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FMH606 Master's Thesis 2022

Energy and Environmental Technology

Modelling and Simulation of an Electrochemically Mediated Biofilm Reactor Biogas Upgrading

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Course: FMH606 Master's Thesis, 2022

Title: Modeling and Simulation of an Electrochemically Mediated Biofilm Reactor for Biogas Upgrading

Number of pages: 53

Keywords: MES, ADM-1, Biogas, Biofilm, AQUASIM

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Summary:

Marzieh Domirani et al. (2021) had developed the mechanistic model with the implementation of integration of microbial electrosynthesis (MES) with anaerobic digestion (AD) technology for biogas upgrading. The model's predictions varied significantly from the real-case scenario and required proper parameter estimation. Model modification and development of a new improved ADM1 based model with the bioelectrochemical CO_2 reduction process in MES biofilm reactor was focused on this thesis to understand MES application. The model considered a single chamber MES biofilm reactor and the AD process also occurred on the same reactor. Microbially active CO_2 reduction to CH_4 was included in the MES biofilm model. The Nernst expression was incorporated as a Monod-type kinetic expression to formulate the reaction rate. For the biofilm reactor compartment (BRC) in AQUASIM, ADM1 was implemented solely as a set of differential equations (DE). Seven dynamics processes (DE) along with one equilibrium process, (input and initial condition as per ADM1) were activated on BRC along with disintegration, hydrolysis, and uptake subprocesses of AD.

The simulation was not achieved in AQUASIM due to a dynamic problem (DAZZL error) during simulation. Checking rate and input in BRC and changing the accuracy of state and program variables were recommended to rectify the error. The maximum CH4 content in upgraded biogas with optimized parameters was expected high (>87%) with efficient biogas yield. CO_2 from external sources could reduce the pH inhibitory effect in the MES-BRC reactor. Furthermore, the possible simulation of the model identifies the key process parameter and understands MES application.

Preface

This thesis is performed as partial fulfillment for the Master study program in Energy and Environmental Technology at the University of South-Eastern Norway (USN), Porsgrunn.

The purpose of this thesis is to develop an improved mechanistic, biogas upgrading model for Microbial Electrosynthesis (MES) and Anaerobic digestion (AD) integrated system to understand biofilm behavior on cathode electrodes and its influence on production rate. In addition, ADM1 model was extended to simulate the system.

I would like to express my sincere gratitude to my main supervisor Gamunu L. Samarakoon Arachchige for his guidance, support, feedback, technical advice, and motivation throughout thesis time. I am very grateful to my co-supervisors Carlos Dinamarca and Vasan Sivalingam for their involvement, suggestions, and comments.

Finally, I am truly thankful to my family, friends, and those who have supported and motivated me directly or indirectly during these times.

Porsgrunn, 18 May 2022

Saroj Neupane

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Nomenclature

Abbreviations/Expressions	Description
AD	Anaerobic Digestion
ADM1	Anaerobic Digestion Model No.1
BES	Bioelectrochemical Systems
BRC	Biofilm Reactor Compartment
CE	Coulombic Efficiency
CH_4	Methane
CHP	Combined Heat and Power Generation
CO_2	Carbon dioxide
CSTR	Continuous flow Stirred Tank Reactor
DAE	Differential Algebraic Equation
DE	Differential Equation
DET	Direct Electron Transfer
DIET	Direct Interspecies Electron Transfer
EET	Extracellular Electron Transfer
GW	Giga Watt
H_2S	Hydrogen Sulphide
HHV	Higher Heating Value
IET	Indirect Electron Transfer
IN	Inorganic Nitrogen
kWh/m^3	Kilowatt hour per cubic meter
LHV	Lower Heating value

MEC	Microbial Electrolysis Cell
MES	Microbial Electrosynthesis
PEM	Proton Electron Chamber
PSA	Pressure Swing Adsorption

1 Introduction

Anaerobic digestion is an ancient process for sludge stabilization and degradation of organic matters from wastewater treatment with the unavailability of oxygen molecules producing biogas and microbial biomass [1], [2]. Biogas can be used as an alternative source of energy that can replace fossil fuels in the future and has a direct impact on reducing greenhouse gas emissions [1], [3]. Biogas is a significant energy source delivering 5.5-7 kWh/m^3 and the energy content is determined by methane content [4]. Biogas is primarily composed of methane (50–80%) and carbon dioxide (20–50%). Other compounds like ammonia, nitrogen, mercaptans, indolum, skatolum, halogenated hydrocarbons, siloxanes, and hydrogen sulphide (H_2S) are also present in biogas but in trace amounts (1–5%) [1]. The removal of components like carbon dioxide (CO_2), H_2S, and siloxanes before direct gas application is called biogas upgrading [5].

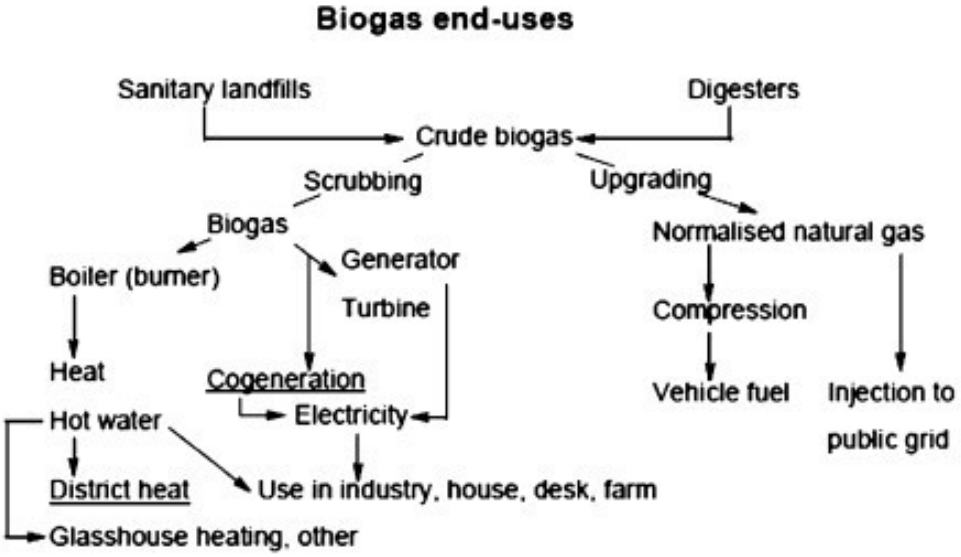

Figure 1. 1 Biogas utilization overview [1]

Figure 1. 1 shows the uses of the biogas in various applications. The crude biogas either from digesters or sanitary landfills can be used for various purposes such as the source of heat by direct burning in boilers or natural gas burners, advanced trigeneration system (Power-heat-cooling coupling), combined heat and power generation (CHP), electricity generation from gas turbine [1]. In 2018, over two-thirds of biogas produced was used to generate energy and heat. The residential area utilized 30% approximately for heating and cooking with the rest upgraded to biomethane and connect to gas networks or used as a transportation fuel. The majority of biogas produced now is used in the power sector approximately 18 GW. Germany, the United States of America, and the United kingdom are the dominant country for power generation running on biogas around the world [6]. The crude biogas has a low calorific value since it constitutes CO_2 [7]. It should be upgraded by increasing the CH_4 content to use for vehicle fuel as well as biomethane generation to add to the public grid [8]. The United States of America is the global leader in the usage of biomethane in the transportation sector [6].

Bio-electrochemical systems (BES) are innovative systems that use wastewater and bacteria as catalysts to turn chemical energy into electrical energy (and vice versa) [9]. Figure 1. 2 shows the schematic diagram of the types of BES [10]. It has been studied in a variety of experimental settings and feed sources. Electric current generation by anode was the focus in the past but recently, the biologically catalyzed cathodic reaction has attracted the attention of researchers [11]. A growing number of studies on the application of various microbial electrochemical technologies have been published in recent years [12]. CO_2 conversion catalyzed by microorganisms to methane by supplying electrical energy is new upgraded BES technology called MES [13]. The surplus energy generated by renewable electricity sources like wind, and solar can be utilized in form of electrical energy [8], [11]. MES is electricity-driven microbial technology that involves microorganisms taking electrons from the solid electrode (cathode) and utilizing electrons within their metabolism to convert CO_2 into value-added product methane (CH_4) [13]. It is an effective technology involving the chemical reaction between CO_2, proton, and electron for upgrading the biogas (reduction of CO_2 to CH_4) [14].

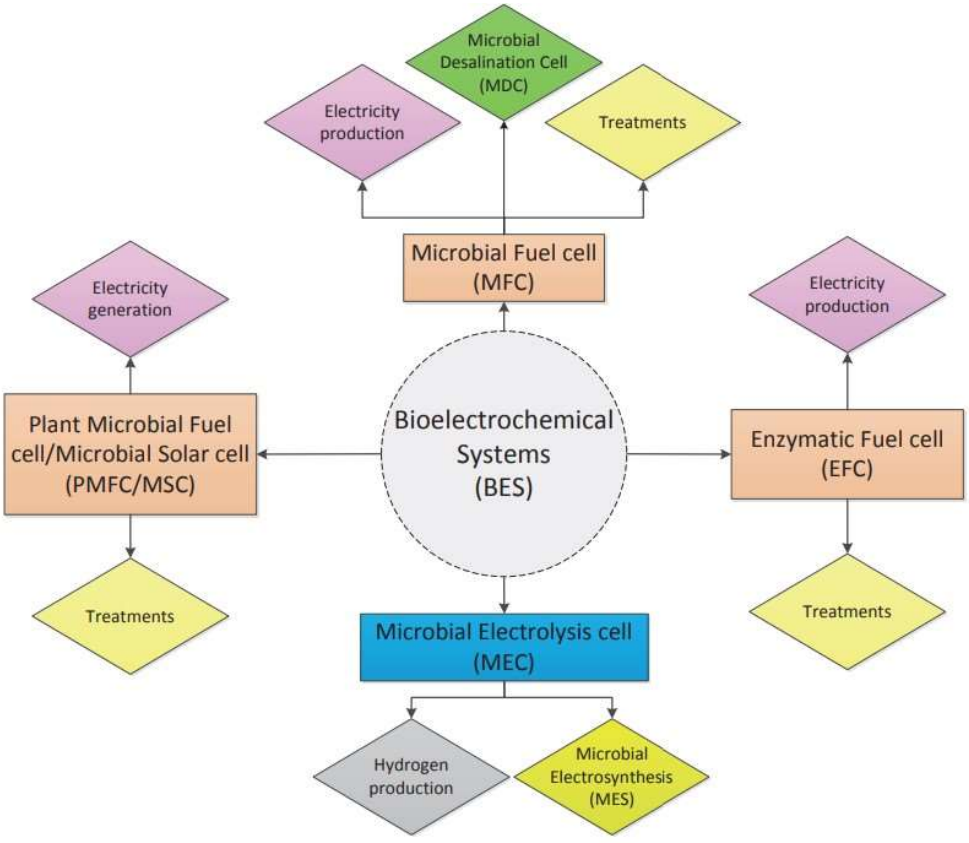

Figure 1. 2: Schematic overview of various types of BES [10]

Nelabhotla et al (2019) suggested an integrated AD-MES system for obtaining higher methane content biogas produced in anaerobic digestion by installing MES in the reject water loop. Thus, obtained biogas can be used as transport fuel [15]. Even though the technology has been validated in the lab, it is not yet mature enough to be used on a large scale. Domairani et al (2021) developed a simple mechanistic model for an electrochemically mediated biofilm reactor for biogas upgrading with MES integration with AD. The model's behavior was far from realistic, and more parameters should be added to the model. To optimize the process, further research is needed, including a better knowledge of the actual mechanisms and the development of mathematical models for both simulation and control. Since the experimental work is impractical or expensive to do in the system for different operating conditions, mathematical modelling can extrapolate such results [14] Modifying the existing mechanistic model and developing of new improved ADM-1 based model with the bioelectrochemical CO_2 reduction process in MES-BRC is emphasized to understand MES application in biogas upgrading processes.

