

MICROBIAL ELECTROSYNTHESIS: Production of green chemicals from CO₂

Name of the author: Bhoomika K N

Affiliation: Student of the R V College Of Engineering

Address: Shravanabelagola, Channarayapatna taluk, Hassan district.

Abstract

At this shift, this will be aided by the lower cost of renewable energy. However, various technological hurdles must be overcome before the MES system can be implemented can attain its full potential. The goal of this research is to objectively examine the roadblocks to industrial MES implementation, taking into account the entire production process (from CO₂ source to marketable goods), and to suggest future options. For site-specific decentralized applications, a modular stack architecture with flat or tubular MES modules and direct CO₂ delivery is necessary. The knowledge obtained by scaling up electrochemical cells (such as electrolysers) may be used to create prototype MES stacks that can be the global level, decarbonization of the economy has become a top issue. Increasing CO₂ abatement rates by focusing on high-rate acetate synthesis can help to boost MES adoption. However, the progress of a repeatable and robust approach for the generation and in-line isolation of relatively high products (e.g., caproic acid and hexanol) at the cathode, as well as substantial exploitation of the currently underutilized anodic processes, can enhance MES cost-effectiveness even further. Furthermore, the utilization of energy storage and smart electronics can help to mitigate renewable energy supply variations. Despite the unsolved issues, the versatile MES technology may be used to decarbonize flue gas from a variety of sources, update industrial and wastewater treatment plants, and manufacture a wide range of sustainable and green chemicals. The combination of these advantages may help MES gain industry acceptance over rival systems.

Keywords: Microbial electrosynthesis, Carbon capture technology, 3-D graphene, Methanogenisis

1.0 Introduction

Climate change has been one of humankind's most difficult problems. After joining the Paris Agreement in 2015, various nations pledged to reduce their greenhouse gas (GHG) emissions in order to keep global warming below 2 degrees Celsius (above pre-industrial levels), with a goal of 1.5 degrees Celsius by 2050[1]. Anthropogenic greenhouse gas emissions, of which CO_2 is the most prominent, are commonly regarded as the primary causes to global warming[2]. As a result, it's no surprise that rising global Carbon dioxide emissions and their influence on climate change have become a major public issue, with significant efforts and expenditures being made in research and engineering to reverse this trend[3]. CO₂ accounts for 65 percent of global greenhouse gas emissions, and the associated environmental difficulties have influenced the paradigm shift toward its recycling[6]. CO₂ is a resource which could be turned into carbon-neutral chemical substances and fuels utilising carbon capture and utilisation (CCU) technology, with a gigatonne-scale future prospects^[7]. CCU technology will reduce Greenhouse gases both directly and indirectly, by collecting CO_2 that would otherwise be discharged into the atmosphere and by replacing fossil fuel-based chemicals and fuels with green alternatives. Every tonne of heavy fuel expelled was predicted to save 300-500 g CO₂eq from entering the environment[8]. Microbial electrosynthesis (MES) is a potential CCU technique for recycling CO₂ into useful chemicals such as organic acids, alcohols, and bioplastics. MES cells are made up of 2 electrodes (cathode and anode)



divided by a cation-exchange membrane (CEM), each of which hosts a reductive (CO_2 bio-reduction) and an oxidative (e.g. water or organic compound oxidation) reaction.

MES is still in its infancy, and its practicality hasn't yet reached the levels necessary for effective electrosynthesis[9]. Electrons in MES are supplied entirely by an external source. The microbes then utilize these electrons to reduce CO_2 to acetate, for example (Reaction 1)[10]. If renewable resources used to produce power resource this process is also called as 'artificial form of photosynthesis[11]. MES-produced fuels and chemicals (from CO_2) are stated to as electro-biocommodities[12].

