SINTEF
PROCEEDINGS
4

Selected papers from the 10th Trondheim Conference on CO_2 Capture, Transport and Storage

TCCS-10

SINTEF Proceedings

Editors:
Nils A. Røkke and Hanna Knuutila

TCCS–10
CO_2 Capture, Transport and Storage
Trondheim 17th–19th June 2019

Selected papers

SINTEF Academic Press

SINTEF Proceedings no 4
Editors: Nils A. Røkke (SINTEF) and Hanna Knuutila (NTNU)
TCCS–10
CO_2 Capture, Transport and Storage. Trondheim 17th–19th June 2019
Selected papers from the 10th International Trondheim CCS Conference

Keywords:
CCS – Carbon Capture, Transport and Storage, CO_2 Capture, CO_2 Transport, CO_2 Storage, CO_2 Utilization, Pre-combustion capture, Post-combustion capture, Oxy-fuel capture, CCS and hydrogen, CO_2 positive solutions, International R&D activities, Whole system issues, Novel CCS technologies, Public Acceptance, Communication, Policy, Business models

Cover illustration: SINTEF Energy

ISSN 2387-4295 (online)
ISBN 978-82-536-1646-9 (pdf)

SINTEF Academic Press
Address: Børrestuveien 3
PO Box 124 Blindern
N-0314 OSLO
Tel: +47 40 00 51 00

www.sintef.no/community
www.sintefbok.no

SINTEF Proceedings
SINTEF Proceedings is a serial publication for peer-reviewed conference proceedings on a variety of scientific topics.
The processes of peer-reviewing of papers published in SINTEF Proceedings are administered by the conference organizers and proceedings editors. Detailed procedures will vary according to custom and practice in each scientific community.

MODELLING BIO-ELECTROCHEMICAL CO_2 REDUCTION TO METHANE

G. Samarakoon[1*], C. Dinamarca[1], A.B.T. Nelabhotla[1], D. Winkler[2], R. Bakke[1]

[1] Department of Process, Energy and Environment

[2] Department of Electrical Engineering, Information Technology and Cybernetics, University of South-Eastern Norway, Kjølnes ring 56, 3918, Porsgrunn, Norway

* Corresponding author e-mail: gamunu.arachchige@usn.no

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 simulations demonstrate the basic concepts of BES for biogas upgrade and its limitations. The simulations show that biogas methane content can be increased up to 85 % under the reactor settings selected for the simulations. The rate of the reduction reaction can be constrained by the local potential of the cathode and the substrate concentration. 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 a 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, biogas is upgraded by removing CO_2 before selling as a transport fuel. Water scrubbing, physical absorption using organic solvents, chemical absorption using amine solutions are 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 also be extended to 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 sources, as a way of storing renewable surplus electricity as methane [4].

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

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

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

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

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 in the production of CO_2.

The 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 biologically relevant conditions at pH 7 and 25 ^{0}C. Additional cathode potential over the thermodynamic potential should be always applied to overcome other potential losses (energy losses) and derive the intended reaction. The other potential losses are mainly a result of activation energy required to drive the electrochemical reactions, ohmic losses as a result of resistance to the flow of charges, concentration losses as a result of mass transfer limitation and bacterial metabolic losses[7].

Electrode "respiring" bacteria 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 the 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. CO_2 reduction to CH_4 (reaction 1) is catalysed by the microbial group, hydrogenotrophic methanogens. It is assumed that this microbial group can acquire electrons directly from the solid cathode).
2. Only hydrogenotrophic methanogens are active on the cathode surface (any other parallel biochemical and bio-electrochemical reactions on the cathode surface are neglected.)
3. The reactor compartment is a continuous flow and complete mixed separate cathode compartment.
4. A separate anode compartment (which is not included in the model modification) supplies an unrestricted proton flow (to the liquid phase of the cathode compartment) and electron current (to the cathode).
5. The biochemical reduction reaction (reaction 1) is the rate-limiting step within the reactor compartment, while the transport of CO_2 and H^+ to the solid cathode is comparatively fast and the electroactive microorganism are abundant on the cathode.

