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Author(s)	Dessi, Paolo; Rovira-Alsina, Laura; Sánchez, Carlos; Dinesh, G. Kumaravel; Tong, Wenming; Chatterjee, Pritha; edesco, MicheleT; Farràs, Pau; Hamelers, Hubertus M.V.; Puig, Sebastià
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1 Microbial electrosynthesis: towards sustainable biorefineries for 2 production of green chemicals from CO₂ emissions

3
4 Paolo Dessì^{a,*}, Laura Rovira-Alsina^b, Carlos Sánchez^c, G. Kumaravel Dinesh^a, Wenming
5 Tong^a, Pritha Chatterjee^d, Michele Tedesco^e, Pau Farràs^a, Hubertus M.V. Hamelers^e, Sebastià
6 Puig^b

7
8 ^a School of Chemistry and Energy Research Centre, Ryan Institute, National University of
9 Ireland Galway, University Road, H91 TK33 Galway, Ireland

10 ^b LEQUiA, Institute of the Environment, University of Girona. Campus Montilivi,
11 Carrer Maria Aurèlia Capmany 69, E-17003 Girona, Spain

12 ^c Microbiology Department, School of Natural Sciences and Ryan Institute, National
13 University of Ireland Galway, University Road, H91 TK33 Galway, Ireland

14 ^d Department of Civil Engineering, Indian Institute of Technology, Hyderabad, India

15 ^e Wetsus, European Centre of Excellence for Sustainable Water Technology, Oostergoweg 9,
16 8911 MA Leeuwarden, The Netherlands

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18 * Corresponding author: Paolo Dessì; E-mail address: paolo.dessi@nuigalway.ie

19 Highlights

- 21 • MES is a resilient technology for recycling CO₂ into various marketable products
- 22 • Increase production rates and minimise costs and footprint are required for scaling-up
23 MES
- 24 • MES can upgrade existing treatment plants to comply with future legislation on CO₂
25 emissions
- 26 • *In-line* product extraction is cost-effective and avoids product inhibition
- 27 • Membranes with selectivity and anti-fouling properties will reduce extraction costs
- 28 • Renewable energy sources pave the ground towards sustainable MES

29 Abstract

30
31 Decarbonisation of the economy has become a priority at the global level, and the resulting
32 legislative pressure is pushing the chemical and energy industries away from fossil fuels.
33 Microbial electrosynthesis (MES) has emerged as a promising technology to promote this
34 transition, which will further benefit from the decreasing cost of renewable energy. However,
35 several technological challenges need to be addressed before the MES technology can reach
36 its maturity. The aim of this review is to critically discuss the bottlenecks hampering the
37 industrial adoption of MES, considering the whole production process (from the CO₂ source
38 to the marketable products), and indicate future directions. A flexible stack design, with flat
39 or tubular MES modules and direct CO₂ supply, is required for site-specific decentralised
40 applications. The experience gained for scaling-up electrochemical cells (*e.g.* electrolyzers)
41 can serve as a guideline for realising pilot MES stacks to be technologically and
42 economically evaluated in industrially relevant conditions. Maximising CO₂ abatement rate
43 by targeting high-rate production of acetate can promote adoption of MES technology in the
44 short term. However, the development of a replicable and robust strategy for production and
45 *in-line* extraction of higher-value products (*e.g.* caproic acid and hexanol) at the cathode, and
46 meaningful exploitation of the currently overlooked anodic reactions, can further boost MES
47 cost-effectiveness. Furthermore, the use of energy storage and smart electronics can alleviate
48 the fluctuations of renewable energy supply. Despite the unresolved challenges, the flexible
49 MES technology can be applied to decarbonise flue gas from different sources, to upgrade

50 industrial and wastewater treatment plants, and to produce a wide array of green and
51 sustainable chemicals. The combination of these benefits can support the industrial adoption
52 of MES over competing technologies.

53

54 **Keywords:** Bioelectrochemistry, Circular economy, CO₂ reduction, Electrochemical cell,
55 Gas fermentation, Microbial electrochemical technologies, Product purification, Scale-up

56

57 **Abbreviations**

58 BMED Bipolar membrane electrodialysis

59 CCS Carbon capture and storage

60 CCU Carbon capture and utilisation

61 CE Coulombic efficiency

62 CEM Cation exchange membrane

63 CHP Combined heat and power

64 COD Chemical oxygen demand

65 ED Electrodialysis

66 EDI Electrodeionisation

67 FO Forward osmosis

68 GDE Gas diffusion electrode

69 GHG Greenhouse gas

70 IL Ionic liquid

71 LED Light emitting diode

72 LLE Liquid-liquid extraction

73 MES Microbial electrosynthesis

74 MFC Microbial fuel cell

75 NF Nanofiltration

76 PEM Proton exchange membrane

77 PMS Power management system

78 SCE Solar conversion efficiency

79 SHE Standard hydrogen electrode

80 TLA Trilaurylamine

81 TOA Trioctylamine

82 TOPO Tri-n-octylphosphine oxide

83 VFA Volatile fatty acid

84

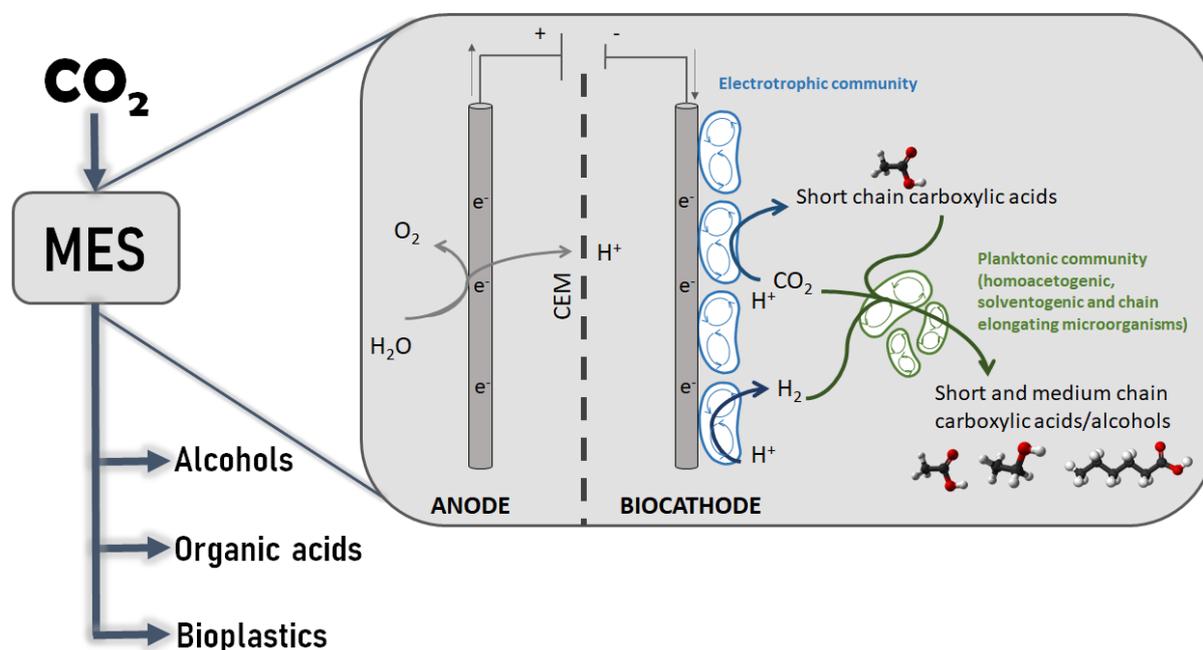
85 **1. Introduction**

86 Climate change has become one of the most challenging issues faced by humanity. After
87 signing the Paris agreement in 2015, most countries worldwide committed to decreasing their
88 greenhouse gas (GHG) emissions to contain global warming to 2°C (above pre-industrial
89 levels), aiming to 1.5°C by 2050 (United Nations, 2015). Accordingly, the European Union
90 (EU) set a target of 20% GHG reduction by 2020, 40% by 2030 and of achieving a net-zero
91 carbon economy by 2050. The legislative pressure of EU on carbon emissions allowed to
92 achieve the 2020 target already in 2017, when a total of 4483 Mt CO₂eq were produced, 22%
93 lower than the emissions in 1990 (European Environment Agency, 2019). However, EU
94 economy remains largely dependent on fossil fuels, which currently account for 65% of the
95 energy supply and 80% of the total GHG emissions (European Environment Agency, 2019).
96 Significant efforts and innovative measures need to be developed to achieve the ambitious
97 target of net-zero carbon emissions by 2050. Such efforts were translated into the European
98 Green Deal, in which the EU will invest over one trillion euros to promote a low-carbon
99 circular economy (European Commission, 2020).

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CO₂ accounts for 65% of GHG emissions worldwide and the resulting environmental issues have contributed to change the paradigm towards its recycling (Aresta et al., 2013). CO₂ is indeed a resource that can be converted to carbon-neutral chemical commodities and fuels using carbon capture and utilization (CCU) technologies, with a future potential at the gigatonne scale (Bains et al., 2017). CCU technologies will mitigate GHG emissions both directly, by capturing CO₂ that would be otherwise released to the atmosphere, and indirectly, by displacing fossil fuel-based chemicals and fuels currently used by industries with green alternatives. It was estimated that every ton of heavy fuel displaced would avoid emissions of 300-500 g CO₂eq to the atmosphere (Masnadi et al., 2018), which is also valid for fossil fuel-derived chemicals.

Microbial electrosynthesis (MES) is a promising CCU technology for bio-electro CO₂ recycling into valuable chemical products, including organic acids (Batlle-Vilanova et al., 2017; Jourdin et al., 2015), alcohols (Arends et al., 2017; Gavilanes et al., 2019; Vassilev et al., 2019), and bioplastics (Pepè Sciarria et al., 2018). MES cells are essentially composed of two electrodes (cathode and anode), typically separated by a cation-exchange membrane (CEM), hosting a reductive (CO₂ bioreduction) and an oxidative (*e.g.* oxidation of water or organic compounds) reaction, respectively (Fig. 1). CO₂ conversion into organic acids is catalysed by microorganisms that uptake electrons directly from the electrode or indirectly through intermediates such as (bio)electrochemically produced hydrogen (Nevin et al., 2010; Rabaey and Rozendal, 2010).



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Figure 1. Schematic representation of a typical MES configuration for biocommodities production from CO₂.

The use of microbial catalysts provides several advantages in comparison to conventional thermo-electrocatalytic CO₂ reduction. Microorganisms are cheap and self-regenerating catalysts that can achieve >80% electricity-to-product conversions under mild temperature (*i.e.* ambient or mesophilic conditions) (Bajracharya et al., 2017a). However, further efforts are required to optimise the conversion rate/yield and purity of products in MES reactors, and

133 research on scaling-up CO₂ reduction processes is still scarce (Sánchez et al., 2019). The
 134 experience acquired in scaling-up related technologies such as commercially available
 135 electrolysers, as well as pilot-scale microbial fuel cells (Dong et al., 2015; Feng et al., 2014;
 136 Liang et al., 2018; Rossi et al., 2019; Vilajeliu-Pons et al., 2017), and microbial electrolysis
 137 cells (Gil-Carrera et al., 2013), can offer guidelines for deploying scalable MES
 138 configurations.