 $2\text{CO}_2 + 6\text{H}_2\text{O} + 8\text{e}^2 \xrightarrow{biocatalyst} \text{CH}_3\text{COOH} + 4\text{H}_2\text{O} + 2\text{O}_2$ (Reaction 1)

Microorganisms catalyse the conversion of Carbon dioxide to organic acids, either directly from the electrode or indirectly via intermediates such as (bio)electrochemically generated hydrogen. In compared to traditional thermo-electrocatalytic CO₂ reduction, the use of microbial catalysts has various benefits. Microorganisms are low-cost, self-regenerating catalysts that can convert >80% of electricity into products at room temperature (i.e. ambient or mesophilic conditions)[10]. The benefits utilising CO₂ as a substrate through MES are numerous. CO₂ is a plentiful source because it can be found in the atmosphere, oceans, and soils. It can be thought of as a government-subsidized cost [13]. Consequently, the use of such a substrate does indeed have drawbacks, the most significant of which is that, due because of its thermodynamic stability, CO₂ requires a large number of electrons for the synthesis of organic compounds. Furthermore, energy is required to initiate the microbial paths for autotrophic growth, which leads to higher costs. Both from an economic and also an environmental standpoint, effective charge use is a key concern.

1.1 Measuring microbial electrosynthesis empirically

MES catalysts were initially thought to be autotrophic microorganisms able to accept electrons [14]. The ability of acetogenic microorganisms to convert CO₂ into acetyl-CoA, that can then be used for biosynthesis, led to their adoption [15]. Microorganisms that satisfy autotrophic requirements frequently fail to satisfy electron acceptor requirements. Genetically engineered microorganisms, including Clostridium ljungdahlii, are a means of improving MES in this line [16,17]. Acetate and methane are among the most popular electrobiocommodities synthesized through MES, which are typically produced by acetogenic and methanogenic cultures [18,19]. The microorganisms chosen are critical for producing the desired product, as they can influence the quality and quantity of the final product. Acetate and methane have been initially produced using pure strain cultures [12], with the use of mixed cultures improved yields [20,21]. The significance of hydrogen was also emphasized in MES systems, with results confirming that increased proton availability enhances product formation, resulting in influence of different polarization capacities in bioproduction [10]. successful in obtaining longer chain alcohols like isobutanol and 3-methyl-1-butanol forward to genetically modifying Ralstonia eutropha H16 [22] also showed that using a mixed culture inoculum with a pure Clostridium ljungdahlii strain produced not only acetate but also butyrate and ethanol. These findings pique interest in manipulating electrode potentials, proton concentrations, and microorganism selection to produce desired products.

1.2 Mathematical estimation of microbial electrosynthesis

For product formation, MES uses complex biological and electrochemical processes. The amount and type of product produced is determined by a number of factors. The total amount and/or species of microorganism, mixing and mass transfer phenomena, anodic and cathodic reactions, voltage or current supplied, and proton exchange performance are the main parameters considered [23].



2.0 Biofilms

It was presumed that steady state biofilms had formed prior to the start-up of the MES plant. On the basis of experimental data, a few biofilm development protocols, parameters, and assumptions were developed [24]. Sometimes biofilms were obtained from waste water. The biofilm used to make aceticacid was mostly made up of bacteria from the Acetobacterium genus (51–60%), Rhodobacteraceae family (15.9–18.7%), and Sulfurospirillum genus (18.9–26.9%). Other evaluated products were made using mixed cultures or pure cultures obtained.

2.1 Mixed culture v/s pure culture in MES

A wide range of microorganisms among all three domains of life also demonstrated the ability to interact with solid electrodes for metabolic purposes [25]. Their ability to transfer electrons to or accept electrons from an electrode classifies them as exoelectrogens or electrotrophs, respectively. Four different types of proteins were detected as liable for electron transfer in between electrode and the cell surface that so far: cellsurface cytochromes, redox proteins such as iron-sulfur and copper proteins, conductive nanowires and Porin-cytochrome complexes. Micro organisms can reduce CO_2 by absorbing electrons directly from the cathode electrode or indirectly through mediators like formate, H_2 , Fe^{2+} , ammonia, or much more complex molecules like self-produced flavins. In MES cells, biocatalysts can be mixed microbial cultural products and pure cultures with specific microorganisms, either natural or genetically manipulated. Each vaccination strategy has its own set of benefits and drawbacks.

2.2 Mixed microbial culture

Advantages:	Disadvantages:
 Easy to operate Widely available Resistant to system fluctuations Resistant to O₂ intrusion Easy start-up upon failure 	 Prone to membrane bio-fouling Low selectivity for products other than acetate Possible competition between acetogens and methanogens and/or establishment of other competitors.