1.1 Task description, objective, and scope

It is essential to realize the role of MES in producing value-added fuels or chemicals with the utilization of renewable electricity from wastewater. This thesis is the continuation project from last year's modeling and simulation of an electrochemically mediated biofilm reactor for biogas upgrading. Marizieh Domirani developed the mechanistic model for biogas upgrading MES technology integration with AD. The drawbacks of the existing model should be minimized and improved the model to get closer model approximations. The development of a model for biogas upgrading by converting CO_2 to CH_4 through MES technology in AD is focused in this thesis. Adoption of AQUASIM software for Anaerobic digestion model no. 1 (ADM-1) in a biofilm compartment should be carried out for the modification of the existing model. ADM-1 is the commonly used model to simulate the biogas process.

The main objectives of the tasks are:

- Implementation of ADM1 in biofilm compartment in AQUASIM tool.
- Literature review on MES modelling.
- Identify the current model limitation and work towards its improvement.
- Process simulation and identify important process parameters.

Task description along with objectives in detail are given in Appendix A.

1.2 Report structure

The first chapter begins with a quick explanation of anaerobic digestion, biogas, and its applications, and an overview of the electrochemical system (MES), followed by a detailed work description, objectives, and scope. Chapter 2 covers the literature on modeling and simulations, existing MES modeling, and existing mechanistic models. In the third chapter (Methodology), the simulation tool AQUASIM 2.1 along with the adoption of anaerobic digestion model no.1 (ADM1), modified model biofilm reactor configuration, and assumptions are described. The results of the simulations for the updated model, as well as their discussions and subsequent analysis, are provided in chapter 4. Thereafter, in Chapter 5, conclusions were drawn, and possible recommendations were offered.

2 Literature Review

The chapter reflects an overview of biogas upgrading, some adopted technologies, and MES. Furthermore, it contains a review of existing MES modeling.

2.1 Background of Biogas upgrading

Raw biogas must be cleaned and upgraded to fuel standard by an increment of calorific values. It is done by removing or reducing the CO_2 and H_2S content in biogas [16]. The energy density is increased as methane is enriched after biogas upgrading [17] [8]. One of the technologies that have generated a lot of attention in the bioenergy business is upgrading biogas to biomethane [16]. Biogas upgrading produces about 90% of the biomethane generated worldwide. About 60% of the biomethane produced today is produced by membrane separation and water scrubbing [6].

2.1.1 Physical and chemical technologies

Absorption, adsorption, and membrane separation are the most common commercial technologies for capturing carbon dioxide in the biogas. The recovery of methane from physicochemical processes can be greater than 96 percent [8]. Some of the techniques used for biogas upgrading are Pressure Swing Adsorption (PSA), Absorption, (Water scrubbing, Organic physical scrubbing, and chemical scrubbing), and Membrane. Among them, PSA, Organic physical scrubbing, and chemical (amine) scrubbing are the most widely used technologies for CO2 capture commercially[17] [7]. Table 2. 1 illustrate the comparison of different biogas upgrading technology [8]. The optimal technology depends on the plant's factors, such as the availability of low-cost heat and the cost of power are selected accordingly. It is frequently possible to reduce methane loss despite increasing energy usage costs. The methane loss, as well as methane content in amine scrubbing, is the most effective one. PSA uses somewhat less energy than water scrubbing, but more than chemical adsorption methods. Some of the newly developed technology is cryogenic upgrading, In-situ methane enrichment for biogas upgrading [17] [16].

Table 2. 1: Comparison of different pilot and commercial biogas upgrading technologies [8].

	Cryogenic	PSA	Water scrubbing	Physical scrubbing	Chemical absorption	Membrane separation
Consumption for raw biogas (kWh/Nm³)	0.76	0.23-0.30	0.25-0.3	0.2-0.3	0.05-0.15	0.18-0.20
Consumption for clean	nf	0.29-1.00	0.3-0.9	0.4	0.05-0.25	0.14-0.26

biogas (kWh/Nm3)						
Heat consumption (kWh/Nm³)	nf	None	None	<0.2	0.5-0.75	None
Heat demand (*C)	- 196			55-80	100-180	
Cost	High	Medium	Medium	Medium	High	High
CH_4 losses (%)	2	< 4	< 2	2-4	< 0.1	< 0.6
CH_4 recovery (%)	97-99	96-98	96-98	96-98	96-99	96-98
Pre-purification	Yes	Yes	Recommended	Recommended	Yes	Recommended
H_2S co-removal	Yes	Possible	Yes	Possible	Contaminant	Possible
N_2 and O_2 Co- removal	Yes	Possible	No	No	No	Partial
Operation pressure (bar)	80	3-10	4-10	4-8	Atmospheric	5-8
Pressure at outlet (bar)	8-10	4-5	7-10	1.3-7.5	4-5	4.-6

2.1.2 Biological technologies

Chemoautotrophic and photoautotrophic are two biological upgrading methods. The chemoautotrophic method relies on hydrogenotrophic methanogens that convert CO2 to CH4 by utilizing H_2 according to the reaction (R 2.1).

$$4H_2 + CO_2 \rightarrow CH_4 + H_2O \qquad \Delta G^{\circ} = -130.7\ \text{KJ/mol} \qquad \text{(R 2.1)}$$

The three types of hydrogen-assisted biogas upgrading configurations namely ex-situ, in-situ, and hybrid design are shown in Figure 2. 1. They have been characterized based on the injection of H2 to either the biogas plant or a separate upgraded biogas plant and the biogas plant's proximity to the upgraded plant. In-situ plant, the direct injection of H2 to a biogas reactor reacts to endogenous CO2 from an anaerobic digester and is converted to CH4 by autochthonous methanogenic archaea. Methane recovery in in-situ is around 99 percent under-regulated operational parameters such as PH. Ex-situ involves upgrading biogas in a separate unit with CO2 from an external source and H2 in an anaerobic reactor with a hydrogenotrophic culture that converts CO2 to CH4. A hybrid method is the combination of ex-situ and in-situ biogas upgrading technology. Ex-situ and in-situ methods have been experimentally verified, while the hybrid design is currently in development [8]. Furthermore, evaluating the energy efficiency of the biological upgrading process employing hydrogenotrophic methanogens is challenging because the technology requires H2, although consuming just a little amount of energy [16].

Photo autotrophic methods use phototrophic organisms as a catalyst like algae either in enclosed or open photobioreactors

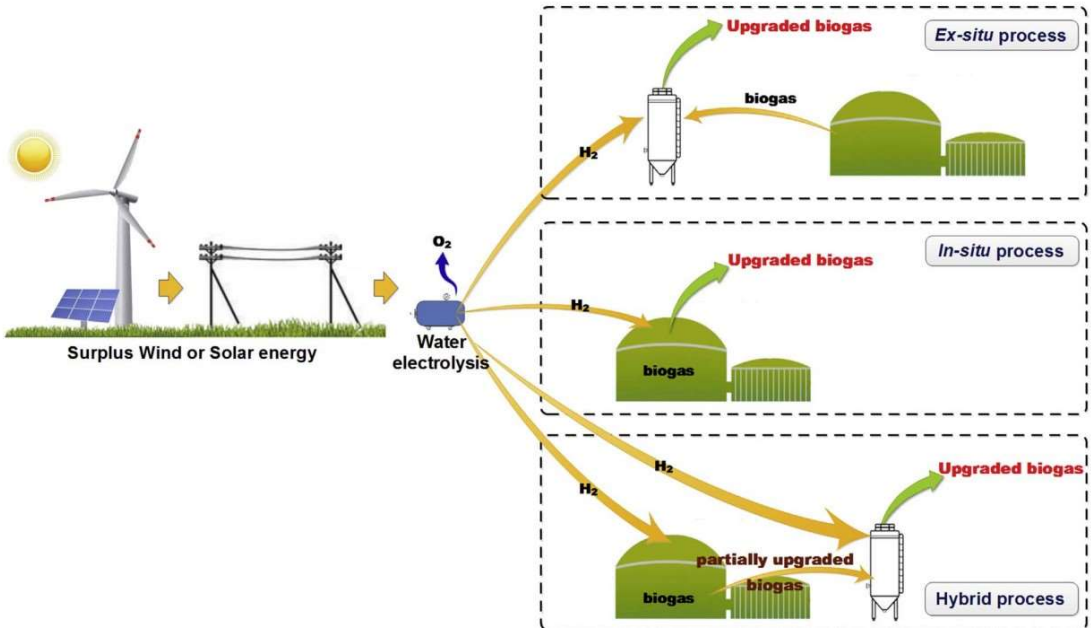

Figure 2. 1: Hydrogen methanation based biological upgrading technologies [8]

2.1.3 Microbial electrochemical methods

A growing number of research in the field of microbial electrochemical technologies have been studied in recent years [12]. The conversion of CO2 to CH4 by BES is a sustainable and cost-effective method for biogas upgrading [8]. Microbial electrochemical approaches involve a Faraday or capacitive interaction between the living microbe and the electrodes. In Faraday capacitive, the oxidation and reduction reaction occurs by pseudo-capacitive (biofilm and cells as supercapacitor get charged or uncharged) processes or microbial electrolysis process (acceleration of electrochemical reaction by microbes based on extracellular electron transfer). In capacitive interaction, the displacement of water molecules and ions from the electrode changes the electrochemical capacity, causing the electric current to flow. Based on the application, microbial electrochemical methods are represented by different terminology like Microbial fuel cells (MFC) for the generation of electricity, Microbial electrolysis cells (MEC) for H2 synthesis, Microbial Electrosynthesis (MES) for the production of value-added chemicals [18]. MES is described in detail in Chapter 2.2.

2.2 Microbial electrosynthesis (MES)

MES is the combination of biotechnology and electrochemistry [19]. It is microbial-driven technology to convert CO_2 to industrially relevant chemicals (alcohols, methane, carboxylic acids) by the electron transfer mechanism from solid-state cathode on the application of electrical energy [19]. Figure 2. 2 shows the schematic diagram of a typical MES including the involved process. It consists of two electrodes biotic cathode and an abiotic anode in two different chambers separated by a proton exchange chamber (PEM) that allows the passing proton from the anodic chamber to the cathodic chamber. Splitting of protons, electrons, and oxygen from water molecules occur in the anodic chamber. The cathodic chamber receives the proton passing through PEM and withdraws the electrons through an external circuit. The cathode is a working electrode since organic compounds like acetate, formate, methane, etc. are produced by direct and indirect electron transfer by utilizing CO_2 [20]. The CO_2 conversion process is catalyzed by microorganisms [21].

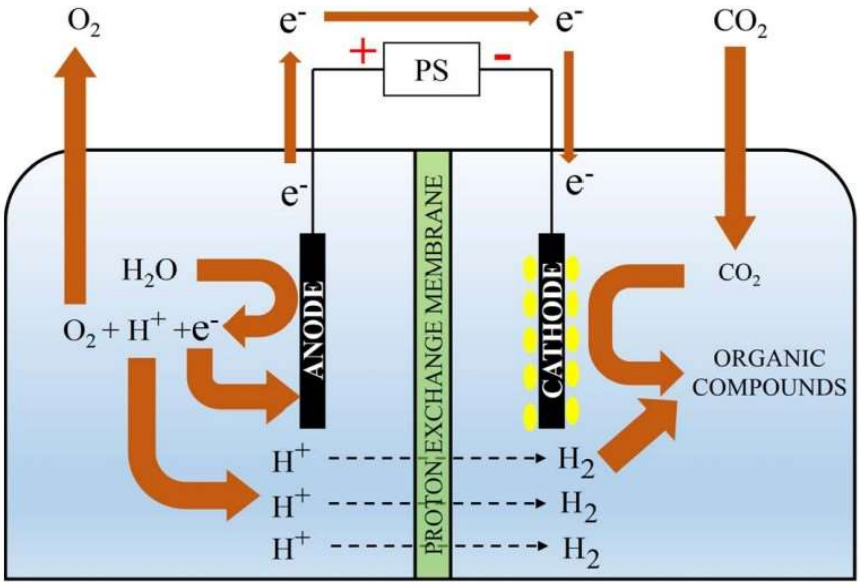

Figure 2. 2: schematic of typical MES and involved processed [20]

The chemical reactions that occurred on MES in electrodes for electrochemical CO_2 reduction to CH_4 are shown in (R 2.2), (R 2.3), (R 2.4), (R 2.5) [22]. The theoretical potential of DET (R 2.2) is less than IET (R 2.3) for CO_2 reduction to CH_4. DET is more efficient than IET as microorganisms involved in DET have higher energy gain [22]. Sporomusa ovata, Clostridium ljungdahlii, Clostridium aceticum, and Moorella thermoacetica are among the microbes that can grow on CO_2 as an electron acceptor and convert it to organic compounds via anaerobic respiration [23].

