

CO₂ abatement and renewable chemicals production by using microbial electrosynthesis within the framework of CO₂ biorefineries

Carla Gil Piñeira

Abstract – As CO₂ emissions continue to be on the rise and the consequent effects of global warming are not to be overlooked, atmospheric CO₂ levels urgently need to be decreased. To tackle this, microbial electrosynthesis, which relies on microorganisms as catalysts for the anoxic reduction of organic compounds, CO₂ in this study, at the cathode at the expense of oxidizing reactions performed at the anode, is presented as a promising approach. Due to the oxidized nature of this carbon molecule, external energy must be supplied for the reaction to be thermodynamically favorable, enabling to store the excess power from non-peak hours in the form of chemical carbon bonds. Altogether, microbial electrosynthesis aims to decrease surplus CO₂ while producing renewable-based and value-added compounds.

Index Terms – bioelectrochemical systems (BES), carbon capture and utilisation (CCU), CO₂ valorisation, microbial electrosynthesis (MES), negative emissions biotechnologies (NEB).

I. INTRODUCTION

The combustion of fossil fuels for the fulfillment of human activities, which mainly are transportation, electricity generation, and heat obtention (1) is causing carbon dioxide (CO₂) levels to increase. As a matter of fact, measurements from the Manua Loa observatory in Hawaii showed that atmospheric CO₂ levels exceeded 417 parts per milion (ppm) in 2021, while pre-industrial levels were 278 ppm (2).

Although carbon dioxide is not a toxic compound it absorbs infrared energy coming from the Earth and emits it back to the planet. Consequently, increased atmospheric levels of CO₂ cause global warming and ocean acidity, being the latter the result of its conversion to bicarbonate (3). Nevertheless, many other worrisome consequences derive, such as ice melting, unleashing sea level rises and floods, alterations on rainfalls, droughts, and changes in biodiversity. Additionally, fossil fuels are consumed at a faster rate than their regeneration time, causing the dwindling of fossil supplies (4).

All things considered, alternative means of meeting the current energy demand while

lowering the CO₂ emissions and not causing the feedstock to be exhausted is a must. This may be the definitive call for renewable energies, which albeit being on the spotlight for greener energy obtention, display an implementation rate which is still far from the ideal in the transportation, electricity and heat sectors. As a result, humanity is on a transition period in which it still relies on fossil raw materials to meet global needs (4).

All in all, while the world is in this transitory period from high to low CO₂ emissions, a contingency plan must be implemented to deal with the generated CO₂ emissions. This is when carbon capture technologies come into play, which mitigate the greenhouse effect by capturing CO₂. Carbon dioxide is currently captured and stored underseas and in forests (5), but alternatively, carbon capture and utilisation (CCU) go a step further, reducing the captured carbon dioxide and generating value-added compounds. Therefore, microbial electrosynthesis (MES), a CCU strategy, will be the topic at issue in this review, which does not only capture CO₂ but converts it into a variety of renewable-based products, reducing CO₂ levels and displacing the exploitation of fossil reserves for both energy and materials obtention.

II. MICROBIAL ELECTROSYNTHESIS

According to the Science Advice for Policy by European Activities, CCU has been defined as “those technologies that use CO₂ as a feedstock and convert it into value added products such as fuels, chemicals or building materials” (6). More specifically, MES employs anaerobic electrophilic microbes as biocatalysts at the cathode for the sequestration of CO₂ and its concurrent transformation into multi-carbon compounds (7).

Currently, the most mature production scheme is that of acetate synthesis, but many other compounds can be produced, such as methane, methanol, butyrate, butanol, caproic acid, hexanol and bioplastics (8). MES systems, therefore, can produce biofuels and biomaterials while reducing CO₂ and simultaneously displacing the consumption of non-renewable feedstocks for its obtention.

Hence, the general configuration consists of two chambers separated by a proton exchange membrane (PEM) as displayed in Figure 1. On the anodic chamber, hydrolysis reactions take place, generating stoichiometric amounts of protons and electrons. While protons diffuse to the cathodic chamber through the selective membrane, electrons pass through an external circuit. Consequently, on the cathodic chamber, an electrophilic microbiome takes up electrons and reduce CO₂, which acts as an electron sink.

As illustrated in Figure 1, the reaction performed on the cathode is not thermodynamically favorable, so that the electric circuit must be reinforced. As a result, MES can be used to store the excess power generated during non-peak hours in the form of chemical carbon bonds (7).

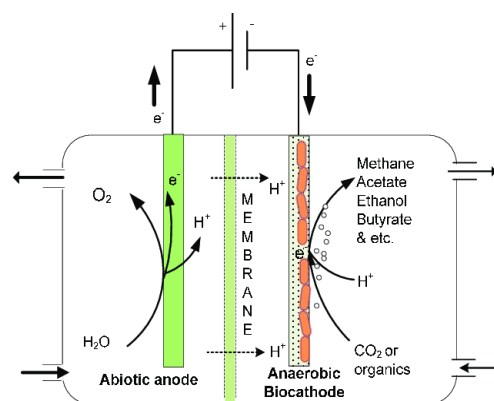


Figure 1: Illustration of a microbial electrosynthesis chamber (9). $E'^{\circ} = 0.82$ V for H₂O/O₂ and $E'^{\circ} = -0.28$ V for HCO₃⁻/acetate (10).