2.3 Pure microbial culture

Advantages:	Disadvantages:
 High selectivity Easy optimization for highest production ratesyields Prevents growth of competitors 	 Laborious start-up procedure Requires a specific growth medium Requires sterilization Vulnerable to system fluctuations Vulnerable to O₂ intrusion

Ι



2.4 Genetically modified microorganisms

Advantages:	Disadvantages:
 Same advantages of pure microbial cultures Wider product spectrum and selective production of high-value molecules Can be made resistant to system fluctuations and O₂. 	 Expensive and laborious start-up procedure Requires a specific growth medium Requires sterilization - Questionable societal acceptance. Requires approval by the government.



Fig. 1. Schematic representations of a traditional MES design for the generation of CO_2 biocommodities (Paolo Dessì et al [29]).

Table 1. A comparison of the various microbial catalysts employed and the products generated using MES[26].

Biocatalyst used	Imposed/Applied potential at cathode (V vs SHE)	Products synthesized
Sporomusa ovate	-0.69	Acetate, H ₂
S. ovate	-0.40	Acetate
S. sphaeroides	-0.40	Acetate, 2-oxobutyrate, formate
S. silvacetica	-0.40	Acetate, 2-oxobutyrate, formate
Clostridium aceticum	-0.40	Acetate, 2-oxobutyrate, formateAcetate, 2-oxobutyrate, formate
C. ljungdahlii	-0.40	Acetate, 2-oxobutyrate, formate
Moorella thermoacetica	-0.40	Acetate, 2-oxobutyrate, formate
Acetobacterium woodii	-0.69	Acetate
C. ljungdhalii	-0.69	Acetate, ethanol, H ₂
S. acidovorance	-0.69	Acetate
S. malonica	-0.69	Acetate
Mixed culture from brewery wastewater sludge	-0.60	Acetate, H ₂ , formate

I



International Journal of Scientific Research in Engineering and Management (IJSREM)

Volume: 05 Issue: 06 | June - 2021

ISSN: 2582-3930

Mixed culture from domestic wastewater treatment plant sludge	-0.85	Acetate, H ₂ , CH ₄
Mixed culture collected from bog sediment	-0.40	Acetate, ethanol, butanol, butyrate, H ₂ , propionate,
Enriched mixed culture from UASB reactor	-1.26	Acetate, H ₂
Mixed culture from anaerobic digester sludge	-0.6	Acetate, CH ₄
Mixed culture from septic tank	-1.10	Acetate, isobutyrate, propionate, 2- piperidinone
Mixed culture from septic tank	-1.0	Acetate, butyrate, propionate
Enriched mixed culture from anaerobic digester	-0.8	Acetate, H ₂
Mixed culture from septic tank	-0.9	Acetate, isobutyrate, propionate, 2-piper-idinone

Cathode surface area-based production rate, UASB - upflow anaerobic sludge blanket, SHE: Standard hydrogen electrode.

3.0 Increasing productivity of MES

3.1 Long-term operation of microbial electrosynthesis cell reducing CO_2 to multicarbon chemicals with a mixed culture avoiding methanogenesis

A biologically derived mixed anaerobic consortium generally creates methane from CO_2 reduction, avoiding the creation of multi-carbon compounds. The goal of one study was to create a stable and strong CO_2 lowering biocathode via a mixed culture inoculum without generating methane.

Based on

- (i) an enrichment technique comprising inoculum pre-treatment and numerous culture transfers in H₂:CO₂ media.
- (ii) a transition from heterotrophic to autotrophic growth.
- (iii) a sequential batch operation, a successful methodology was proven.



I



Fig. 6: Microbial electrosynthesis of organic compounds from CO_2 production techniques. Market pricing for acetic acid, ethanol, and butyric acid were gathered from marketsandmarkets.com, transparencymarketresearch.com, or alibaba.com (caproic acid and hexanol). Mixed cultures can be used to produce selective acetic acid and methane. Longer-chain carboxylic acid synthesis, whether employing pure or mixed cultures, necessitates more stringent control of operating parameters including pH, hydrogen and CO_2 partial pressures (PH₂ and PCO₂), and electrolyte composition(Paolo Dessì et al [29]).

