generering af syre og alkali, CO_2 binding, biogas opgradering og COD fjernelse alt sammen opnået samtidigt. Under de optimale forhold på 1.2 V ekstern spænding, og 19.6 mL/h tilstrømning af gas, kunne pH i regenerations- og katodekamrene nå henholdvis 1.34±0.04 og 9.19±0.11; det maksimale metan indhold var oppe på 97.0±0.2% og COD reduktionseffektiviteten nåede 98.2±2.6%. Energiforbruget for opgraderingen af biogas var omkring 0.17 kWh/m^3 rå biogas. Derudover kan H_2 fra vandhydrolysen potentielt kompensere for 23.4% af energiforbruget.

Det er blevet bevist at udviklingen af effektiv, billig, hurtig og pålidelig VFA overvågning med et bredt detektionsinterval kan realiseres i BES, som er bæredygtigt og miljøvenligt. Den udviklede teknologi kunne let installeres som et online overvågningssystem for at optimere AD processen. Herudover kunne BES blive en bæredygtig økonomisk teknologi til opgradering af biogas til biometan, og ville derved kunne øge værdien af biogas. Resultaterne af projektet i laboratorieskala giver ideer til udvidelse af brugen af BES.

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Abbreviations

AD	Anaerobic digestion
AEM	Anion exchange membrane
AOC	Assimilable organic carbon
ARB	Anode respiring bacteria
ATP	Adenosine-triphosphate
BES	Bioelectrochemical systems
BOD	Biochemical oxygen demand
BPM	Bipolar membrane
CE	Coulombic efficiency
CEM	Cation exchange membrane
COD	Chemical oxygen demand
CSTR	Continuous flow stirred-tank reactor
CV	Cyclic voltammetry
DO	Dissolved oxygen
GC	Gas chromatographic
GTO	Glyceryle trioleate
MDC	Microbial desalination cell
MEC	Microbial electrolysis cell
MES	Microbial electrosynthesis
MFC	Microbial fuel cell
SDS	Sodium dodecyl sulphate
SHE	Standard hydrogen electrode
tVFA	Total volatile fatty acids
VFAs	Volatile fatty acids

1 Introduction

1.1 Background

The rapid growths in population and industrialization have increased consumption of fossil fuels and generation of municipal/industrial waste. Increasing pressure on world fossil fuel reserves, and the need to reduce greenhouse gas emissions by burning these fuels, has increased the demand for seeking renewable energy sources to decrease the reliance on fossil fuels. In the last decade, ambitious energy policies have been published constantly by countries. For instance, the EU has set a target of a 20% share of renewable energies in overall EU energy consumption by 2020 (Böhringer et al., 2009). They also set a long-term goal of reducing greenhouse gas emissions by 80-95% compared to levels in 1990 by 2050. Denmark's long-term energy goal is to become completely independent of fossil fuels use by 2050 (Sovacool, 2013).

Anaerobic digestion (AD), which can convert diverse waste to biogas, has been widely applied in many European countries and is receiving increased attention. AD can bring many benefits such as management and disposal municipal/industrial waste, generation of renewable energy, and recovery of nutrients. The biogas production is carbon-neutral and there is no contribution to greenhouse gas emissions (Bohutskyi et al., 2016). Government policies have provided incentives to use biomass and biogas via AD process which has promoted its use and driven its facilities significantly. At the end of 2013 in Denmark, the total number of biogas plants is 174 (Edwards et al., 2015) and the building of 40-50 new large-scale biogas plants is required along with the increasing of biogas production potential since 50% of the animal manure will be supplied to biogas plants by 2020 (Thygesen et al., 2014). However, there are still problems which impede the efficiency and there is still room for improvement. For instance, process instability triggered by ammonia inhibition, organic overload, clogging and foaming may cause a failure and serious economic losses. Only when it is properly monitored, will an anaerobic digester function effectively. What's more, produced raw biogas with approximately 30-40% v/v CO_2 and other impurities presence exhibits a significantly low heating value which can adversely affect the engine performance (Sun et al., 2015b). It is essential to upgrade biogas to the natural gas quality for various biogas utilization pathways.

Therefore, it is necessary to develop technologies capable of solving the aforementioned problems. To ensure a stable biogas production and to upgrade the raw biogas, a monitoring system and an upgrading system are needed to be established.

1.2 Anaerobic digestion process

AD is a complex biological process in which several groups of bacteria convert organic material (polymers such as carbohydrates, protein and lipids) to methane and carbon dioxide with small amount of water, hydrogen, hydrogen sulphide, and ammonia (Weiland, 2010) under anaerobic conditions. Functioned by several groups of bacteria, AD can be divided into four steps which are hydrolysis, acidogenesis, acetogenesis and methanogenesis (Angelidaki et al., 2011).

In AD, hydrolysis is the first step by which polymeric compounds are hydrolysed into smaller units such as glucose, xylose, amino acids and long-chain fatty acids facilitated by various enzymes produced from fermentative bacteria (Xue et al., 2015). The products in hydrolysis are the substrates for the following steps. However, the presence of lignin or lignocellulose waste such as grass, wood and pulping waste can be a problem since they are practically undegradable under anaerobic conditions. Hydrolysis will be the rate-limiting step if cellulose is the main substrate and some physicochemical pretreatments may be needed. If the substrate is mainly composed of easily degradable material, the decomposition of acetate to methane will be the rate-limiting step.

In the second stage, hydrolysis products are further transformed to smaller compounds by the fermentative bacteria (Karthikeyan et al., 2016). The main part of the organic matter is converted to hydrogen, carbon dioxide and acetate. And approximately 30% is converted to other short-chain fatty acids and alcohols. If the process is out of balance, more volatile fatty acids (VFAs) will be produced and accumulate. Especially, when the generated hydrogen is not consumed fast enough and the increasing hydrogen partial pressure can inhibit the hydrogen production process. As a result, the microorganisms change their metabolism pathway to produce more VFAs like propionate and butyrate.

During acetogenesis, acetate is transformed from other VFAs and alcohols by different microbial members (Seitz et al., 2016). Hydrogen plays a vital intermediary role in this process, for instance, the conversion of propionate to acetate (Equation 1) is only achievable at low hydrogen partial pressure. To keep the hydrogen concentration within a certain limit, flocks and microbial consorts form so that a direct hydrogen transfer happens from the hydrogen producing bacteria to the hydrogen consuming bacteria.

$$CH_3CH_2COO^- + 3HO_2 \leftrightarrow CH_3COO^- + H^+ + HCO_3^- + 4H_2 \quad (1)$$

Methanogenesis is the final stage of AD in which biogas is produced. Biogas is mainly composed of methane and non-combustible carbon dioxide (Demirel and Scherer, 2008). About 70% of methane comes from acetate degradation by aceti-

clastic methanogens (Equation 2) while the remaining 30% is converted from H_2/CO_2 or formate executed by hydrogenotrophic methanogens (Equation 3 and 4).

$$CH_3COO^- + H^+ \rightarrow CH_4 + CO_2 \qquad \Delta G^{0'} = -32.5KJ/molCH_4 \qquad (2)$$

$$4H_2 + CO_2 \rightarrow CH_4 + 2HO_2 \qquad \Delta G^{0'} = -130.4KJ/molCH_4 \qquad (3)$$

$$4HCOO^- + 2HO_2 \rightarrow CH_4 + 3CO_2 + 2HO_2 \qquad \Delta G^{0'} = -119.5KJ/molCH_4 \qquad (4)$$

Methanogens which are responsible for this process are strict anaerobes and commonly considered to be the most sensitive to interruptions and toxicity in the AD process.

1.3 Challenges in the AD process and conventional solutions

1.3.1 Challenges in the AD process

The AD process is a complex biologically mediated process. After numerous academic and industrial studies, only a few principles of the process are known. The AD process can be divided by four steps: hydrolysis, acidogenesis, acetogenesis and methanogenesis (Madsen et al., 2011). There are many interesting reactions and phenomena during the AD process. Some of the former reactions proceed from hours to days, while some of the latter reactions proceed in seconds to minutes. Hence, a well-balance between products from the previous process and substrates for the next process is the prerequisite for a healthy AD process. However, most of the microbial consortium involved in the process is unknown and the complex interaction among them is not fully understood either (Falk et al., 2015). Therefore, to maintain a stable process is a challenge for every biogas plant operator.

On the other hand, although a stable process and consistent biogas production is obtained, upgrading biogas quality to nature gas can be another challenge. Raw biogas mainly contains methane and carbon dioxide, with small amount of hydrogen sulphide, ammonia, hydrogen, nitrogen, oxygen and carbon monoxide (Andriani et al., 2014). Apart from methane, the other impurities have significant negative impacts on the utilization system (Sun et al., 2015). The large share of carbon dioxide and small amounts of other noninflammable components in biogas lower its calorific value and can be corrosive to engines. Besides, the transportation of raw biogas is much costly than the transportation of upgraded biomethane over long distance (Budzianowski et al., 2016). Therefore, it is important to remove the unwanted components and upgrade biogas to a higher fuel quality.

1.3.2 Conventional VFAs monitoring technologies

To avoid complete failures, effective monitoring of the AD process is necessary. Many researchers have favoured VFAs as indicators since these short-chain acids are the headmost parameters to reflect the metabolic imbalance of the biochemical process. Currently, many analytical methods, such as titration, chromatographic, and spectroscopy have been established for a measure of their concentrations.