The use of MES to produce organic chemicals by reducing CO₂ has several advantages: (i) the technology does not require arable land, rendering it free from the debate of food vs. fuel, and sometimes nor even freshwater, (ii) it does not require the addition of high quality nutrients, since it normally uses wastewater, (iii) it displays higher efficiency than that of biological photosynthetic biofuel obtention and, moreover, it requires an easier downstream processing (see section VI) and (iv) it does not pose any threat regarding the emission of toxic compounds (7).

A. ANODIC ELECTRODES

Anodic electrodes are mainly made of carbonaceous materials (graphite sticks, carbon cloths and fibers) (10). However, if a current density of 5 mA·cm⁻² is to be driven, an overpotential¹ of more than 600 mV is required for carbon electrodes to display intrinsic OER², thus, a high energy input is required. It is for this reason that approaches such as the mixture of small amounts of noble catalysts (Ni or Pt) on non-noble electrodes, the utilisation of photo-anodes and the use of alternative reactions for

¹ Difference between the thermodynamically determined potential and the experimentally observed potential of half reaction (9).

² Limiting step for the water splitting process.

electron production (10) can yield better results.

To start, the use of solar energy can be employed to achieve the so-called artificial photosynthesis. More specifically, photo-electrochemical (PEC) systems consist in the production of oxygen and hydrogen through water splitting via titanium dioxide (TiO₂) nanowire arrays (10).

Lastly, bacteria can oxidize organic matter in the anode, reducing the chemical oxygen demand (COD) of wastewater and decreasing the overpotential at the anode. For this, *Shewanella* and *Geobacter* are commonly used (10). Indeed, the implementation of bioanodes includes MES within the concept of biorefineries since it can simultaneously treat wastewater in the anode while generating chemical commodities in the cathode.

B. CATHODIC ELECTRODES

Cathodes are usually made of carbonaceous, metallic, and carbo-metallic materials or modifications of those, such as the derivatisation of carbon cloth electrode with chitosan, which resulted in a 7.6 fold improvement in acetate production (10). This is because the addition of chitosan confers the electrode with a positively charged layer, circumventing the repulsive force from the negatively charged electrodes that averts cell adhesion. That is why it favours biofilm formation and, consequently, increases the production titer.

Moreover, since the rate of CO₂ fixation is dependent on the electrode surface area (which oscillates between 1-50 cm² in preliminar trials), its surface to volume ratio, and the current density (11); electrodes must display high conductivity and adhesion area, chemical stability, and high electron transfer rate (12).

C. MICROORGANISMS

Microorganisms act as biocatalysts, decreasing the overpotential at the electrodes (9), and the employed microorganisms are chemolithoautotrophs which can use H₂, formate, sulfide, and metal ions as electron donors mainly via the Wood-Ljungdahl pathway. Acetogens and methanogens are the most used microorganisms for biocathodic reactions, being species from the genus *Methanococcus*, *Clostridium*, *Moorella* and *Sporomusa* (10, 12) the most common. Besides, photosynthetic microorganisms can also be used, which assimilate CO₂ via the Calvin Benson cycle (8).

Furthermore, metabolic and protein engineering are usually applied for the optimization of the chosen strain, reducing the energy cost while increasing the overall productivity (13).

Both pure and mixed cultures are currently used, depending on several factors. Pure cultures, on the one hand, achieve highly selective production, higher electron recovery efficiencies and it is easier to perform genetic engineering on them, nevertheless, they are expensive if used at large scale. On the other hand, mixed cultures are cheaper and easier to grow, reducing the operation costs, and, due to the intricate microbial communities formed, they are more robust towards changes in operational parameters and more versatile in terms of product synthesis, but at the cost of the obtention of mixed products. Thus, they will require more complex downstream processing (12).

As for the electron transfer, it can either happen directly, through redox mediators, or a mixture of both. Direct electron transfer (DET) implies strict contact between the electrode and the microorganism; which uses intracellular substances such as NADH delivering enzyme, coenzyme Q, and ubiquinone (12); whereas indirect electron transfer (IET) employs electron carriers (8). Electron carriers consist of secondary metabolites such as phenazines, flavins, hydrogen, neutral red, methyl viologen

and thionin (9), all of which can be supplied to the medium provided toxic concentrations are not reached (9). Consequently hydrogen-related metabolic systems benefit from H₂ producing cathodes. That is why metals like molybdenum carbide in carbon felt resulted in higher rates of CO₂ reduction since they unleashed an increased evolution of H₂ in the cathodic chamber (14). It is important to note that IET displays higher electron losses compared to DET, so that the coulombic efficiency³ tends to be lower for the former (7).