The maximal acetate generation rate was 400 mg $L_{catholyte}^{-1}d^{-1}$ at -1 V (vs. Ag/AgCl) after biomass growth and progressive adaptation to CO₂ electroreduction. During the more than 300 days of operation, no methane was identified. Providing a (80:20) CO₂:N₂ mixture at -0.9 to -1 V (vs. Ag/AgCl) resulted in the accumulation of acetate up to 7-10 g L⁻¹ on many occasions. CO₂ reduction also resulted in the production of ethanol and butyrate. By using the specific culture enrichment with operating protocols, a robust CO₂ reducing biocathode may be generated from a mixed culture while avoiding methane formation and without the need of a chemical inhibitor[27].

3.2 3-D graphene functionalized cathodes fabricated via solvothermal synthesis

Conditions for optimum electron transport in between cathode and the microbial catalyst should be adopted to maximise MES production. The creation of a 3D-graphene(3D-G) functionalized carbon felt composite cathode for quicker electron transmission to the microbial catalyst Sporomusa ovata in a MES reactor is described. The electrosynthesis rate of acetate from CO_2 was increased by 6.8 times after the 3D-graphene network was modified. It also improved biofilm density and current consumption significantly. The creation of more extensive biofilms was explained in part by a 2-fold increase in specific surface area of the 3D-graphene/carbon felt composite cathode compared to the untreated control. Furthermore, the current response of the 3D-graphene/carbon noticed composite cathode was greater in cyclic voltammetry study. The findings suggest that developing a 3D-network cathode is a viable strategy for improving microbe-electrode interactions and resulting in productive MES systems. The results of this work show that using 3D-G to functionalize the cathode of a S. ovata-driven MES system improves current consumption density as well as chemical production rates dramatically. The enhanced performance of MES systems equipped with 3D-graphene carbon felt cathode (3D-G-CF) composite cathodes is attributable to an increase in the electrode surface area accessible for electron exchange with microorganisms, a greater electrical conductivity, and the production of a larger biofilm, according to cyclic voltammetry (CV) analysis, Scanning Electron microscopy(SEM), and Confocal Laser Scanning Microscopy (CLSM) pictures. Other bioelectrochemical experiments have found that bioelectrodes treated with 3D-G are more efficient at generating electricity using microbial fuel cells (MFCs). 3D-G is expected to boost the electrode's specific surface area and conductivity, as well as the intensity of electrostatic interactions seen between electrode and the microorganisms, resulting in higher bacterial adherence in those MFC reactors. Apart from productivity, the integration of a 3D-G composite cathode in a MES reactor would be particularly appealing in terms of cost-effectiveness, because graphene synthesis costs are substantially cheaper via wet-chemical processes than other carbon nanomaterials utilised to improve the performance of MES cathodes, such as carbon nanotubes. This is one of the primary reasons graphene is a desirable material for a variety of applications, including solar cells, batteries, and biosensors [37]. For the construction of cathode for high-performance MES, unfunctionalized 3D-G would likewise be a more cost-effective material than TEPA-modified graphene [21]. As a result, the increased production rates and lower costs associated with the 3D-G-CF cathode bode well for the future industrial growth of MES technology [28].

4.0 Downstream processing

Extraction, fractionation, concentration, & purification are all steps in the downstream processing of MES products that can account for more than 60% of the total cost of production. To accomplish large-scale manufacturing of bio-based chemicals, the development of a cost-effective extraction and separation



process is critical. For the extraction and segregation of major MES products, like C2-C6 monocarboxylic acids, many extraction strategies have been developed.

4.1 Conventional separation processes

Adsorption and liquid-liquid extraction (LLE) are two common methods for separating organic acids that have been studied extensively. The ion exchange among carboxylate groups and functionalized solid sorbents, such as amine-based anion exchange resins, is the basis for adsorption. In most instances, the sorbent's performance is determined by pH of the solution. Because an increasing pH causes an increase in acid concentration in ionized form but a decrease in amine concentration in protonated form, high adsorption potentials are achieved at optimal pH values (6.5).

4.2 Concentration-driven and pressure-driven membrane processes

Pertraction is a membrane technique that separates the feed from a permeate by immobilising an organic solvent within the pores of a hydrophobic microfiltration membrane (by capillary forces). Organic molecules from the feed can be continually back-extracted on the permeate side by diffusing through the organic solvent in the membrane. Because the membrane primarily serves as a mechanical support, extraction selectivity is solely dependent on the extractant. Pertraction has been frequently used for Volatile fatty acid(VFA) extraction because it offers various benefits over traditional LLE, including

- i) The use of less organic solvent.
- ii) Simultaneous extraction and solvent stripping.
- iii) Lower operating expenses.