Titration can be an alternative for quantification of VFAs if merely a measure of total acidity is pursued with respect to the low cost and simplicity. Molina el al. (2009) presented a validation procedure to determine VFA and alkalinity via an on-line titrimetric system which was the AnaSense analyser. A pilot upflow sludge bed filter was monitored using the sensor based on two-point titrimetric methods. Results exhibited good performances with high accuracy for VFA and bicarbonate determination with the range of 13-1900 mg/L and 2.5-49.5 mEq/L, respectively. Purser el al. (2014) tested 154 samples from energy crop, slurry and food waste digestates for VFA quantification using two auto-titrators based on commonly utilized two-end-point titration methods. Compared with the results from HPLC and modified by statistical analysis software SigmaPlot 12, two empirical bivariate linear regression equations were derived. The improved titration model was applied to a food waste dataset and it cut the absolute tVFA mean errors by a factor of 10 from ±3828 to ±576 $mg \cdot kg^{-1}$tVFA. The model was more accurate for tVFA determination aiming to specific digestates.

To distinguish between the VFA acids and quantify their concentrations, chromatographic methods have been commonly used in research laboratories and industry. Boe et al. (2007) proposed an online VFAs monitoring system based on headspace gas chromatography. A lab-scale CSTR reactor treating manure was monitored and results exhibited good agreement with off-line analysis. The authors stated that the method is appropriate for full-scale reactors with short sensor response time (10 min) and a lack of filtration units. de Sá et al. (2011) described a method for the simultaneous determination of VFAs and carbohydrates (sucrose, glucose and fructose) by using high-performance liquid chromatography. It was argued that those compounds could be successfully quantified and the methodology could be applied for monitoring the anaerobic fermentation. Boe et al. (2012) developed a VFA sensor based on headspace chromatography. A pilot-scale manure digester was monitored by the on-line sensor and controlled using a programmable logic control system by adjusting the feed flow automatically while VFAs concentrations were used as the alarm threshold. The control system could successfully optimize the biogas production without organic overload during the process. However, the authors argued that routine maintenance of the mechanical parts is crucial to obtain the optimal performance.

Recently, spectroscopy has been proven to be an alternative for VFA measurement without problems such as sample preparation and biofouling. Falk et al. (2014) installed a spectrometer for VFAs monitoring on the basis of mid-infrared spectroscopy. Individual VFA concentration was evaluated and the partial least square models were developed according to a calibration. The accuracy was validated and the installed setup could automatically measure samples from the digester over 6 months without logging or biofouling problems. However, the authors stated that further investigation on the long term stability and installation on an industrial AD system would take into account.

1.3.3 Conventional biogas upgrading technologies

The number of biogas plants is increasing in Europe and around the globe, and so is the biogas production. The raw biogas is primarily composed of 60-70% v/v methane (CH_4) and 30-40% v/v carbon dioxide (CO_2), small amounts of hydrogen sulfide (H_2S) and ammonia (NH_3), trace amounts of hydrogen (H_2), nitrogen (N_2) and other gases. Since a large share of CO_2 present, the calorific value of the biogas decreases significantly which hinders its application. Therefore, the removal of CO_2 from biogas to reach a natural gas quality is essential and technologies that are performed commercially today are water scrubbing, organic solvent scrubbing, pressure swing adsorption, chemical adsorption, membrane separation, etc.

In water scrubbing, CO_2 is absorbed by the water at high pressure as the solubility of CO_2 in water is much higher than that of CH_4 (Nie et al., 2013). In a water scrubber, water is introduced at the top of the absorption column while the compressed biogas (under 5-10 bar) is injected from the bottom to produce countercurrent flow. The column is usually filled with random packing to maximum the gas-liquid contact area. In principle, H_2S is preseparated since dissolved H_2S can cause corrosion problems. The upgraded methane can reach a purity of 80-99% according to inseparable gases such as H_2 and N_2. The CH_4 loss is normal between 3% and 5% due to the dissolution in water. The method is cost effective and less complicated since water is used as solvent and fewer infrastructures are required (Budzianowski et al., 2016).

The principle of organic solvent scrubbing is the same as that of the water scrubbing (Rochelle, 2009). Organic solvents such as methanol, polyethylene glycol ethers and propylene carbonate can be used to absorb CO_2. Since the solubility of CO_2 in those organic solvents is much higher than that in water, the volume of the absorption column can be decreased significantly. However, heating of the organic solvent is needed for regeneration and cooling is operated before being injected to the column.

In pressure swing adsorption process, porous materials with large specific surface areas are used to absorb gases under higher pressure. CH_4 can be separated from the other noninflammable gases since the strength of the physical interaction between

gas molecules and adsorbents are different. H_2S is removed prior to the absorption process for it is considered toxic to adsorption materials. Typical adsorbents are activated carbons, silica gels, zeolite, alumina and carbon molecular sieves (Petersson and Wellinger, 2009). A shortcoming of this technology is that it has a low CH_4 recovery.

Chemical absorption is an efficient technology to remove CO_2 from gas mixture. Alkali liquor and amines are widely used as chemical solvents and high concentration of CH_4 can be obtained. Tippayawong and Thanompongchart (2010) reported a chemical absorption system designed for small-scale biogas plants. Sodium hydroxide, calcium hydroxide and mono-ethanolamine were employed and created CH_4 enrich fuel with concentrations between 95% and 98%. The non-regenerable nature of the solvents and requirement of large volume are the issues of the technology.

Membrane technology separates the gases at molecular size. The membranes retain CH_4 while CO_2 and H_2S permeate through the membranes under a pressure of 5-20 bars. Deng and Hägg (2010) tested a CO_2-selective polyvinylamine /polyvinylalcohol blend membrane with two-stage recycled processes. They found a CH_4 recovery of 99% with a purity of 98% at a low running cost. With the technology development, more advanced designs on membrane gas separation units have been accepted and offered by the manufacturers.

1.4 Objectives and thesis structure

This PhD project aims to integrate microbial electrochemical technologies with AD for process optimization. New concepts for VFAs concentrations online monitoring and biogas upgrading have been proposed and investigated by integrating innovative bioelectrochemical systems (BES) and AD. In this thesis, new solutions to the key problems existing in the AD process are offered which brings environmental and economic benefits to both Danish and international societies. Specific objectives and thesis structure are introduced below.

- Demonstrate the feasibility of a microbial desalination cell (MDC) as a simple, sensitive and reliable VFAs biosensor. (**Paper I**)
- Provide the relationship between current densities and VFAs concentrations under various conditions. (**Paper I**)
- Explore the robustness of the system to complex organic matter. (**Paper I**)
- Analyse the system applicability with real AD effluent. (**Paper I**)
- Modify the MDC-typed biosensor in architecture and construct a microbial electrolysis cell (MEC) for VFAs concentrations detection. (**Paper II**)

- Establish the correlation between biosensor's signal outputs and VFAs concentrations. (**Paper II**)
- Study the influencing parameters and verify the selectivity of the system. (**Paper II**)
- Demonstrate the feasibility of an innovative BES for biogas upgrading by varying the biogas flow rates as well as the external voltages. (**Paper III**)
- Evaluate the system performance in terms of the current output, chemical oxygen demand (COD) removal efficiency, quality of the outlet gas and energy input. (**Paper III**)
- Evaluate the systems on environmental and economic aspects. (**Paper I, II and III**)

In Chapter 2, a state-of-the art overview of the promising BES with two application aspects: using BES as biosensors and using BES to upgrade biogas quality has been displayed.

In chapter 3, an innovative biosensor based on the principle of MDC for VFAs concentrations monitoring are presented. The mechanism of the process and the outcome of the system are explained. Moreover, the effect of varied operational conditions on the performance of the sensor was investigated. The detailed approaches and results are reported in Paper I**.**

In chapter 4, according to the results reported in chapter 3, a more advanced system is exhibited for VFA quantification using a MEC. Moreover, the effect of various external voltage, VFA composition, and ionic strength on the performance of the sensor was investigated. Advantages and perspectives of the method to predict the AD process state are discussed. (Paper II)

In chapter 5, a novel strategy to simultaneously realize biogas upgrading, CO_2 recovery and COD removal in a bioelectrochemical system is reported. It was conducted in a microbial electrolytic system for ex-situ biogas upgrading. The effect of various biogas flow rates and external applied voltages on the system performance was investigated. (Paper III)

2 BES technology and the applications

BES are a promising and versatile technology which can convert the chemical energy embedded in organic waste streams into electricity and valuable products by microorganisms (Berk and Canfield, 1964). BES share one common principle which oxidation happens in anode and reduction happens in cathode. In anode, generally, electron donors (mainly soluble organic matter in waste streams) are introduced to specific microbial consortia (i.e. exoelectrogens) and electrons are released through oxidation (Wang et al., 2015). In addition to a certain amount of electrons used for microorganism metabolism, the residual electrons are transferred to the anode electrode and then go through an external circuit to the cathode. The electrons are then captured by the abiotic or biotic acceptor in cathode. Charge balance/neutralization is realized by ionic specie migration. The electrons can be trapped directly via the external circuit for electricity generation (microbial fuel cells, MFCs) or used for chemical production (microbial electrolysis cells, MECs; microbial electrosynthesis, MES), or water desalination (microbial desalination cells, MDCs) (Figure 1).