1) Cathode:

Direct Electron Transfer (DET)

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \qquad E^\circ = -0.244\ V\ vs\ NHE \qquad \text{(R 2.2)}$$

Indirect Electron Transfer (IET)

$$8H^+ + 8e^- \rightarrow 4H_2 \qquad E^\circ = -0.414\ V\ vs\ NHE \qquad \text{(R 2.3)}$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad \text{(R 2.4)}$$

2) Anode:

$$H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad E^\circ = 0.82V\ vs\ SHE \qquad \text{(R 2.5)}$$

The main product of MES has been reported as acetate [20], [13]. Later, methane was recognized as an energy-rich product [24]. The application of MES reducing CO_2 to CH_4 using renewable electricity has been shifted [22]. The conversion of CO_2 to CH_4 required anaerobic conditions because the microorganisms involved in conversion processes are generally anaerobic [25]. The integration of MES with AD for bioelectrochemical CO_2 reduction (to CH_4) for biogas yielding was implemented by Nelabhotla et al. (2019). A cathode is a working electrode where the conversion of CO_2 to CH_4 occurs either through direct electron transfer (R 2.2) or indirect electron transfer (R 2.3) (R 2.4) [15]. Electroactive microorganisms growing on biofilm using CO_2 as a carbon source, perform the DET [26]. The important factors influencing the performance of MES are the microbial catalyst, electrode materials, and reactor design [27]. Cathode potential, electron donor, operational parameters, Inoculum type, and system design are some other factors affecting the CH_4 production MES [11]. Major advantages and drawbacks of MES are highlighted in Figure 2. 3 [20]. Due to the complexity (diffusion and migration of species in fluid boundary layers, microbial growth, acid/base, and electrochemical reaction, consumption and production of species, gas/liquid mass transfer, etc) of the bioelectrochemical system in MES, only limited studies had been performed towards scaled and optimized system [28]

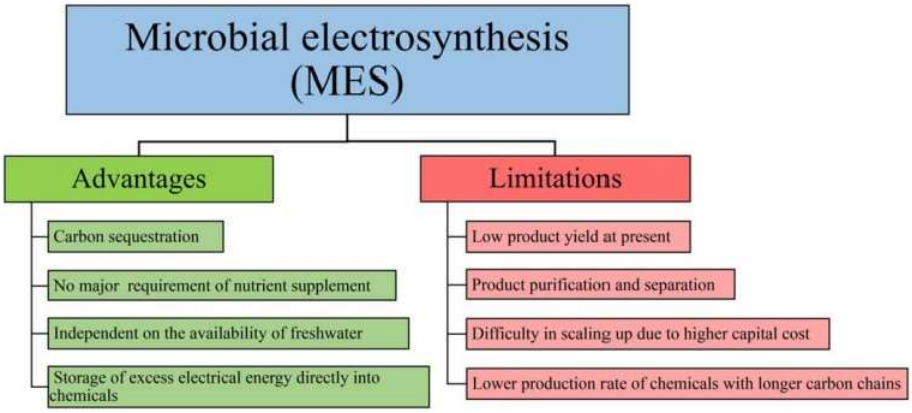

Figure 2. 3: Major advantages and drawbacks of MES [20]

2.2.1 Extracellular electron transfer (EET) mechanism

EET is the exchange process of intracellular electron of microorganism with extracellular electron donor/acceptor including (natural or artificial electrodes) across the cell membrane [13]. Several investigations on electron transfer between microorganisms and (metals and) electrodes have been conducted [29]. The extracellular electron transfer by both direct and indirect methods (intermediate production of hydrogen) was indicated by Villano et al (2010) [30] for CO_2 reduction to CH_4. For both mechanisms, cathode potential was a key process parameter [30]. In an MES, methane can be produced primarily by three methods as shown in Table 2. 2 [22], [31].

Table 2. 2: Methods of methane production in MES

SN	Methods	Process	References
1	Acetoclastic methanogenesis	Acetate utilization for methane production	[31]
2	Hydrogenotrophic methanogenesis	Methane production form Hydrogen production at cathode	[24]
3	Direct electron transfer at cathode	Avoiding mediated electron transfer	[30]

Electron is transferred from cathode surface to electrotrophs by two mechanisms either direct electron transfer (DET) or indirect electron transfer (IET) as shown in reaction (R 2.2), (R 2.3), (R 2.4). DET exists when electrodes (cathode) and bacteria (biofilm) are in direct contact for a long period [22] [20]. Losing electrons in the electrolyte is insignificant in direct electron transfer enhancing the process's faradic efficiency. Furthermore, while using a continuous mode of operation, the loss of biocatalysts is negligible.

The depending factors like production of the final product applied cathode potential, system's operation mode and microbial inoculum source are characterized for selection of electron transfer mechanism[20] [32]. It's worth highlighting that DET might be more advantageous for

continuously run systems, although both approaches could be employed effectively for batch processes. The other mode of electron transfer is mediated through numerous electron shuttles, which is mostly applicable to planktonic cells that remain in suspension in the catholyte. The electrons can also be mediated through molecules of H_2, soluble or insoluble mediators and capacitive particles [32].

2.2.2 Direct interspecies electron transfer (DIET)

In a complex AD system, many redox reactions and interspecies electron transfer exist. Electrons are transferred across methanogenic archaea through electrically conductive pili (also called nanowires) in DIET methane synthesis [33], [22]. CO_2 reduction was achieved through DIET between Geobacter metallireducens and Methanosaeta harundinacea by [22]. On MEC-AD, the conductive material, carbon cloth was found to be effective [34]. DIET's biocathode allows for high current flow at low voltage [35]. Based on theory, DIET improves AD process efficiency. The additional conductive material can be used to improve, although the mechanism is unclear [22].

2.2.3 Biocathodes

Biocathode involve in either direct or indirect electron transfer using microorganisms in the cathode compartment of MES for synthesizing the product [11],[13]. The commonly used metal cathode in MEC and MFC such as platinum was used as it displayed efficient results in past to reduce the overpotentials. But it had a negative impact on the environment, was poisoned by CO (carbon monoxide) and Sulphur, and was expensive as well. Researchers were focused on cost-effective, environment-friendly, self-generating properties, high resistivity to impurities like Sulphur with promising performance catalyst. The reactor size and flow pattern of the cathode had effects on microbes of biocathode biofilm [36]. Cathode material strongly influenced the microbial electric-driven CO_2 conversion process [27]. Figure 2. 4 shows the MES application at the biocathode for CO_2 reduction to CH_4.

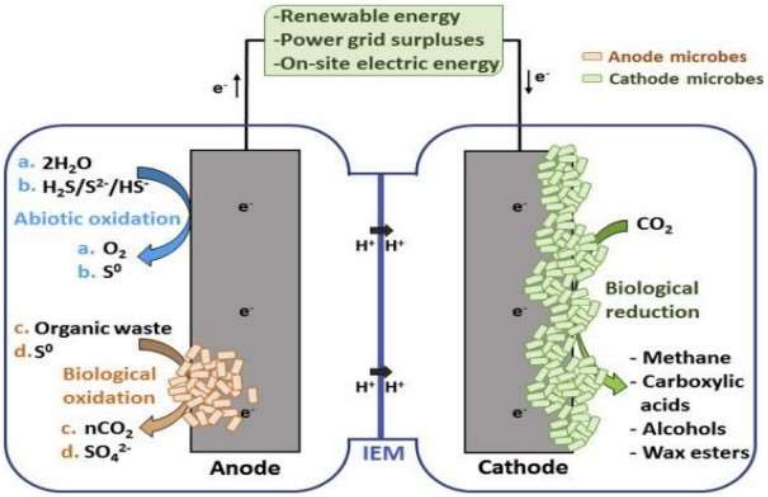

Figure 2. 4: MES application (CO_2 reduction to CH_4) at biocathode [37].

For the first time, biocathode was used in a single chamber BES to generate methane [38]. CO_2 was converted to methane at biocathode in two-chamber BES by a direct bioelectrochemical process [35]. Biofilm-based biocathodes possess a high efficiency for the reduction process due to the high chance of direct electron transfer. The major factors like electrostatic attraction, hydrogen bonding, and van der Wall interaction affect the attachment and detachment of biofilm on the electrode surface [22]. In 2010 graphite block cathode demonstrated CO_2 for the first time [39]. For the cathode as an assembly of graphite felt and stainless steel, the mixed culture microbes was preferred rather than pure one for preventing simultaneous product degradation [40]. Aryal et al (2017) [27] reviewed the cathode materials for microbial CO_2 conversion and suggested three-dimensional cathodes for increasing production efficiencies. Some of the biocathodes (biofilm formed), utilized to form methane as main product of economical cathode materials are listed on Table 2. 3.

Table 2. 3: List of biocathodes forming biofilms as methane product on economical cathode materials [22]

Cathode material	Biofilm	Voltage (V) vs SHE	Columbic efficiency (%)	Anode properties
Carbon cloth	Methanobacterium palustre	-0.5 to -0.8	96 (at -0.8V)	Graphite brush
Graphite granules	Mixed methanogenic cultures	-0.85	74	Graphite granules
Graphite granules	Mixed methanogenic cultures	+0.5 (anode)	100 (approx.)	Graphite granules with G. sulfurreduccens
Carbon fiber	Mixed methanogenic cultures	-0.65, -0.60 and -0.55	100 (approx.)	Carbon fiber brush
Graphite plate	Methanobacterium	0.7 (cell voltage)	< 100 (bog) and > 100 (AD)	Graphite plate
Graphite rod	Hydrogenotrophic methanogens	-0.7	80-85	Graphite rod
Carbon cloth (Pt coated)	Mixed cultue	0.8 (cell voltage)	Not available	Graphite brush

2.3 Review on MES Modelling

Limited modelling studies on MES and dynamics of microorganisms and operating parameters have been performed. Most of the modelling articles are focused on studying impact of operational parameter on MES's general performance. Since there is knowledge gap in MES about the microbial growth rates and microbial kinetics, it is difficult to break through the higher process performance [19]. Many previous models has focused on batch or fed-batch systems without considering physical phenomena like gas/liquid mass transfer [28]. Metabolic networks model is complex mathematical expressions, useful when investigating the pathways present in specific microorganism and MES processes as well [19].

Pinto et al (2011) developed a multi-population dynamic model of microbial electrolysis cell (MEC). The authors used MEC current and cathode efficiency to create an expression for hydrogen production rate at the chemical cathode. The metabolic activity and growth of microorganism like electricigenic, fermentative, methanogenic hydrogenophilic and methanogenic acetoclastic at anode are described by multiplicative Monod kinetics. This ordinary differential equations model assumed that the anaerobic degradation of wastewater can be described by a single hydrolysis and fermentation stage of complex organic matter conversion to acetate. Though this model is not directly developed for MES and does not consider any biocatalyst at the cathode, it can be used as a preliminary step for more comprehensive numerical models for various microbial electrochemical cell [41].