The target chemicals are recovered through partial vaporisation via a membrane, with the permeate side kept under vacuum, in pervaporation. High-molecular-weight alkyl amines such as trioctylamine (TOA), trilaurylamine (TLA), and tri-n-octylphosphine oxide (TOPO) are the most commonly utilised extractants because they have a high boiling point, low viscosity, and poor water solubility Nanofiltration separated organic acids in lignocellulosic biomass digestion liquors using commercial NF membranes, reaching an 86 percent recovery rate (except for butyric acid, likely due to interactions with other components in the digestion liquor). The osmotic pressure differential between the input and a draw solution preserved at the same hydrostatic pressure is exploited in forward osmosis (FO). The composition and concentration of said draw solution have a significant impact on process efficiency, fouling, and energy consumption.

4.3 Electro-membrane processes

At the industrial scale, Electrodialysis (ED) is the most frequently used electro-membrane technique, and it has also been extensively studied for organic acid recovery. VFA extraction from hydrogen fermentation broths was up to 99 percent, and the application of ED for in-line VFA extraction was proven. However, because ED has a low selectivity for organic acids, it extracts other anions (such as Cl-) as well, especially if they are present in large concentrations. Membrane electrolysis also an ED-based technique in which the anode and cathode produce H+ and OH-, respectively, as part of the process. Membrane electrolysis was used (in conjunction with pertraction) to specifically extract caproic acid via a fermentation broth, with a pH gradient maintained electrochemically between the two chambers and no chemicals used.

4.4 Reactive extraction processes

The use of ionic liquids (ILs) for selective extraction of organic acids has been researched. ILs are used to concentrate and esterify acetic acid generated by MES at the same time (extracted via membrane



electrolysis). Using a bis(trifluoromethylsulfonyl)-imide IL, acetic acid was concentrated up to 80 mM, followed by esterification to ethyl acetate when ethanol was added, with a maximum conversion of 90%. This proof-of-concept research paves the way for MES to expand its product line.

4.5 Perspectives for integrated MES-VFA extraction systems

One of the most difficult aspects of upscaling VFA biological production is achieving selective separation of VFAs from dilute aqueous streams. Several variables impact separation selectivity, including pH, mobility, hydrophobicity, molecular weight, and ionisation degree of the target product. Due to its low product concentration using MES, this is extremely difficult. Due to product inhibition, MES reactors can only generate up to 7–10 g/L acetate. When compared to commercial fermentation procedures, where organic acid concentrations of 20–200 g/L may be produced, these concentrations are not yet sufficient for economically upscaling[29].

5.0 Development of sustainable MES biorefineries

5.1 Renewable energy sources to power MES

For (bio)electrochemical processes, electric energy represents a significant expense. Using an optimistic CE of 90% and a 3 V operational voltage, it was calculated that 12 kWh_{el} are required to produce 1 kilogramme of acetic acid, and this power consumption effectively doubles for caproic acid production. Without including operating, maintenance, and downstream processing expenses, the power cost for manufacturing 1 kg of acetic acid (0.83 €) is already more than its market worth . Furthermore, if fueled by fossil-fuel-based electricity, MES might result in net carbon emissions creation rather than mitigation. As a result, using renewable, low-cost energy is a critical strategic aspect for MES biorefineries to be sustainable. Over the period 2007–2017, renewable energy capacity in the EU expanded from 258 to 512 GWe, with solar photovoltaics (+1966%), offshore wind (+1365%), onshore wind (+180%), and biofuels (+94%) showing particularly strong development. Renewable energy adoption is expected to reduce power prices by at least 20-30%, making it more competitive with fossil-fuel-based energy. Renewable energy sources may be incorporated into MES in two ways: indirectly, through using renewable electric energy generated by solar, wind, geothermal, hydro, or biomass to power MES, or directly, through solarto-product conversion utilizing photoactive electrodes to create the requisite power density. The indirect strategy looks to be particularly useful for storing the low-cost extra electricity generated by renewable sources that are intrinsically variable as multi-carbon compounds. Variable electric supply, on the other hand, might temporarily reduce MES production rates or even alter the metabolic route from carboxylic acid to methane generation. Using batteries and special electrical circuits to give a continuous current to the MES reactor, this problem may be eliminated [29].