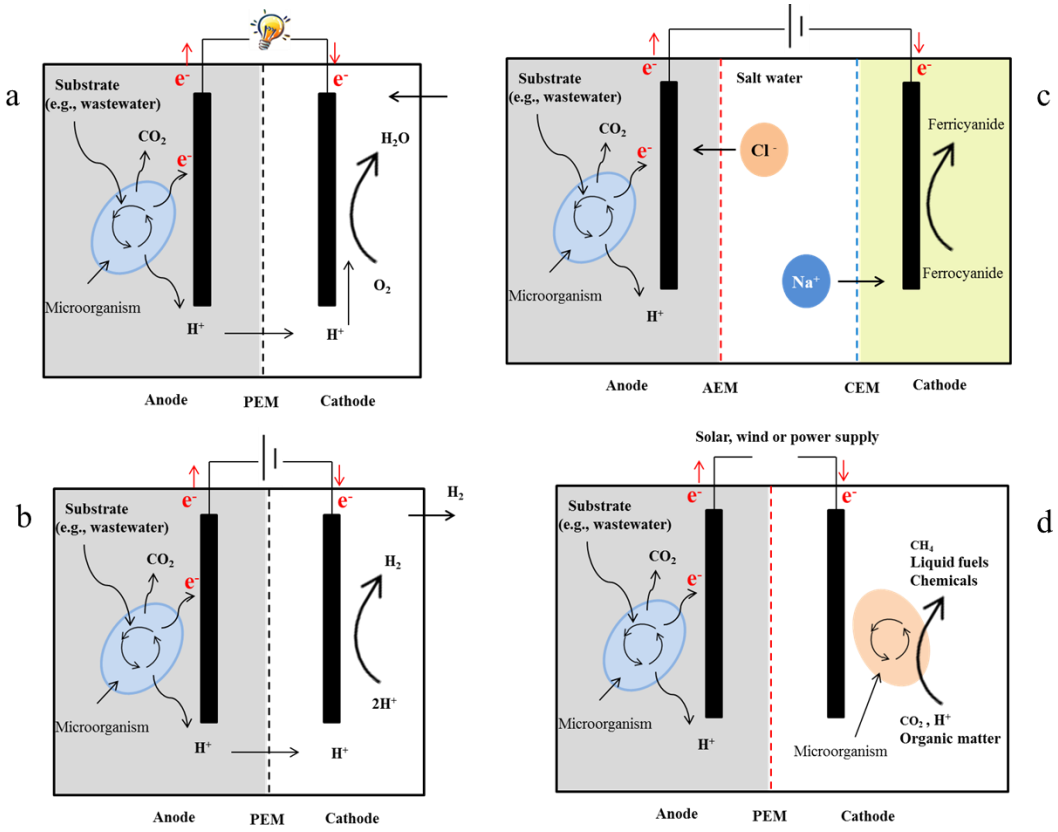

Figure 1. The schematic of a microbial fuel cell (a); microbial electrolysis cell (b); microbial desalination cell (c); and microbial electrosynthesis (d).

Based on the principal feature, BES are potentially used in several aspects: biosensors for water quality monitoring (e.g., BOD, DO, microbial activities and toxicants) and biogas upgrading in biotic and abiotic ways. This chapter targets to review and discuss the applications of BES in biosensors and biogas upgrading.

2.1 Biosensors

2.1.1 Organic substrate monitoring (BOD, COD, AOC, VFAs)

Microbial substrate oxidation rate is relevant to and can be interpreted as generated current. Under unsaturated condition, any variations in organic contents should be directly proportional to the output current. Therefore, BES have a unique ability to measure the contaminant concentrations (Lei et al., 2006). What's more, an electrical signal transducer is not required since the direct signal is already the easily readable electrical current.

In recent years various MFC-typed biosensors for BOD concentration determination have been demonstrated. Kim et al. (2003) tested a MFC-type sensor to detect BOD of wastewater and found a good correlation between the produced coulomb and the BOD values up to 206 ppm. The sensor was operated by employing diluted samples for over 5 years without any service. However, the detection range was limited and the response time was quite long with higher sample strength. Lorenzo et al. (2009) simplified the MFC configuration and established a single-chamber MFC with an air cathode to measure BOD concentrations. The biosensor output increased linearly with the BOD levels. The measuring range was larger with a better oxygen supply to the cathode. Peixoto el al. (2011) proposed a compact reactor with an anode electrode connected to a rectangular cathode chamber. The sensor was submerged in anaerobic wastewater for online and in situ monitoring of biodegradable organic content. Accurate and producible results were obtained indicating the application in real-time wastewater quality monitoring. Later, Lorenzo et al. (2014) reported a small-scale air-cathode MFC fabricated by rapid prototyping layer-by-layer 3D printing for continuous water quality monitoring. The linear detection range of COD was 3-164 ppm and the response time was as short as 2.8 min due to the improvement of mass transport element via miniaturization.

Apart from BOD determination in wastewater and AD effluents, the monitoring of assimilable organic carbon (AOC) in seawater to avoid biofouling of desalination plants is another application of the BES-typed biosensor (Quek et al., 2014). In oxygenated seawater, trace levels of AOC could still be detected in a hexacyanoferrated-adapted MFC biosensor (Cheng et al., 2014). Quek et al. (2014) investigated AOC biosensor based on a MEC principle where the anode potential was controlled by a potentiostat. The response of the system was rapid, sensitive

and showed a linear relationship between trance amounts of acetate and produced signals with a high correlation coefficient factor (R^2>0.99).

BES could also be used to monitor the AD process stability by detecting VFAs concentrations including acetate, propionate and butyrate. To discriminate and measure different VFA species (acetate, butyrate and propionate), Kaur et al. (2013) evaluated the MFC technology based on two electrochemical methods: coulombic efficiency (CE) and cyclic voltammetry (CV). The correlation between VFAs levels and coulomb generation exhibited good linearity. However, CE was not applicable since it gave a slow response of longer than 24 h when the substrate concentration exceeded 20 mg/L. By using CV, distinctive shapes of specific VFA along with the quantification could be obtained at a consistent scan rate with a rapid response time of 2 min. And from the oxidation peak linear correlations between VFA concentration and produced peak current were found. Nevertheless, the detection range was from 5 to 40 mg/L and was quite limited while the normal VFA concentrations in the AD reactor could reach several grams per liter. What's more, though the anode bacteria has been acclimated prior of its deployment, the bacterial communities might be influenced and even lose its function during long-term exposure with actual AD effluents. To protect the pre-acclimated microbial community from the sample matrix, Kaur et al. (2014) improved their system by modifying the anode with both natural polymer and polypyrrole to immobilize anode bacteria. Compared to the system performance with an unmodified electrode, the voltage output was improved, start-up time was reduced, and the system showed better stability and repeatability with the modified anodes. The detection range was widened up to 60 mg/L which still required further improvement. Since a real digestion effluent contains different microbial groups and various organic contaminants, the biofilm may be renewed continuously and adapt to other substrates. The biosensor behaviour may be affected in a long-term operation. To address the aforesaid issues, a MDC-based system was established for VFA measurement (Jin et al., 2015). Artificial wastewater was dosed in the middle chamber and VFA could penetrate to the anode chamber with the utilization of ion-selective membrane which led to a lack of direct contact between biofilm and the sample matrix. To simplify the structure and reduce the capital cost, a MEC-typed biosensor was developed to monitor VFAs concentrations (Jin et al., 2016). The response time was short (1 h) and linear relationships between VFA levels and current densities were found in the range of 5 to 100 mM.

2.1.2 Toxicant detection

If BES function at saturated fuel values and other parameters such as pH, temperature and conductivity are constant, then undesired variations in the current output can be explained by the presence of toxicants in the feeding solution. The used of MFC for toxic compound detection has been demonstrated recently. The principle is that the biosensor is set at a fixed current and changes on the current are recorded with the addition of toxic compounds. Stein et al. (2012b) investigated the effect of membrane type, current and potential on the response of the MFC-typed biosensor. They found the type of membrane (anion, cation, monovalent cation exchange membranes and bipolar membrane) seemed unlikely to affect the sensitivity of the sensor for nickel detection. While both a higher current density and overpotential could lead to a higher sensitivity. Afterwards, Stein et al. (2012a) established a MFC-based biosensor for sodium dodecyl sulphate (SDS) detection. They investigated the effect of different external resistor values and anode potential on sensor sensitivity and the time required by the bacteria to recover. They found a small resistance led to a more sensitive sensor while a large resistance favoured a short recovery time. High sensitivity and longer recover time was observed with a high current (>0.5 mA) or anode potential (>-0.4 V) control. The relationship between signal outputs and SDS values has not been discussed yet. Shen et al. (2013) developed a single-chamber air-cathode reactor for fast monitoring of the Cu(II) toxicity. They discovered that the sensor sensitivity could be affected by biofilm characteristics such as density, porosity and extracellular polymeric substances which were controlled by flow rate and nitrogen sparging. The sensitivity of MFC-based toxicity sensor was also affected by the mass transfer rate and control mode. Jiang et al. (2015) observed better sensitivity with flow-through anode and controlled anode potential while the flow-by anode and constant external resistance contributed little to the sensitivity. Rasmussen and Minteer (2015) developed a MFC-based sensor for long-term arsenic monitoring. The power output decreased with the presence of arsenate or arsenite warning whether the concentration was too high. Current output deceased linearly along with the increasing arsenic concentrations and the detection limit for arsenate and arsenite were 46 μM and 4.4 μM, respectively.