Biria et al (2015) modelled MES cathode in the reversed microbial fuel cell (R-MFC) for CO_2 reduction to acetate. The model was based on electron direct conductive in biofilm and implemented in MATLAB software package. It was purposed to predict variation in the current density, biofilm thickness, cathodic potentials, CO_2 concentration and acetate production as well. Additionally, the model determined coulombic efficiency with respect to cathode potential and CO_2 concentration. It was observed that high CO_2 concentrations with constant cathodic potential reduced coulombic efficiency, whereas a larger cathodic potential with constant CO_2 concentrations enhanced coulombic efficiency. The model was validated by comparing the results with experimental values [23].

For the first time, Gadkari et al (2019) developed robust one-dimensional dynamic model (considering kinetics on both anode and cathode) with two populations for double chamber MES converting CO_2 to carboxylic acid. The model allowed to analyse the effect of operational parameters such as initial substrate concentration at both electrodes and operational cycle time on product formation rate, substrate consumption and coulombic efficiency (CE). Their results showed that increasing initial substrate concentration generally have positive influence on product formation rates, but decreased substrate consumption and CE. Also, the reduction of operating cycle time favoured product formation rate but decreased substrate consumption and CE was concluded [42].

Samarakoon et al (2019) studied biogas upgrading model with adoption of ADM1 by adding of bio-electrochemical active CO_2 reduction to CH_4 reaction. Monod-type kinetic expression was formulated for the reaction rate, controlled by local potential. The model considered continuous flow cathode compartment only. Model's result showed that biogas methane content in AD with MES could be reached up to 85%. The affecting factor for reduction reaction were local potential and substrate concentration. It was reported that some buffering from CO2 partial pressure is required to prevent pH inhibition [43].

Abel and Clark (2020) designed a biomass-generating system that electrochemically converts CO_2 to formate, that is subsequently utilised aerobically by planktonic microbes to grow. The dynamics of CO_2, Oxygen (O_2) and biomass growth, including the effect of operational parameters on reactor's performance were studied. Mass transfer of O_2 and CO_2 were limiting factor for formate-mediated reactor. Their research showed that gas recycling was significant parameter utilizing maximum overall CO_2 usage for higher efficiency. The process design for CO_2 reduction to renewable chemical feedstocks are guided by the coupled MES model analysis [28].

Salimijazi et al (2020) developed a mathematical model for predicting highest theoretical electrical to biofuel conversion efficiency of MES process. The model was based on the use of highly engineered microbes, using H_2 (Hydrogen) oxidation and DET. The maximum conversion efficiency 52% was achieved. Their study showed that the conversion efficiency, resistivity and biofilm thickness were interdependent. Increased in the biofilm resistivity while decreasing its thickness but increased its area to achieve given efficiency was concluded [44]

Peinado et al (2021) used thermodynamic approach for predicting cellular growth and current consumption relatable to microbial metabolism through the link between microbial metabolism and intracellular mediator's electrochemical reduction. The author implemented a dynamic black-box model of a MES reactor for CO_2 conversion to acetate (further elongated to n-butyrate and n-caproate) including microbial kinetic with product inhibition and integrated chain elongation on MATLAB software. The model was bioelectrochemical reactor incorporated mass balance equations as well as electrochemical and biological kinetics with four domains (gas-liquid mass transfer compartment, cathode biofilm, bulk liquid compartment each on cathode and biofilm side). The simulation was based on mass balances, net reaction rate in biofilm and CO2 gas/liquid transfer. The model was validated and the information regarding microbial kinetics (growth, product inhibition and chain, elongation) and reactor performance (current density) in MES operating in batch, fed batch, and continuous mode was provided. Model results highlighted CO_2 dissolved concentration and its delivering method as key parameter in MES for increasing production rate. The simulation data indicated continuous mode significantly improves microbial growth in biofilm-driven reactors, allowing for denser biofilm formation and higher current densities [19].

Domirani et al (2021) developed MES mechanistic model for biogas upgrading with adoption of ADM1 in AQUASIM 2.1 software. The model considered two reactors continuous flow stirred tank reactor (CSTR) reactor and MES biofilm reactor coupled through recycle loop. The microbial CO_2 reduction to CH_4 occurred in MES biofilm reactor and it was expressed as Nernst expression by incorporating Monod type kinetic expression. The result showed that maximum 87% CH_4 content was achieved but rise in pH due to CO_2 conversion to CH_4 was also observed. A decrease in the rate of generation of bigas was also noticed[14].

Due to less information related to species interaction in mixed microbial biofilms, biofilm structure, mass transport process in MES, the models are hardly suitable for generalized study at a reactor scale [19]. Modelling studies have not yet focussed on mediated MES system or continuous operation schemes, which would be required for industrial processing [28].

3 Methodology

This chapter includes the description of simulation tool AQUASIM with the adoption of ADM1 model for model modification. It also contains the information regarding the reactor specification and configuration along with operating conditions, model parameters used or modified, assumptions for the simulations and planned simulation outline as well.

3.1 AD-MES-BRC Reactor

The reactor configuration of model is as shown in Figure 3. 1. It consists of single chamber AD-MES biofilm reactor. The sludge from a wastewater treatment plant is injected directly to the reactor. The volume of the reactor is 28 m^3 operated under the mesophilic condition (35°C). The biogas production processes with anaerobic digestion occurred on the reactor till 50 days then MES biofilm reactor is activated for the biogas upgrading by converting byproduct CO_2 into CH_4. The power source for MES is surplus or unutilized energy from renewable source like wind energy, solar energy etc.

For MES process, cathode is working electrode where electroactive microbes growing on biofilms are attached to cathode's surface, perform reaction of direct electron extracellular transfer as shown in (R 2.2) [26]. The microbes involved is electroactive methanogens grow on cathode surface. These microbes utilize CO2 as carbon source for their growth. Electron from cathode is taken by the bacteria to CO2. The anode supplies proton (H^+) in biofilm.

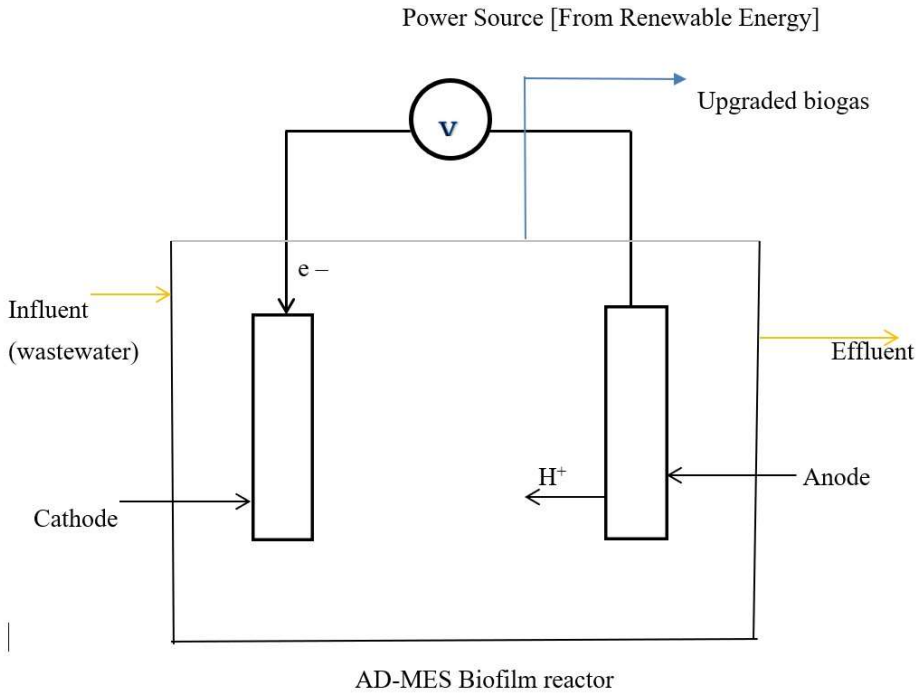

Figure 3. 1: Schematic diagram representing AD – MES biofilm reactor

3.2 Simulation tool and model.

The simulation tool, Version 2.1 of AQUASIM software with the adaption of anaerobic digestion model no. 1 (ADM1) is used for model modification of the existing mechanistic model.

3.2.1 AQUASIM

AQUASIM is designed for aquatic systems that are crucial in environmental research. The tool performs simulations, sensitivity analysis, and parameter estimations using measured data for the model defined by the user. Systems Sciences department of Swiss Federal Institute of Environmental Science and Technology (EAWAG) introduced the first version 1.0 in the years 1991-1994 in computer. From then now, it has been updating the program and introduced the latest 2.17 version in 2022. It is applicable for research use and freely available to public [45].

The four subsystems (variables, processes, compartment, and links) are mutually dependent for defining the model as shown in Figure 3. 2. Variables with numeric value define processes, compartments as well as links. Program's user is free to active any set of state variables and transformation processes in compartment. It enables the user to update the model structure and parameter values easily. It also allows user for the model modification, identification of new key process parameters [17].

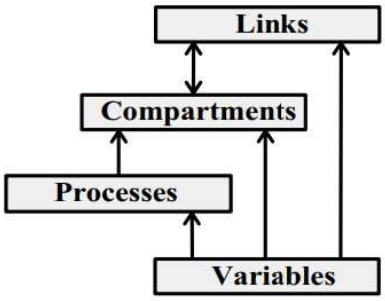

Figure 3. 2: Main components of model structure

3.2.2 Anaerobic digestion model no. 1 (ADM1)

It is structured model based on anerobic digestion process, proposed by IWA Task Group for Mathematical Modelling of Anaerobic digestion processes in 2002. Many research and studies have been explored on biogas process modeling and even established the new model from ADM1 as common basis. The application of this model leads to the growth of a broad understanding of anaerobic processes, that increases the use of sustainable wastewater treatment for energy production processes.

The two important conversion processes involved in anaerobic digestion are biochemical and physico-chemical. Biochemical reaction and physico-chemical reactions are implemented as irreversible and reversible respectively in ADM1.

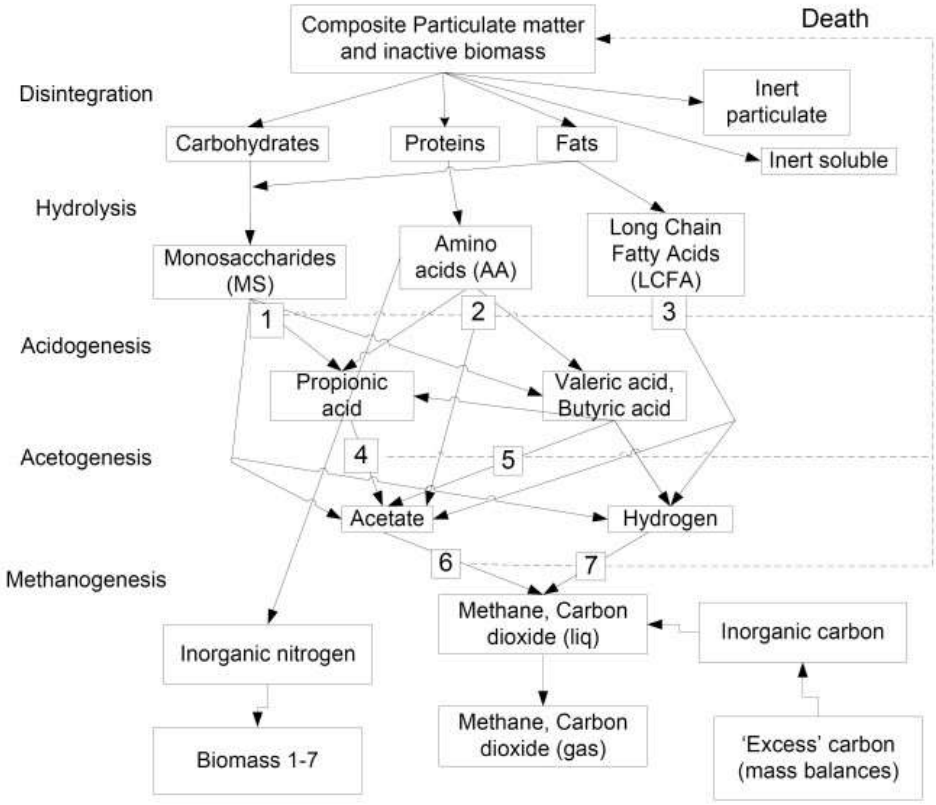

Figure 3. 3: The reaction paths described in ADM1, with the following microbial groups: (1) Sugar degraders, (2) amino acid degraders, (3) LCFA degraders, (4) propionic acid degraders, (5) butyric and valeric acid degraders, (6) acetoclastic methanogens, and (7) hydrogenotrophic methanogens [14], [46].