Since electron transfer can happen directly and indirectly, microorganisms can either be creating a biofilm or in a planktonic manner in the electrolyte⁴.

D. DOWNSTREAM PROCESSING

Product extraction often represents a considerable economic cost of the process (10) that should be considered. Currently, acetate extraction is performed via anionic exchange resins, hollow fiber membranes (7) and liquid-liquid extraction (15). Nevertheless, *in situ* extraction is another strategy under development, in which an extraction chamber is located and separated from the cathode using an anionic membrane and from the anode using a PEM. As a result, the product is accumulated in the middle chamber (16), this strategy is used to produce bioplastics from acetate (see section V.D).

III. ECONOMIC ANALYSIS

Microbial electrosynthesis has been presented as a versatile and promising approach to reduce the greenhouse effect caused by CO₂ emissions, however Bian *et al* demonstrated the economic

inviability of MES implementation under the current state-of-the-art (10). More specifically, the economic analysis is based on one stack with an average cathodic surface of 45 m² that can assimilate 3.94 ton_{carbon dioxide} and produce 5.37 ton_{acetate} yearly, producing acetate at a rate of 10 g m⁻² h⁻¹. If the cost of electricity is around 406 EUR ton_{product}⁻¹ with 30% of electrical efficiency; the overall electricity cost per stack is 2,180 EUR year⁻¹ plus the reagent costs (membranes and electrodes) which are around 50 EUR m⁻² (10). The outcome is that 4,430 EUR must be spent for electricity obtention and reagent costs per year, not including installation and maintenance costs nor downstream processing.

Therefore, if the current market price of acetic acid is accounted (0.6 EUR kg⁻¹), the overall benefits are 3,222⁵ EUR year⁻¹ (10), labelling the process as economically non-viable. However, higher acetate yields could be obtained, as it was the case in Jourdin *et al.*, who achieved 1,330 g_{acetate} m⁻² day⁻¹ (17), increasing the economic profitability.

Alternatively, the use of renewable energies can play an essential role in MES scale-up. Following the previous economical analysis, Bian *et al*, found out that it can pose a huge economic reduction, as the total energy cost for renewable energy is around 162.4-243.6 EUR ton_{product}⁻¹. Nevertheless, it must be considered however that energy storage systems are often required to store excess energy from production peaks and deliver it later at a constant rate (15), increasing the overall cost.

Additionally, conversion of acetate to medium-chain carboxylic acids can also increase the economic benefit of the process as they display higher market price. As a matter of fact, caproic acid has a price of 1.6 EUR kg⁻¹ and butyric acid 3.5 EUR kg⁻¹ (10). It must be manifested, however, that acetate, ethanol, butyric acid,

³ Efficiency of charge transfer from the electron donor to the anode and from the cathode to the electron acceptor. It is the same as electron recovery.

⁴ Electrically conductive substance through the movement of ions.

⁵ $5.37 \text{ ton year}^{-1} \cdot \frac{10^3 \text{ kg}}{1 \text{ ton}} \cdot \frac{0.6 \text{ EUR}}{1 \text{ kg}}$

butanol, hexanoic acid and hexanol require 8, 12, 20, 24, 32, and 36 electrons respectively (18), reducing the obtained production rate and titer as the length of the product increases. Indeed, Jourdin *et al.* (19) stated that at 3 V: 10.9 kWh kg_{acetate}⁻¹, 18.4 kWh kg_{butyrate}⁻¹, and 22.3 kWh kg_{caproate}⁻¹ were required. Thus, only two times more power is required to produce caproate whereas its market price is more than double than that of acetate.

Additionally, anodic oxidation reactions also yield value-added products, promoting the economic sustainability of the process. For instance, current MES configurations generate oxygen, which can find a place in the chemical market. Moreover, other oxidation reactions can take place such as the production of chlorine (10), used for the tertiary treatment of wastewater and as a bleaching agent, or the desulphurisation of gases, obtaining sulphate, which finds application as a cleansing and foaming agent.

IV. MES SCALING-UP

The current technology readiness level (TRL) of MES is 4 (20) on a scale of 1 to 9, meaning that the technology at issue has only been validated at laboratory level, thus making the scale-up a challenge.

Firstly, one of the main drawbacks that averts MES implementation are the low obtained titers and the low electron recoveries, which is mainly due to limitations on electron supply and low electron utilisation rates.

Secondly, accumulation of protons is observed at the anode upon scale-up, as proton diffusion is not complete. Consequently, the pH at the vicinity of the cathode gets alkaline (21) affecting the biocathodic capacity to reduce

CO₂, since homoacetogenic bacteria are acidophiles.