The most important role of MFC-based sensor is bacteria which oxidize a carbon source, release the electrons and translate directly into an electrical signal. Any changes in water quality can be reflected by the signal produced by bacteria. Therefore, MFC can be used as biosensors to detect compounds such as toxic organic compounds and heavy metals which could inhibit the microbial metabolic activity.

2.1.3 Microbial activity and DO assessment

Since the produced current by BES directly reflects the metabolic activity of the exoelectrogens at the anode, BES have the potential to provide useful information on microbial respiration rate. Based on the correlation between microbial respiration and contaminant reduction, Tront et al. (2008) developed a MFC-biosensor to monitor analyte concentrations and related microbial activity. The biosensor inoculated with Geobacter sulfurreducens were operated with media at varying acetate concentrations. A correlation between current outputs (0-0.30 mA) and acetate levels (0-2.3 mM) was established. Therefore, the respiration rate of G. sulfurreducens was also expressed as the electric current. In an interesting work, a submersible MFC was proposed to monitor microbial activity and BOD in groundwater (Zhang and Angelidaki, 2011). Fresh anode without biofilm was installed for microbial activity measurement, while biofilm enriched anode was used for BOD content quantification. The active microorganism concentrations were expressed as microbial adenosine-triphosphate (ATP) concentrations since they are energy carrying molecules in all living cells. With biofilm-colonized anode, linear relationship between current outputs and BOD up to 250 mg/L was observed. By switching the anode, current density increased linearly from 0.6 to 12.4 mA/m^2 along with the active microorganism concentrations from 0 to 6.52 nmol-ATP/L. Then the biosensor was tested with real contaminated groundwater to verify its practicability.

Since in MFCs electrons shuttled from anode substrate oxidation are all accepted by oxygen at cathode, MFCs can also be used as a DO sensor. Zhang and Angelidaki (2012) presented a submersible signal-chamber MFC to monitor DO in situ. When constant substrate concentrations were employed in anode, the biosensor gave different responses in current outputs at varying DO levels. With an external resistance of 1000 Ω, the current densities increased proportionally to DO levels (0-8.8 mg/L).

Overall, the practical application of BES as biosensors to monitor organic substrate concentrations, toxicants, microbial activity and DO is quite promising. It is a prerequisite for bioprocess real-time monitoring to better understand and improve the process.

2.2 Biogas upgrading

Methane produced from AD is the only valuable gas and biogas upgrading is essential to improve the heating value and promote the application. In BES, biogas upgrading can be realized by bioelectrochemical conversion of CO_2 to methane or physicochemical CO_2 capture and separation.

2.2.1 Bioelectrochemical conversion

Recently, many researches demonstrated hydrogenotrophic methanogens could be enriched in bioelectrochemical reactors, CO_2 conversion to CH_4 was realized according to Equation 3 when sufficient H_2 was supplied. Villano et al. (2010) established a MEC with a microbial biocathode. Wastewater was oxidized in anode to release CO_2 and electrons which were converted to the cathode containing hydrogenophilic methangenic culture. When cathode potential was more negative than -650 mV vs. SHE, CH_4 was produced from CO_2 reduction. Apart from via abiotically produced hydrogen gas, the authors claimed that CH_4 generation could also be realized by direct extracellular electron transfer (Equation 5) which was highly dependent on the set cathode potential. And the CH_4 production rate increased along with the electrode potential became more negative up to -900 mV vs. SHE. Based on the results, the system can be operated with AD in series while the effluent of AD can be polished by the anode and biogas can be introduced into the cathode for bioelectrochemical reduction of CO_2 to CH_4.

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \quad (5)$$

The concept of integration of AD and a CH_4 producing MEC was proved by Villano et al. (2013) in the laboratory. The bioanode was poised at +0.200 V vs. SHE and a diluted stream containing acetate was introduced into anode to mimic low-strength AD effluent while a gaseous stream containing 30% CO_2 was bubbled in the biocathode to simulate the biogas derived from AD. At the anode, acetate removal efficiency reached 94% and the effluent COD concentration remained around 38±6 mg/L. At the cathode, when pH was controlled around 8.2, CH_4 was the only measured end-product indicating H_2 and/or electric current driven reduction of CO_2. Apart from high COD removal and efficient conversion of CO_2, other merits such as very low biomass growth and ammonium migration to the cathode make the system very promising.

Xu et al. (2014) proposed a method for bioelectrochemical removal of CO_2 which cooperated with AD for biogas upgrading. In the ex-situ system, biogas generation from a digester bottle was bubbled into a biocathode, while in the in-situ one, the electrode was inserted into the digester bottle where biogas production and upgrading were achieved simultaneously. The inlet CO_2 content was around 30%

and the outlet CO_2 content in the ex-situ system was kept below 10% while the in-situ system had a better performance with faster gas-liquid transfer rate. An interesting thing in the systems was that the increased CH_4 production was consistently lower than the total removed CO_2. The authors concluded that apart from reduction of CO_2 by electro- and/or hydrogenotrophic methanogenesis, CO_2 might be absorbed by the alkali produced in the cathode.

Recently, a process coupling of MEC and AD for in situ converting CO_2 to CH_4 has been proposed (Bo et al., 2014). Anode was inserted into a stainless steel anaerobic digested reactor which served as cathode. Outlet CH_4 content from the coupling system exceeded 98% and CH_4 yield was increased 2.3-fold that of single AD process. At the anode, hydrogenotrophic methanogens were dominant and their electrochemical activity was demonstrated by clear oxidation peaks via CV technology. The authors concluded the hydrogenotrophic methanogens are electromethanogens.

In BES for biogas upgrading, methane production mechanism in biocathodes remains unclear. A process called ‘electromethanogenesis’ was proposed which electromethanogens can directly accept electrons from cathode electrodes for CO_2 reduction (Blasco-Gómez et al., 2017). In another process, hydrogenotrophic methanogens remove CO_2 by using H_2 generated from water electrolysis in the cathode. And both of these contribute to the CO_2 removal.

2.2.2 Physicochemical CO_2 capture and separation

The chemical adsorption of CO_2 is an efficient and low energy consumption way for biogas upgrading. In MECs with an external voltage, hydroxyl ions can be produced via water split in the cathode compartment which can drive CO_2 adsorption. A MEC system with biocathode has been established and the CO_2 removal mechanisms have been investigated by Zeppilli et al. (2016). A gas mixture (30% CO_2 and 70% N_2) to simulate the raw biogas from AD process was bubbled into the cathode. Based on the mass balance calculation of the inorganic carbon, the authors concluded CO_2 reduction to CH_4 by hydrogenotrophic methanogens accounted for 4% and 15% with AEM and PEM, respectively of the total CO_2 removal. CO_2 removal contributed by alkalinity adsorption was 94% and 73% of the overall values with AEM and PEM, respectively. The study highlighted the main mechanism of CO_2 removal was its adsorption as bicarnonate ion with high concentration in cathode due to alkalinity generation. Later, they studied the effect of real effluents from two-phase AD on CO_2 removal (Zeppilli et al., 2017). A MEC with PEM was used and the anode was fed with real effluents from a pilot-scale two-phase AD while the cathode was fed by a CO_2-rich gas phase. Fed with fermentate-digestate mixture, the COD removal was 360±41 mg/d (by taking into account sCOD only) and the removal efficiency reached 28±3%. CE was high at 119±28% and the current transferred to cathode to reduce the CO_2 which

contributed to CO_2 removal of 3.5±0.9 mmol C/d. Since alkalinity generation from water electrolysis, CO_2 absorption and dissolution in cathodic liquid caused CO_2 removal of 25±3 mmol C/d. Coupling AD and MEC as a post treatment has many merits such as low microbial growth, low-strength COD removal, CO_2 removal, ammonium removal and comparable energy consumption.

Except water electrolysis in MEC cathode, alkali can also be produced in employed bipolar membranes (BPM) via water dissociation with supplied voltage. Chen et al. (2012) established a bipolar membrane electrodialysis (BPMED)-MFC to produce alkali on site for biogas upgrading. Powered by a MFC, the BPMED produced alkali via water dissociation in the BPM and pH in the alkali generation chamber reached 9.8. With 0.5 V applied voltage, the produced alkali solution had a maximum pH of 11.6 which reduced CO_2 content and upgraded CH_4 to 100%. BPMED has quite low investment and operation cost while alkali production on site will cut the transportation cost which is very appealing (Chen et al., 2013). Recently, in a novel BES system, alkali and acid were produced and used in situ for biogas upgrading and CO_2 recovery (Paper III) (Jin et al., 2017). CO_2 was removed from the synthetic biogas via alkalinity adsorption in cathode and CH_4 content could reach as high as 97.0±0.2%. Without electromethanogens, produced H_2 was present in the outlet mixture which enhanced the Wobbe index.