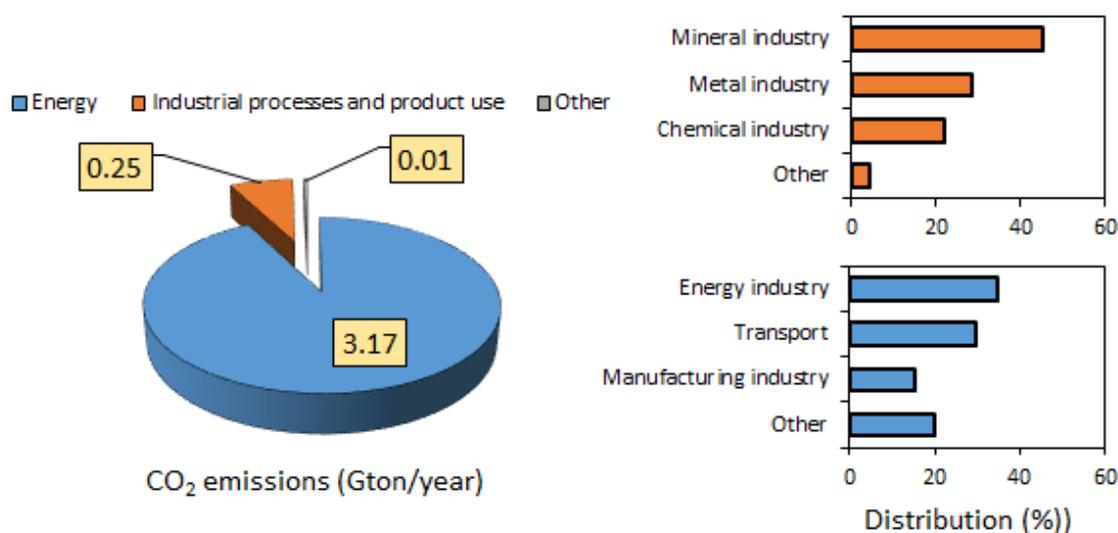
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 140 MES is currently a hot topic in biotechnology, and recent reviews gave an excellent summary
 141 of key aspects of the technology, from fundamental microbiology and electron transfer
 142 aspects (Karthikeyan et al., 2019; Logan et al., 2019) to the current state-of-art and future
 143 perspectives (Bian et al., 2020; Fruehauf et al., 2020; Jiang et al., 2019; Jiang and Jianxiong
 144 Zeng, 2018; PrévotEAU et al., 2020), as well as techno-economic feasibility (Jourdin et al.,
 145 2020). Here we reviewed the main aspects hindering MES commercialisation, including the
 146 integration of MES reactors in industrial plants, reactor design, product synthesis and
 147 purification, and use of renewable electricity. Key issues were individuated, and future
 148 directions were suggested, based on previous experience on similar technologies, for putting
 149 forward resilient and sustainable CO₂ recycling MES biorefineries.

150
 151 **2. Integration of MES into industrial plants**

152 **2.1 CO₂ sources for MES**

153 Energy supplies, together with industry and transportation, generate most greenhouse gas
 154 emissions in EU (1.27, 0.88 and 0.95 Gton CO₂eq/year, respectively). The energy sector
 155 accounts for 92.4% of the total CO₂ emissions, where energy generation (34.8%), transport
 156 (29.6%), and the manufacturing industry (15.4%) are the main contributors. The remaining
 157 non-energy related CO₂ emissions are mainly produced by the mineral, metal, and chemical
 158 industry (Fig. 2). MES is a bio-electrochemical recycling platform for CO₂ conversion to
 159 valuable products that can be directly applied for decarbonisation of flue gases from the
 160 energy supply and carbon-intensive industry sectors such as steel mills (20-30% CO₂),
 161 ceramic (15-20% CO₂), glass (10-15% CO₂), refineries (10-20% CO₂), cement industries (25-
 162 30% CO₂), and power plants (10-15% CO₂). Furthermore, MES can potentially recycle CO₂
 163 produced from biological processes such as anaerobic digestion, fermentation and
 164 conventional wastewater treatment, which has been estimated to produce around 4.4×10^{-3}
 165 Gton CO₂/year worldwide (Rosso and Stenstrom, 2008).

166



168 **Figure 2.** Sectorial distribution of the CO₂ production in EU and relative contributions of
169 CO₂ emissions from the energy (blue) and industrial processing (orange) sectors. The graphs
170 were generated from the European Environmental Agency (EEA) database 2018.
171

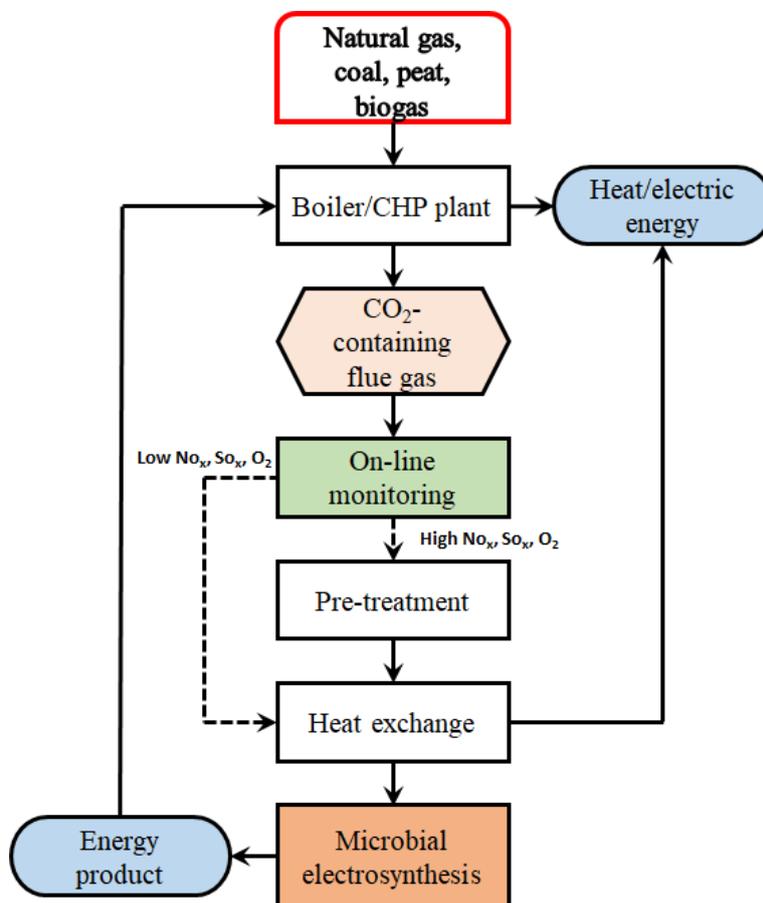
172 **2.2 CO₂ capture and utilisation in MES devices**

173 Applying MES to industry requires infrastructures for gas transportation to the MES reactor,
174 which inevitably lead to a higher footprint and costs. By performing a sensitivity analysis on
175 the major costs associated to the adoption of carbon capture and storage (CCS) technologies
176 in the iron and steel, cement and petroleum refining industries, Leeson et al. (2017) estimated
177 that CO₂ capture and transportation can cost as high as 180 €/ton CO₂. Hence, integrated
178 MES plants on industrial sites (*i.e.* close to the CO₂ emission sources) present a more
179 economically viable solution than centralised plants. This highlights the need for designing
180 flexible MES reactors, adaptable to the gas volumes and composition of the specific industry
181 requiring gas treatment. Furthermore, when spent gasses are released during combustion, *e.g.*
182 in boilers on combined heat-power (CHP) plants, reducing the temperature to 20-30°C is
183 required prior to feeding it to the MES cell. Such excess of heat can be recovered, using heat
184 exchangers, and used for warming up the MES reactors, or recycled to other applications to
185 further reduce operational costs. Another option is to operate MES reactors under
186 thermophilic conditions, thereby increasing the production kinetics and reducing the risk of
187 microbial contamination, although the lower gas solubility at high temperature may limit the
188 carbon and energy availability (Rovira-Alsina et al., 2020).
189

190 Depending on waste gas components, a pre-treatment may be required to remove impurities
191 and toxic compounds for the MES microbial community (Fig. 3). This is the case, for
192 example, of power plants powered by coal, peat or crude oil combustion, producing a gas
193 containing CO, O₂, SO_x, NO_x, HCl and particulate ash besides CO₂ (Aouini et al., 2014; Pihu
194 et al., 2017). In contrast, CO₂ constitutes nearly 96-99% of flue gas produced in natural gas
195 processing and alcohol fermentation. Complete natural gas combustion with air generates a
196 clean flue gas stream of nitrogen (72% wt.), CO₂ (15-17%) and moisture (10-11%) (Sonibare
197 and Akeredolu, 2004), which can be directly fed to MES reactors due to the absence of toxic
198 compounds. Lab-scale MES reactors were indeed successfully operated on N₂:CO₂ 80:20%
199 mixture gas feed (Deutzmann and Spormann, 2017; Nevin et al., 2010; Russell, 2013; Tahir
200 et al., 2020; Zhang et al., 2013). In case of incomplete combustion, CO, NO_x and residual O₂,
201 detrimental for the microbial community, are also released, and on-line monitoring of the flue
202 gas is thus required to prevent system breakdown. Nevertheless, regulations on CO, SO_x and
203 NO_x emissions are, or will be, in place at the global level and thus, industries already have,
204 or will require, a technology to remove these contaminants from flue gas. Oxygen
205 concentration should also be minimised, since it can reduce MES efficiency by inhibiting the
206 strictly anaerobic microorganisms, particularly in the absence of oxygen scavenging species
207 (*e.g.* when oxygen-sensitive pure cultures are used as a microbial catalyst) (Giddings et al.,
208 2015). Furthermore, O₂ exposure causes a decrease of the Coulombic efficiency (CE) by
209 promoting the biological oxidation of MES organic products (Marshall et al., 2013), as well
210 as diverging electrons towards O₂ electrochemical reduction into water.
211

212 The carbon capture cost is highly variable concerning the flue gas composition and increases
213 with the level of CO₂ purity required (Bains et al., 2017; d'Amore et al., 2019; Leeson et al.,
214 2017). In MES, the pre-treatment target is to reduce contaminants (*e.g.* NO_x, SO_x, and O₂)
215 below the tolerance limit of the microorganisms, rather than generating a pure CO₂ stream,
216 resulting in lower costs. Several SO_x and NO_x removal technologies are commercially
217 available, being desulfurisation with lime or limestone, and catalytic NO_x reduction,

218 respectively, the most commonly applied worldwide (Sun et al., 2016). Furthermore, since
 219 CO₂ is a by-product of both processes when urea is used as reductant, it will contribute to the
 220 overall CO₂ feedstock for the MES cells. If the O₂ concentration in flue gas exceeds the
 221 tolerance of the MES community, a CO₂/O₂ separation step, such as adsorption or membrane
 222 separation (Wilberforce et al., 2019), is also required.
 223



224
 225 **Figure 3.** Example of integration of MES for treatment of CO₂-containing flue gas from the
 226 combustion of carbonaceous fuels. MES energy products (e.g. methane or alcohols) can be
 227 blended to the fossil fuels, further decreasing the carbon footprint of power plants.
 228

229 2.3 Reactor design for scale-up

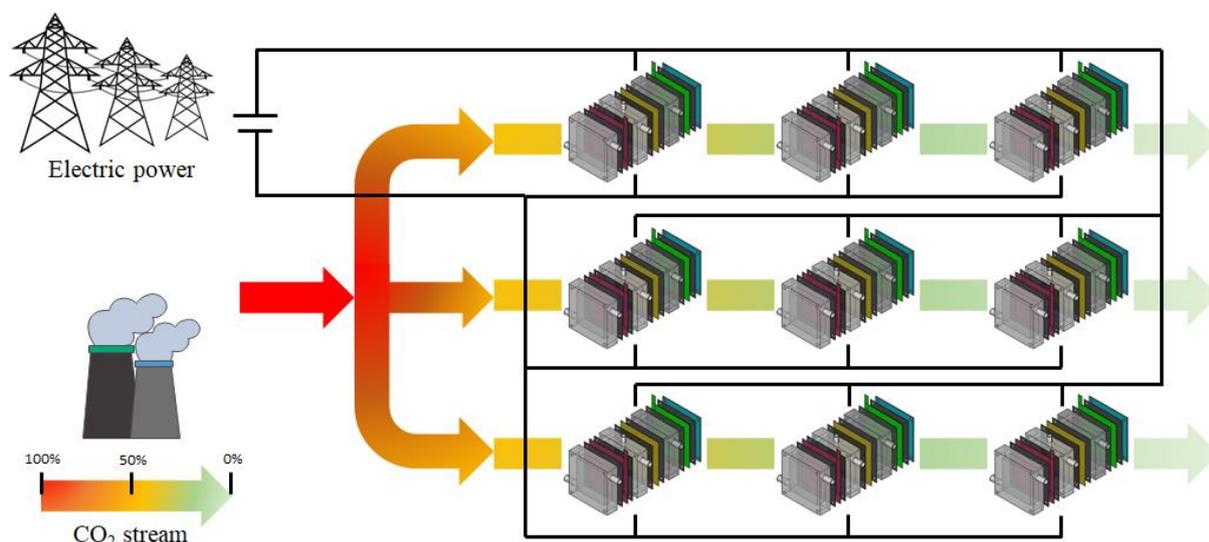
230 Due to their simplicity, H-type MES cells have been commonly used for lab-scale
 231 experiments (Deutzmann and Spormann, 2017; Gavilanes et al., 2019; Mohanakrishna et al.,
 232 2020). Such design, however, is not an optimal solution for scale-up, due to (i) the large area
 233 requirements, (ii) the lack of modularity and versatility, and (iii) the high ohmic losses
 234 associated to low electrode surface/volume capability, low membrane surface, inefficient
 235 hydrodynamics, and a large distance between anode and cathode.
 236