Thirdly, diffusion limitations increase with the working volume, leading to an increased power requirement (9). Indeed, a proposed solution to that could be the use of gas diffusion electrodes (22) as displayed in Figure 2, which will help to provide CO₂ to the electrochemically active bacteria attached on the electrode directly on-site at controlled rates, minimizing the mass transfer limitations from solution to electrode.

Fourthly, other features that should be optimized for an economically feasible scale-up include low product specificity and end-product inhibition (10).

All things considered, scaling-up of MES can be done pursuing two objectives: (i) maximization of the production titers, or (ii) production of value-added products. In the context of CO₂ abatement, however, the first strategy appears to be wiser in the short term.

Finally, the input of CO₂ can either be atmospheric or from point sources. CO₂ capture and transportation, however, has a high impact on the final cost of the process which is often overlooked in the preliminar economic analysis. As a matter of fact, it is estimated that CO₂ capture and transportation costs for the iron and steel, cement and petroleum refineries has a cost of approximately 180 EUR ton_{carbon dioxide}⁻¹ (15).

MULTIPLE STACK DESIGN

Since the electrolyte, electrodes and membrane suffer from ohmic losses⁶ and overpotentials which increase with the reactor's size (21), the scaling-up of MES differs from the classical strategy for bioreactors, in which the fermenter volume increases for higher production figures.

⁶Internal resistances that occur due to the resistance of the flux of electrons through the electrodes, and the flux of ions in the

electrolyte and membrane (21).

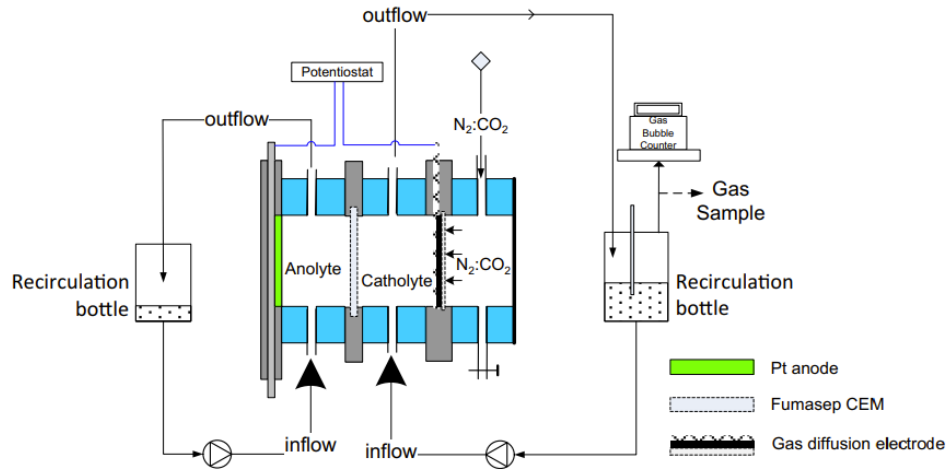


Figure 2: Experimental setup for a MES reactor with a gas diffusion cathode (22).

Indeed, the ohmic drop of the electrolyte will constitute a significant portion of the cell voltage (13), so that the anode should be the closest possible to the cathode (21).

Considering the above, if industrial implementation is sought, a multiple stack design is the most attractive strategy. Advantageously, stackable cells display an ease of maintenance, since stopping individual cells can be performed for cleaning and reparations without affecting other cells.

Regarding hydraulic and electric connections, MES chambers can be configured either in series or in parallel. While parallel chambers receive the same feeding rate, promoting replicability; chambers connected in series receive decreasing CO_2 concentrations, henceforth increasing the removal efficiency but, on the flip side, chambers are more exposed to contaminants in the CO_2 source (15). Thereby, a hybrid configuration can be employed in which parallel circuits connect the chambers, which are, in turn connected in series, as illustrated in Figure 3. The number of chambers connected in series will depend on the desired removal efficiency while the number of parallel lines will depend on the amount of gas to be treated.

V. MES APPLICATIONS

Several products can be obtained from MES. Generally and with an increased number of carbons are: methane (C1), acetate and ethanol (C2); propanol, lactate, and glycerol (C3), butyrate (C4), valerate (C5), and caproate (C6).

A. ANAEROBIC DIGESTION BIOGAS PURIFICATION

MES have been reported to purify biogas from anaerobic digestion, which usually contains 40-60% CO_2 (14), by using methanogenic cultures. Methanogens belong to the Archaea domain and they can convert CO_2 and H_2 into methane (hydrogenotrophic methanogenesis), but they can also convert acetate into methane (acetoclastic methanogenesis), so that methanogens are inactivated when acetate or other products are desired. The inlet of biogas usually contains toxic gases like H_2S , NH_3 and sulphur oxides, which can alter the pH of the electrolyte. It is for this reason that it is advisable to attach a gas filter at the entrance of the chamber (7).