Biochemical processes in model divided into disintegration, hydrolysis, acidogenesis, acetogenesis and methanogenesis steps as shown in Figure 3. 3. The first step disintegration is non-biological that converts the complex organic matter into inerts (particulate and soluble), particulate carbohydrates, proteins, and lipids. The next step i.e., hydrolysis of those particulates carbohydrates, proteins and lipids to monosaccharides, amino acids, and long chain fatty acids (LCFA) respectively. Both the steps disintegration and hydrolysis are extracellular solubilization steps and their processes are expressed by first order kinetics. Monosaccharides and amino acids undergo fermentation and degrades to organic acids (Propionic acid, Valeric acid and butyric acid), hydrogen and carbon dioxide. Acetogens converts organic acids to acetate, hydrogen, and carbon dioxide by utilizing LCFA, butyrate and valerate (one group), and propionate. Thus, formed acetate and hydrogen is finally converted to methane and carbon dioxide by acetoclastic methanogens and hydrogenotrophic methanogens respectively. The processes disintegration and hydrolysis are extracellular. The other processes acidogenesis, acetogenesis and methanogenesis are intracellular processes and substrate uptake rates (resulting biomass growth and decay) is based on Monod type substrate kinetics equations [46]. The biochemical kinetics describes 19 sub-processes for 24 (12 each soluble and particulate) compounds in details by authors.

Physico-chemical process are not biologically mediated and include ion association/dissociation (acid-base reaction) and liquid-gas transfer as relative kinetic rates but exclude precipitation in ADM1. Acid- base equilibrium are described by algebraic equation set

or additional kinetic rates. There are 26 dynamic state concentration variables, 19 biochemical kinetic processes, 3 gas-liquid transfer kinetic processes and 8 implicit algebraic variables as per liquid vessel as a differential and algebraic equation (DAE). There are 32 dynamics state concentration variables and additional 6 acid-base kinetic processes per vessel as a differential equation set. Batstone et al has described in details about the related information regarding the model [3].

3.2.3 Model development Approach

One-dimensional system has been assumed in this model to describe biofilm metabolism. The external sources (electricity from renewable source) supply the electron current. The assumptions for AD-MES-BRC modelling are listed below:

1. Biofilm surface area (A) is constant at stated values for the simulation.
2. Only electroactive methanogens (hydrogenotrophic methanogens) are present on cathode surface. Neglecting other parallel bio-electrochemical and biochemical reactions on the cathode surfaces.
3. The reactor compartment is a continuous flow.
4. The Inhibition describing the growth of electroactive microbial growth due to extreme pH conditions (I_{ph}) is neglected.
5. Only the reaction at cathode is considered.
6. Reduction of CO_2 to CH_4 is catalyzed by electroactive methanogens and assumed direct electron transfer process from solid cathode.
7. The reaction at anode side is not considered. Anode supplies an unrestricted proton flow to the cathode side.

3.3 Bio-electrochemical kinetics equation and model parameter

Bio-electrochemical active CO_2 reduction to CH_4 reaction associated with extracellular electron transfer (EET) are defined in ADM1. Only hydrogenotrophic methanogens (biofilm) at cathode involving only direct electron transfer (DET) as stated in (R 2.2) is considered for CO_2 reduction to CH_4 [43]. For microbial growth, kinetics on all substrates in ADM1 is described by Monod equation. Hydrogenotrophic methanogens take electrons from the cathode (final donor) directly and transfer them to CO_2 as final acceptor. The bacteria utilize CO_2 as carbon source for their growth. The rate of reaction for both soluble substrates (electron donor i.e., solid cathode and electron acceptor i.e., CO_2) can be defined in equation (3.1). as the rate is restricted by availability of electron donor and acceptor [43], [47].

$$\rho = k_m^{\circ} X \frac{S_a}{K_a + S_a} \frac{S_d}{K_d + S_d} \tag{3.1}$$

where,

ρ = Growth kinetic rate

k_m° = Maximum uptake rate

X = Concentration of microorganisms

S_a and S_d = Concentration of two limiting-substrate (acceptor and donor respectively)

K_a and K_d = Half-maximum rate concentration of S_a and S_d respectively

$\frac{S_a}{K_a+S_a}$ = Monod expression for CO_2 (i.e., soluble)

$\frac{S_d}{K_d+S_d}$ = Monod expression for solid cathode without concentration

The electrical-potential gradient permits electrons to pass through the solid cathode. And the Nernst equation is used to relate the soluble concertation of the donor component to the cathodic potential [48]. The overall rate equation can be expressed in equation (3.2).

$$\rho = k^{\circ}_{m\_eet}\, X_{eet} \left(\frac{S_{CO2}}{K_{S\_CO2} + S_{CO2}}\right)\left(\frac{1}{1 + exp\left[-\frac{F}{RT}\eta\right]}\right) \tag{3.2}$$

Where $k^{\circ}_{m\_eet}$ and X_{eet} are maximum uptake rate and concentrations respectively for electrically active microorganisms. S_{CO2} and K_{S_CO2} are concentration and half maximum rate concentration of CO_2. *F* is Faraday constant, *R* is ideal gas constant, *T* is absolute temperature and η is local potential in reference to E_{KA}. The potential at which the substrate consumption rate reaches half of the maximal rate (analogous to K_d) is called E_{KA}. Local potential (η) is defined by equation (3.3).

$$\eta = E_{KA} - E_{cathode} \tag{3.3}$$

Where E_{KA} is taken as reference potential (E ≡ 0) then equation (3.3) become $\eta = -E_{cathode}$.

The term $\left(\frac{1}{1+exp\left[-\frac{F}{RT}\eta\right]}\right)$ is referred as Nernst-Monod term as it is derived from Monod equation. Microbial kinetics control the electron consumption is the main assumption. The Nernst-Monod term illustrates that when the local potential increases, the rate of substrate uptake increases until a constant maximum level is reached.

Samarakoon et al (2019) derived equation (3.4) from equation (3.3) by incorporating two inhibitors describing microbial growth I_{ph} (due to extreme pH conditions) and *I_NH_limit* (due to limitation of soluble inorganic nitrogen) [43].

$$= k^{\circ}_{m\_eet}\, X_{eet} \left(\frac{S_{CO2}}{K_{S\_CO2} + S_{CO2}}\right)\left(\frac{1}{1 + exp\left[-\frac{F}{RT}\eta\right]}\right) I_{ph} I\_NH\_limit \tag{3.4}$$

The process ($dec_{X_{eet}}$) is the first order decay process of electrically active microorganisms (X_{eet}) in MES-BRC is shown in equation (3.5).

$$dec_{X_{eet}} = X_{eet}\, k_{dec\_eet} \tag{3.5}$$

Where X_{eet} and k_{dec_eet} are concentration and first-order decay rate of electrically active microorganisms.

Equations (3.4) and (3.5) are the reaction rate for bio-electrochemical process (i.e, MES in our model)

The model parameters used for bioelectrochemical processes in MES-BRC are listed on Table 3. 1. The diffusion coefficients through pure water of components were taken from Cunningham (2001) and the values are 0.6 times the corresponding diffusion coefficients. For those whose value is not available is taken as 0.004147 m^2/d [49]. The diffusivity of cation, anion, H^+, OH^- are selected as 0.1 m^2/d.

Table 3. 1: Model parameters used for bioelectrochemical processes in MES-biofilm reactor compartment

Parameters	**Description**	**Unit**	**Value**	**References**
D_S_co2	Diffusivity of Carbon dioxide	m^2d^{-1}	0.0001273	[50]
D_S_ch4	Diffusivity of Methane	m^2d^{-1}	0.0000988	[50]
D_S_IN_nh4_ion	Diffusivity of Total Inorganic nitrogen/ionic Ammonium	m^2d^{-1}	0.0001306	[50]
D_S_hco3_ion	Diffusivity of bicarbonate	m^2d^{-1}	0.0000782	[50]
D_S_bu_ion_bu	Diffusivity of Butyrate/ Ionic Butyrate	m^2d^{-1}	0.0000577	[50]
D_S_h2	Diffusivity of elemental Hydrogen	m^2d^{-1}	0.0002984	[50]
D_S_pro_ion_pro	Diffusivity of propionate/ Ionic propionate	m^2d^{-1}	0.0000703	[50]
D_S_ac_ion_ac	Diffusivity of acetate/ Ionic acetate	m^2d^{-1}	0.0000802	[50]
D_S_h_ion	Diffusivity of hydrogen ion	m^2d^{-1}	0.1000000	Assumed
D_S_oh_ion	Diffusivity of hydroxide ion	m^2d^{-1}	0.1000000	Assumed
D_S_an	Diffusivity of anions	m^2d^{-1}	0.1000000	Assumed
D_S_cat	Diffusivity of cations	m^2d^{-1}	0.1000000	Assumed
D_S_su	Diffusivity of monosaccharides (Glucose)	m^2d^{-1}	0.0000444	[50]

D_S_aa	Diffusivity of amino acids (Valine)	m^2d^{-1}	0.000055	[50]
D_S_OS	Diffusivity of free ammonia/ Ionic Valerate/ total valerate/ Long chain fatty acid/ Soluble inert COD	m^2d^{-1}	0.004147	[51]
D_X	Diffusivity of biomass	m^2d^{-1}	0.0000001	[52]
rho	Biomass density	Kg COD m^{-3}	25	[52]
Ks_co2	Half saturation constant for CO2 reduction	M	0.06	[43]
T	Temperature	K	308	[43]
F	Faraday's constant	C mol-e^{-1}	94485	[43]
R	Ideal gas constant	J mol^{-1} K^{-1}	8.314	[43]
km_eet	Maximum electron uptake rate	Kmol-e Kg COD Xd^{-1}	4.5	[43]
Y_eet	Yield of bio-electroactive biomass	Kg COD-X/Kmol-e	0.48	[43]
Kdec_x_eet	First order decay rate of X_eet	d^{-1}	0.02	[43]
I_NH_limit	Microbial growth inhibition due to limitation of inorganic nitrogen		reported formula	[3]
X_eet	Concentration of electroactive biomass	Kg COD m^{-3}	m.d	
S_co2	concentration of dissolved CO2	M	m.d	
uf	Growth velocity of biofilm	md^{-1}	m.d	
LL	Biofilm Layer thickness	m	0.0001	[52]
LF	Biofilm thickness	m	m.d	

η	Local Potential	V	Change	
A	Cathode biofilm Area	m^2	Change	

3.4 Model Modification

The current existing model is modified by the removal of Continuous-flow stirred-tank reactor (CSTR) resulting single chamber AD-MES biofilm reactor as shown in figure 3.4.

