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An interdisciplinary roadmap towards future research and application**

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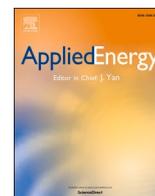
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Techno-economic assessment of microbial electrosynthesis from CO₂ and/or organics: An interdisciplinary roadmap towards future research and application

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HIGHLIGHTS

- Techno-economic assessment of microbial electrochemical production was performed.
- CO₂ and/or organics were considered as carbon-feedstock for carboxylates production.
- 28 keys parameters were analysed, sole performance improvement allows profitability.
- Anode cost is the main CAPEX while electricity utilization is the main OPEX.
- Current density, electron distribution, energy efficiency are improvement targets.

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ABSTRACT

Microbial electrosynthesis (MES) allows carbon-waste and renewable electricity valorization into industrially-relevant chemicals. MES has received much attention in laboratory-scale research, although a techno-economic-driven roadmap towards validation and large-scale demonstration of the technology is lacking. In this work, two main integrated systems were modelled, centered on (1) MES-from-CO₂ and (2) MES from short-chain carboxylates, both for the production of pure, or mixture of, acetate, n-butyrate, and n-caproate. Twenty eight key parameters were identified, and their impact on techno-economic feasibility of the systems assessed. The main capital and operating costs were found to be the anode material cost (59%) and the electricity consumption (up to 69%), respectively. Under current state-of-the-art MES performance and economic conditions, these systems were found non-viable. However, it was demonstrated that sole improvement of MES performance, independent of improvement of non-technological parameters, would result in profitability. In otherwise state-of-the-art conditions, an improved electron selectivity ($\geq 36\%$) towards n-caproate, especially at the expense of acetate, was showed to result in positive net present values (i.e. profitability; NPV). Cell voltage, faradaic efficiency, and current density also have significant impact on both the capital and operating costs. Variation in electricity cost on overall process feasibility was also investigated, with a cost lower than 0.045 € kWh⁻¹ resulting in positive NPV of the state-of-the-art scenario. Maximum purification costs were also determined to assess the integration of a product's separation unit, which was showed possible at positive NPV. Finally, we briefly discuss CO₂ electroreduction versus MES, and their potential market complementarities.

1. Introduction

The concept of circular economy is a solution to series of challenges

such as waste generation, resource scarcity, and sustaining economic benefits. Circular economy is an economy which is environmentally and economically regenerative [1]. The microbial conversion of CO₂ and

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organic wastes into chemicals, fuels, feed, and food without any harmful emission into the environment could have the potential to contribute to the envisioned circular biobased economy [2]. Microbial electrosynthesis (MES) is an electrified biotechnology, i.e. an electricity-driven production platform, that allows converting electrical power and carbon building blocks into valuable chemicals such as medium chain carboxylic acids (MCCAs), as schematized in Fig. 1 [3]. MES relies on electroactive microorganisms, i.e. biocatalysts which utilize electrons from a solid-state electrode as their main energy source, for the conversion of CO₂ and/or organics. MES could allow to store and increase the value of electrical energy produced from intermittent renewable sources such as solar and wind [4]. Moreover, MES uses minimal amounts of water (ca. 1–5 kg_{H₂O} kg⁻¹_{product}), when calculated from current density and considering water oxidation at the anode electrode.

There has been a significant amount of laboratory-scale research investigating the MES conversion of CO₂ to organics [5]. However, there have only been very limited research activities attempting to understand the costs of such MES technologies to date. ElMekawy et al. investigated the feasibility to produce formic, acetic, and oxalic acids from CO₂ by MES [6], while Christodoulou et al. studied the integration of MES from CO₂ to anaerobic fermentation [7], as well as MES for the production of C1-3 organics from CO₂ [8]. Several important questions remain unanswered. For example, how economically feasible is the state-of-the-art of MES from CO₂ and/or organics for the production of chemicals up to six carbon? What are the constraints on the viability of the technology? What key parameters are the most impactful to the profitability of the technology? With this study we provide an analytical framework and the tools to answer these questions.

Mainly short to medium chain carboxylates have been produced from MES to date, namely acetate, n-butyrate, and n-caproate, as well as lower amount and rates of their respective alcohols. The most valuable of them is n-caproate, which was produced continuously and concomitantly with n-butyrate and acetate [3]. These MES were operating in the range of the highest current densities reported of –100 to –175 A m⁻² (normalized to projected surface area) at electron to carboxylic acid recoveries up to 88%. Application examples of n-caproate are as follows: antimicrobial agent in the pharmaceutical industry, livestock feed additives, flavor additive in the food industry, feedstock for the chemical

industry, and precursor in production of biofuels [9]. Although n-caproate can also be obtained from coconut and palm kernel oils through fractional distillation, it corresponds to less than 1% of the composition of both oils [9]. The limitation and non-sustainable nature of the above resources have limited n-caproate to a relatively small market. However, its market is expected to expand tremendously upon discovering novel ways to produce it. A commercial demonstration factory is starting ethanol-based chain elongation to produce a mixture of carboxylate salts for use as feed additive in the agro-food industry in the port of Amsterdam, The Netherlands [10]. Based on these technical and application developments, the pure and/or mix carboxylic acids were selected as end product(s) of this study.