Fu *et al.* (23) obtained an upgrading of 98.3% of methane at a rate of $20.6 \mu\text{mol}_{\text{methane}} \text{h}^{-1}$ ($0.008 \text{ g}_{\text{methane}} \text{day}^{-1}$) and an efficiency removal of about 92%. Moreover, H_2S was converted to elemental

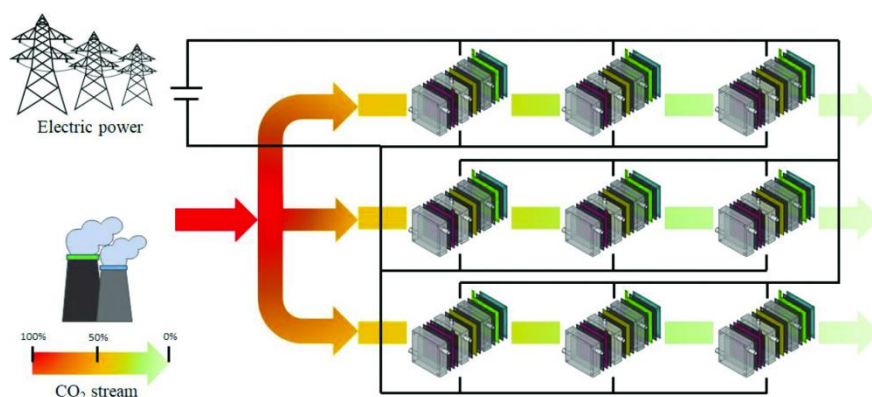


Figure 3: Example of MES stacks with hydraulic connections both in parallel and in series, and electric connections in parallel (15).

sulphur particles at the anode while carbon dioxide was reduced to methane at the cathode, using carbon paper as electrodes, by a pure culture of *Methanococcus maripaludis*. Furthermore, Enzmann *et al.* (24) developed a scaled-up 50 liter reactor and achieved $10.24 \text{ mmol m}^{-2} \text{ d}^{-1}$ ($0.16 \text{ g}_{\text{methane}} \text{ m}^{-2} \text{ day}^{-1}$) at 1.1 A m^{-2} and a coulombic efficiency of 113%, the fact that it is higher than 100% is since it considers the consumption of electrons from the cathode, which is feasible since corrosion took place.

B. ACETATE, BUTYRATE AND CAPROATE PRODUCTION

Nevin *et al.* (11) first obtained obtained acetic acid ($1.3 \text{ g}_{\text{acetate}} \text{ m}^{-2} \text{ day}^{-1}$) in 2010 and later in 2016 Jourdin *et al.*, achieved $1,330 \text{ g}_{\text{acetate}} \text{ m}^{-2} \text{ day}^{-1}$ with 99% electron recovery, and a current density of 102 A m^{-2} by using 3D RVC with CNT (carbon nanotubes), the highest reported values for acetate production (17).

Likewise, Ganigué *et al.* first achieved the production of butyrate from CO_2 in 2015 (25), obtaining a concentration of $1.82 \text{ mMC}^7 \text{ d}^{-1}$ ($0.16 \text{ g}_{\text{butyrate}} \text{ L}^{-1} \text{ d}^{-1}$) by *Clostridium kluyveri* at a coulombic efficiency of 32%. Later in 2017, Batlle-Vilanova *et al.* (26) increased the partial pressure of hydrogen *in situ* to push the reaction towards butyrate production when acetate

reached a high concentration, in an acid pH, obtaining 87.5 mMC of butyrate and 34.7 mMC of acetate at a maximum production rate of $7.2 \text{ mMC}_{\text{butyrate}} \text{ d}^{-1}$ ($0.21 \text{ g}_{\text{butyrate}} \text{ L}^{-1} \text{ d}^{-1}$)(10) at a coulombic efficiency of 63%, by *Megasphaera sueciensis* at current density of 2.74 A m^{-2} .

Furthermore, caproate was obtained from chain elongation by Jourdin *et al.* in 2019 (19) and $160 \text{ g}_{\text{butyrate}} \text{ m}^{-2} \text{ day}^{-1}$ and $46 \text{ g}_{\text{caproate}} \text{ m}^{-2} \text{ day}^{-1} \text{ d}^{-1}$ were reached when $370 \text{ g}_{\text{acetate}} \text{ m}^{-2} \text{ day}^{-1}$ were obtained. The employed current density was 147 A m^{-2} and 12.8% electron recovery was reached for caproate production on the most productive period.

Lastly, it was proven that a high concentration of organic acids in the presence of reducing power leads to the conversion of carboxylic acids into their corresponding alcohols. This is a survival mechanism since undissociated organic acids can penetrate the cell's membrane and cause such a proton gradient that can make the cell collapse. Thus, Srinanth *et al.* (27) used gas diffusion electrodes to produce volatile fatty acids from CO_2 , which were later accumulated and reduced to ethanol and butanol, obtaining $8.46 \text{ g}_{\text{ethanol}} \text{ m}^{-2} \text{ day}^{-1}$ at 26% coulombic efficiency and $3.12 \text{ g}_{\text{butanol}} \text{ m}^{-2} \text{ day}^{-1}$ at 11.56% coulombic efficiency.