5.2 Integrated MES devices for CO₂ recycling and wastewater treatment

The oxygen evolution process requires high potentials or costly catalysts when CO_2 reduction at the cathode is paired with water oxidation at the anode. Furthermore, some of the oxygen created at the anode might pass to the cathode, preventing purely anaerobic microbes from growing. An integrated system incorporating CO_2 reduction at the cathode and pollutant oxidation at the anode would not only reduce MES's energy requirement, but will also solve two key industry concerns at the same time reduction of CO_2 emissions and wastewater treatment. A bio-cathode with a current density of 0.04 mA/cm2 created by a bio-anode supplied by synthetic wastewater containing 4 g/L sodium acetate had a maximum acetic acid production rate of 83 mg/(m3 d). At a low cell potential of 1.4 V, the COD elimination rate reached 87 percent. Additionally, acetic acid synthesis from CO_2 was proven at potentials as low as 0.8 V, but at a



slower pace. Furthermore, CO_2 created during anode wastewater treatment may be returned to the cathodic chamber and used as a chemical precursor[29].

5.3 Energy storage and smart electronic design for MES

MES reactors have proved their resiliency to current variations, but for a reliable 24/7 operation, a steady electrical source is necessary. When variable energy sources are utilized to power MES, energy storage devices are necessary to collect surplus energy from manufacturing peaks and provide it to the MES reactors at a steady flow. In the last five years, the cost of storage technologies, particularly batteries, has dropped by 60%, reaching the 100 ϵ /kWh mark. Power storage costs in Germany have been estimated at 0.085 ϵ /kWh for a 7-hour storage period, which is low enough to encourage the installation of batteries for solar power harvesting, and is expected to drop to 0.065 ϵ /kWh within four years. MFCs that treat wastewater can also be used to generate electricity to charge energy storage devices, which are then released to power MES reactors. Even when the cells are coupled in parallel, potential management in MES stacks is more difficult than in solely electrochemical electrolysers. Non-uniform charge distribution on a MES electrodes can be caused by fundamentally in homogeneous microbial catalysts[29].

6.0 The success of MES from CO_2 will require a pinch of realism, solid evidence, and some out of the box thinking

In addition to the intriguing basic science still in the field, a drive is being developed to resolve a real-life problem by developing a solution. Essentially, irrespective of the intended procedure, one has to consider the feasibility of expanding the system and retrieving an actual product of set specifications at an appropriate production rate and investments in capital (adequate reactor life). Rigorous techno-economic analysis should be undertaken, including CO_2 effect, in order to enable objective comparisons between present processes of fossil fuel and other alternative technologies for target product and carbon capture production. Chemical commodities are necessarily energized using (bio) electrochemical processes. For example, the relatively low 16 Mt of global production of acetic acid expected in 2020 [30](more than 150 Mt of ethylene is produced yearly) would account for an electrolysis energy of 3 V and 90% of the electron recovery process for a total of 190 TW h (calculation of the additional material). Approximately 1 percent of world energy generation, or a third of photovoltaic electricity was produced in 2018. Green energy prices in the near future provide attractive prospects. However, low-carbon electric energy is a worldwide requirement and should be utilised mostly for the most sensible purposes. Ultimately, all of the above will determine if the MES from CO_2 is sensible or not, and if so, how, where and at what size[31].

7.0 Conclusions

The versatility of MES, which can convert CO_2 containing gas from a variety of sources into a variety of chemical compounds, could be a crucial difference for entering the market. Prior to commercialization, however, considerable difficulties must be overcome. To examine the technology from a technoeconomic standpoint, MES stacks must be constructed and run under relevant conditions (e.g., in a pilot scale). MES can assist in the recovery of these biorefinery contaminants as resources, hence reducing environmental discharges. Biorefineries and MES systems could work together to improve product yields and selectivities, as well as overall efficiency, and so address the fundamental difficulties with upscaling both technologies. When methanol, ethanol, as well as formic acid are synthesised, employing gaseous CO_2 as a substrate provides environmental benefits, according to the sustainability evaluation. Because of the thermodynamic properties of CO_2 and the production of water molecules during synthesis, product production and purification need a lot of energy. As a technology, MES can assist reduce greenhouse gas emissions while simultaneously lowering production costs and boosting the economy. This presents a



promising possibility for MES to be used and scaled up for industrial intake. Heat pretreatment, which was utilised as a technique for specifically enriching homoacetogenic bacteria, was found to be effective in the establishment of a Clostridiaecea-dominated microbial community.