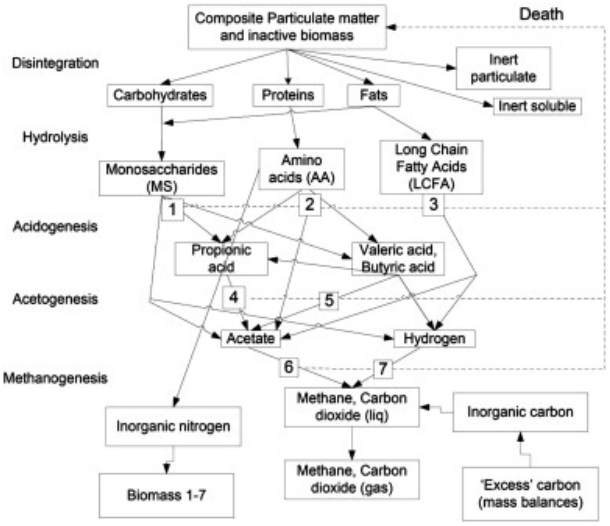

Figure 1: The reaction paths described in ADM-1 [10], with the following microbial groups: (1) sugar degraders, (2) amino acid degraders, (3) LCFA degraders, (4) propionic acid degraders, (5) butyric and valeric acid (VFA) degraders, (6) acetoclastic methanogens, and (7) hydrogenotrophic methanogens, 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 particulate constituents into sugars, amino acids and long-chain fatty acids (LCFAs). The hydrolysis products are then fermented into volatile fatty acids (Acidogenesis). These acids are broken down to acetate and hydrogen (Acetogenesis). The final step is Methanogenesis in which the Acetoclastic methanogenesis converts acetate to methane, and hydrogenotrophic methanogenesis converts carbon dioxide and hydrogen to methane.

The rate expressions and stoichiometric coefficients of these steps as biological processes are given in a Peterson matrix [12]. The matrix incorporates the biological processes as rate equations, the components and the stoichiometric coefficients of the 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 from 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]:

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

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, the overall rate equation can be defined as rate equation (r2):

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

The last term in the parenthesis (r2) which is derived from the 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 the 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 $\eta = E_{KA} - E_{cathode}$. Since E_{KA} is used as reference potential ($E \equiv 0$), η becomes $-E_{cathode}$.

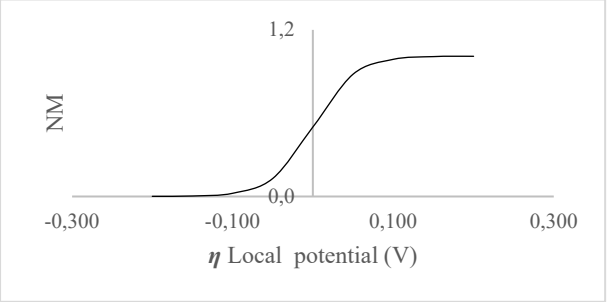

Figure 2**:** Plot of the Nernst-Monod (NM) term for E_{KA} = 0 V and T = 308 K and the local potential (η) from -0.2 to 0.2 V.

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).

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

Table 1**:** Parameters used for the bio electrochemical process

Parameters	Description	Unit	value
$k_{m\_eet}^0$	Maximum electrons uptake rate	Kmol-e kg COD X d^{-1}	4.5
X_eet	Concentration 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

2.2.1 Kinetic and stoichiometric parameters

The developed ADM-1 modification is relatively simple, and the main objective is to use it as a 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.

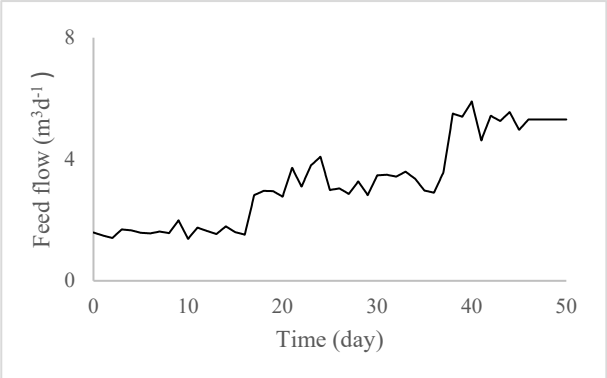

Figure 3**:** The sludge feed flow to the AD reactor [16].

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, a 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 the 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 constraints.
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 the rate of its conversion to biogas. It could be hypothesized that the overall methane production capacity might be increased by increasing the input of gaseous carbon from external sources. Thereby, a source of soluble CO_2 was added to the digester with BES activated when running 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.

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, the biogas production rate increases. The reactor produces biogas with ~ 65 % methane (CH_4) content.