⁷ mM of carbon

C. INTEGRATED DESIGN FOR WASTEWATER TREATMENT

The oxidation of organic compounds from wastewater can take place at the anode, which is of low potential (0.7 V) (10). Thus, the circuit requires very little energy input, circumventing the issues of OER, plus the required cathodes are cheaper compared to that for water splitting (9). Additionally, this strategy does not generate oxygen at the anode, which is hazardous for the required strict anoxic conditions of the cathode.

More specifically, Xiang *et al.* (28) developed an efficient bioanode for treating wastewater using a bipolar membrane (BPM) as a separator, which splits water into protons and hydroxides, as showed in Figure 4 acting as a pH buffer. This partially solves the proton accumulation issue that takes place at the anode plus prevents the use of phosphate buffers at large-scale, which increase the overall cost.

More specifically, Xiang *et al.* used a planktonic cell culture from previous bioelectrochemical cultures at the anode and granular sludge from brewery plus domesticated syngas mixtures at the cathode, operated at current densities that ranged from 0.072 to 0.078 A m⁻². As a result, 87% COD removal was achieved and 0.826 g_{acetate} L⁻¹ d⁻¹ were obtained. Moreover, the electron recovery rates were lower in BPM-MES (44-52%) compared to that of PEM-MES (60-66%), and it was hypothesized that the hydrolysis reaction that takes place consumed part of the electrons.

D. BIOPLASTICS PRODUCTION

To improve the added value of MES, Zhang *et al.* (29) used *Ralstonia eutropha* to produce polyhydroxybutyrate (PHB), an environmentally friendly product completely biodegradable.

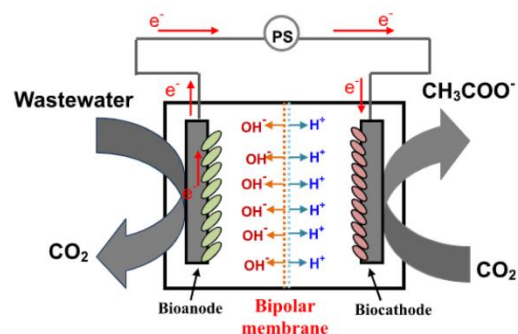


Figure 4: Schematic representation of MES using a BPM membrane (28)

Firstly, acetate was generated from CO₂ at the cathode, which was extracted on a central chamber, obtaining 5 g L⁻¹ of acetate (and traces of ethanol (0.165 g L⁻¹), caproate (0.09 g L⁻¹) and butyrate (0.08 g L⁻¹)). The obtained mixture had its pH adjusted to 6.8 using saturated sodium bicarbonate and, later, *R. eutropha* was cultivated *ex situ*, consuming 3.76 g L⁻¹ acetate (and by-products) and producing 0.46 g L⁻¹ of PHB at an average coulombic efficiency of 71% at a current density of 5.68⁸ A m⁻².

VI. MES COMPARED TO CONVENTIONAL BIOFUEL OBTENTION

The use of MES powered with solar energy allows to obtain biofuels at a higher efficiency than the current microalgae-based method. If solar panels can achieve up to 40% efficiency (sunlight to power) with 200 W per m² ground surface per 12 hours per day, using the derived power at 2V, a current of 100 A m⁻² is required. Thus, if a 50% electron butyrate to butanol conversion efficiency is assumed; 252 tonnes of butanol hectare⁻¹ annum⁻¹ could theoretically be produced. This figure is staggering compared to the average 50 tonnes biomass dry weight generated by algae per hectare per annum (9).

⁸ 14.2 mA · $\frac{1A}{10^3 mA} \cdot \frac{1}{2500 mm^2} \cdot \frac{10^6 mm^2}{1 m^2}$

Additionally, lipid extraction from biomass and its consequent transformation processes for fuel obtention are not required, making the downstream process simpler and cheaper.

VII. OUTLOOK AND FUTURE PERSPECTIVES

Microbial electrosynthesis incorporates the use of electricity to drive bio-production schemes based on CO₂ reduction, resulting not only in lower CO₂ levels, but also in lower consumption of fossil materials for the production of fuels and commodity chemicals. Nevertheless, as observed in the field cases, low titers are usually obtained, which currently classifies the project as economically non-viable under the current state-of-the-art, as demonstrated by Bian *et al.*

At long last, however, the first proof-of-concept of MES was in 2010 by Nevin *et al.*, and only a decade has passed since. Indeed, it took 30 years for reverse osmosis of seawater desalination to reach full industrial implementation from proof-of-concept (30), which entails that the presented results should not be underestimated since MES is in its first decade of life and further investigation should be conducted.