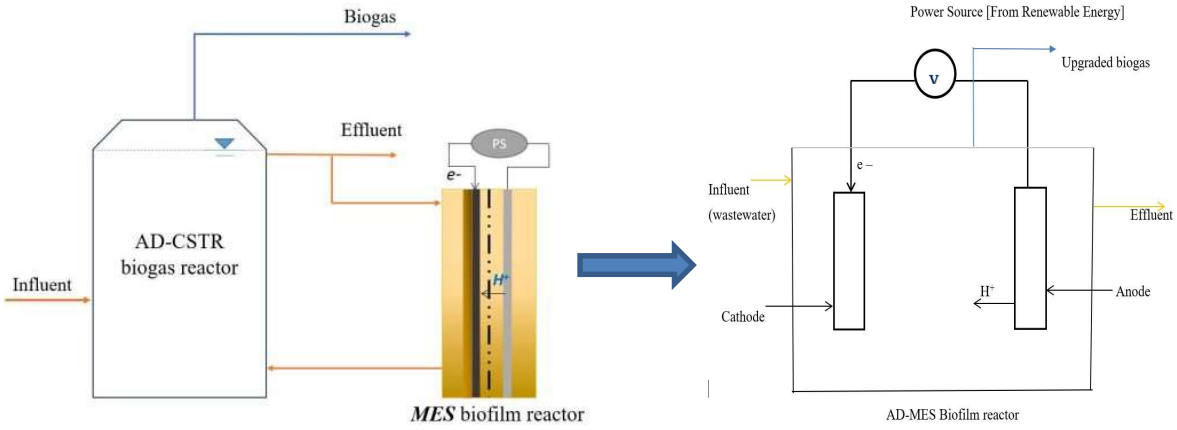

Figure 3. 4: Reactor configurations of existing and modified model

The ADM1 model must be built exclusively as a set of differential equations to use the AQUASIM Biofilm Reactor Compartment without numerical mistakes. The conversion of program structure from DAE to DE for biofilm reactor compartment is explained clearly by botheju at el [51]. Under DE implementation, six dynamic process, one equilibrium expression and conversion of acid base concentration variables to dynamics volume state variables are introduced in the model [51].

3.4.1 Variables in ADM1

To implement the dynamic processes in BRC the associated variable to the rate is changed to dynamic and volume type. The first eight variables (1 to 8) as shown in Table 3. 2 is changed to dynamic and volume type and 24 variables are activated on MES-BRC.

Table 3. 2: Modified variables added to MES-BRC

Newly added activated Variables

Modified and added

SN	Name	Description	Unit	Type
1	S_ac_ion	Ionic acetate	Kg COD*m-3	Dynamic & volume
2	S_bu_ion	Ionic butyrate	Kg COD*m-3	Dynamic & volume
3	S_h_ion	Hydrogen Ion	M	Dynamic & volume
4	S_nh3	Free ammonia	M	Dynamic & volume
5	S_nh4_ion	ionic ammonium	M	Dynamic & volume
6	S_oh_ion	Hydroxide ion	M	Dynamic & volume
7	S_pro_ion	Ionic propionate	Kg COD*m-3	Dynamic & volume
8	S_va_ion	Ionic Valerate	Kg COD*m-3	Dynamic & volume
9	S_cat	Cation	M	Dynamic & volume
10	S_an	elemental anions	M	Dynamic & volume
11	S_aa	Amino acids	Kg COD*m-3	Dynamic & volume
12	S_ac	Total acetate	Kg COD*m-3	Dynamic & volume
13	S_bu	Total butyrate	Kg COD*m-3	Dynamic & volume
14	S_fa	Long chain Fatty acid	Kg COD*m-3	Dynamic & volume
15	S_h2	Elemental Hydrogen	Kg COD*m-3	Dynamic & volume
16	S_hco3_ion	Bicarbonate	M	Dynamic & volume
17	S_I	Soluble inert COD	Kg COD*m-3	Dynamic & volume
18	S_pro	Total propionate	Kg COD*m-3	Dynamic & volume
19	S_su	Monosaccharides	Kg COD*m-3	Dynamic & volume
20	S_va	Total valerate	Kg COD*m-3	Dynamic & volume
21	X_ch	Particulates carbohydrates	Kg COD*m-3	Dynamic & volume
22	X_I	Particulates inert	Kg COD*m-3	Dynamic & volume
23	X_li	Lipids	Kg COD*m-3	Dynamic & volume
24	X_pr	Proteins	Kg COD*m-3	Dynamic & volume

3.4.2 Processes in ADM1

Seven dynamics processes along with one equilibrium process were activated on BRC along with disintegration, hydrolysis, and uptake subprocesses of anaerobic digestion. The dynamic charge balance equation is modified with rate expression as per Botheju et al (2010) [53].

$$R = K_{A/B\,,CO2}\left\{S_{H+} - 0.5\left(f + \sqrt{f^2 + 4k_w}\right)\right\} \tag{3.6}$$

Where,

$f = S_{HCO3^-} + S_{An^-} - S_{NH4^+} + {}^{S_{Ac^-}}/_{64} + {}^{S_{Pr^-}}/_{112} + {}^{S_{Bu^-}}/_{160} + {}^{S_{va^-}}/_{208}$

k_w = water dissociation constant (Ka_h2o in ADM1 model)

$K_{\frac{A}{B},CO2}$ = Kinetic constant for CO_2-HCO_3 acid-base reaction

As per Botheju et al [49], the rate equation for dynamic process (Inorganic Carbon) under DE implementation is given by equation (3.7).

$$R_{A/B\,CO2} = K_{A/B\,CO2}\{S_{HCO3^-}\,.S_{H+} - K_{a,CO2}\,.S_{CO2}\} \tag{3.7}$$

Similarly, For Inorganic Nitrogen

$$R_{A/B\,NH4} = K_{A/B}\left\{S_{NH3}\,.S_{H+} - K_{a,NH4}\,.S_{NH_4^+}\right\} \tag{3.8}$$

For acetate

$$R_{A/B\,ac} = K_{A/B}\left\{S_{ac\_ion}\,.S_{H+} - K_{a,ac}\,.S_{ac}\right\} \tag{3.9}$$

For butyrate

$$R_{A/B\,bu} = K_{A/B}\left\{S_{bu\_ion}\,.S_{H+} - K_{a,bu}\,.S_{bu}\right\} \tag{3.10}$$

For proponiate

$$R_{A/B\,pro} = K_{A/B}\left\{S_{pro\_ion}\,.S_{H+} - K_{a,pr}\,.S_{pro}\right\} \tag{3.11}$$

For valerate

$$R_{A/B\,va} = K_{A/B}\left\{S_{va\_ion}\,.S_{H+} - K_{a,va}\,.S_{va}\right\} \tag{3.12}$$

Where $K_{A/B}$ is kinetic constant for acid-base reaction and $K_{a,CO2}$, $K_{a,NH4}$, $K_{a,ac}$, $K_{a,bu}$, $K_{a,pr}$, $K_{a,va}$ are acetate acidity constant of carbon dioxide, ammonium ion, acetate, butyrate, propionate and valerate respectively.

All the new processes added on MES-BRC in comparison to existing model in AQUASIM along with its kinetic rate are listed in Table 3. 3. All the related nomenclatures are described by ADM1 [3]. The bioelectrochemical processes of MES as mentioned by equation (3.4) and (3.5) along with decay processes of biomass are activated on the reactor.

Table 3. 3: Processes added to the MES-BRC for modified model.

SN	Processes	Description	Rate
1	dyn_charge	dynamic charge balance	kAB*(S_h_ion-0.5*(f+sqrt(f^2+4*Ka_h2o)))
2	dyn_ac	acetate dynamic	kAB*((S_ac_ion*S_h_ion)-(Ka_ac*S_ac))
3	dyn_bu	bu dynamic	kAB*((S_bu_ion*S_h_ion)-(Ka_bu*S_bu))
4	dyn_E_IN	NH4/NH3 dynamic	kAB*((S_nh3*S_h_ion)-(Ka_nh4*S_nh4_ion))
5	dyn_prop	dynamic	kAB*((S_pro_ion*S_h_ion)-(Ka_pro*S_pro))
6	dyn_va	va dynamic	kAB*((S_va_ion*S_h_ion)-(Ka_va*S_va))
7	dyn_acid_base_co2	Pseudo acid-base equilibria for CO_2-HCO_3 acid-base pair	kAB_co2*(S_hco3_ion*S_h_ion-Ka_co2*S_co2)
8	equilib_IN_bal	inorganic nitrogen balance	S_nh3+S_nh4_ion-S_IN = 0
9	disintegration	first order disintegration of complex particulates	kdis*X_c
10	hyd_ch	first order hydrolysis of carbohydrates	khyd_ch*X_ch
11	hyd_li	first order hydrolysis of Lipids	khyd_li*X_li
12	hyd_pr	first order hydrolysis of proteins	khyd_pr*X_pr
13	uptake_aa	uptake of amino acids	km_aa*X_aa*S_aa/(Ks_aa+S_aa)*I_ph_bac*I_NH_limit
14	uptake_ac	uptake of acetate	km_ac*X_ac*S_ac/(Ks_ac+S_ac)*I_ph_ac*I_nh3_ac*I_NH_limit
15	uptake_bu	uptake of butyrate	km_c4*X_c4*S_bu/(Ks_c4+S_bu)*1/(1+S_va/S_bu)*I_ph_bac*I_h2_c4*I_NH_limit
16	uptake_h2	uptake of h2	km_h2*X_h2*S_h2/(Ks_h2+S_h2)*I_ph_h2*I_NH_limit
17	uptake_fa	uptake of propionate	km_fa*X_fa*S_fa/(Ks_fa+S_fa)*I_ph_bac*I_h2_fa*I_NH_limit
18	uptear	uptake of propionate	km_pro*X_pro*S_pro/(Ks_pro+S_pro)*I_ph_bac*I_h2_pro*I_NH_limit
19	uptake_su	uptake of monosaccharides	km_su*X_su*S_su/(Ks_su+S_su)*I_ph_bac*I_NH_limit
20	uptake_va	uptake of valerate	km_c4*X_c4*S_va/(Ks_c4+S_va)*1/(1+S_bu/S_va)*I_ph_bac*I_h2_c4*I_NH_limit

3.4.3 Compartment

The BRC properties are defined in AQUASIM dialog box as shown in appendix. The reactor type was set to be confined (Reactor with a constant total volume for biofilm and bulk fluid). 36 variables, 29 processes are activated on the reactor. The initial condition and water inflow input was taken with reference to the reactor compartment from ADM1 model. The details are shown in appendix c.

The properties of (13 no.) particulates variables are defined by density (rho) and boundary layer resistance whereas for (23 no.) dissolved variables case only boundary layer resistance. The boundary layer resistance is given by eqn.

$$Boundary\ layer\ resistance = \frac{Molecular\ Boundary\ Layer\ (LL)}{Diffusivity\ of\ variables} \qquad (3.13)$$

The reactor volume was set to 28 m^3. The properties of pore volume were defined as liquid phase only (No suspended solids in pore water). Rigid biofilm matrix was set (No diffusive mass transport of solids). The biofilm area was described by A variables (5 m^2). For the porosity of biofilm keeping constant, the rate porosity was set to zero. The surface detachment of solids from biofilm was set to be global velocity (detachment of solids from biofilm as per their relative occurrence at surface of biofilm) and was set initially as 0.63 times biofilm's growth velocity as purposed by Botheju et al (2008) [51].

3.5 Simulation outline

Simulation was planned to run in single chamber AD-MES-BRC undergoing AD processes only without activating bio-electrochemical process for 50 days. The feed's composition of influent is defined in Table 3. 4. The expected sludge feed flow from wastewater plant for AD reactors only is illustrated in Figure 3. 5 The feed load is gradually increased after days 16 and 37. After 50 days, The influent flow rate to AD-MES biofilm reactor is constant corresponding to the value 5. 31 m^3/d.

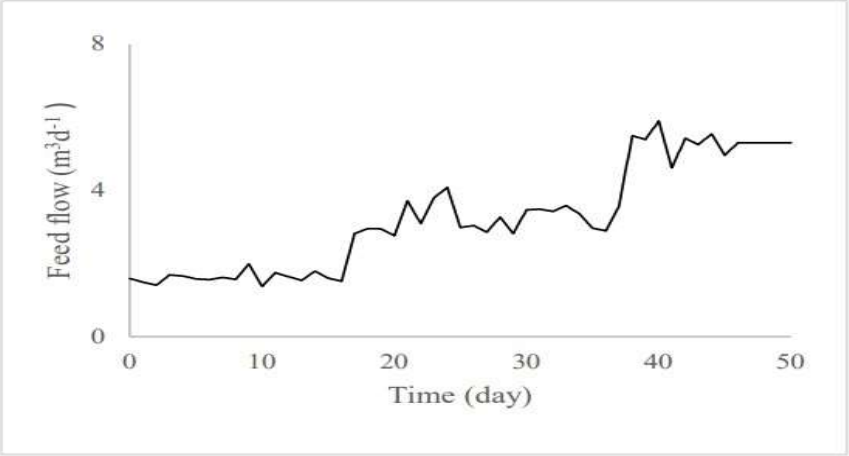

Figure 3. 5: Sludge feed flow to the reactor [14], [43].