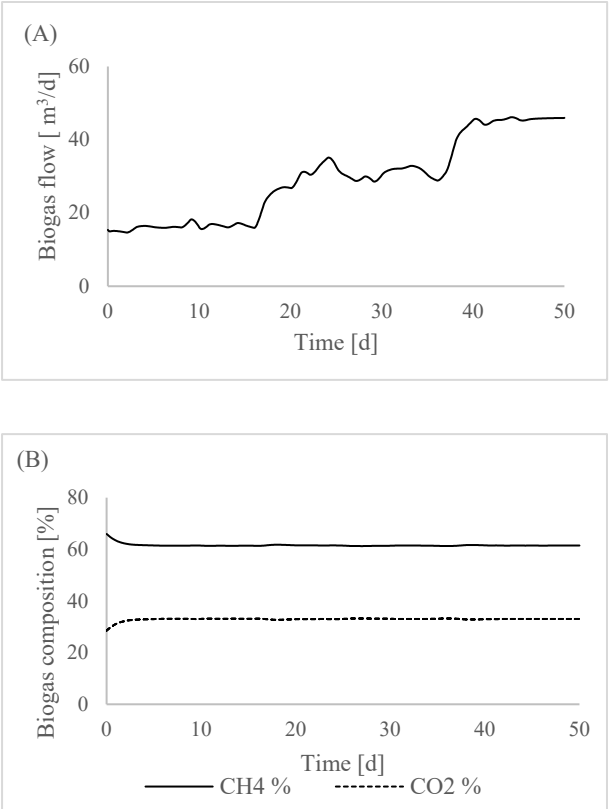

Figure 4**:** Biogas production rate (A) and composition (B) for the conventional biogas reactor (selected to simulate for the baseline data). The feed rate changes at day 16 and 37.

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 shown in Figure 5. Increasing η further does not rise the biogas methane

content. The simulation demonstrates that 30 % methane increase could be expected by employing BES in this reactor settings chosen for the study.

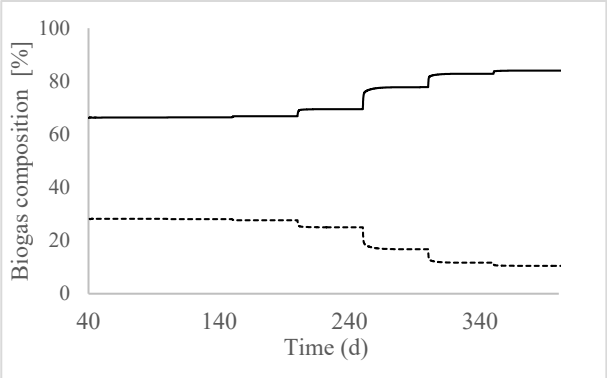

Figure 5: Response of biogas composition (— CH_4 %, ··· CO_2 %) to step increases of the local potential (η) from -0.2 to 0.2 V (step size =0,05). The bio-electrochemical process is activated at day 50.

When the local potential is sufficiently high, the cathodic donor saturates, and it is acceptor, in this case, dissolved CO_2 that limits the rate. Figure 6 shows how the value which accounts for the electron acceptor part of the rate expression decreases as the local potential increases. However, it should be noted that the effect shown here is qualitative and the exact values depend on the values 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 in 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.

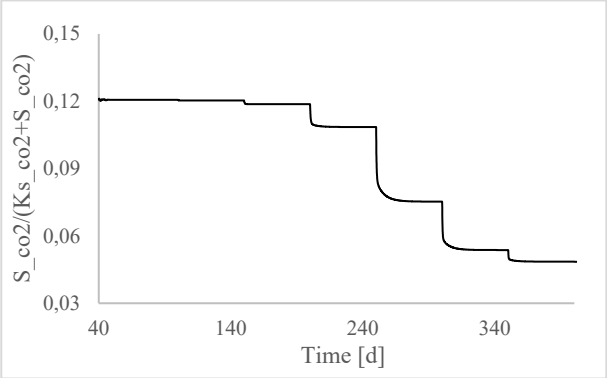

Figure 6: The Monod-type kinetic expressions (r3) due to available electron acceptor (soluble substrate, CO_2) after the bio-electrochemical process is activated at day 50, and the local potential (η) from -0.2 to 0.2 is increased stepwise (step size =0.05).

pH is one of the main parameters that can affect the performance of AD. Figure 7 shows the variation of pH in the digester. The digester with the conventional settings (selected to simulate for the baseline data) has pH at 7.2. The pH of the digester with BES increases as the local potential increases. The pH rises because of a fall in the bicarbonate strength due to depletion of headspace CO_2 as it is converted to methane. The elevated 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 pathway. The simulation result showed an increased acetate concentration and slight reduction in total biogas production (The results are not presented). Here, the pH elevation 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].