Fundamentally, MES main strong points are (i) requirement for little amount of water and, sometimes not even freshwater, (ii) it does not need arable land, rendering it free from the debate of food vs. fuel, (iii) ease in the biofuel obtention process (see section VI), and (iii) the possibility of (renewable) energy storage.

Nevertheless, some limiting factors that must be improved are (i) good CO₂ availability, (ii) high electron recoveries at low overpotentials, (iv) increase in the production rates and specificity, and (v) effective and economic downstream processing.

For this, development of porous membrane electrodes to enhance biofilm development, biological and electrode upgrading to reduce the overpotentials that limit the current density,

strain engineering to increase the overall titers and selectivity, and downstream engineering to reduce the cost of the separation and purification is a must for a future industrial implementation.

Indeed, microbial engineering can be the cornerstone of microbial electrosynthesis. Genetic and metabolic engineering will enable to increase the selectivity and coulombic efficiency of MES but, even further, will open the door to new production schemes. This is the case for ethylene and succinate production, located at the core of the petrochemical industry (12). The synthesis of these products will expand the product portfolio of MES, providing alternatives to non-petrochemical based production schemes of industrial essential products, reducing carbon dioxide emissions and the consumption of depleting feedstocks.

Overall, an industrial implementation of MES altogether with the use of renewable energies will allow to satisfy the needs of the upcoming generations. Firstly, the former will capture the generated CO₂ and synthesize renewable chemicals and, secondly, the latter will minimize CO₂ emissions; enabling to fulfill the requirements of the transportation, heat and electricity as well as the materials sector in a sustainable manner.

VIII. RESEARCH METHODOLOGY

This literary review has been based on scientific publications, starting with review articles, and followed by specific papers, frequently found via cross-references or key words (bioelectrical systems, carbon capture and utilisation, microbial electrosynthesis) by using the CCUC (Catàleg Col·lectiu de les Universitats de Catalunya), Science Direct, Springer Link, Web of Science, and Wiley Online Library databases. As a result, scientific publications from diverse magazines have been useful, mainly coming from the magazines: Elsevier, Nature, and Springer. Additionally, a project portfolio as well as a poster of this thesis has been deposited in

the virtual campus of the Autonomus University of Barcelona.

All in all, the objectives of the thesis were: (i) evaluation of the current state of CO₂ emissions and abatement, (ii) study of MES materials and microorganisms, (iii) research on economic viability reviews and scale-up strategies, and (iv) analysis of real production schemes.

Lastly, it is important to note that some of the provided data has been simplified or slightly processed for the purpose of understanding.

REFERENCES

1. International Energy Agency. Greenhouse Gas Emissions from Energy. <https://www.iea.org/data-and-statistics/data-product/greenhouse-gas-emissions-from-energy>. 2021.
2. Betts R. Met Office: Atmospheric CO₂ now hitting 50% higher than pre-industrial levels. 2021 Mar 16 [cited 2022 Mar 1]; Available from: <https://www.carbonbrief.org/met-office-atmospheric-co2-now-hitting-50-higher-than-pre-industrial-levels>
3. Farrelly DJ, Everard CD, Fagan CC, McDonnell KP. Carbon sequestration and the role of biological carbon mitigation: A review. *Renewable and Sustainable Energy Reviews*. 2013 May;21:712–27.
4. Osman AI, Hefny M, Abdel Maksoud MIA, Elgarahy AM, Rooney DW. Recent advances in carbon capture storage and utilisation technologies: a review. *Environmental Chemistry Letters*. 2021 Apr 22;19(2):797–849.
5. Leung DYC, Caramanna G, Maroto-Valer MM. An overview of current status of carbon dioxide capture and storage technologies. *Renewable and Sustainable Energy Reviews*. 2014 Nov;39:426–43.
6. SAPEA. Novel carbon capture and utilisation technologies. Vol. 2. Berlin: SAPEA; 2018.
7. Das S, Diels L, Pant D, Patil SA, Ghangrekar MM. Review—Microbial Electrosynthesis: A Way Towards The Production of Electro-Commodities Through Carbon Sequestration with Microbes as Biocatalysts. *Journal of The Electrochemical Society*. 2020 Jan 12;167(15):155510.
8. Kajla S, Kumari R, Nagi GK. Microbial CO₂ fixation and biotechnology in reducing industrial CO₂ emissions. *Archives of Microbiology*. 2022 Feb 21;204(2):149.
9. Rabaey K, Rozendal RA. Microbial electrosynthesis — revisiting the electrical route for microbial production. *Nature Reviews Microbiology*. 2010 Oct 16;8(10):706–16.
10. Bian B, Bajracharya S, Xu J, Pant D, Saikaly PE. Microbial electrosynthesis from CO₂: Challenges, opportunities and perspectives in the context of circular bioeconomy. *Bioresource Technology*. 2020 Apr;302:122863.
11. Nevin KP, Woodard TL, Franks AE, Summers ZM, Lovley DR. Microbial Electrosynthesis: Feeding Microbes Electricity To Convert Carbon Dioxide and Water to Multicarbon Extracellular Organic Compounds. *American Society for Microbiology*. 2010 Jun 29;1(2).
12. Zhang S, Jiang J, Wang H, Li F, Hua T, Wang W. A review of microbial electrosynthesis applied to carbon dioxide capture and conversion: The basic principles, electrode materials, and bioproducts. *Journal of CO₂ Utilization*. 2021 Sep;51:101640.
13. PrévotEAU A, Carvajal-Arroyo JM, Ganigué R, Rabaey K. Microbial electrosynthesis from CO₂: forever a