Table 3. 4: Influent feed composition to AD-MES-BRC [14], [43].

Compounds	Concentrations (*Kg COD/m^3*)
Amino acids	4.2
Fatty acids	6.3
Monosaccharides	2.8
Complex particulates	10.0
Total	23.3

Table 3. 5: Checking parameters for simulation in AD-MES-biofilm reactor. shows the parameters to be checked by changing its values to understand the processes and identify the key process parameters for modified model.

Table 3. 5: Checking parameters for simulation in AD-MES-biofilm reactor.

Parameters	Description	Unit	Changes for simulation
A	Cathode biofilm Area	m^2	5, 10,15 stepwise
η	Local Potential	V	from -0.2 to +0.2 (Stepwise=0.05)
	Detachment velocity	md^{-1}	0.2, 0.4, 0.6* biofilm growth velocity (uf)
Qin_new	Influent Flow rate	m^3d^{-1}	Change the value of 5.31 (stepwise ±1)
input_CO2	External CO_2 flow	Md^{-1}	Changes
LL	Initial biofilm layer thickness	m	0.001, 0.002, 0.003 (stepwise ±0.001)
D_S_h_ion	Diffusivities of hydrogen ion	m^2d^{-1}	0.001, 0.01, 0.1
D_S_oh_ion	Diffusivities of hydroxide ion	m^2d^{-1}	0.001, 0.01, 0.1
D_S_an	Diffusivities of anion	m^2d^{-1}	0.0005, 0.001, 0.005
D_S_cat	Diffusivities of cation	m^2d^{-1}	0.0005, 0.001, 0.005

4 Results and Discussion

Figure 4. 1 shows the production rate of biogas and its composition (CH_4 and CO_2 content) under conventional condition before the activation of MES-BRC reactor [14], [54]. This result is taken as baseline results. The biogas production rate increases as the feed rate is increased for first 50 days. The feed rate changes at day 16 and day 37. The graph illustrates the biogas flow is approximately 45m^3/d at day 50 with approximately 65% methane (CH_4) content.

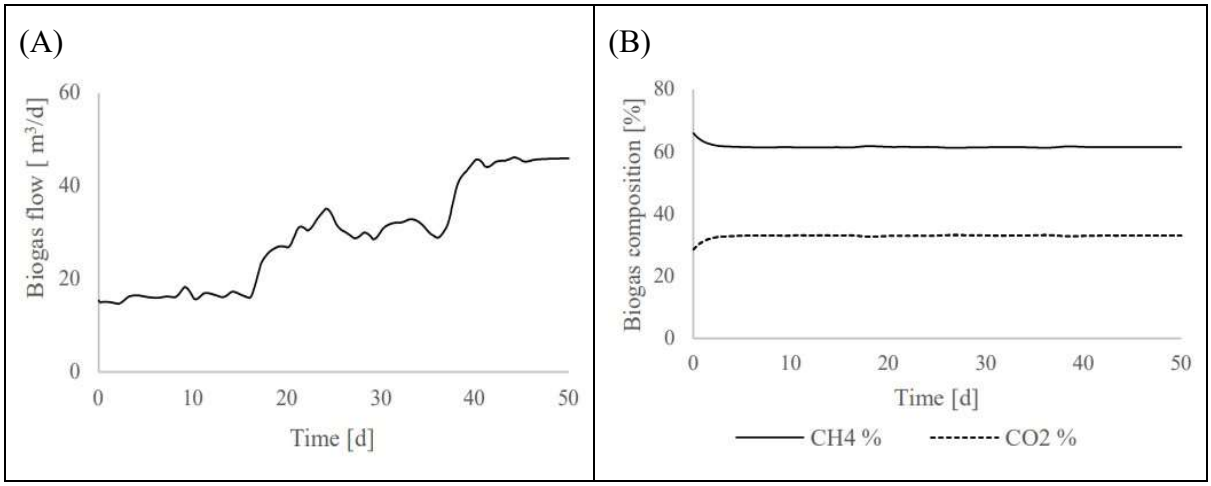

Figure 4. 1: Biogas production rate (A) and its composition (B) from the AD-MES-BRC reactor (but without activation of MES-BRC).

4.1 Simulation result

The bioelectrochemical process was activated at day 50. The model was modified as mentioned on Chapter 3.4. Simulation on AQUASIM couldn't be achieved for the modified model.

4.1.1 Error during the initialization

After the modification of the existing model by defining the parameters for the system on AQUASIM, the problem during the initialization was occurred. The log file of AQUASIM for the error is shown in Figure 4. 2. The content of the log file provided some important information for the error [55]. The error was FORMVAR numerical problem: illegal value in variable BifFlux for the calculation of consistent initial condition. It was discussed among the supervisors as well, but it took long time to understand the error. Later, it was rectified by checking all the seven variables (State, Program, Constant, Real list, Variable list, Formula and Probe) and corrected it accordingly as per the outline of model. The error during the initialization was solved.

Figure 4. 2: Log file display of problem during the initialization

4.1.2 Error during dynamic simulation

The problem during the dynamic simulation was occurred. It was a major problem recognized by the integration algorithm that cannot be solved by the reduction of integration step size and order [55]. The log file of AQUASIM for the error (with information) during the dynamic simulation is shown in Figure 4. 3. It visualized the occurrence of DASSL error that is most difficult to interpret [55]. Figure 4. 4 shows the DASSL error message that the error test failed repeatedly. Removal of the error was attempted several times by changing the values of diffusivity coefficient of soluble components and biomass, biofilm Area, flow rate, Molecular

Boundary layer, Volume of reactor, Local potential etc. But simulation was not achieved during the period.

aquasim - Notepad

File Edit View

```
AQUASIM Version 2.1f (win/mtc) - Log File

*******************************************************************************

Start of Session:  05/02/2022  13:50:24


Calculation of consistent initial condition
-------------------------------------------

   Number of codiagonals considered:                  1000
   Time of initial condition:                         0

   05/02/2022 13:50:54  Start of calculation
   05/02/2022 13:50:54  End of calculation

   Number of equations:                               885
   Number of integers needed for calculation:         885
   Number of reals needed for calculation:            1573530

   Number of steps taken:                             0
   Number of evaluations of the jacobian:             0


Dynamic calculation
-------------------

   Number of codiagonals considered:                  1000
   Maximum internal step size:                        10

   05/02/2022 13:50:56  Start of calculation
   05/02/2022 13:50:56  Integration at time 0
   DASSL--  AT T = 0 AND STEPSIZE H = 9.2465407e-026
   DASSL--  THE ERROR TEST FAILED REPEATEDLY
   DASSL--  OR ABS(H) = HMIN.
   05/02/2022 13:50:57  End of calculation

   *** Calculation stopped due to numerical problems ***

   Number of equations:                               885
   Number of integers needed for calculation:         905
   Number of reals needed for calculation:            791230

   Current integration time:                          0
   Current step size:                                 0
   Current order of integration:                      0
   Number of steps taken:                             0
   Number of function evaluations:                    2
   Number of evaluations of the jacobian:             1
   Number of error test failures:                     1
   Number of convergence test failures:               0
```

Figure 4. 3: log file display of Problem during dynamic simulations

4.1.3 Possible causes and solution for the problem (DASSL ERROR)

The possible causes for the error in AQUASIM could be failure to fulfill error test criterion while the algorithm repeatedly tried to reduce the integration step size. Finding the source of the numerical problem was challenging. At the point in time (i.e., T=0) where the DASSL error occurred, an input or rate could be discontinuous [55].

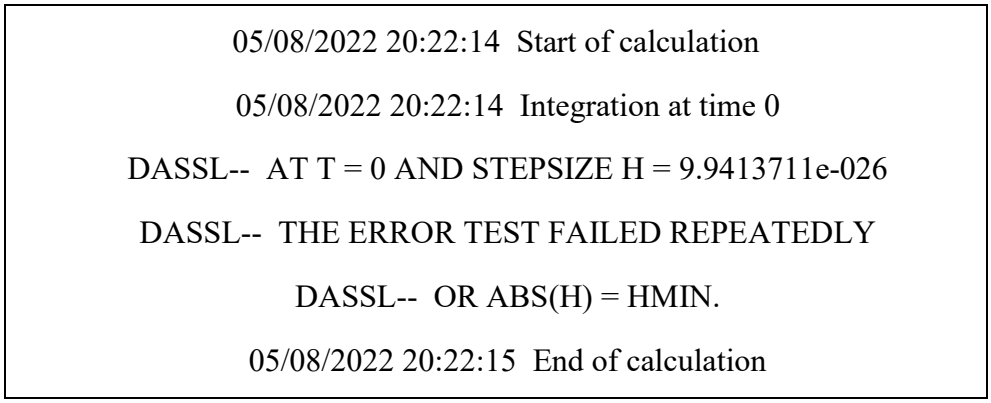

Figure 4. 4: DASSL error message

Since I had changed the values of different variables (diffusion coefficient, flow rate, molecular Boundary layer, volume of reactor, local potential) along with the discussion with supervisors for the solving the error so that simulation could be achieved. But for every different case, error occurred at same point of time (T=0). It means a rate, or an input is discontinuous at that time. The rate and input in the compartment should be checked. Time series plot of important system variables can also give an idea about the strange behavior at that point of time. The possible solution of the problem may be achieved by changing the accuracy of state and program variables. The implementation of varying the integration accuracy of state and program variables is covered in section 3.5 of the AQUASIM 2.0 user manual [55].

4.2 Expected result and discussion

The methane content in biogas could increases in AD-MES-BRC reactor when influent flow rate increases [14]. Higher influent flow rate resulting the higher production rate of CO_2 and conversion of these dissolved CO_2 (available in the reactor) to CH_4 could be reason behind it. The maximum CH_4 content in upgraded biogas in this model with optimized parameters (Local potential, cathode surface area, Influent flow rate) were expected more (greater than 87%) than the previous model. But the local potential might not have significant effect on the conversion process as dissolved CO_2 limits the rate [14].

According to a prior experimental investigation by Nelabhotla et al (2019), MES could enhance CH_4 production by 10-15% when compared to a reactor without MES operation [15]. It is expected that biogas production rate could be increased along with higher CH_4 yield with the implementation of optimized parameters (Cathode biofilm area, Initial biofilm layer thickness,

detachment velocity, influent flow rate). The relationship of these parameters for increasing CH_4 rate should be highlighted.

Increment in cathode area (attached biofilm) causes higher electron flow for the growth of biofilm [56], [22], [57]. The expected result could illustrate that increasing area always don't have positive impact on CO_2 reduction process until it reached the proper biofilm area for the conversion process. Even with a large cathode surface area, increasing biofilm thickness can be a limiting factor in reaching higher CH4 content. Thicker biofilms provide higher resistance to substrate transfer within the biofilm. It could be highlighted that the need of keeping a consistent biofilm thickness throughout the processes.

The conversion process (CO_2 to CH_4) at higher influent flow rate could result in elevated pH in the reactor and it might reduce CH_4 production rate. To avoid inhibition, it is critical to maintain a correct pH. The increased pH can cause ammonium ions to deprotonate, producing free ammonia. Acetoclastic methanogens, responsible for acetate decomposition to methane are completely inhibited by free ammonia. In AD, this acetate pathway produces a significant amount of biogas. The reduction of inhibition is possible since free ammonia can oxide at anode for actual MES application as per Sivalingam et al (2020) [58]. CO_2 from external source could also reduce the pH inhibitory effect in the MES-BRC reactor [43].