Overall, these reports indicate that employing BES as a post treatment unit to simultaneously recover electric energy from AD effluent, generate a better quality final effluent, enrich CH_4 and remove CO_2 of an AD biogas is quite appealing.

3 Realizing VFAs monitoring in a microbial desalination cell

3.1 Main scientific challenges related to VFAs monitoring in BES

VFAs monitoring in AD has been considered as a valid solution for the AD process control. During the AD process, imbalance triggered by organic overloading and ammonia inhibition can cause VFAs accumulation and then pH decrease (Kretzschmar et al., 2015). Therefore, the AD process state can be evaluated by VFAs levels so that swift solutions can be proposed when a problem occurs.

Recently, there has been accelerating interest in BES-based biosensors. BES-based biosensor has been demonstrated its feasibility for organic substrate determination, such as COD, AOC and VFAs. All of them share one common principle (Sun et al., 2015a). Organic substrates are oxidized by exoelectrogens enriched in the anode. Electrons are released and transfer from the anode to the cathode via an external circuit. In the cathode, electrons are accepted by the final electron acceptor which is oxygen usually (Wang et al., 2015). Since the amount of transferred electrons is dependent on the microbial respiration and proportional to the amount of oxidized organic material, the current/voltage generated from BES should be proportional to the fuel concentration when the anode biofilm is in steady state.

In most researches on BES-based biosensors, acetate was commonly used as the model substrate on behalf of COD and AOC (Di Lorenzo et al., 2014; Chouler and Di Lorenzo, 2015). In general, samples were dosed in the anode which could cause a series of problems. First, pre-acclimated biofilm could be influenced by microorganisms, organic matter, toxicants present in the samples which could affect the system performance. Secondly, since substrate was directly available for the microorganisms, the saturated concentration was usually around several dozens milligram per liter. The detection range was quite limited while VFA concentrations in real AD effluent could always reach several grams per liter (Banks et al., 2011; Madsen et al., 2011; Kaur et al., 2013). And sample dilution would make the technology more complex and unpractical.

3.2 An innovative concept to overcome technical issues on VFAs monitoring in BES

In order to overcome the technical issues associated with VFAs monitoring in BES, a microbial desalination cell (MDC) has been developed in Paper I (Figure 2). The MDC consisted of three chambers which were anode, middle and cathode chamber. They were separated by an AEM and cation exchange membrane (CEM),

respectively. Samples containing various VFAs concentrations were measured in the middle chamber. The hypothesis was that VFAs in their ionized form could diffuse through the AEM to the anode where they were oxidized by exoelectrogens attached on the anode electrode. Electricity was produced the current signal might be proportional to the VFAs concentrations. What's more, complex organic matter such as protein and lipids would be retained by the AEM. MDC could be used for VFAs detection rather than a measurement of total organic matter.

The experiment aimed to seek a correlation between VFAs concentrations and the current output from the biosensor; investigate the effect of ionic strength and external resistance on the biosensor's performance; verify the reliability of the biosensor with the presence of other organic matter in samples and real AD effluents.

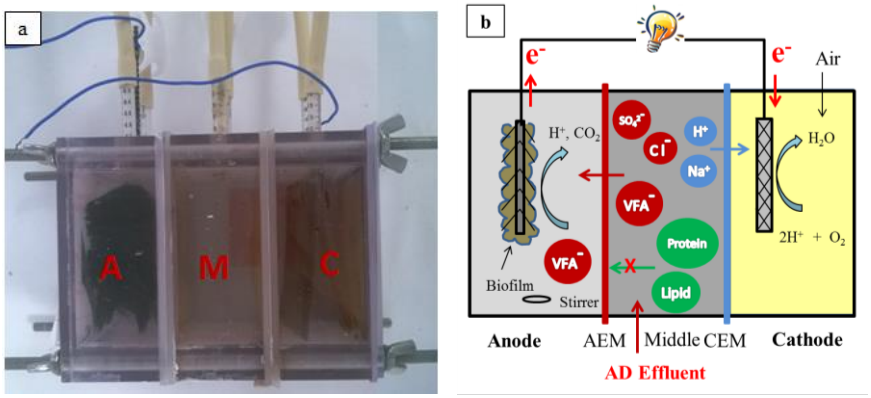

Figure 2. Sensor prototype (a) and schematic diagram (b). A, the anode chamber; M, the middle chamber; C, the cathode chamber; AEM, the anion exchange membrane; CEM, the cation exchange membrane. **(Paper I)**

The working volume of each chamber was 250 mL. The anode and cathode chamber was filled with buffer solution (Kvesitadze et al., 2012) and NaCl solution, respectively. Instead of releasing it in the anode in other studies, synthetic digestate with various VFAs concentrations were dosed in the middle chamber. Synthetic digestate contained acetate, propionate, butyrate and formate at a concentration ratio of 10:2:2:1 to mimic the actual AD effluent (Hollinshead et al., 2014). A resistance was connected in the system and the voltage across it was monitored using a digital multimeter with 30 min internals. The anode and middle chamber was performed in the anaerobic condition while the cathode was aerated for oxygen reduction.

3.3 Effect of VFAs concentrations on the system performance

Outcomes of this study showed that the current output increased along with VFAs concentrations (Figure 3). When VFAs concentrations were low (1 and 5 mM), the mass transfer rate driven by concentration gradient to the biofilm surface was far lower than the rate of substrate (VFAs) consumption which limited the current output (Quek et al., 2015). When VFAs concentrations were high (100 and 120 mM), the mass transfer rate increased along with the bulk VFAs concentrations and the maximum current was soon achieved within 2 hours.

VFAs diffused through the AEM and accumulated in the anode. When the biosensor was operated for 5 hours, the amount of VFAs in the anode increased positively along with the bulk VFAs in the middle chamber. The linear correlation agreed well with Fick's first law ($J = -D\frac{d\varphi}{dx}$). Additionally, the current outputs observed at 5 h were plotted against VFAs levels and two linear relationships with good correlation coefficient factors were obtained (Figure 4). In the first stage with VFAs concentrations from 1 to 30 mM, the current density increased linearly from 0.04±0.01 to 8.50±0.32 mA/m^2 with a steep slope. In the second stage, the current density grew from 8.50±0.32 to 10.80±0.72 mA/m^2 with VFAs concentrations ranged from 30 to 120 mM. Substrate was the limiting factor in the first stage while other parameters (e.g. architecture, material, conductivity, microorganisms et al.) played an important role in the current output in the second stage (Rismani-Yazdi et al., 2011; Lefebvre et al., 2012).

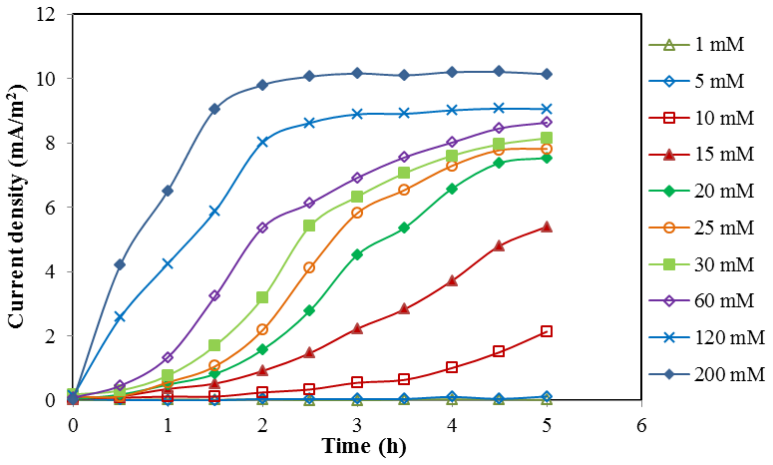

Figure 3. Typical current generation from the biosensor during the batch mode experiment while a 1000 Ω external resistance was used to connect the anode and cathode. **(Paper I)**

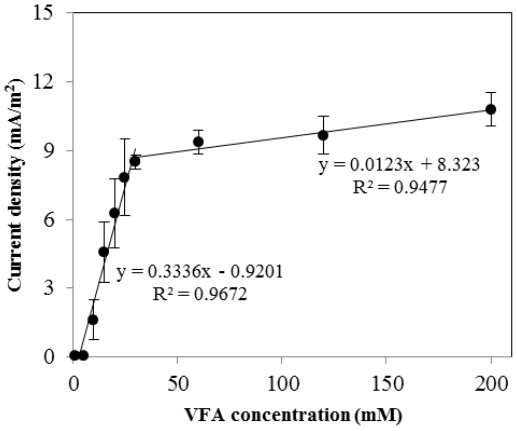

Figure 4. The relationship between current density and VFAs concentrations at 5 h. **(Paper I)**

3.4 Effect of varied operational conditions on the system performance

To study the effect of ionic strength, certain amounts of salt were added into the samples. When the increment of ionic strength was less than 100%, the increased ionic strength was advantageous for the electricity production. The increased conductivity facilitated proton transfer and therefore decreased the internal resistance (Lefebvre et al., 2012). However, when the ionic strength increased further, more inorganic anions existed and penetrated through the AEM. The competition between inorganic anions and ionized VFAs was intense and less VFAs diffused to the anode. The current density decreased when the increment of conductivity was larger than 150%.