237 Since in bioelectrochemical systems the overpotential (*i.e.* the extra-voltage required for a
 238 reaction to occur in comparison to the theoretical) unavoidably increases with the reactor size
 239 (Rossi et al., 2019), a small, compact, and stackable reactor design is preferable for scaling-
 240 up rather than a single, large volume reactor (Greenman and Ieropoulos, 2017). Furthermore,
 241 stacks with several MES cells facilitate maintenance, since individual cells can be stopped
 242 without affecting the operation of the other cells. Multi-chamber reactors with flat
 243 (Bajracharya et al., 2016; Srikanth et al., 2018b) or tubular (Batlle-Vilanova et al., 2017;
 244 Blasco-Gómez et al., 2019; Pepè Sciarria et al., 2018) structures are examples of easily

245 scalable and stackable configurations to increase the electrode surface/volume ratio and
246 reduce area requirements. Projected surface/volume ratios above 1 cm²/mL are achievable
247 with flat MES configurations (Srikanth et al., 2018b), and can be further optimised, although
248 the limitations of the microbial catalysts will hamper to reach the extremely low electrolyte
249 volumes of up-to-date electrochemical electrolyzers (Haas et al., 2018; Yin et al., 2019).

250
251 MES stacks can be operated with either series or parallel hydraulic and electric connections.
252 Modules hydraulically connected in parallel receive the same feed rate, favouring
253 replicability, whereas modules connected in series will receive a decreasing CO₂ load,
254 thereby resulting in higher overall CO₂ removal efficiency (Fig. 4). However, the
255 configuration in series is more exposed to the toxic effect of contaminants, if present in the
256 flue gas to be treated, whereas the contaminant load is distributed when MES cells are
257 connected in parallel. Therefore, a hybrid configuration, with parallel lines connected in
258 series (Fig. 4), could be an advantageous solution. The number of parallel lines required can
259 be dimensioned based on the waste flue gas production and reaction rates, whereas the length
260 of the cell series is proportional to the required CO₂ removal efficiency. When comparing the
261 electric configurations, superior performance of parallel than series connection was reported
262 for bioelectrochemical systems stacks (Jafary et al., 2013; Liu et al., 2016). Connection in
263 series could cause operation problems such as polarity reversal and substrate cross-
264 conduction effect, and the resulting parasitic current flows (Gurung and Oh, 2012; Zhuang et
265 al., 2012). Thus, connections in parallel appear preferable for MES, since a reliable cathode
266 potential control (*e.g.* between -0.6 and -1.0 V vs. standard hydrogen electrode, SHE) is
267 required, and because of connections in parallel result in higher current densities than in
268 series (Gurung and Oh, 2012). However, since MES cells are not identical, low resistance
269 paths may occur in the MES stacks, requiring further potential control, as explained in
270 Section 5.3.

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273

274 **Figure 4.** Example of MES reactor stacks with hydraulic connections both in parallel and in
275 series, and electric connections in parallel.

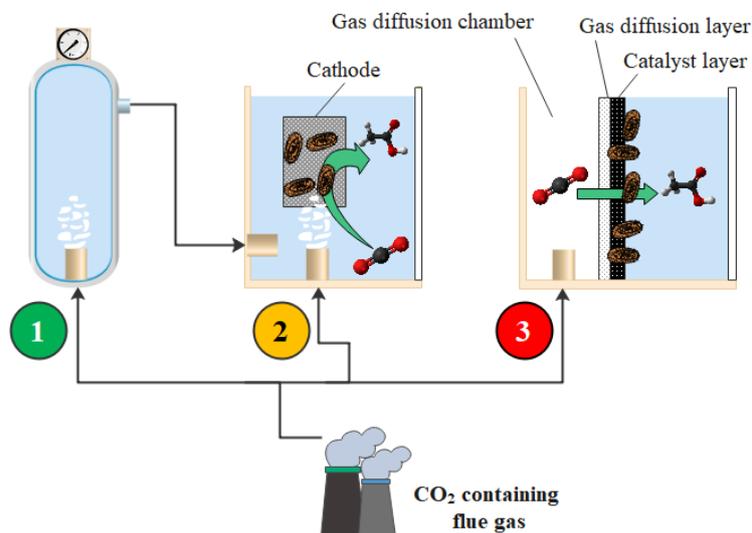
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277 Reporting on MES scaling-up is highly limited, and to date no pilot- or full-scale MES
278 system is reported for CO₂ conversion. However, design of commercially available
279 electrochemical cells, such as electrolyzers, can be potentially applied to scale-up the MES

280 systems with minor modifications, and available pilot-scale studies on other
281 bioelectrochemical systems, such as microbial fuel cells (MFCs), can provide useful
282 guidelines. Configurations of scaled-up, stacked bioelectrochemical systems have been
283 applied for the treatment of swine manure (Vilajeliu-Pons et al., 2017), brewery wastewater
284 (Dong et al., 2015), and municipal wastewater (Feng et al., 2014; Liang et al., 2018; Rossi et
285 al., 2019), as well as ammonia recovery (Zamora et al., 2017). So far, the largest scaled-up
286 bioelectrochemical system is a 1000 L MFC (Liang et al., 2018), a device in which electric
287 energy is produced by biological oxidation of organic or inorganic contaminants and
288 subsequent electron transfer to an electric circuit. It consisted of 50 squared modules (20 L
289 each), electronically connected in parallel. A similar configuration, with the integration of
290 CO₂ feeding lines, can be adapted to MES cells.

291
292 Flue gas can be delivered to MES reactors essentially in three ways: (i) CO₂ solubilisation
293 and feeding as bicarbonate, (ii) direct gas feeding using gas spargers, or (iii) gas diffusion
294 electrodes (Fig. 5). Dissolving CO₂ into a liquid bicarbonate-containing stream could
295 simplify MES operation and improve the carbon conversion efficiency (Srikanth et al.,
296 2018a). However, it requires an additional step for CO₂ solubilisation, leading to higher costs
297 and area requirement. Direct gas utilisation requires more sophisticated design and control
298 (*e.g.* gas composition and pressure monitoring) but is a more viable option in terms of costs
299 and space utilisation. When gas spargers are used in MES, promoting contact between CO₂
300 and microorganisms is key to reach high production rates. This can be achieved by (i)
301 maximising the active electrode surface by filling the cell with conductive granules (Vassilev
302 et al., 2018), (ii) using electrodes with a high specific active surface such as multi-walled
303 carbon nanotubes (Jourdin et al., 2016, 2015), (iii) forcing the CO₂ flow towards the
304 electrode, *e.g.* using hollow fibre cathode electrodes (Katari et al., 2018), or (iv) recirculating
305 gas from the reactor headspace (Mateos et al., 2019).

306



307

308 **Figure 5.** CO₂ feeding strategies to MES reactors. CO₂ can be solubilised in a pressurised
309 reactor and then delivered to the MES reactor (1), or directly delivered to the MES reactor
310 through a sparger (2) or gas diffusion electrode (3).

311

312 Gas diffusion electrodes (GDEs) represent an effective alternative for decoupling the MES
313 process from CO₂ solubilisation. GDEs, first applied to a MES reactor by Bajracharya et al.
314 (2016), consist of a combination of hydrophobic polymeric gas diffusion and catalyst layers,

315 enabling a three-phase (gas-liquid-solid) interphase that allows keeping high CO₂
316 concentrations in proximity of the (bio)catalyst. GDEs have been applied in lab-scale MES
317 devices to produce both carboxylic acids and alcohols with production rates of 238 mg/(L·d)
318 acetic acid (Bajracharya et al., 2016), 360 mg/(L·d) formate and 141 mg/(L·d) ethanol
319 (Srikanth et al., 2018b). Multi-panel GDEs have also been applied as air diffusion cathodes in
320 pilot-scale MFCs treating municipal wastewater with each panel having a surface of 324 cm²
321 (Hiegemann et al., 2019; Rossi et al., 2019). Both studies reported a reduction of MFC
322 performance over time due to fouling, which, nevertheless, is a minor issue in MES reactors
323 owing to the low growth rate of autotrophic microorganisms and the relatively pure catholyte.
324 Therefore, with such flexibility and efficiency, GDEs are promising electrodes for scaling-up
325 MES.

326
327 Minimising the electrolyte volumes along with circulating the catholyte and anolyte towards
328 and away from the respective electrodes is a scalable design solution discerning cell
329 architecture, which is adopted in commercial-scale water electrolyzers and fuel cells (Weekes
330 et al., 2018). Such setup requires a separator to split apart the reduction and oxidation
331 reactions occurring at the cathode and anode, respectively, promoting proton transfer while
332 limiting O₂ flow from the anodic to the cathodic chamber. Proton exchange membranes
333 (PEMs) such as Nafion, widely used in MES lab-scale devices (Kracke et al., 2019;
334 Mohanakrishna et al., 2020; Srikanth et al., 2018b), are expensive. PEMs can cost as high as
335 2500 €/m² and represent up to 30-40% of the capital costs in both electrolyzers and MFCs
336 (Chakraborty et al., 2020; Mayyas et al., 2019). Cheaper options such as textile separators
337 (Dong et al., 2015), as well as membrane-electrode assemblies (Salar-García et al., 2016) and
338 membrane-less configurations (Feng et al., 2014; Hiegemann et al., 2019; Thung et al., 2019;
339 Walter et al., 2020) have been generally preferred for scaling-up MFCs for wastewater
340 treatment, and are potential solutions for MES as well. Low-cost ceramic separators were
341 shown to achieve comparable, or even higher CE than Nafion membranes in MFCs (Khalili
342 et al., 2017). Porous ceramic diaphragm separators are already available at commercial scale
343 for alkaline electrolysis (Ursúa et al., 2012), and can replace expensive ion exchange
344 membranes in MES.

345
346 Membrane-less MES systems can eliminate the costs and ohmic drops associated to
347 separators, but oxygen diffusion towards the cathode needs to be prevented (Butler and
348 Lovley, 2016). A membrane-less MES reactor, in which the CO₂-containing gas sparged
349 from the bottom of the reactor was used to mitigate oxygen diffusion from the anode towards
350 the cathode, was proposed by Giddings et al. (2015). However, the acetic acid production rate
351 of 1.7-2.2 g/(m²·d) achieved using *Sporomusa ovata* was substantially lower than that of 2.7-
352 3.4 g/(m²·d) obtained with the same strain using Nafion membranes (Russell, 2013; Zhang et
353 al., 2013). A membraneless cell was also proposed for biomethane production from CO₂,
354 achieving a production rate of 4.7 L/(m²·d) (Giang et al., 2018). Microfluidic cells, with
355 anode and cathode divided by a thin layer of electrolyte in which CO₂ diffuses, are an
356 emerging technology for CO₂ electrolysis (Weekes et al., 2018), potentially applicable to
357 designing membrane-less MES reactors with minimal distance between electrodes. However,
358 scaling-up of such technology, hardly operable under pressure, is more problematic than
359 traditional setups with membranes (Sánchez et al., 2019).