References

- 1. United Nations, 2015. Paris Agreement [WWW Document]. URL. <u>https://unfccc.int/file</u> <u>s/essential_background/convention/application/pdf/english_paris_agreement.pdf</u>.
- Pearson, R.J.; Eisaman, M.D.; Turner, J.W.G.; Edwards, P.P.; Jiang, Z.; Kuznetsov, V.L.; Littau, K.A.; Di Marco, L.; Taylor, S.R.G. Energy Storage via Carbon-Neutral Fuels Made from CO₂, Water, and Renewable Energy. Proc. IEEE 2012, 100, 440–460. [CrossRef]
- Manan, Z.A.; Mohd Nawi, W.N.R.; Wan Alwi, S.R.; Klemeš, J.J. Advances in Process Integration research for CO₂ emission reduction—A review. J. Clean. Prod. 2017, 167, 1–13. [CrossRef]
- 4. Otto, A.; Grube, T.; Schiebahn, S.; Stolten, D. Closing the loop: Captured CO2 as a feedstock in the chemical industry. Energy Environ. Sci. 2015, 8, 3283–3297. [CrossRef]
- Zdeb, J.; Howaniec, N.; Smoli ´nski, A.; Zdeb, J.; Howaniec, N.; Smoli ´nski, A. Utilization of Carbon Dioxide in Coal Gasification—An Experimental Study. Energies 2019, 12, 140. [CrossRef]
- Aresta, M., Dibenedetto, A., Angelini, A., 2013. The changing paradigm in CO2 utilization. J. CO2 Util. 3–4, 65–73. <u>https://doi.org/10.1016/j.jcou.2013.08.001</u>
- 7. Bains, P., Psarras, P., Wilcox, J., 2017. CO2 capture from the industry sector. Prog. Energy Combust. Sci. 63, 146–172. doi:https://doi.org/10.1016/j.pecs.2017.07.001
- Masnadi, B.M.S., El-Houjeiri, H.M., Schunack, D., Li, Y., Englander, G., Badahdah, A., Monfort, J., Anderson, J.E., Wallington, T.J., Bergerson, J.A., Gordon, D., Koomey, J., Azevedo, I.L., Bi, X.T., Duffy, J.E., Heath, G.A., Keoleian, A., Mcglade, C., Meehan, D.N., Yeh, S., You, F., Brandt, A.R., 2018. Global carbon intensity of crude oil production. Science (80-.). 361, 851– 853
- 9. T. deCamposRodrigues, M.A. Rosenbaum, Microbial electroreduction: screening for new cathodic biocatalysts, ChemElectroChem 1 (11) (2014) 1916–1922
- 10. A. ElMekawy, H.M. Hegab, G. Mohanakrishna, A.F. Elbaz, M. Bulut, D. Pant, Technological advances in CO2 conversion electro-biorefinery: a step toward commercialization, Bioresour. Technol
- 11. D.R. Lovley, Powering microbes with electricity: direct electron transfer from electrodes to microbes, Environ. Microbiol. Rep. 3 (1) (2011) 27–35
- 12. D.R. Lovley, K.P. Nevin, Electrobiocommodities: powering microbial production of fuels and commodity chemicals from carbon dioxide with electricity, Curr. Opin. Biotechnol. (2013)
- 13. Styring, E.A. Quadrelli, K. Armstrong, Carbon Dioxide Utilisation: Closing the Carbon Cycle, first edition, (2014) .
- 14. P.L. Tremblay, T. Zhang, Electrifying microbes for the production of chemicals, Front. Microbiol. 6 (2015)
- 15. B. Schiel-Bengelsdorf, P. Dürre, Pathway engineering and synthetic biology using acetogens, FEBS Lett. 586 (15) (2012) 2191–2198
- 16. C. Leang, T. Ueki, K.P. Nevin, D.R. Lovley, A Genetic system for Clostridium ljungdahlii: achassis for autotrophic production of biocommodities and a model homoacetogen, Appl. Environ. Microbiol. 79 (4) (2013) 1102–1109
- 17. A. Banerjee, C. Leang, T. Ueki, K.P. Nevin, D.R. Lovley, Lactose-inducible system for metabolic engineering of clostridium ljungdahlii, Appl. Environ. Microbiol. 80 (8) (2014) 2410–2416