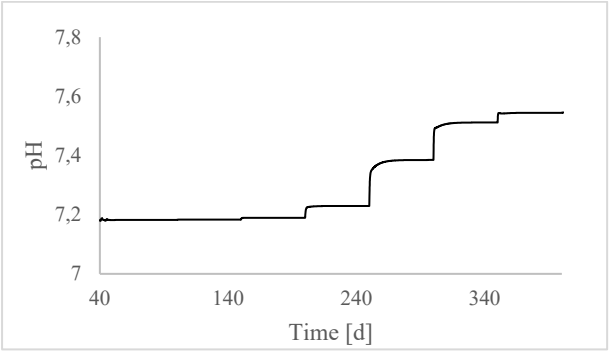

Figure 7: Response of pH in the digester to stepwise increases of the local potential (η) from -0.2 to 0.2 (step size =0.05). The bio-electrochemical process is activated at day 50.

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 increases 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 increases (Figure 8, C). In order to keep the methane content at the desired level (e.g. 85%), the rate of CO_2 input to the digester, should thus be controlled according to the rate of the reduction reaction (r3). 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.

It can be anticipated that the reduction of CO_2 from an 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 the reduction of CO_2 from both endogenous and external sources demonstrates that 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 also overcome.

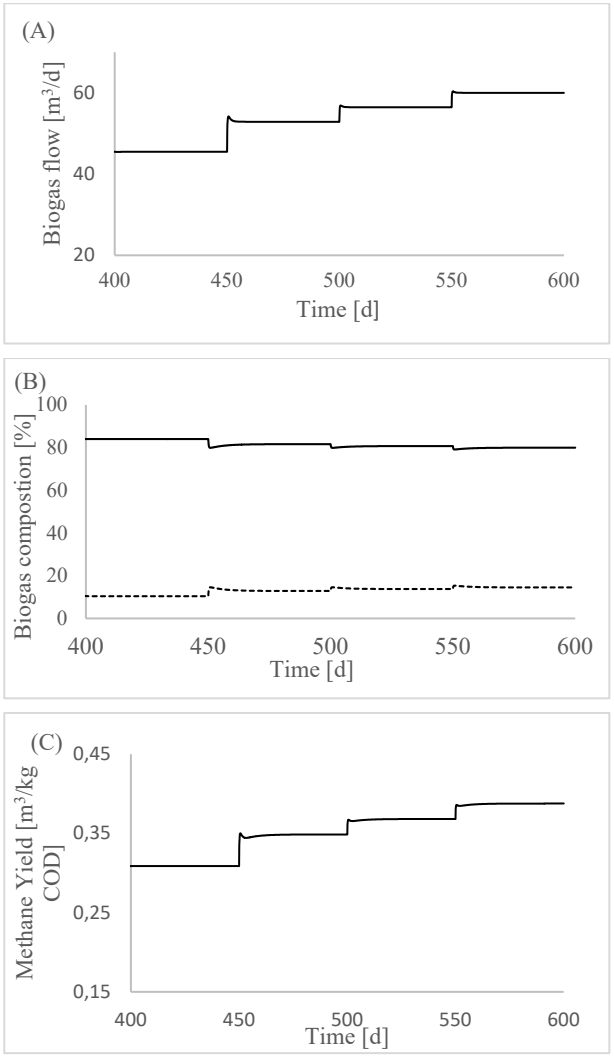

Figure 8: Biogas production rate (A), biogas composition (B) ─ CH_4 %, ··· CO_2 %, methane yield (C); after CO_2 addition form external source to the digester (AD with BES) at day 450. (η=0.200 V). The CO_2 loading rate simulated were 0.01, 0.015; and 0.02 M d^{-1}.

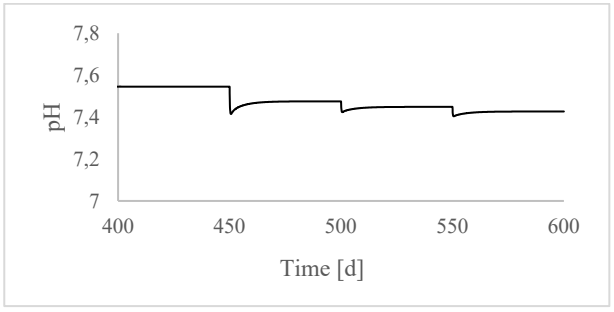

Figure 9**:** pH variation in the digester (AD with BES) after CO_2 addition form external source to the digester at day 450. (η=0.200 V). The CO_2 loading rate simulated were 0.01, 0.015, and 0.02 M·d^{-1}.

4. Conclusion

- The proposed model modification 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 simulations show that by employing BES in AD, the methane content in biogas can be increased (up to 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 concentration.
- 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 a minimum 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 constraints of the applied organic load.