360

361 **3. Carbon recycling in MES**

362 **3.1 Biocatalysts**

363 Numerous microorganisms from all three domains of life have revealed ability to interact
364 with solid electrodes for their metabolism (Logan et al., 2019). They are classified as
365 exoelectrogens or electrotrophs, respectively, based on their ability of transferring electrons
366 to, or accepting electrons from, an electrode. So far, four types of proteins have been
367 identified to be responsible for electron transfer between electrode and cell surface: (i) porin-
368 cytochrome complexes, (ii) cell-surface cytochromes, (iii) conductive nanowires and (iv)
369 other redox proteins, including copper and iron-sulfur proteins (Costa et al., 2018).
370 Electrotrophs are the core of MES cells, acting as the catalyst for CO₂ conversion to a wide
371 array of valuable products (Lee et al., 2019). They can reduce CO₂ by uptaking electrons
372 either directly from the cathode electrode, or through mediators such as H₂, formate,
373 ammonia, Fe²⁺, or even more complex molecules such as self-produced flavins (Tremblay et
374 al., 2017). Mixed microbial consortia and pure cultures of specific microorganisms, either
375 natural or genetically modified, can act as biocatalyst in MES cells. Each inoculation strategy
376 has its own advantages and disadvantages, as summarized in Table 1.

377
378 Mixed cultures from natural and anthropogenic environments have been widely used as
379 biocatalyst in bench-scale MES cells for production of methane (Geppert et al., 2019; Jiang et
380 al., 2013), acetate (Jourdin et al., 2015; Mateos et al., 2019), as well as mixtures of medium-
381 chain carboxylic acids (Batlle-Vilanova et al., 2017; Vassilev et al., 2019, 2018) and alcohols
382 (Arends et al., 2017; Blasco-Gómez et al., 2019; Gavilanes et al., 2019; Srikanth et al.,
383 2018b) from CO₂. Mixed cultures represent the easiest and cheapest inoculation strategy for
384 MES, but the low product selectivity (except for acetate) and the possible competition
385 between acetogenic and methanogenic microbial communities are still unresolved challenges.

386 In comparison to mixed cultures, pure cultures offer higher product selectivity and eliminate
387 competition issues. However, handling of pure cultures is laborious, requiring sterilization
388 and a stable ecosystem. Nonetheless, avoiding contamination in CO₂-fed cells appears easier
389 than in reactors treating solid or liquid waste, making the use of pure cultures suitable for
390 industrial MES applications. Among pure cultures, acetogenic bacteria including *Sporomusa*
391 *ovata*, *S. sphaeroides*, *Clostridium ljungdahlii* and *Moorella thermoacetica* have been
392 confirmed to reduce CO₂ to acetate by accepting electrons from a MES cathode (Nevin et al.,
393 2011, 2010), whereas other microorganisms such as *Acetobacterium* sp. exploit locally
394 produced H₂ as the electron source (Marshall et al., 2017). Indirect (H₂-mediated)
395 electromethanogenesis was reported by using a pure culture of *Methanococcus maripaludis*
396 that converted CO₂ and on-site electrochemically produced H₂ to methane (Kracke et al.,
397 2020). H₂-mediated electron transfer has been postulated to be less energy efficient than
398 direct electron transfer (Karthikeyan et al., 2019), in which, nevertheless, the production
399 yields can suffer of low electron exchange rates.

400 Genetic engineering approaches have been proposed to overcome the limitation of
401 microorganisms in terms of electron transfer rates and cathode interaction, as well as to
402 manipulate the metabolic pathways to target specific biocommodities (Shin et al., 2017).
403 Metabolic engineering can provide a reliable method to go beyond the low-value chemicals
404 naturally produced at the cathode (e.g. acetate), and achieve high-rate production of more
405 valuable chemicals that are typically obtained in traces (e.g. multi-carbon chain biochemicals

406 and biofuels (Kracke et al., 2018). However, an insufficient knowledge of the fundamental
 407 mechanisms is limiting the adoption of genetic engineering in MES, and research efforts are
 408 required to expand the toolset available for manipulating electricity-driven metabolic
 409 pathways. Furthermore, the high costs, as well as the legislative requirements, summarized in
 410 the review from Voeikova et al. (2020), make this approach complicated and economically
 411 dependent on the production capacity and value of the output products.

412 **Table 1.** Advantages and disadvantages of the different biocatalysts for MES.

Type of biocatalyst	Advantages	Disadvantages
Mixed microbial culture	+ Easy to operate + Widely available + Resistant to system fluctuations + Resistant to O ₂ intrusion + Easy to start-up upon failure	- Prone to membrane biofouling - Low selectivity for products other than acetate - Possible competition between acetogens and methanogens and/or establishment of other competitors
Pure microbial culture	+ High selectivity + Easy optimisation for highest production rates-yields + Prevents growth of competitors	- Laborious start-up procedure - Requires a specific growth medium - Requires sterilisation - Vulnerable to system fluctuations - Vulnerable to O ₂ intrusion
Genetically modified microorganisms	+ Same advantages of pure microbial cultures + Wider product spectrum and selective production of high-value molecules + Can be made resistant to system fluctuations and O ₂	- Expensive and laborious start-up procedure - Requires a specific growth medium - Requires sterilisation - Questionable societal acceptance - Requires approval by the government

413

414 **3.2 Production rates and product selectivity**

415 Acetic acid is, to date, the major product obtained with MES. The highest specific production
 416 rate of 790 g/(m²·d) was achieved using three-dimensional (3D) macroporous cathodes, far
 417 beyond the production rate obtained with unmodified carbon-based electrodes (Jourdin et al.,
 418 2018, 2016). Acetic acid can be produced from CO₂ in MES with high selectivity (>90%),
 419 and CE exceeding 85% (Nevin et al., 2010). Despite the developments in electrode design,
 420 the acetic acid production rate is limited by the low current densities, typically below 20
 421 mA/cm², which is one order of magnitude lower than those achieved in electrolyzers
 422 (PrévotEAU et al., 2020). In MES, besides the inherent limitations of the biological catalysts,
 423 the current density is limited by the kinetically unfavourable oxygen evolution reaction at the
 424 anode. This is particularly relevant when carbon electrodes are used, resulting in potential
 425 differences as high as 3 V, or even more, between cathode and anode (Bian et al., 2020).
 426 Furthermore, the anode has been individuated as the highest contributor to capital
 427 expenditure in MES cells (Jourdin et al., 2020). Using photoanodes, or exploiting less
 428 energy-demanding (bio)reactions at the anode, such as the oxidation of organic pollutants, are
 429 potential solutions currently under investigation (described in Section 5.2).

430

431 Methane can be produced at biocathodes in alternative to acetic acid. So far, the highest
 432 methane production rate of 12.5 L/(L·d), with 65% current-to-methane efficiency, was
 433 achieved using a mixed culture from a biogas plant in a galvanostatic flow-cell designed to

434 maximise surface area ($2 \text{ cm}^2/\text{cm}^3$) and optimise flow distribution (Geppert et al., 2019). In
435 this study, the methane production rate was shown to increase linearly with the applied
436 current (in the range $0.5\text{-}3.5 \text{ mA}/\text{cm}^2$), although hydrogen was detected at currents above 2.5
437 mA/cm^2 , suggesting metabolic limitations of the biocatalyst. Methane has often been reported
438 as co-product in acetogenic MES (Marshall et al., 2013; Patil et al., 2015). When mixed
439 cultures are used as inoculum, and when MES cells are operated at neutral pH, methanogenic
440 organisms can indeed compete with acetogens for H_2 , or even convert carboxylic acid into
441 methane. Methanogenic growth can be prevented by pre-treating the inoculum, *e.g.* by heat
442 (Bajracharya et al., 2017c) or chemical treatment (Marshall et al., 2013), although these
443 procedures do not ensure their permanent elimination.

444
445 The product spectrum of MES has expanded away from acetic acid towards more valuable
446 compounds in the past few years, being butyrate and caproate two of the main products of
447 interest (Table 2). Chemical commodities such as formate (Tashiro et al., 2018) and 3-
448 hydroxybutyrate (Chen et al., 2018) have been obtained *via* MES from CO_2 as the sole
449 carbon source using pure cultures and metabolic engineering tools. However, the scalability
450 of this approach remains arguable and requires further investigation. Mixed cultures from
451 different sources, nevertheless, have shown potential for the production of carboxylic acids
452 and alcohols from CO_2 in MES, up-to six-carbon chains (Vassilev et al., 2018). Operation
453 conditions, in particular pH, hydrogen partial pressure and inorganic carbon concentration,
454 can be fine-tuned to steer the production of the target compound (Blasco-Gómez et al., 2019).
455 In MES, pH can be controlled by CO_2 sparging, without the need for added chemicals
456 (Bajracharya et al., 2017c; Ganigué et al., 2015), which represents a key advantage for full-
457 scale applications. Low pH (< 5.5) has been observed to promote solventogenesis, whereas
458 pH close to neutrality is more favourable for butyric and caproic acid formation *via* chain
459 elongation (Vassilev et al., 2018). Based on this observation, a dual biocathode arrangement
460 was proposed to set an optimal pH of 6.9 for acetogenesis and chain elongation in one
461 chamber, and a pH of 4.9 to promote solventogenesis in a second chamber (Vassilev et al.,
462 2019). High hydrogen partial pressure was shown to promote acetic acid production rates, as
463 well as solventogenesis, when combined with low pH (Blasco-Gómez et al., 2019), whereas
464 low H_2 partial pressures turned out to favour biological H_2 evolution (Philips, 2020).
465 Otherwise, a high concentration of dissolved CO_2 promotes acetic acid production, but results
466 in lower product diversification (Arends et al., 2017).

467

468 **Table 2.** Biochemicals and biofuels obtained from CO₂ in MES cells operated in potentiostatic (*i.e.* constant voltage operation) or galvanostatic
 469 (*i.e.* constant current) mode under different operational conditions.

Product	Highest production rate (g/(L·d))	Main carbon sources	pH	T (°C)	Potentiostatic control (V vs. SHE)	Galvanostatic control (mA/cm ²)	Cathode	Reference
<i>Biochemicals</i>								
Acetate	77	NaHCO ₃	5.2	35	-1.10	n.a	3D-reticulated vitreous carbon	Jourdin et al. (2016)
	66	NaHCO ₃	6.7	35	-0.85	n.a	Multi-walled carbon nanotubes	Jourdin et al. (2015)
	18.72	CO ₂	7.0	25	n.a.	-83	Reticulated vitreous carbon foam	LaBelle and May (2017)
	9.85	CO ₂ :N ₂ 30:70%	5.8	32	-0.85	n.a.	Carbon felt	Jourdin et al. (2018)
	0.26	Brewery flue gas (98% CO ₂)	7.0	28	-0.80	n.a.	Graphite plate	Roy et al. (2021)
Butyrate	5.70	CO ₂ :N ₂ 30:70%	5.8	32	-0.85	-5 to -12	Carbon felt	Jourdin et al. (2019)
	0.54	Acetate, (NH ₄) ₂ CO ₃ and CO ₂	5.5	30	n.a.	-0.93	Carbon felt	Raes et al. (2017)
	0.16	CO ₂	6.3	38	-0.80	n.a.	Carbon cloth	Battle-Vilanova et al. (2017)
	0.04	CO ₂	6.4	35	-0.80	n.a.	Carbon cloth	Ganigué et al. (2015)
Caproate	2.41	Ethanol, CO ₂ and NaHCO ₃	7.0	30	n.a.	-1.0	Carbon felt	Jiang et al. (2020)
	2.00	CO ₂ :N ₂ 30:70%	5.8	32	-0.85	-5 to -12 ^a	Carbon felt	Jourdin et al. (2019)

Formate	0.36	CO ₂	8.0	29	-0.80	n.a.	Gas diffusion electrode	Srikanth et al. (2018b)
<i>Biofuels</i>								
Butanol	0.06	CO ₂	8.0	29	-0.80	n.a.	Gas diffusion electrode	Srikanth et al. (2018b)
Ethanol	0.18	CO ₂	8.0	29	-0.80	n.a.	Gas diffusion electrode	Srikanth et al. (2018b)
	0.05	CO ₂	5.4	25	-0.80	n.a.	Granular graphite	Blasco-Gómez et al. (2019)
Isopropanol	0.06	CO ₂ :N ₂ 10:90%	5.0	30	n.a.	-0.5	Carbon felt	Arends et al. (2017)
Methane	12.5 ^b	NaHCO ₃	7	30	n.a.	-1.0 to -3.5	Graphite felt	Geppert et al. (2019)
	0.53 ^b	CO ₂	n.a.	30	-0.85	n.a.	Carbon felt	Jiang et al. (2013)

470 ^a The cell was first operated in potentiostatic mode, and successively in galvanostatic mode; ^b Units in L/(L·d); n.a.: non-available.