Τ



- 18. S. Cheng, D. Xing, D.F. Call, B.E. Logan, Direct biological conversion of electrical current into methane by electromethanogenesis, Environ. Sci. Technol. 43 (10) (2009) 3953–3958
- 19. K.P. Nevin, T.L. Woodard, A.E. Franks, Z.M. Summers, D.R. Lovley, Microbial electrosynthesis: feeding microbes electricity to convert carbon dioxide and water to multicarbon extracellular organic compounds, mBio 1 (2) (2010)
- Y. Jiang, M. Su, Y. Zhang, G. Zhan, Y. Tao, D. Li, Bioelectrochemical systems for simultaneously production of methane and acetate from carbon dioxide at relatively high rate, Int. J. Hydrogen Energy 38 (8) (2013) 3497–3502
- P. Batlle-Vilanova, S. Puig, R. Gonzalez-Olmos, M.D. Balaguer, J. Colprim, Continuous acetate production through microbial electrosynthesis from CO2 with microbial mixed culture, J. Chem. Technol. Biotechnol. 91 (4) (2016) 921–927
- 22. S. Bajracharya, R. Yuliasni, K. Vanbroekhoven, C.J.N. Buisman, D.P.B.T.B. Strik, D. Pant, Long-term operation of microbial electrosynthesis cell reducing CO2 to multi-carbon chemicals with a mixed culture avoiding methanogenesis, Bioelectrochemistry 113 (2017) 26–34
- 23. V.B. Oliveira, M. Simões, L.F. Melo, A.M.F.R. Pinto, Overview on the developments of microbial fuel cells, Biochem. Eng. J. 73 (2013) 53–64
- 24. C.W. Marshall, D.E. Ross, E.B. Fichot, R.S. Norman, H.D. May, Long-term operation of microbial electrosynthesis systems improves acetate production by autotrophic microbiomes, Environ. Sci. Technol. 47 (11) (2013) 6023–6029
- Logan, B.E., Rossi, R., Ragab, A., Saikaly, P.E., 2019. Electroactive microorganisms in bioelectrochemical systems. Nat. Rev. Microbiol. 17, 307–319. https://doi.org/ 10.1038/s41579-019-0173-x
- 26. Review—Microbial Electrosynthesis: A Way Towards The Production of Electro-Commodities Through Carbon Sequestration with Microbes as Biocatalysts To cite this article: Sovik Das et al 2020 J. Electrochem. Soc. 167 155510
- 27. Long-term operation of microbial electrosynthesis cell reducing CO2 to multicarbon chemicals with a mixed culture avoiding methanogenesis Suman Bajracharya1,2, Rustiana Yuliasni2, Karolien Vanbroekhoven1, Cees J.N. Buisman2, David P. B. T. B. Strik2#, Deepak Pant1*
- 28. Enhanced microbial electrosynthesis with three-dimensional graphene functionalized cathodes fabricated via solvothermal synthesis Nabin Aryala , Arnab Halderb , Pier-Luc Tremblaya,c , Qijin Chib , Tian Zhanga,c, *
- 29. Microbial electrosynthesis: Towards sustainable biorefineries for production of green chemicals from CO2 emissions Paolo Dessì a,* Laura Rovira-Alsina b, Carlos Sanchez ´c, G. Kumaravel Dinesh a, Wenming Tong a, Pritha Chatterjee d, Michele Tedesco e, Pau Farras`a, Hubertus M.V. Hamelers e, Sebastia `Puig b
- 30. Christodoulou X, Okoroafor T, Parry S, Velasquez-Orta SB: The use of carbon dioxide in microbial electrosynthesis: advancements, sustainability and economic feasibility. J CO2 Util 2017, 18:390-399
- 31. Microbial electrosynthesis from CO2: forever a promise? Antonin Pre´ voteau1,2,3 , Jose M Carvajal-Arroyo1,2,3 , Ramon Ganigue´1,2,3 and Korneel Rabaey1

Τ