Notably, the biosensor showed different current outputs with different external resistances. External resistance could affect the electron flow rate and microbial communities (Rismani-Yazdi et al., 2011; Jung and Regan, 2011). Lower external resistances resulted in higher current outputs. A higher current output was an evidence of a faster microbial respiration rate and therefore more VFAs consumption. A highly sensitive biosensor can be constructed with a low external resistance since the signals will be amplified. However, large deviations in current outputs were observed with low external resistances. This can be explained by the relatively high internal resistance which can be easily influenced by the operational conditions and sample quality.

In other biosensor studies, sample measurement was usually conducted in the anode. The current output from the BES-based biosensor was proportional to all degradable substrates concentrations (Madsen et al., 2011; Kim et al., 2003; Zhang and Angelidaki, 2011). In the MDC-typed biosensor, the ion-selective membrane allowed

ionized VFAs to enter into the anode while other organic matter such as protein and lipids were retained. Apart from the interference from various organic matter, real AD effluents are more complex (Fradler et al., 2014). In tests with real AD effluents, results calculated from the biosensor agreed well with those measured by GC regardless of sample quality and reactor operational parameters. The MDC-typed biosensor has been proved to be robust and reliable.

4 Improving VFAs monitoring in a microbial electrolysis cell

4.1 A novel concept describing VFAs detection in MEC

In chapter 3, MDC has been demonstrated its feasibility as a VFA biosensor. However, the MDC-based VFA biosensor consists of three chambers and two pieces of membrane which increases the capital cost to some extent. To reduce the capital cost, a simple microbial electrolysis cell (MEC) was constructed in Paper II (Figure 5) for fast VFAs monitoring. The MEC had two chambers (i.e. anode and cathode) which were separated by a piece of AEM. Apart from a 10 Ω resistance, a power supply was connected in the system to provide an additional voltage to the circuit. Samples with varied VFAs concentrations were quantified in the cathode chamber. The hypothesis was that, besides diffusion driven by concentration gradient, ionized VFAs could also migrate under the external voltage through the AEM to the anode where they were microbially oxidized and converted into current signals. The VFAs monitoring process was accelerated and hydrogen was produced in the cathode from electrolysis as byproduct during the process. The purpose of the experiment was to build relationships between VFAs concentrations and the current output from the MEC-typed biosensor. Moreover, different operational parameters such as the external voltage, ionic strength and VFA composition ratio were investigated. In order to verify the robustness of the biosensor, interruptions such as the presence of other organic matter, anode exposure to oxygen and samples with low pH were introduced to the reactor. Finally, the biosensor performance with real effluents from a lab-scale AD reactor has been evaluated.

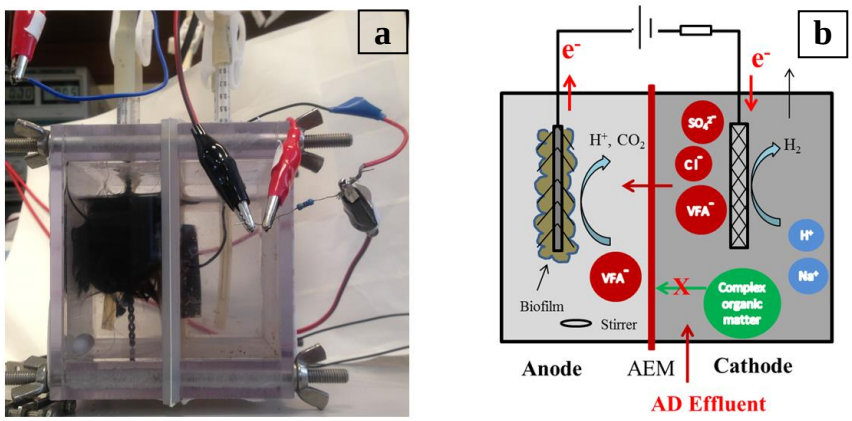

Figure 5. Prototype (a) and schematic diagram (b) of the bio-electrolytic sensor. **(Paper II)**

4.2 Effect of VFAs concentrations on the system performance

Under operating conditions with 0.5 V external voltage and a 5:1:1concentration ratio of acetate, propionate and butyrate, the current density from the MEC-typed biosensor increased along with VFAs concentrations with a range of 5 to 120 mM (Figure 6a). Under each concentration, the current density rose rapidly along with the time and a platform was observed without obvious increase after 4 hours (data was not shown). Equilibrium between VFAs transportation and microbial consumption was reached within 4 hours. Moreover, no matter from low to high concentrations of VFAs or vice versa, the current density was independent from the sequence of measurement and showed a good reproducibility. When VFAs were removed from the sample, little current density was observed. After a period of starvation, the biosensor responded immediately once VFAs were introduced into the system. When the operation time was 1 hour, the current density observed (0.03±0.01 to 2.43±0.12 A/m^2) increased linearly with VFAs concentrations (5 to 100 mM).

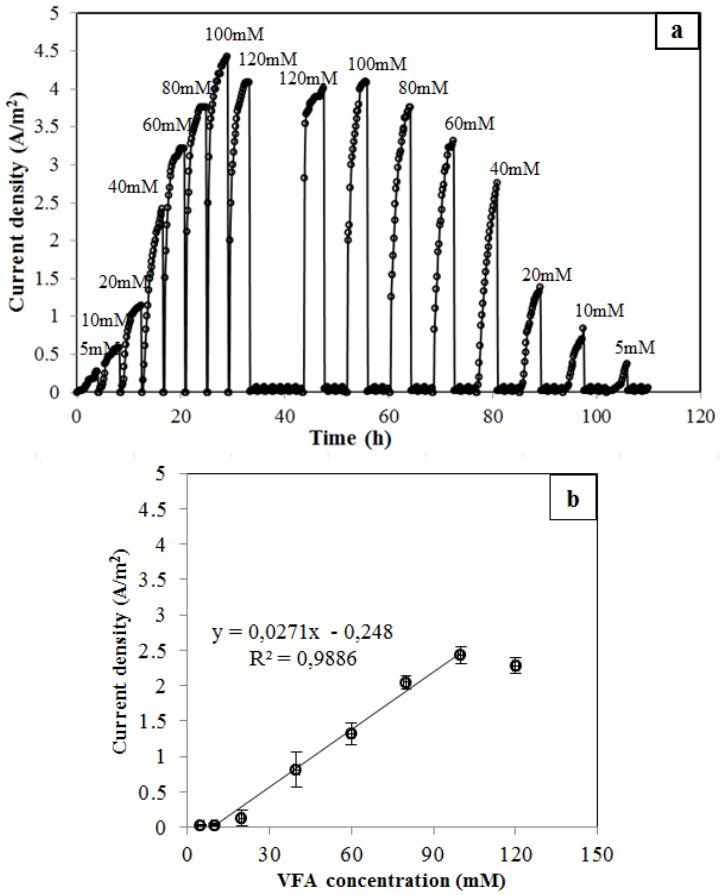

Figure 6. Typical current density generation along with time from the biosensor (a) and the relationship between current density generated at 1 h and initial VFA levels in the artificial AD effluent (b). **(Paper II)**

4.3 Effect of varied operational conditions on the system performance

The system was influenced by external voltage, VFA concentration ratio and ionic strength. The current density increased with the increasing external voltage. The applied voltage induced fast electron transfer kinetic and compensated the electrode overpotential, which enhanced VFAs consumption by anode respiring bacteria (ARB) (Lee et al., 2009). The difference in concentrations between the bulk VFAs in the cathode and those in the anode was increased. Thus, more VFAs transported to the anode and consumed by the ARB with the assistance of external power, and higher current density was obtained. VFAs composition influenced the anode microbial community, the anion transportation across the AEM (Jung and Regan, 2011), as well as the signal outputs. Results showed that the proportion of acetate had an important impact on the biosensor. Acetate is the favorable substrate for most of ARB such as Geobacter while propionate and butyrate may need to be first degraded to acetate with the help of fermentative bacteria (Yang et al., 2015). Besides, the transportation rate of acetate through the AEM was faster than those of propionate and butyrate (Zhang and Angelidaki, 2015). When the proportion of acetate was above 70%, the influence of VFAs composition on the biosensor was limited. The increased ionic strength within a certain range was advantageous for the bioelectricity production. High ionic strength benefited the system by reducing the internal resistance (Liu et al., 2005). However, when the conductivity increment was larger than 150%, no further increase in the current density was observed indicating the saturation of the system. When a certain amount of VFAs were available for the microorganism and substrate was not the limiting factor, the operational parameters were dominant in the electricity production.

Prior to the installation of MEC, enrichment of biofilm with VFAs was conducted to establish specific electrogenic functionality. Apart from bacterial community acclimation, the overall selectivity of the biosensor was improved by using an AEM which allowed selective negative-charged ions transport across the membrane. The AEM allowed VFAs to transport while ionisable species (glucose, cellulose, protein and lipids) were retained. In real AD effluent, organic contents such as glucose, long-chain fatty acids, and amino acids rather than short-chain VFAs take up a part. Therefore, in our systems, the interference from other organic matter was eliminated. Moreover, our systems were robust against interruptions such as temporary anode exposure to oxygen injection and samples with low pH.

In tests with real effluents from a lab-scale AD reactor, the biosensor showed reliable results for VFA monitoring compared with that measured by GC (Figure 7). Though VFAs concentrations fluctuated during the monitoring process, the biosensor could easily handle samples with a wide concentration range and exhibit accurate results.