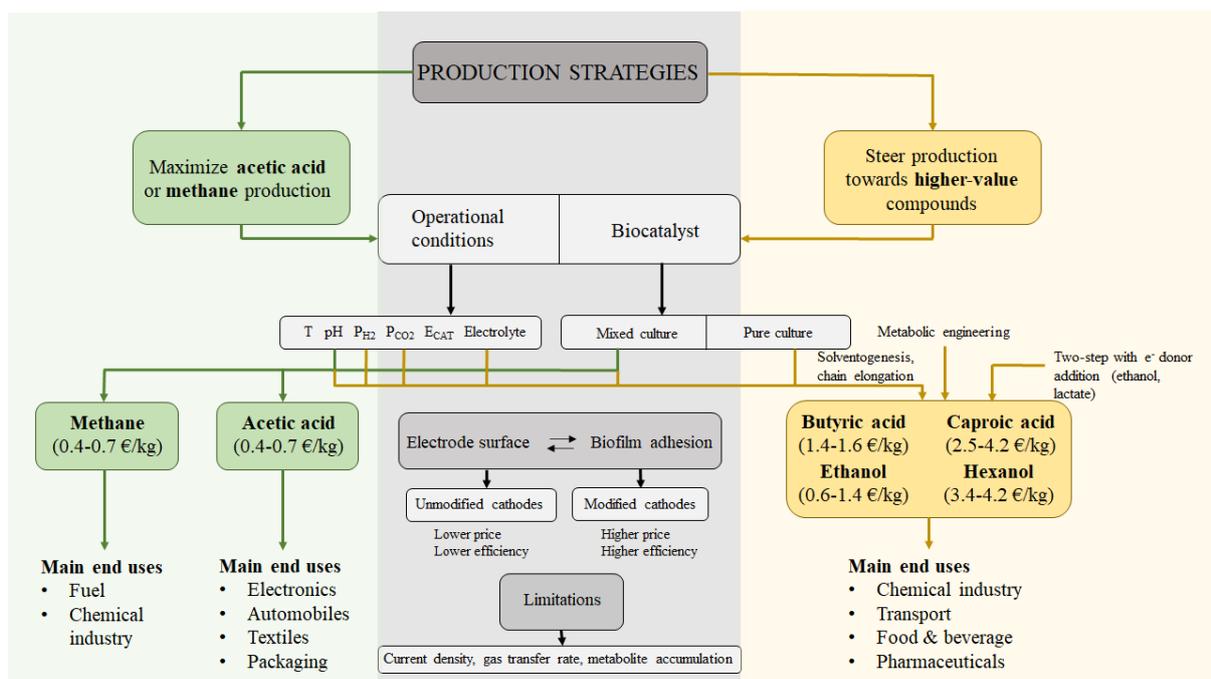
471

472 Butyrate production from CO₂ in MES was achieved for the first time by Ganigué et al.
473 (2015), with a production rate of 0.04 g/(L·d). Batlle-Vilanova et al. (2017b) triggered its
474 selective production by operating the reactor at pH close to 5 and hydrogen partial pressure
475 above 1 atm, reaching a maximum rate of 0.16 g/(L·d). Jourdin et al. (2019) reinforced
476 butyrate and caproate production (maximum rates of 5.7 and 2.0 g/(L·d), respectively) by
477 increasing the CO₂ loading rate up to 173.2 L/d. In this study, ethanol was first produced by
478 acetate reduction and then acted as the electron donor for chain elongation. However, in
479 another study (Jourdin et al., 2018), caproate was produced at a rate of 0.95 ± 0.05 g/(L·d),
480 together with acetate (9.8 ± 0.65 g/(L·d)) and butyrate (3.2 ± 0.1 g/(L·d)), but without ethanol
481 production, suggesting that the cathode was acting as the sole electron donor. At low pH,
482 butyric and caproic acid were reduced to the corresponding alcohols (butanol and hexanol),
483 opening possibilities of producing high-value biofuels in MES, although low titers of 0.8 and
484 0.2 g/L, respectively, were achieved (Vassilev et al., 2018). On the other hand, isopropanol
485 production could be triggered in MES at pH 5 by maintaining low dissolved CO₂
486 concentrations in the catholyte. The production rate was stable at $5.85 \pm 0.17 \times 10^{-2}$ g/(L·d)
487 working under a hydraulic retention time of 5 days (Arends et al., 2017).
488

489 **3.3 Production strategies**

490 Development of cost-effective MES reactors for CO₂ recycling involves two diverging
491 strategies: (i) maximise production rate of low-value products with high market request (*i.e.*
492 acetic acid or methane), or (ii) steer production towards more valuable products, though at
493 lower production rates (Fig. 6). The first strategy, in which the main target is the abatement
494 of high CO₂ volumes, appears as the most feasible in the short term. Selective acetic acid
495 production *via* MES, with both pure and mixed cultures, has been extensively demonstrated
496 from different inorganic carbon sources, including bicarbonate (Jourdin et al., 2015), pure
497 CO₂ gas (Song et al., 2017), and brewery flue gas (Roy et al., 2021). Versatile mixed cultures
498 can achieve comparable, or even higher, acetic acid production rates than pure cultures, with
499 similar specificity and CEs (Jiang et al., 2019). High product selectivity will make the
500 product downstream processing easier and cheaper. Similarly, methane can be selectively
501 produced in MES cells using widely available methanogenic cultures from biogas plants
502 Geppert et al. (2019).
503

504 Despite the technological advances of the field, production rates far beyond the current record
505 are required for MES commercialisation, due to the low value of acetic acid and methane
506 (0.4–0.7 €/kg). When modelling for an industrial production of 1000 tons/year with an
507 assumption of 69% CE, an unsustainable production cost of about 6.6 €/ton acetic acid was
508 estimated, which could be reduced by 33% using renewable energy. Other products such as
509 ethanol (1.0 €/kg) and formate (0.4 €/kg) are more cost-attractive (Christodoulou et al.,
510 2017). Ethanol was also shown to have the most positive effect on GHG emissions, with a
511 negative global warming potential of -753 t CO₂eq (Christodoulou et al., 2017).
512



513
514 **Figure 6.** Production strategies for microbial electrosynthesis of organic compounds from
515 CO₂. Market prices have been obtained from marketsandmarkets.com (acetic acid, ethanol
516 and butyric acid), transparencymarketresearch.com (methane) or alibaba.com (caproic acid
517 and hexanol). Selective acetic acid and methane production can be achieved using mixed
518 cultures. Production of longer-chain carboxylic acid, both using pure and mixed cultures,
519 requires a stricter control of operation parameters such as pH, hydrogen and CO₂ partial
520 pressure (P_{H₂} and P_{CO₂}), and electrolyte composition. Alternatively, engineered
521 microorganisms, or a two-step process combining MES to fermentation with an added
522 electron donor, are viable strategies to produce high-value chemicals.

523
524 Beyond acetic acid and ethanol, conversion of CO₂ to longer-chain carboxylic acids or
525 alcohols, though with lower production rates, offers an interesting economic perspective.
526 Such products are currently mainly manufactured *via* chemical synthesis from fossil-fuel
527 based precursors. The expected dynamic growth in their market size, in combination with the
528 fees (up to 99 €/ton, with an increasing trend) associated to CO₂ emission (Luckow et al.,
529 2016), can foster the use of CO₂ as an alternative feedstock. Increasing demand for so-called
530 cosmeceutical products is catalysing the global carboxylic acid market, in which compounds
531 such as butyric and caproic acid are extensively used (Future Market Insights, 2020; Global
532 Market Insights, 2020). Due to their high energy density and low hygroscopicity, higher
533 alcohols such as butanol and hexanol have been the focus of recent research initiatives
534 (Vassilev et al., 2018). Butanol can be directly incorporated in the current fuel infrastructure,
535 whereas hexanol, besides being an alternative to petrol-derived gasoline, has multiple end-
536 uses in the pharmaceutical, cosmetic, textile, food (both as pesticide and flavouring agent),
537 and leather industry (Fernández-Naveira et al., 2017).

538
539 MES has the potential for meeting the future demand of the chemical industry, but further
540 research is required to achieve production costs comparable to the currently applied chemical
541 synthesis. Furthermore, despite the efforts aimed at understanding the metabolic pathways
542 governing MES, and how they are affected by the operation conditions (Blasco-Gómez et al.,
543 2019; Vassilev et al., 2018), a replicable, robust strategy for the selective production of
544 carboxylate molecules other than acetic acid has not yet been developed.

545

546 **4. Downstream processing**

547 Downstream processing of MES products, including extraction, fractionation, concentration
 548 and purification, can account for more than 60% of the production cost (PrévotEAU et al.,
 549 2020). Thus, development of a cost-effective extraction and separation method is crucial to
 550 achieve large-scale production of bio-based chemicals. Several extraction techniques have
 551 been proposed for extraction and separation of typical MES products, such as C2-C6
 552 monocarboxylic acids (Table 3), described in the following sections.
 553

554 **Table 3.** Main investigated technologies for extraction and separation of organic acids from
 555 fermentation broths.

Technology	TRL ^a	Advantages	Disadvantages	References
<i>Conventional separation processes</i>				
Adsorption in ion exchange resins	Industrial	Low CAPEX ^b ; no pretreatment needed	Ion-exchange influenced by pH	Bajracharya et al. (2017b); Rebecchi et al. (2016); Reyhanitash et al. (2017); Saito et al. (2009)
Liquid–liquid extraction	Industrial	High extraction efficiency	High OPEX ^c (compared to pertraction) and large use of extractant	Alkaya et al. (2009); Bekatorou et al. (2016); Reyhanitash et al. (2016); Saboe et al. (2018)
<i>Concentration-driven and pressure-driven membrane processes</i>				
Pertraction (membrane liquid–liquid extraction)	Industrial	High extraction efficiency; low OPEX; selective extraction possible (based on hydrophobicity)	Selectivity depends on solvent	Agler et al. (2012); Aydin et al. (2018); Battle-Vilanova et al. (2017); Dessì et al. (2020); Nuchnoi et al. (1987); Outram and Zhang (2018); Plácido and Zhang (2018); Yesil et al. (2014)
Pervaporation	Lab	Simultaneous extraction and liquid–vapour phase change	Loss of extractant <i>via</i> evaporation; selectivity depends on permeate pressure (high vacuum needed)	Choudhari et al. (2015); Qin et al. (2003)
Nanofiltration	Industrial	Low CAPEX/OPEX; high rejection of high-molecular weight solutes	Separation strongly affected by pH and electrostatic interactions with membrane	Cho et al. (2012); Xiong et al. (2015); Zacharof et al. (2016)
Forward osmosis	Demo	High rejection of organics	Membrane biofouling and VFA degradation; rejection rates dependent on availability and concentration of draw solution	Blandin et al. (2019); Cho et al. (2012)
<i>Electro-membrane processes</i>				
Electrodialysis (ED)	Industrial	Low OPEX; easily scalable	Low selectivity among carboxylates and other anions	Cerrillo et al. (2016); Jones et al. (2017, 2015); Scoma et al. (2016); Zhang and Angelidaki (2015)
Membrane electrolysis	Industrial	Reduced chemical dosage thanks to in-situ production of H ⁺ /OH ⁻	Membrane fouling; less easily scalable than ED (because of non-modular unit)	Gildemyn et al. (2015); Xu et al. (2015)

Electrodeionization (EDI)	Industrial	Possibility to treat very diluted streams; reduced energy consumption	Higher pressure drops and fouling tendency (compared to ED)	Lopez and Hestekin (2015)
Bipolar electro dialysis (BMED)	Lab/demo	Reduced chemical dosage thanks to in-situ production of H ⁺ /OH ⁻	No selectivity for a specific organic acid; higher membrane costs (compared to ED)	Arslan et al. (2017); Shi et al. (2018); Xue et al. (2017)
Reactive extraction processes				
Reactive extraction with ionic liquids	Lab	Simultaneous extraction and esterification	High costs of ionic liquids with good extraction properties; ionic liquid losses	Andersen et al. (2016)
Reactive extraction in supercritical CO ₂	Lab	Higher partition coefficient than physical extraction	Product losses due to formation of acid-amine complexes	Djas and Henczka (2018); Henczka and Djas (2016)

^a Technology readiness level; ^b Capital expenditures; ^c Operational expenditures.