The CO_2 reduction rate can also be altered by the diffusion coefficient. It could be expected that the diffusivity constant (substrates) will influence CH_4 production at lower local potentials [14].The addition of CO_2 coming from external sources could increase overall biogas production and rise methane content (compared to conventional AD). The biogas production could be increased by simultaneous biomethanation from the reduction of CO_2 from both external and endogenous sources beyond organic loading limitation [43].

4.3 Importance of results

The simulation results take one step ahead in implementation of MES integrated with AD for biogas upgrading. Since the physicochemical processes (acid-based equilibrium and charge balance) in MES-BRC reactor is considered in the biofilm-model, it may determine the required pH and IN (Inorganic Nitrogen) concentrations for efficient biological processes. Thus, the current model can be used to investigate the impact of physicochemical processes on biofilm formation.

The modelling results provide the outline for the lab experiments in micro and macro level for understanding MES and implementing it commercially. The simulations provide information regarding the critical process parameters for monitoring and controlling electrochemically mediated biofilm reactor involving in biogas upgrading.

4.4 Limitation of Previous model

Marzieh et al. [14] developed the mechanistic model for MES integrated in AD for biogas upgrading by conversion of CO_2 to CH_4 . The following limitations of the model were identified:

1. The model was simplified by considering only bio electrochemical CO2 reduction process and decays of microbial in MES-BRC.

2. All the microbe's processes like growth were not considered on cathodic biofilm as the model considered only one electroactive microorganism (X_{eet}).
3. Charge balance and acid-base equilibrium are not explored in biofilm modelling (MES-BRC), even though they are critical for pH and inorganic nitrogen. The effect by those processes to the biofilm growth couldn't be studied further.
4. The current model provided only qualitative understanding of the use of MES-BRC for CO_2 to CH_4 reduction. Thus, the model's predictions may differ significantly from real-world scenarios.

4.5 Future works

There is indeed much investigation to be carried out under this topic especially in the new model developed to understand the real scenario behind the application of MES. It will be preferable to first investigate the simulation error of the current developed model (Modified on ADM1) in AQUASIM software. Further investigation on the effect of process parameter (like Cathode potential, biofilm thickness, flow rate, Cathode biofilm area, detachment velocity etc.) on the MES process is recommended to identify the key processes parameter for monitoring and controlling the biofilm MES process. More use of computational modeling of MES for developing new model to explore knowledge on process optimization and system understanding. In addition, experiment at lab must be done for understanding of the microbial growth rates and microbial kinetics.

5 Conclusion

The simulation of the modified model was not achieved in AQUASIM as dynamic problem (DAZZL error) occurred during the simulation process. The possible causes of the error could be failure to fulfill error test criterion while the algorithm repeatedly tried to reduce the integration step size. Since the error is most complicated to find the cause, solving the error (identifying the origin of the problem) is most challenging task. Checking rate and input in biofilm reactor compartment (BRC) and changing the accuracy of state and program variables were recommended to rectify the error. The maximum CH4 content in upgraded biogas with optimised parameters is expected higher (>87%) than previous model with efficient biogas yield. It could be expected that the diffusivity constant (substrates) will influence CH4 production at lower local potentials. At higher influent flow rate, the conversion process (CO_2 to CH_4) could result in elevated pH in the reactor and reduce CH_4 production rate as well. The pH inhibitory effect in the MES-BRC reactor can be reduced by adding CO_2 from external sources. The influence of diffusion coefficient of substrate could be expected for CH_4 production at lower local potentials. Furthermore, the possible simulation of the model could estimate or identifies the key process parameter, validate the model based on real case scenario to understand MES application.

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Appendices

Appendix A Master Thesis Description (Signed copy)

Appendix B Additional variables in ADM1 for previous model

Appendix C Total input added to new purposed ADM1 based model in AQUASIM

Appendix D Biofilm Reactor compartment properties in AQUASIM (New model)

Appendix A Master Thesis Description (Signed copy)

University of South-Eastern Norway

Faculty of Technology, Natural Sciences and Maritime Sciences, Campus Porsgrunn

FMH606 Master's Thesis

Title: Modelling & simulation of an electrochemically mediated biofilm reactor for biogas upgrading

USN supervisor: Gamunu Samarakoon, Vasan Sivalingam, Carlos Dinamarca

External partner:

Task background:
Anaerobic digestion (AD) process is a highly economical and efficient method to produce methane (CH_4) from organic matter. It produces biogas containing 50 -70 % CH_4 and 50-30 % CO_2 (carbon dioxide), meaning that the typical biogas has a low calorific value, which limits its use, e.g., as a transport fuel. Therefore, biogas is upgraded by removing CO_2 to increase the calorific value. Recently, Microbial Electrosynthesis (MES) for biogas upgrading by converting CO_2 to CH_4 has received attention. MES refers to the chemical synthesis of desired products through chemical reactions catalysed by microorganisms and powered by electrical energy.

The proposed thesis intends to develop a mechanistic model that contributes to the integration of MES in AD to reduce CO_2 to CH_4. The experimental work requires large efforts to test a wide variety of operational conditions, while mathematical modelling can extrapolate on such results and enhance our understanding of MES. We have developed a mechanistic model that contributes to this application. The tasks of this work include identification of the limitation of the current model and improving it further.

Task description:
The commonly accepted anaerobic digestion model no.1 (ADM-1) as a common platform will be used for the model modification. The main task is to improve the said mechanistic model to understand the biofilm growth on electrode(s), particularly on the cathode and its limitation to achieve desired production rates. The modelling work is carried out on the simulation tool, AQUASIM 2.1. The task includes the following activities,

- Review existing literature on MES modelling.
- Identify the current model limitation and work towards its improvement.
- Model modification (*also* includes identification of key process parameters for monitoring and controlling and, incorporating them with model parameters).
- Run different simulation cases to assist the lab experiments conducted at USN campus Porsgrunn.

This work is a part of USN's BEC-AD strategic project.

Student category: EET or PT students

Is the task suitable for online students (not present at the campus)? Yes

Practical arrangements: The simulation tool, AQUASIM will be provided. The modified model and original ADM -1 are also available.

Supervision:
As a general rule, the student is entitled to 15-20 hours of supervision. This includes necessary time for the supervisor to prepare for supervision meetings (reading material to be discussed, etc).

Signatures:

Supervisor (date and signature): Gamuuu Samarakoon 26-01-2022

Student (write clearly in all capitalized letters): SAROJ NEUPANE

Student (date and signature): 01/30/2022

Appendix B Additional variables in ADM1 for previous model

New variables added to ADM1 model in previous model in AQUASIM.

SN	Terminology	Symbol used	Types	Unit	Expression
1	Concentration of electron up taking organism	X_eet	State Variable	kg COD m-3	Type: Dynamic Volume
2	Biofilm Thickness	LF	Program	m	Reference to biofilm thickness
3	Growth velocity of biofilm	uf	Program		Reference to velocity of biofilm
4	Biofilm Area	A	Constant	m2	
5	Faraday's Constant	F	Constant	Cmol-e-1	96485
6	Kinetic constant for acid base reaction	KAB	Constant	d-1	1.00E+14
7	decay rate for degarding organisms	kdec_X_eet	Constant	d-1	0.02
8	Maximum Electrons Uptake rate	Km_eet	Constant	kgmol-e kg COD X.d-1	4.5
9	Half saturation constant for CO2 reduction	Ks_co2	Constant	M	0.06
10	Recycle	Recycle	Constant		0.6
11	Local Potential	nue_dyn	Real List	V	Std Deviation : Global
12	Diffusivity of S_Ch4	D_S_ch4	Formula	m2/d	0.000164653
13	Diffusivity of S_co2	D_S_co2	Formula	m2/d	0.000212171
14	Diffusivity of S_hco3_ion	D_S_hco3_ion	Formula	m2/d	0.000130397
15	Diffusivity of S_IN	D_S_IN	Formula	m2/d	0.000217696
16	Diffusivity of Particles	D_X	Formula	m2/d	1.00E-07
17	Volume Fraction of X_eet	esp_X_eet	Formula		X_eet/rho
18	Microbial growth inhibiton due to PH	I_ph	Formula		if pH<I_ph_h2_ul then exp(-3*((pH-I_ph_h2_ul)/(I_ph_h2_ul-I_ph_h2_ll))^2) else 1 endif
19	Biofilm Length	LL	Formula	m	0.0001

20	Maximum growth rate of X_eet	mue_X_eet	Formula	d-1	km_eet*X_eet*S_co2/(Ks_co2+S_co2)*I_ph_bac*I_NH_limit*Y_eet
21	Constant Local Potential	nue	Formula	Local Potential	0.2
22	Inflow	Qin_new	Formula	m^3/d	5.31
23	Recirculation flow	Qrec	Formula	m^3/d	Recycle*Qout_CSTR
24	Rate of EET	rate_eet	Formula		km_eet*X_eet*(S_co2/(Ks_co2+S_co2))*(1/(1+exp(-F*nue/R*T)))*I_ph*I_NH_limit
25	Density	rho	Formula	kg COD m-3	25
26	Yield of Bioelectriactive biomass uptake of electron	Y_eet	Formula	kg cOD. X/Kmol-e	0.48*1
27	Outflow from CSTR	Qout_CSTR	Probe	m^3/d	

Appendix C Total input added to new purposed ADM1 based model in AQUASIM

SN	Variables	Zone	Intial Condition	SN	Variables	Zone	Intial Condition
1	LF	Biofilm matrix	0.001	30	S_va	bulk volume	0.0117245
2	X_eet	biofilm matrix	0.1*rho	31	S_aa	Pore water	0.0056389
3	X_aa	biofilm matrix	0.1*rho	32	S_ac	Pore water	0.0492285
4	X_ac	biofilm matrix	0.1*rho	33	S_an	Pore water	0.0035714
5	X_c	biofilm matrix	0.1*rho	34	S_bu	Pore water	0.0148542
6	X_c4	biofilm matrix	0.1*rho	35	S_cat	Pore water	0.04
7	X_ch	biofilm matrix	0.1*rho	36	S_ch4	Pore water	0.0542531
8	X_fa	biofilm matrix	0.1*rho	37	S_co2	Pore water	0.0078805
9	X_h2	biofilm matrix	0.1*rho	38	S_fa	Pore water	0.109845
10	X_l	biofilm matrix	0.1*rho	39	S_h2	Pore water	0.000000255
11	X_li	biofilm matrix	0.1*rho	40	S_hco3_ion	Pore water	0.0671877
12	X_pr	biofilm matrix	0.1*rho	41	S_h_ion	Pore water	5.79E-08
13	X_pro	biofilm matrix	0.1*rho	42	S_I	Pore water	1.67072
14	X_su	biofilm matrix	0.1*rho	43	S_IN	Pore water	0.0324451
15	S_aa	bulk volume	0.0056389	44	S_pro	Pore water	0.0179604
16	S_ac	bulk volume	0.0492285	45	S_su	Pore water	0.0126099
17	S_an	bulk volume	0.0035714	46	S_va	Pore water	0.0117245
18	S_bu	bulk volume	0.0148542	47	X_aa	bulk volume	0.356823
19	S_cat	bulk volume	0.04	48	X_ac	bulk volume	0.470399
20	S_ch4	bulk volume	0.0542531	49	X_c	bulk volume	1.04006
21	S_co2	bulk volume	0.0078805	50	X_c4	bulk volume	0.144876
22	S_fa	bulk volume	0.109845	51	X_ch	bulk volume	0.0103452
23	S_h2	bulk volume	0.000000255	52	X_fa	bulk volume	0.390669
24	S_hco3_ion	bulk volume	0.0671877	53	X_h2	bulk volume	0.223732
25	S_h_ion	bulk volume	5.79E-08	54	X_l	bulk volume	19.9414
26	S_I	bulk volume	1.67072	55	X_li	bulk volume	0.0155177
27	S_IN	bulk volume	0.0324451	56	X_pr	bulk volume	0.0103452
28	S_pro	bulk volume	0.0179604	57	X_pro	bulk volume	0.0609795
29	S_su	bulk volume	0.0126099	58	X_su	bulk volume	0.354125

Appendix D Biofilm Reactor compartment properties in AQUASIM (New model)