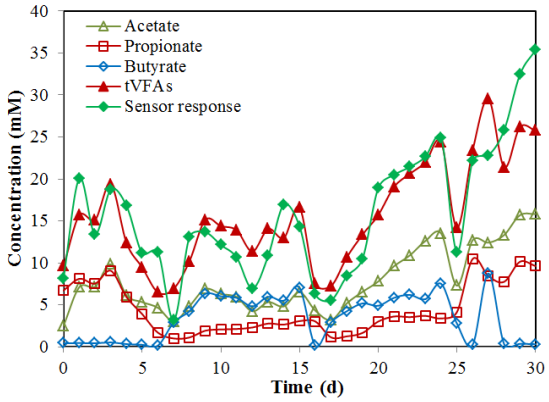

Figure 7. Monitoring test of a lab-scale CSTR**. (Paper II)**

4.4 Strengths and outlook of the technology

The merits of the biosensor are obvious. The biosensor isolated the biofilm from samples which could protect the microbial community from inocula and inhibitors in the samples. The biosensor could distinguish VFAs, rather than conduct a measurement of all degradable organic matter. Moreover, the detection range was widened significantly that sample dilution was not required. The detection time was quite short (1 hour) compared with that in other studies (Kaur et al., 2013). During the monitoring process, hydrogen (H_2) was produced from water hydrolysis. The produced H_2 could contribute for the energy needs for operating the biosensor. And a self-sustaining system can be pursued.

Integrating BES with AD in other applications such as AD effluent polishing, electricity generation and biogas quality upgrading, the scale up of BES technology is certainly needed for industrial applications. However, the major challenge for system scale up is that the maximum power density generated by a BES and the performance of the reactor is not directly proportional to the size of the reactor (Du et al., 2007). In contrast, the down scale or even miniaturization of BES-based biosensor should be pursued. A smaller size reactor could make a better performance and shorter response time which are limited by the mass transfer to the biofilm. Therefore, the technology will be less costly and more practical.

5 Realizing CO_2 capture and separation from biogas in a novel BES

5.1 A novel BES for biogas upgrading

Energy crisis and climate change are global issues in these days. Renewable energy resources, which are recognized as clean sources of energy, receive great interest (Nematollahi et al., 2016). Biogas is a clean renewable energy as an alternative of fossil fuels and the production process is carbon-neutral. The utilization of biogas generated from biomass degradation contributes to achieve a sustainable bioenergy ecosystem for countries (Sun et al., 2015a). Biogas consists of mainly methane (CH_4) and carbon dioxide (CO_2), as well as small amounts of ammonia (NH_3), hydrogen sulphide (H_2S), nitrogen (N_2), oxygen (O_2), hydrogen (H_2) and carbon monoxide (CO) (Sun et al., 2015). Since the presence of impurities, especial CO_2 which usually accounts for 30-40%, the heating value of raw biogas is quite low which limits its industrial application (Andriani et al., 2014). Biogas upgrading is necessary and the upgraded biogas could be injected into the natural gas grids or compressed for vehicles (Budzianowski et al., 2016). In the current work, a novel microbial electrolytic capture, separation and regeneration cell (MESC) was proposed for biogas upgrading. The system consisted of three chambers which were anode, regeneration and cathode chamber. They were separated by a BPM and an AEM, respectively (Figure 8).

In the anode, organic matter were microbial oxidized to release electrons, protons and CO_2. Electrons transferred via external circuit to the cathode. With an external voltage, electrons and protons were chemically reduced; H_2 evolved and alkaline generated in the cathode. Water dissociation happened inside the BPM and H^+ was produced in the regeneration chamber. The hypothesis was that raw biogas was introduced into the cathode chamber via a diffuser. Then CO_2 was absorbed by alkaline to form HCO_3^- and CO_3^{2-}. These negative charged species could pass through the AEM to maintain charge balance or driven by concentration gradient. In the regeneration chamber, produced H^+ from water splitting reacted with HCO_3^- and CO_3^{2-} and regenerated CO_2. The experiment mainly studied the system performance with regard to enriched methane concentrations, COD removal efficiency and current output under different external voltage and biogas flow rate.

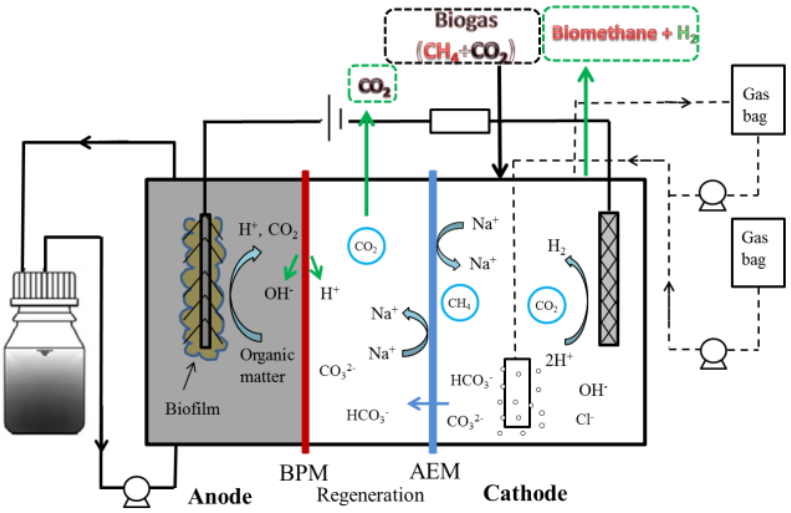

Figure 8. The schematic diagram of the MESC reactor. BPM, bipolar membrane; AEM, anion exchange membrane (**Paper III**)

5.2 The MESC reactor performance

Under operating conditions with 1.2 V external voltage and 19.6 mL/h gas flow rate, outcomes of the system was shown in Figure 9. A maximum current density of 1.7 A/m^2 was produced during the process. And COD decreased from 2341±320 to 41.2±12 mg/L with removal efficiency at 98.2%. The current output was mainly influenced by the substrate concentrations and exoelectrogens (Lu et al., 2015). The lowest pH in the regeneration chamber and the highest pH in the cathode chamber reached 1.34±0.04 and 9.19±0.11, respectively. Acid and alkali were produced in the regeneration and cathode chamber, respectively. The highest conductivity in the regeneration chamber was 22.79±0.75 mS/cm which was mainly contributed by H^+ produced via the BPM (Cao et al., 2009). Alkali in the cathode was used to absorb CO_2 in situ. During the whole process, notably, the portion of CH_4 was higher than 90% and even up to 97.0±1.3%. The minimum portion of CO_2 reached 0.5±0.2%. The diminished CO_2 was mainly converted to (bi)carbonate in the cathode which accounted for 37% of the total initial CO_2. The (bi)carbonate in the regeneration chamber shared 12% of the total initial CO_2 and the regenerated CO_2 made up a small percentage of the total (only 2%). Therefore, acid and alkali production, COD removal, current production and biogas upgrading were realized simultaneously in a single reactor.

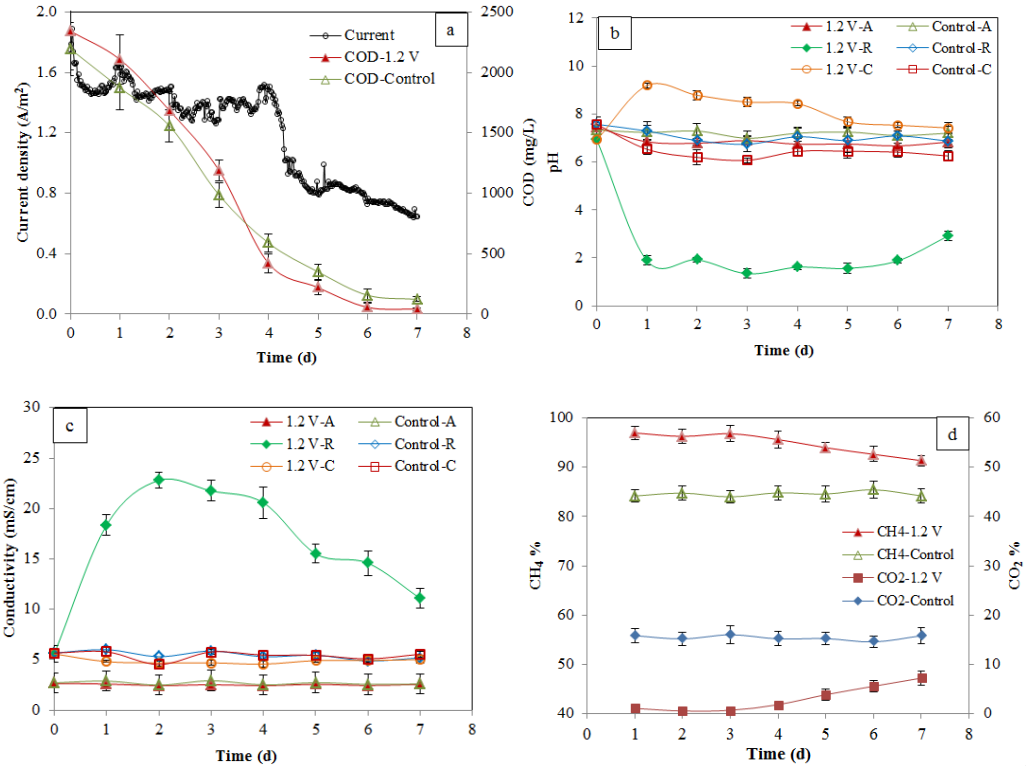

Figure 9. MESC performance at 19.6 mL/h gas flow rate with 1.2 V and control experiement. A, anode chamber; R, regeneration chamber; C, cathode chamber. The current density output and COD changes (a); pH profiles in three chambers (b); conductivity profiles in three chambers (c); methane and carbon dioxide contents in the outlet gas (d). **(Paper III)**