556
557

4.1 Conventional separation processes

559 Conventional processes widely investigated for separation of organic acids are adsorption and
560 liquid-liquid extraction (LLE). Adsorption is based on the ion exchange between carboxylate
561 groups and functionalized solid sorbents, *e.g.* amine-based anion exchange resins (Rebecchi
562 et al., 2016; Reyhanitash et al., 2017). In most cases, the performance of the sorbent depends
563 on the pH of the solution. High adsorption capacities are achieved at intermediate pH values
564 (~6.5), since an increasing pH causes an increasing concentration of acid in ionized form, but
565 also a reduction of the amine concentration in protonated form (Rebecchi et al., 2016).

566
567 LLE is also a well-studied technology for separation of organic acids (Alkaya et al., 2009;
568 Reyhanitash et al., 2016). Organophosphates such as tri-*n*-octylphosphine oxide (TOPO), tri-*n*-
569 butyl phosphate and aliphatic amines have been identified as the most suitable extractants.
570 Alkaya et al. (2009) used TOPO in kerosene to recover VFAs from a fermentation broth of
571 sugar beet processing waste, reaching VFA recoveries of 61–98%, where the efficiency
572 increases with increasing TOPO concentration (up to 20 wt%).

573

4.2 Concentration-driven and pressure-driven membrane processes

575 Pertraction is a membrane process where an organic solvent is immobilized (by capillary
576 forces) inside the pores of a hydrophobic microfiltration membrane, thus separating the feed
577 from the permeate (Dzygiel and Wiczorek, 2010). Organic compounds from the feed diffuse
578 through the organic solvent in the membrane and can be continuously back-extracted on the
579 permeate side. The membrane only acts as mechanical support, thus the extraction selectivity
580 relies only on the extractant. Pertraction has been widely adopted for VFA extraction (Table
581 3), since it has several advantages compared to conventional LLE, such as (i) small amounts
582 of organic solvent required, (ii) simultaneous extraction and solvent stripping, and (iii) lower
583 operational costs. When using hollow fibre membranes, the organic phase is typically fed on
584 the shell side and the aqueous feed on the tube side, although the opposite configuration
585 could result in higher mass transfer rates (Pabby and Sastre, 2013). Recently, the use of
586 silicone membranes has also been proposed, with water as extractant, showing good
587 selectivity towards VFAs based on hydrophobicity (isovaleric > butyric > acetic) (Outram
588 and Zhang, 2018). A silicone membrane was applied *in-line* to a cheese whey fermentation
589 process by Dessì et al. (2020), achieving selective extraction of butyric acid over propionic

590 and acetic acid. However, low pH (as close as possible to carboxylic acid pK_a) is required,
591 since only undissociated acids can be extracted. The process was also shown suitable for
592 alcohol extraction, whereas nutrients were retained, highlighting its potential for *in-line*
593 product extraction from the MES catholyte.

594
595 In pervaporation, the target compounds are extracted *via* partial vaporization through a
596 membrane, by maintaining the permeate side under vacuum. The extractant must have high
597 boiling point, low viscosity, and low solubility in water, and the most used extractants are
598 high-molecular-weight alkyl amines such as trioctylamine (TOA), trilaurylamine (TLA), and
599 tri-*n*-octylphosphine oxide (TOPO) (Nuchnoi et al., 1987; Qin et al., 2003).

600
601 Nanofiltration (NF) has been also widely investigated for VFA separation. Xiong et al.
602 (2015) used commercial NF membranes to separate organic acids in lignocellulosic biomass
603 digestion liquors, achieving 86% recovery (except for butyric acid, likely due to interactions
604 with other components in the digestion liquor). In NF, the pH affects both the surface charge
605 of the membrane and the degree of ionization of the acids. Acetic acid rejection increased
606 from 0 to 62% with pH increase from 3 to 7 (Xiong et al., 2015), since at high pH the
607 membrane (negatively charged) rejects carboxylate ions due to electrostatic effects.
608 Therefore, low pH (in the range of 2.9-3.0) is advantageous for acetic acid separation via NF
609 (Cho et al., 2012), which could preclude its *in-line* application to MES.

610
611 Forward osmosis (FO) exploits the osmotic pressure difference between the feed and a draw
612 solution kept at the same hydrostatic pressure. The process efficiency, fouling and energy
613 consumption are strongly influenced by the composition and concentration of the draw
614 solution. Blandin et al. (2019) used FO to concentrate VFAs (mainly acetic acid) from
615 domestic wastewater, achieving rejection rates >80% at pH 7.5. At pH 4, instead, the
616 rejection drastically decreased, since the separation becomes mostly steric for undissociated
617 acids (*i.e.*, small molecules such as acetic acid can pass through the FO membrane, while
618 larger molecules are rejected), thus showing the possibility to achieve selective separation.
619 Rejection is also affected by molecule geometry (*e.g.*, *n*-butyric acid shows higher rejection
620 than iso-butyrac acid), hydrophilicity, electrostatic and specific solute-membrane interactions.
621 In general, anti-fouling strategies (*e.g.* backwashing) are crucial to limit VFA biodegradation
622 on the membrane surface.

623 624 **4.3 Electro-membrane processes**

625 Electrodialysis (ED) is the most widely applied electro-membrane technology at industrial
626 scale, and has also been widely investigated for organic acid recovery (Huang et al., 2007).
627 Jones et al. (2017, 2015) achieved up to 99% VFA recovery from hydrogen fermentation
628 broths, and also demonstrated the use of ED for *in-line* VFA extraction. However, ED suffers
629 from low selectivity towards organic acids, and other anions (such as Cl⁻) are also inevitably
630 extracted, especially if present at high concentration (Scoma et al., 2016).

631
632 Membrane electrolysis is an ED-based technology where anode and cathode play a crucial
633 role in the process by producing H⁺ and OH⁻ (Xu et al., 2015). Membrane electrolysis has
634 been applied (in combination to pertraction) to selectively extract caproic acid from a
635 fermentation broth, in which a pH gradient between the two chambers was electrochemically
636 maintained, without chemicals addition (Xu et al., 2015).

637
638 Another alternative is bipolar membrane electrodialysis (BMED), *i.e.* an ED-like system that
639 contains a bipolar membrane to promote water dissociation into H⁺ and OH⁻ *via* a catalysed

640 protonation-deprotonation mechanism. The main advantage of BMED is the *in-situ*
641 production of H⁺ and OH⁻ on the membrane surface, thus allowing pH change in the cell
642 without dosing chemicals. BMED has been proposed for simultaneous electrochemical
643 production and recovery of acetic acid (Zhang et al., 2011) and propionic acid (Boyaval et al.,
644 1993).

645
646 A possible strategy to further enhance the separation efficiency is to use electrodeionisation
647 (EDI), *i.e.*, an ED-like system where the compartments are filled with ion exchange material
648 (*e.g.* beads or wafers), to enhance ion transport in dilute stream conditions. Lopez and
649 Hestekin (2015) used an EDI cell with ion exchange wafer and ionic liquids to remove
650 butyrate and acetate from a synthetic fermentation broth, showing current efficiency up to
651 90% and energy consumptions of 1.25-2.80 kWh/kg acid recovered.

652 653 **4.4 Reactive extraction processes**

654 Ionic liquids (ILs) have been investigated for selective extraction of organic acids. Andersen
655 et al. (2016) used ILs for the simultaneous concentration and esterification of MES-produced
656 acetic acid (extracted *via* membrane electrolysis). Acetic acid was concentrated up to 80 mM
657 using a bis(trifluoromethylsulfonyl)-imide IL, followed by esterification to ethyl acetate,
658 upon ethanol addition, with a maximum conversion of 90%. This proof-of-concept study
659 opens opportunities for widening the product spectrum of MES.

660
661 Another proposed strategy to recovery VFAs is the reactive extraction using organic solvents
662 in supercritical CO₂ (Djas and Henczka, 2018). Henczka and Djas (2016) investigated the
663 reactive extraction of acetic and propionic acid (0.07-1.04 M) using TOA in supercritical CO₂
664 (at 35-65°C and 80-160 bar), reaching a highest extraction efficiency of 94.7% for propionic
665 acid, although part of the product was lost due to the formation of acid-amine complexes.
666 Both pressure and temperature significantly influence the separation efficiency, due to the
667 effect on the density and solvating power of supercritical CO₂.

668 669 **4.5 Perspectives for integrated MES-VFA extraction systems**

670 Achieving selective separation of VFAs from dilute aqueous streams is still one of the biggest
671 challenges for upscaling VFA biological production. The separation selectivity is influenced
672 by several factors, such as pH, mobility, hydrophobicity, molecular weight, and ionization
673 degree of the target product (Moon et al., 1998). This is especially challenging in MES, due
674 to the low product concentration. For instance, MES reactors can only produce up to 7–10
675 g/L acetate, due to product inhibition (Bajracharya et al., 2017c). These concentrations are
676 not yet sufficient for economically upscaling if compared to industrial fermentation
677 processes, where concentrations of 20–200 g/L of organic acids can be achieved (López-
678 Garzón and Straathof, 2014). In this regard, the maximisation of MES production rates is
679 strictly linked to the development of an efficient *in-situ* extraction system, to minimise
680 product degradation and alleviate the inhibition caused by the end-product accumulation
681 (Batlle-Vilanova et al., 2017).

682
683 Since both extraction and concentration of VFAs are pH-dependent processes, an efficient pH
684 control is of outmost importance to minimize the operational costs. In this regard,
685 technologies that can provide *in-situ* production of H⁺ and OH⁻ (such as BMED, or
686 membrane electrolysis) are advantageous to reduce the chemical dosage for pH control. For
687 membrane-based extraction processes, one of the challenges in process integration with MES
688 is preventing fouling. Pretreatment of the fermentation broths is required to remove
689 suspended solids and colloids that can cause fouling, and tailored membrane with anti-fouling

690 properties and increased selectivity toward organic anions should be designed. Since ED-
691 based technologies suffer of low selectivity towards the target products, they can be deployed
692 as final concentration step after extraction using membrane technologies with higher selective
693 extraction capabilities, such as pertraction, forward osmosis, or pervaporation (especially in
694 the case of VFAs).

695
696 Very limited information is available in literature on capital and operation costs for VFA
697 purification, which depend on the maturity and market of the separation technology, and on
698 the economy of scale of the MES process. Jourdin et al. (2020) estimated a capital cost of
699 1000 €/ton, and an operation cost of 344 €/ton for the separation of caproic acid produced as
700 the sole product in a MES cell. However, such rough estimation did not take into account the
701 economy of scale factor, and costs will inevitably increase when separating specific products
702 from mixtures of organic compounds, which appears as a more realistic scenario with the
703 current state-of-art MES technology.