- promise? Current Opinion in Biotechnology. 2020 Apr;62:48–57.
14. Quraishi M, Wani K, Pandit S, Gupta PK, Rai AK, Lahiri D, et al. Valorisation of CO₂ into Value-Added Products via Microbial Electrosynthesis (MES) and Electro-Fermentation Technology. Fermentation. 2021 Nov 30;7(4):291.
15. Dessì P, Rovira-Alsina L, Sánchez C, Dinesh GK, Tong W, Chatterjee P, et al. Microbial electrosynthesis: Towards sustainable biorefineries for production of green chemicals from CO₂ emissions. Biotechnology Advances. 2021 Jan;46:107675.
16. Gildemyn S, Verbeeck K, Jansen R, Rabaey K. The type of ion selective membrane determines stability and production levels of microbial electrosynthesis. Bioresource Technology. 2017 Jan;224:358–64.
17. Jourdin L, Freguia S, Flexer V, Keller J. Bringing High-Rate, CO₂-Based Microbial Electrosynthesis Closer to Practical Implementation through Improved Electrode Design and Operating Conditions. Environmental Science & Technology. 2016 Feb 16;50(4):1982–9.
18. Kantzow C, Mayer A, Weuster-Botz D. Continuous gas fermentation by *Acetobacterium woodii* in a submerged membrane reactor with full cell retention. Journal of Biotechnology. 2015 Oct;212:11–8.
19. Jourdin L, Raes SMT, Buisman CJN, Strik DPBTB. Critical Biofilm Growth throughout Unmodified Carbon Felts Allows Continuous Bioelectrochemical Chain Elongation from CO₂ up to Caproate at High Current Density. Frontiers in Energy Research. 2018 Mar 1;6.
20. Omid M, Mashkour M, Biswas JK, Garlapati VK, Singh L, Rahimnejad M, et al. From Electricity to Products: Recent Updates on Microbial Electrosynthesis (MES). Topics in Catalysis. 2021 Sep 1;
21. Jourdin L, Burdyny T. Microbial Electrosynthesis: Where Do We Go from Here? Trends in Biotechnology. 2021 Apr;39(4):359–69.
22. Bajracharya S, Vanbroekhoven K, Buisman CJN, Pant D, Strik DPBTB. Application of gas diffusion biocathode in microbial electrosynthesis from carbon dioxide. Environmental Science and Pollution Research. 2016 Nov 20;23(22):22292–308.
23. Fu XZ, Li J, Pan XR, Huang L, Li CX, Cui S, et al. A single microbial electrochemical system for CO₂ reduction and simultaneous biogas purification, upgrading and sulfur recovery. Bioresource Technology. 2020 Feb;297:122448.
24. Enzmann F, Holtmann D. Rational Scale-Up of a methane producing bioelectrochemical reactor to 50 L pilot scale. Chemical Engineering Science. 2019 Nov;207:1148–58.
25. Ganigué R, Puig S, Batlle-Vilanova P, Balaguer MD, Colprim J. Microbial electrosynthesis of butyrate from carbon dioxide. Chemical Communications. 2015;51(15):3235–8.
26. Batlle-Vilanova P, Ganigué R, Ramió-Pujol S, Bañeras L, Jiménez G, Hidalgo M, et al. Microbial electrosynthesis of butyrate from carbon dioxide: Production and extraction. Bioelectrochemistry. 2017 Oct;117:57–64.
27. Srikanth S, Singh D, Vanbroekhoven K, Pant D, Kumar M, Puri SK, et al. Electro-biocatalytic conversion of carbon dioxide to alcohols using gas diffusion electrode. Bioresource Technology. 2018 Oct;265:45–51.

28. Xiang Y, Liu G, Zhang R, Lu Y, Luo H. High-efficient acetate production from carbon dioxide using a bioanode microbial electrosynthesis system with bipolar membrane. *Bioresource Technology*. 2017 Jun;233:227–35.
29. Zhang K, Zhou Y, Song T, Xie J. Bioplastic Production from the Microbial Electrosynthesis of Acetate through CO₂ Reduction. *Energy & Fuels*. 2021 Oct 7;35(19):15978–86.
30. Elimelech M, Phillip WA. The Future of Seawater Desalination: Energy, Technology, and the Environment. *Science* (1979). 2011 Aug 5;333(6043):712–7.