5.3 The effect of operational conditions on system performance

The system was influenced by external voltage and biogas flow rate. When the applied voltage was changed from 0, 1.0 to 1.2 V at around 19.6 mL/h gas flow rate, the highest pH in the cathode were 6.44±0.05, 7.37±0.12 and 9.19±0.11, respectively. The maximum CH_4 content of the output gas increased from 85.5±0.3%, 89.2±0.4% to 97.0±0.2%. The applied voltage induced fast electron transfer kinetic and compensated the electrode overpotential, which enhanced the substrate consumption by ARB (Lee et al., 2009) and favorite the electrolysis process. The current density, cathodic pH and upgrading performance increased with the increasing external voltage supply. When the gas flow rate was around 28 mL/h, CH_4 contents were not improved further with a higher voltage at 1.4 V. Other factors limited the system performance.

When the external voltage was fixed at 1.2 V, the gas flow rate changed from 13.4, 19.6, 25.3 to 27.7 mL/h. A low gas flow rate (13.4 mL/h) resulted in relative low

current densities. Raw biogas introduction to the catholyte functioned as mixing and affected H_2 bubble release and mass transfer. A low COD removal efficiency (78.7±3.5%) was found which was affected by the reduction process in the cathode. When gas flow rate was higher than 13.4 mL/h, the current output and COD removal exhibited similar results along with the operation time. With the gas flow rate increasing, cathodic pH declined obviously due to the more CO_2 absorption in the alkaline catholyte. However, the upgrading performance decreased and the portion of CH_4 dropped to 86.0±0.3% at 27.7 mL/h gas low rate. Low gas flow rate resulted in a small treatment capacity while high gas flow rate decreased the purity of CH_4. Therefore, a proper feeding gas flow rate is crucial to improve the system performance.

In a continuous mode, the system was operated for 40 days without salt solution switch. For the whole period, CH_4 content kept above 88% with a maximum value at 97.5±0.74% (Figure 10). CO_2 content was kept below 9%. The adsorption capacity was huge since ionized HCO_3^- and CO_3^{2-} was transferred to the regeneration chamber and separated from the system as CO_2. To obtain the natural gas quality, a two-stage process which may potential lead to further biogas purification and high process efficiency could be investigated.

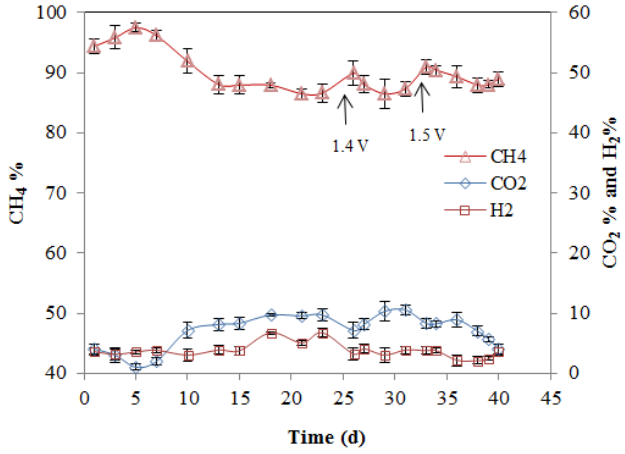

Figure 10. Methane, hydrogen and carbon dioxide contents in the outlet gas in the continuous mode. **(Paper III)**

5.4 Energy consumption and capital cost

Energy consumption derived from peristaltic pumps and power source. For the batch experiment in Figure 9, energy consumptions from pumps were 7×10^{-5} kWh which was quite small in lab scale. Energy input from the external power supply was 4.8×10^{-4} kWh. Therefore, the energy consumption for biogas upgrading was around 0.17 kWh/m^3 raw biogas. The electrical energy consumed in water scrubbing is around 0.2-0.32 kWh/Nm^3 raw gas, and 0.15-0.22 kWh/Nm^3 with membrane technology (Sun et al., 2015; Bauer et al., 2013). Apart from the dominant methane, H_2 was produced during the process and collected at the end of the batch which could compensate part of the energy consumption.

At present, it is still very challenging to scale up the technology for industrial application since the capital cost is a big barrier. The cost of a pilot scale reactor can be estimated around several thousand euros per m^3 according to Table 1. A pilot MEC plant with 100 L in size treating domestic wastewater in the UK cost equivalent around 2800 €/m^3 (Heidrich et al., 2014). Keeping cost down requires choosing better and cheaper materials and producing more valuable products rather than sole electricity such as hydrogen.

Table 1. Construction material price list for BES plants

Category	USD	EUR
Polycarbonate Reactor (/m^3)	5000	4400
Bipolar membrane (/m^2)	1300	1144
Cation /Anion exchange membrane (/m^2)	120	105.6
Plain carbon cloth anode (/m^2)	320	281.6
Pt-catalyst cathode (/m^2)	600	528

6 Conclusions

This thesis mainly focused on the optimization of AD process with BES technology. The AD process state was evaluated by VFAs monitoring in MDC/MEC-typed biosensors. Biogas upgrading and COD removal were conducted in a MESC. The main findings are summarized:

- The feasibility of MDC technology as a simple and reliable VFAs biosensor has been proved. Two linear correlations between current density and VFA levels were obtained in the system. The VFA detection range (1 to 120 mM) was much broader than that of other studies. The biosensor had no response to protein and lipids suggesting its selectivity. The response time was 5 h which is adequate for frequent VFA monitoring in AD reactors.
- The MEC technology has been demonstrated feasible as a VFAs biosensor. The relationship between current density and VFA concentrations up to 100 mM was linear. The external voltage, VFA composition and ionic strength affected the sensor performance. However, linear relationships between current density and VFA levels were always observed. H_2 was collected during the process which could compensate the energy consumption. The VFAs transportation was accelerated by an external voltage and a short response time (1 h) was obtained.
- In MDC/MEC-typed biosensors, other organic matter (glucose, protein, lipids) rather than VFAs was retained by the AEM and their interference was eliminated. When explored with real AD effluent, the results from MDC/MEC-typed biosensors were reliable because no significant differences between results from biosensors and GC were observed.
- The proof of concept of the MESC for simultaneous CO_2 capture, separation and regeneration, biogas upgrading and COD removal was demonstrated. At the optimum conditions, COD removal efficiency reached 98.2±2.6% and the maximum methane content was up to 97.0±0.2%. Energy consumption for biogas upgrading was around 0.17 kWh/m^3 raw biogas. H_2 was detected which could compensate for part of the energy consumption.
- BES assisted by exoelectrogenic microorganisms as biocatalysts are quite environmental friendly since no expensive or toxic mediators are employed. With value-added products such as hydrogen, methane and hydrocarbons, the system could be energy self-sufficient which is very promising. However, the capital cost is one of barriers for scale-up and commercialization of BES.

7 Future Perspectives

In this thesis, the novel concept of using BES to monitor VFAs concentrations or upgrade biogas has been proposed. Influencing parameters have been investigated and satisfied results have been achieved. However, further improvement and modification might be still needed.

- In the MDC-based VFA biosensor, energy consumption derived from aeration which can be removed by employing air-cathode. The feasibility of the new architecture as VFAs biosensor should be verified and the effect of operation parameters such as conductivity, temperature, external resistance on the system performance should be investigated.
- In the MEC-based VFA biosensor, since AD effluent was directly introduced to the cathode chamber where anaerobic condition was maintained, a single-chamber reactor may still function well. It can submerge into an AD reactor which serves as the cathode. The performance of the further simplified reactor in terms of feasibility, detection range, response time and reliability should be investigated. At present, the valid volume of our biosensor reactors is several hundred milliliters. Miniaturization of the reactors to several milliliters could accelerate the mass transfer, short the response time and reduce the capital cost which is the future direction of research.
- In the MESC reactor for biogas upgrading, the outlet CH_4 content in the continuous mode was around 88% which still needs to be improved to meet the natural gas quality. A two-stage process may be employed to achieve further biogas purification and high process efficiency. In the future, synthetic gas with different gas compositions (e.g. 80% CH_4 and 20% CO_2; 90% CH_4 and 10% CO_2) should be tested in the continuous mode. What's more, in order to implement the MESC technology in a commercial application, a detailed environmental and economic impact assessment should be conducted.

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In this online version of the thesis, **paper I-III** are not included but can be obtained from electronic article databases e.g. via www.orbit.dtu.dk or on request from.

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The department dates back to 1865, when Ludvig August Colding, the founder of the department, gave the first lecture on sanitary engineering as response to the cholera epidemics in Copenhagen in the late 1800s.

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