704

705 **5. Development of sustainable MES biorefineries**

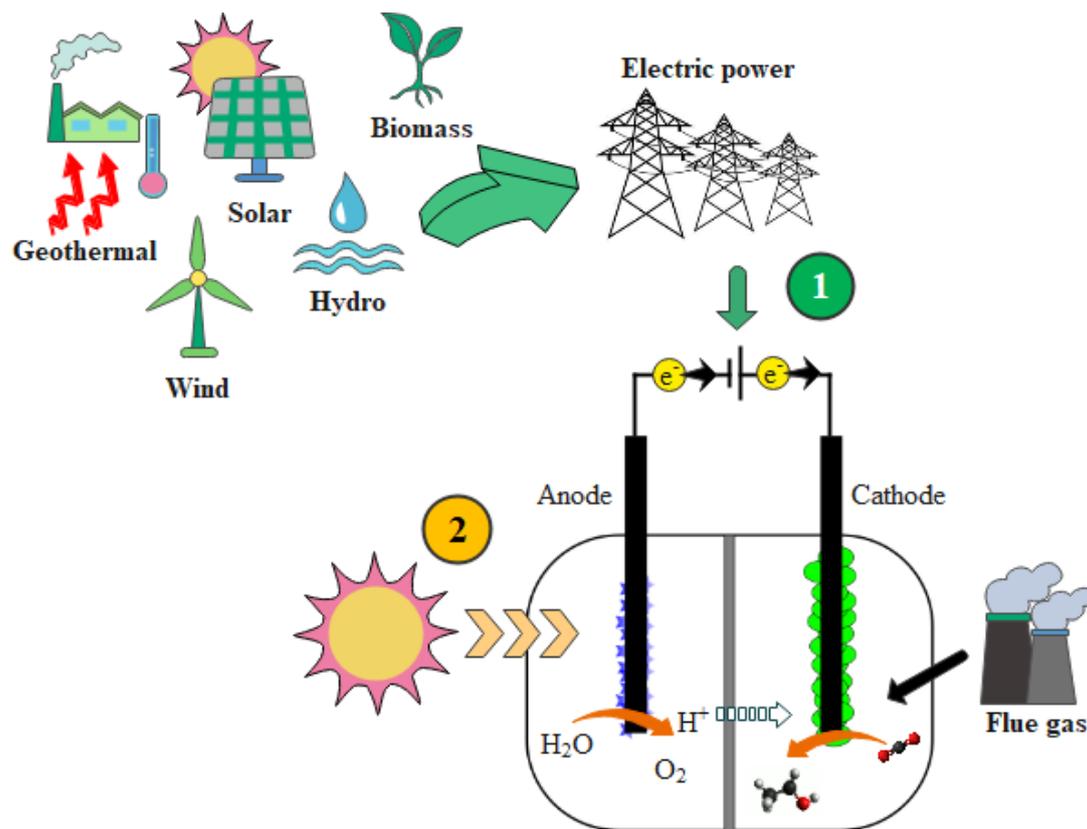
706 **5.1 Renewable energy sources to power MES**

707 Electric energy is a major cost for (bio)electrochemical processes. When assuming an
708 optimistic CE of 90% and an operational voltage of 3 V, it was estimated that about 12 kWh_{el}
709 are necessary for producing 1 kg of acetic acid, and such power consumption nearly doubles
710 for producing caproic acid (PrévotEAU et al., 2020). Considering the current average price of
711 69 €/MWh (Child et al., 2019), the electricity cost for producing 1 kg of acetic acid (0.83 €)
712 is already higher than its commercial value, without taking into account operational,
713 maintenance and downstream processing costs. Furthermore, if powered with fossil fuel-
714 based energy, MES could cause a net generation, rather than mitigation, of carbon emissions
715 (Christodoulou et al., 2017). Thus, the use of renewable, low-cost energy is a crucial strategic
716 factor for sustainable MES biorefineries. Renewable energy capacity in EU increased from
717 258 to 512 GWe over the period 2007–2017, with an exceptional growth of solar
718 photovoltaics (+1966%), offshore wind (+1365%), onshore wind (+180%) and bioenergy
719 (+94%). The adoption of renewable energy is forecasted to push down the electricity price by
720 20-30% at least, increasing competitiveness with fossil-fuel-based energy (Child et al., 2019).

721

722 Renewable energy sources can be integrated into MES either indirectly, by using renewable
723 electric energy produced from solar, wind, geothermal, hydro or biomasses to power MES, or
724 directly, by solar-to-product conversion using photoactive electrodes producing the required
725 power density (Fig. 7). The indirect approach appears particularly convenient for storing the
726 low-cost excess power produced by the inherently fluctuating renewable sources as multi-
727 carbon chemicals (Patil et al., 2015). However, fluctuating electric supply could temporarily
728 decrease the production rates in MES, or even shift the metabolic pathway from carboxylic
729 acid to methane production (Mateos et al., 2020). Such an issue can be avoided by using
730 batteries and dedicated electronic circuits to deliver a constant current to the MES reactor
731 (more details in Section 5.3).

732



733
 734 **Figure 7.** Indirect (1) and direct (2) power supply for microbial electrosynthesis (MES) cells.
 735 In the indirect approach, electric energy is generated from renewable sources and then used to
 736 drive water splitting (at the anode) and CO₂ bio-electrochemical reduction (at the cathode). In
 737 the direct approach, water oxidation is obtained from solar energy using a photoanode.
 738

739 The direct approach entails the key advantage of being independent of an electricity source
 740 (Bushuyev et al., 2018). However, photo-MES cells must be equipped with a power storage
 741 unit (see section 5.3) or light emitting diodes (LEDs) to ensure a continuous current delivery
 742 to the cathode. In the last decade, photoelectrochemical cells for water splitting have been
 743 technologically advanced, and are currently capable to deliver sufficient currents (up-to 5.8
 744 mA/cm²) to drive electrochemical CO₂ reduction (Kirner and Finke, 2017). Hybrid systems,
 745 with biological cathodes coupled to photoelectrochemical anodes, have been thus
 746 demonstrated for self-sustained methane, isopropanol or acetic acid production from CO₂
 747 (Table 4). An average solar conversion efficiency (SCE) of 0.62%, about three times higher
 748 than the global natural photosynthesis, was achieved for biological conversion of CO₂ to
 749 methane deploying the reducing current generated by a TiO₂ CdS photoanode (Xiao et al.,
 750 2020). Methane was generated at the cathode with a production rate of 15 L/(m²·d), which
 751 further increased to 20.8 L/(m²·d) (0.86% SCE) when a Cu₂ZnSnS₄ light adsorbing sensitiser
 752 was added to the photoanode. Liu et al. (2015) reported acetic acid concentrations as high as
 753 6 g/L in a hybrid system with *Sporomusa ovata* and TiO₂ nanowires as the bio- and
 754 photocatalyst, respectively, which is comparable to the concentrations achieved in
 755 conventional MES cells (PrévotEAU et al., 2020). Enzymatic biocathodes have been also
 756 employed for CO₂ reduction (Lee et al., 2016), although the high production and operation
 757 costs of enzymatic electrodes, requiring periodic regeneration, discourages their use in full-
 758 scale MES applications.
 759

760 **Table 4.** Hybrid systems combining biocathode and photoanode for self-sustained CO₂
 761 recycling. The photocatalytic current, main product, coulombic efficiency (CE) and solar

762 conversion efficiency (SCE) are reported. In all studies, the photoanode was exposed to a
763 light intensity of 100 mW/cm².

Inoculum	Cell design	Cathode	Anode	Current (mA/cm ²)	Main product (yield/final concentration)	CE (%)	SCE (%)	Reference
Engineered <i>Ralstonia eutropha</i>	One-chamber	NiMoZn or stainless steel	CoP _i	0.5-1.1	Isopropanol (216 mg/L)	3.9	0.7	Torella et al. (2015)
Enriched methanogenic community	Two-chamber	Carbon cloth	TiO ₂ nanowire array	0.07-0.09	Methane (1.92 L/(m ² ·d))	95	0.1	Fu et al. (2018)
<i>Sporomusa ovata</i>	Two-chamber	Si and TiO ₂ nanowires arrays	TiO ₂ nanowires	0.3	Acetic acid (6 g/L)	86	0.38	Liu et al. (2015)
Effluent from methanogenic MES	Two-chamber	Chitosan-modified carbon cloth	TiO ₂ /CdS on FTO ^a (with CZTS ^b sensitiser)	0.6	Methane (15 L/(m ² ·d), 20.8 L/(m ² ·d) with CZTS)	93	0.62 (0.86 with CZTS)	Xiao et al. (2020)

764 ^a Fluorine-doped tin oxide; ^b Copper zinc tin sulphide.

765 5.2 Integrated MES devices for CO₂ recycling and wastewater treatment

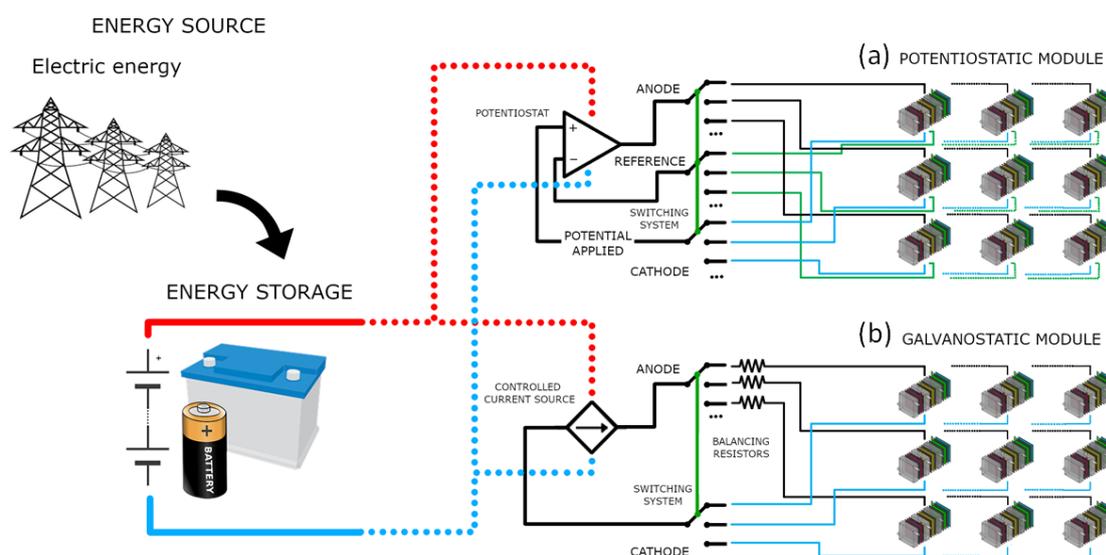
766 When CO₂ reduction at the cathode is coupled to water oxidation at the anode, high potentials
767 or expensive catalysts are required to obtain the oxygen evolution reaction (Bian et al., 2020).
768 Furthermore, a share of the oxygen produced at the anode can diffuse towards the cathode
769 inhibiting the strictly anaerobic microorganisms. An integrated process combining CO₂
770 reduction at the cathode and oxidation of pollutants at the anode not only will decrease the
771 energy demand of MES, but will also simultaneously address two major challenges faced by
772 industries (reduction of CO₂ emissions and wastewater treatment). A maximum acetic acid
773 production rate of 83 mg/(m³·d) was reported for a biocathode at a current density of 0.04
774 mA/cm² generated by a bioanode fed with synthetic wastewater containing 4 g/L sodium
775 acetate. The COD removal rate reached 87% at a relatively low cell potential of 1.4 V (Xiang
776 et al., 2017). Furthermore, acetic acid production from CO₂ was demonstrated at potentials as
777 low as 0.8 V though with a corresponding decrease in production rate. In addition, CO₂
778 produced from wastewater treatment at the anode can be recycled to the cathodic chamber
779 and act as a precursor for chemical production (Zhao et al., 2012). Photocatalytic oxidation
780 can also be exploited for selective oxidation of target compounds such as alkenes (Farràs et
781 al., 2015). However, optimisation of both the cathodic and anodic reaction in integrated
782 systems can be difficult, and further studies involving real wastewaters are required to assess
783 the feasibility of this approach.

785 5.3 Energy storage and smart electronic design for MES

786 Although MES reactors demonstrated their resiliencies to current fluctuations, a constant
787 electricity supply is required for a robust 24/7 operation. Thus, when fluctuating energy
788 sources are used to power MES, additional investment is required for energy storage systems
789 to recover excessive energy from the production peaks and deliver it to the MES reactors at a
790 constant flow. The price of storage technologies, batteries in particular, decreased by 60% in
791 the past five years, approaching the threshold of 100 €/kWh (Berckmans et al., 2017). Power
792 storage costs of 0.085 €/kWh have been estimated in Germany for 7 hours storage duration,
793 low enough to incentivise the installation of batteries for harvesting solar power, and
794

795 projected to further decrease to 0.065 €/kWh within four years (Comello and Reichelstein,
 796 2019). As an alternative, MFCs treating wastewater can be used to produce electric energy
 797 for charging energy storage devices, which are subsequently discharged to power MES
 798 reactors (Hatzell et al., 2013).