References

[1] Angelidaki, I., L. Treu, P. Tsapekos, G. Luo, S. Campanaro, H. Wenzel, and P.G. Kougias, *Biogas upgrading and utilization: Current status and perspectives.* Biotechnology Advances, 2018. **36**(2): p. 452-466.

[2] Blasco-Gómez, R., P. Batlle-Vilanova, M. Villano, M.D. Balaguer, J. Colprim, and S. Puig, *On the Edge of Research and Technological Application: A Critical Review of Electromethanogenesis.* International Journal of Molecular Sciences, 2017. **18**(4): p. 874.

[3] Nelabhotla, A.B.T. and C. Dinamarca, *Electrochemically mediated CO2 reduction for bio-methane production: a review.* Reviews in Environmental Science and Bio/Technology, 2018. **17**(3): p. 531-551.

[4] Geppert, F., D. Liu, M. van Eerten-Jansen, E. Weidner, C. Buisman, and A. ter Heijne, *Bioelectrochemical Power-to-Gas: State of the Art and Future Perspectives.* Trends in Biotechnology, 2016. **34**(11): p. 879-894.

[5] Cheng, S., D. Xing, D.F. Call, and B.E. Logan, *Direct Biological Conversion of Electrical Current into Methane by Electromethanogenesis.* Environmental Science & Technology, 2009. **43**(10): p. 3953-3958.

[6] Logan, B.E., B. Hamelers, R. Rozendal, U. Schröder, J. Keller, S. Freguia, P. Aelterman, W. Verstraete, and K. Rabaey, *Microbial Fuel Cells: Methodology and Technology.* Environmental Science & Technology, 2006. **40**(17): p. 5181-5192.

[7] Kadier, A., M.S. Kalil, P. Abdeshahian, K. Chandrasekhar, A. Mohamed, N.F. Azman, W. Logroño, Y. Simayi, and A.A. Hamid, *Recent advances and emerging challenges in microbial electrolysis cells (MECs) for microbial production of hydrogen and value-added chemicals.* Renewable and Sustainable Energy Reviews, 2016. **61**: p. 501-525.

[8] Tremblay, P.-L., L.T. Angenent, and T. Zhang, *Extracellular Electron Uptake: Among Autotrophs and Mediated by Surfaces.* Trends in Biotechnology, 2017. **35**(4): p. 360-371.

[9] Recio-Garrido, D., M. Perrier, and B. Tartakovsky, *Modeling, optimization and control of bioelectrochemical systems.* Chemical Engineering Journal, 2016. **289**: p. 180-190.

[10] Batstone, D.J., J. Keller, I. Angelidaki, S.V. Kalyuzhnyi, S.G. Pavlostathis, A. Rozzi, W.T.M. Sanders, H. Siegrist, and V.A. Vavilin, *The IWA Anaerobic Digestion Model No 1 (ADM1).* Water Science and Technology, 2002. **45**(10): p. 65-73.

[11 Lauwers, J., L. Appels, I.P. Thompson, J. Degrève, J.F. Van Impe, and R. Dewil, *Mathematical modelling of anaerobic digestion of biomass and waste: Power and limitations.* Progress in Energy and Combustion Science, 2013. **39**(4): p. 383-402.

[12] Henze, M., W. Gujer, T. Mino, and M.C. van Loosdrecht, *Activated sludge models ASM1, ASM2, ASM2d and ASM3*. 2000: IWA publishing.

[13] Monod, J., *The Growth Of Bacterial Cultures.* Annual Review of Microbiology, 1949. **3**(1): p. 371-394.

[14] Bae, W. and B.E. Rittmann, *A structured model of dual-limitation kinetics.* Biotechnology and Bioengineering, 1996. **49**(6): p. 683-689.

[15] Marcus, A.K., C.I. Torres, and B.E. Rittmann, *Conduction-based modeling of the biofilm anode of a microbial fuel cell.* Biotechnology and Bioengineering, 2007. **98**(6): p. 1171-1182.

[16] Siegrist, H., D. Vogt, J.L. Garcia-Heras, and W. Gujer, *Mathematical Model for Meso- and Thermophilic Anaerobic Sewage Sludge Digestion.* Environmental Science & Technology, 2002. **36**(5): p. 1113-1123.

[17] van Leerdam, R.C., F.A.M. de Bok, M. Bonilla-Salinas, W. van Doesburg, B.P. Lomans, P.N.L. Lens, A.J.M. Stams, and A.J.H. Janssen, *Methanethiol degradation in anaerobic bioreactors at elevated pH (⩾8): Reactor performance and microbial community analysis.* Bioresource Technology, 2008. **99**(18): p. 8967-8973.