799
 800 In MES stacks, even if the cells are connected in parallel, the potential control is more
 801 challenging than in purely electrochemical electrolyzers. The inherently inhomogeneous
 802 microbial catalysts can indeed cause non-uniform charge distribution on the MES electrodes.
 803 This creates uneven potentials between the cells in the stack, that may cause a shift of the
 804 microbial communities (when mixed culture are used) or metabolic pathways underpinning
 805 CO₂ recycling (Sánchez et al., 2020). Balancing charge distribution in MES stacks could find
 806 inspiration in power management systems (PMS) already available in battery stacks. PMS are
 807 capable of detecting overvoltage and overloading, switching off the connection to prolong the
 808 lifespan, and reducing stress on battery units (Stroe et al., 2018). Similarly, MES could use
 809 smart electronics to optimise voltage or current delivery (Fig. 8), allowing a stable chemical
 810 output. Such switching systems have already been implemented to improve the energy output
 811 in MFC grids (Kim et al., 2011). Potentiostatic cell control is costly, but enables a precise
 812 electrode potential control that allows to operate the cells under optimal conditions.
 813 Galvanostatic control is cheaper, but can result in fluctuations and divergence among the
 814 cells.
 815



816
 817 **Figure 8.** Example of application of power managing system and smart electronics for
 818 potential or current control in MES stacks. (a) Each stack shares the same potential control
 819 amplifier which allows potential control in each cell through a multiplexer. (b) The cells are
 820 controlled in galvanostatic mode, and balancing resistors are connected in series to minimise
 821 differences among the cells. In case of failure, a stack can be switched off for maintenance
 822 without affecting the other stacks.

823
 824 **6. Outlook and future perspectives**

825 The environmental incentives and increasing CO₂ emission costs as carbon taxes are pushing
 826 industries towards the use of carbon conversion technologies. Although CCS technologies are
 827 already available at commercial scale, the emerging CCU technologies such as MES have the
 828 potential to gradually replace the existing chemical production facilities, producing a revenue

829 stream that can offset the operation costs (Grim et al., 2020). When coupled to renewable
830 energy, electrochemical CO₂ conversion technologies can produce chemicals with a negative
831 carbon footprint (De Luna et al., 2019), and their development is further incentivised by the
832 decreasing electric energy cost. MES is a flexible technology with several market entry
833 opportunities and potentially applicable to decarbonise industrial CO₂-containing flue gas
834 while producing fuels and chemicals that find application in the packaging, food,
835 preservatives, rubber, metallurgy, pharmacy, polymers, chemical and renewable energy
836 industry (ElMekawy et al., 2016).

837
838 Various platform chemicals and fuels can be produced in MES, raising argument about which
839 products are the most viable from an economic perspective. Though a rough estimation on
840 the techno-economic viability of different MES routes can be obtained with thermodynamic
841 calculations, more in-depth techno-economic analyses are required. However, to date, no
842 results on scaled-up MES reactors and operation under relevant conditions are available to
843 support techno-economic analyses. Up to now, acetic acid is the only chemical that is
844 produced in MES with selectivity >90%, and substantially higher rates than other chemicals
845 (>100 g/(m²·d)), and has thus the highest decarbonisation potential (Jiang et al., 2019).
846 Furthermore, acetic acid has a huge market size of about 13 Mtons/year and can be used as a
847 precursor for many valuable products. As such, it currently represents one of the most
848 compelling targets. However, the economic viability of acetic acid production in MES is
849 limited by its low market value (Christodoulou et al., 2017). Thus, research efforts are
850 currently directed towards the selective production of more valuable compounds with
851 reasonably high production rates. The main ongoing European research projects dealing with
852 bio-electro CO₂ recycling, such as [BioRECO2VER](#), [SCALIBUR](#), [BIOCON-CO₂](#), [BAC-TO-FUEL](#),
853 and [Celbicon](#), are making a step beyond in demonstrating the technical feasibility for
854 the production platform of valuable biochemicals and biocommodities (*e.g.* isobutene, lactic
855 acid, biofuels, biopolymers, and surfactants). This is in line with the European strategy of
856 seeking renewable fuels with high energy densities and low hygroscopicity, to be blended, or
857 even to replace, fossil-based fuels for direct use in engines. Hybrid systems, in which
858 enzymes or genetically modified organisms are applied to produce high-value compounds
859 from electrochemically-produced building blocks, is another emerging field that is expected
860 to play a key role in the future of CO₂ recycling (Bushuyev et al., 2018).

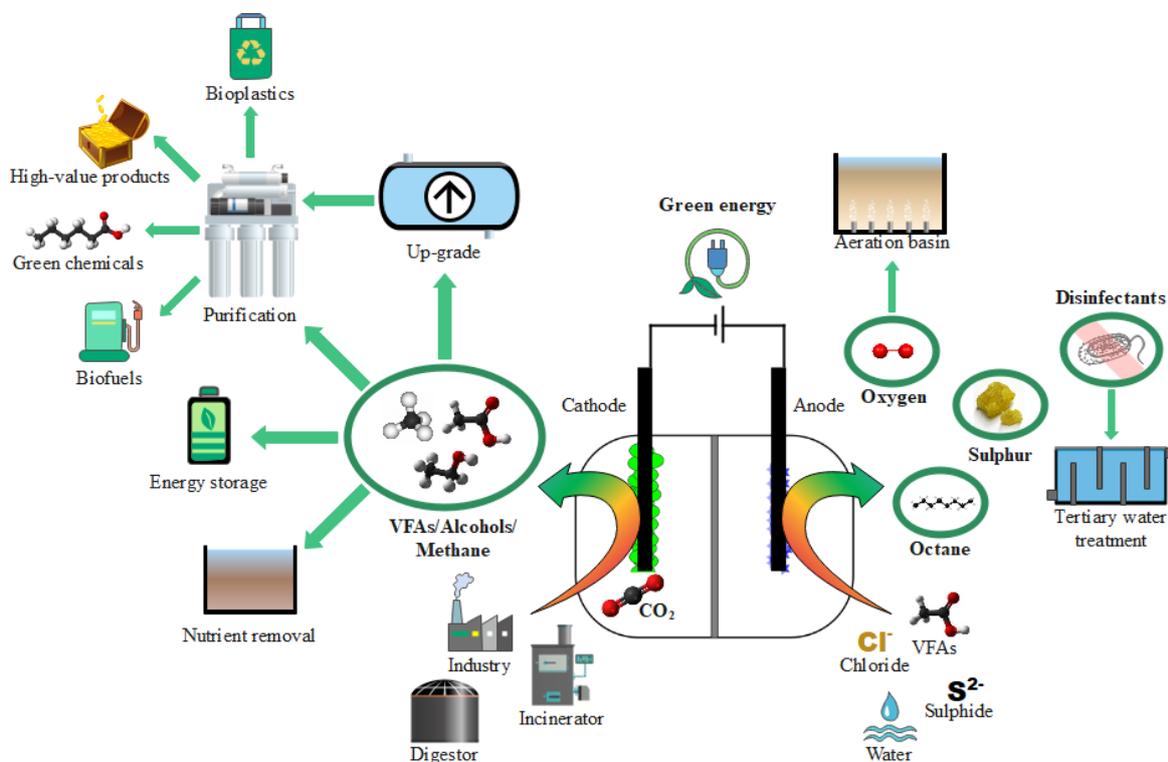
861
862 Besides commercial purposes, MES-derived chemicals can find application within the same
863 industry they are produced. Such approach can decrease the costs of infrastructure required
864 for product purification and transportation. For example, MES can be applied in existing
865 power plants, as renewable energy storage during peak production, or in wastewater
866 treatment plants, to convert CO₂ into organic substrates for processes such as denitrification
867 (Osset-Álvarez et al., 2019). MES can also be seen as part of a biorefinery aiming at cleaning
868 wastewater at the anode while upgrading biogas into biomethane at the cathode and recycling
869 the resulting CO₂ to produce further methane, or for other purposes (Sadhukhan et al., 2016).
870 Similarly, MES can provide reducing equivalents for syngas fermentation (Zhang and
871 Tremblay, 2018). Biofuels produced from CO₂ can be used within the company as an
872 alternative fuel for boilers, combined heat and power (CHP) plants and transportation.
873 Integration of MES into bioethanol production plants would help increase the energetic
874 efficiency of the whole process by recycling energy that is initially lost in the liquid waste,
875 and increase the ethanol yield by recycling the CO₂ produced by solventogenic fermentation.
876 Electrosynthesis products such as H₂, CH₄, CO and VFAs can be further upgraded to longer
877 chain carboxylates, biofuels, bioplastics, polysaccharides and protein *via* multi-step

878 bioconversions (Bian et al., 2020; Haas et al., 2018), or even in the same MES cell (Vassilev
879 et al., 2019).

880

881 To date, most research interest in MES has been directed towards cathodic products, whereas
882 anodic reactions have been overlooked. It was estimated that the anode, particularly when
883 coated with expensive catalysts such as Pt, can generate as high as 59% of the capital costs
884 (Jourdin et al., 2020). However, several value-added products can be obtained through
885 oxidative reactions at the anode (Fig. 9), which could complement biocathodic products to
886 increase the economic sustainability of MES. As an example, a relatively pure oxygen stream
887 is generated by water oxidation at the anode, which can find a plethora of application in the
888 chemical and manufacturing industry, as well as in waste and wastewater treatment facilities.
889 Anodic reactions can be also exploited for producing disinfectants such as chlorine (Batlle-
890 Vilanova et al., 2019), or ozone (Yan et al., 2020), although particular care should be given to
891 prevent their cross-over to the biocathode. Oxidation reactions at the anode can also be
892 applied for resource recovery. Hydrogen sulphide has been proposed as an electron donor in a
893 MES for concomitant acetic acid production from CO₂, and sulphur/sulphate formation
894 (Gong et al., 2013). Such process could be applied to sulphide-containing flue gas, allowing
895 sulphur/sulphate recovery at the anode while reducing the power required for CO₂ reduction
896 at the cathode in comparison to water oxidation. However, biological anodic processes, in
897 particular when heterotrophic microorganisms are present, can result in a higher risk of
898 membrane biofouling in comparison of MES cells where only the cathodic process is
899 biological. Finally, the anodic process can be potentially applied to upgrade MES products
900 (*i.e.* carboxylic acids), *e.g.* to octane *via* Kolbe electrolysis (Stang and Harnisch, 2016).

901



902
903 **Figure 9.** Integration of cathodic and anodic processes in MES. CO₂ is biologically converted
904 into short-chain fatty acids, alcohols or methane. Such products can be used as energy
905 storage, or purified for use in the chemical industry or as biofuel, or up-graded into
906 bioplastics or other high-value products. Anodic reactions can be exploited to produce useful

907 chemical such as oxygen and disinfectants for application in water treatment, for sulphur
908 recovery from sulphide, or to upgrade carboxylic acids to octane *via* Kolbe electrolysis.

909
910 In summary, several challenges need to be overcome to push MES technology towards
911 industrial adoption. Further research efforts are required to decrease the capital costs
912 associated to carbon capture and cell materials (in particular the anode electrode). Increasing
913 the production rates, and developing strategies to selectively produce and extract high-value
914 products, can boost the economic viability of the process. Powering the MES stack is
915 essential to ensure carbon-neutrality, and more attention is required to the anodic reaction to
916 reduce current consumption, possibly generating a secondary revenue stream. MES
917 technology is approaching the maturity level required to finally overstep the laboratory, and
918 operation of pilot plants under relevant industrial conditions will corroborate its techno-
919 economic feasibility.

920

921 **Conclusions**

922 MES has shown potential for replacing fossil-fuel based synthesis of platform chemicals or
923 energy products, and significant opportunities for its establishment are yet to arise in response
924 to the stringent legislation on carbon emissions and the decreasing cost of electric energy.
925 The flexibility of MES, applicable to convert CO₂ containing gas from different sources to a
926 plethora of different chemical products, can represent a key differentiator to enter the market.
927 However, significant challenges need to be tackled before commercialisation. MES stacks
928 need to be designed and operated under relevant condition (*e.g.* in pilot scale) to assess the
929 technology from a techno-economic point of view. Efficient *in-line* product extraction and
930 purification, as well as valorisation of the anodic reaction to obtain further commercial or
931 commodity products, are key aspects in this regard. Since decarbonising the energy and the
932 production sector is a priority, abatement of high CO₂ loads, even if producing low-value
933 compounds such as acetic acid, appears as the most feasible approach for commercialising
934 MES in the short term.

935

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954

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