We propose three designs for integrated systems to either (1) capture CO₂ from an emitter such as listed in Fig. 1, electrochemically reducing it with microorganisms to form a mixture of acetate, n-butyrate, and n-caproate, and purifying the end-product(s) of interest (Fig. 2A), or (2) ferment organic waste streams to short chain carboxylic acids (SCCA) and either, electrochemically reducing them by MES (Fig. 2B), or oxidizing them with a bioanode coupled to reducing the produced CO₂ in a biocathode (Fig. 2C), both for the production of the same mixture of products as from (1) and separating the targeted end-product(s). More details on the integrated systems and MES process can be found in the methodology section.

The objective of the present study was to evaluate the techno-economic feasibility and competitiveness of the three selected MES configurations. To accomplish our goals, we created an engineering and economic model in a spreadsheet representing the integrated systems in Fig. 2. The model solves the material and energy balance of these systems and conducts an economic analysis utilizing capital and operating costs to calculate the cost of production and evaluate economic performance indicators. Material and energy balance calculations were conducted utilizing relevant MES parameters with state-of-the-art performance based on recent lab-scale research. Sensitivity analyses were included to evaluate the impact of important assumptions made to describe which variables are most important for moving the technology towards commercialization. Such a framework and tools will be valuable as an interdisciplinary roadmap for future research and development of microbial electrosynthesis technologies. We found that solely

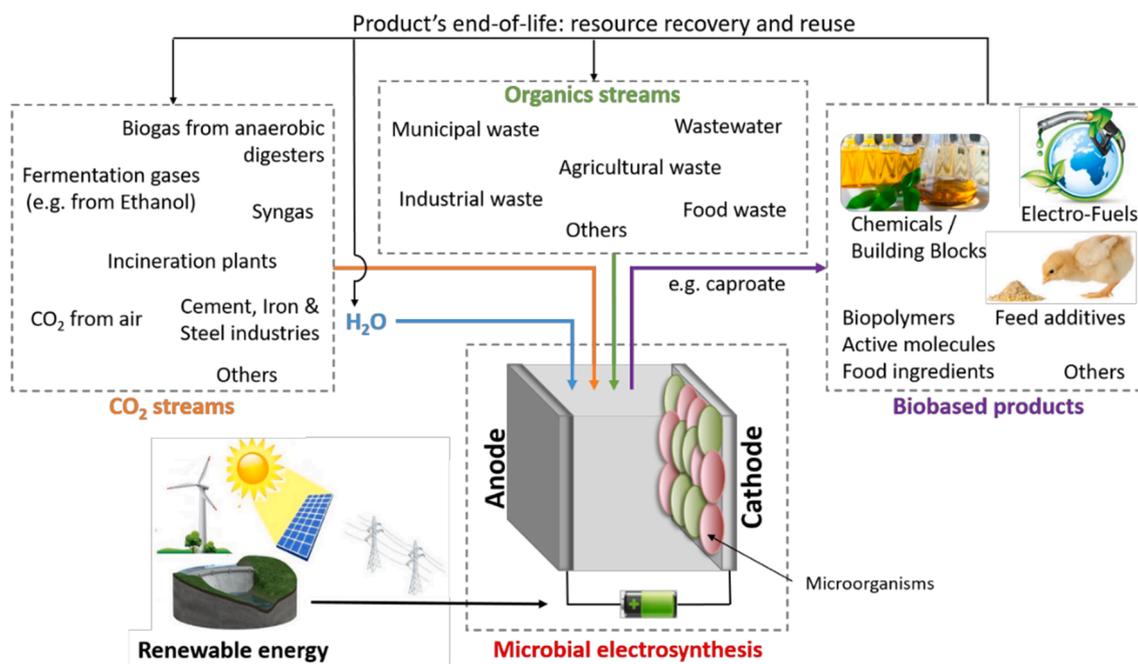


Fig. 1. Simplified representation of microbial electrosynthesis technology versatility displaying some of its possible implementation within a biobased circular economy, with recovery and reuse of resources (example of a biofilm-driven biocathode).

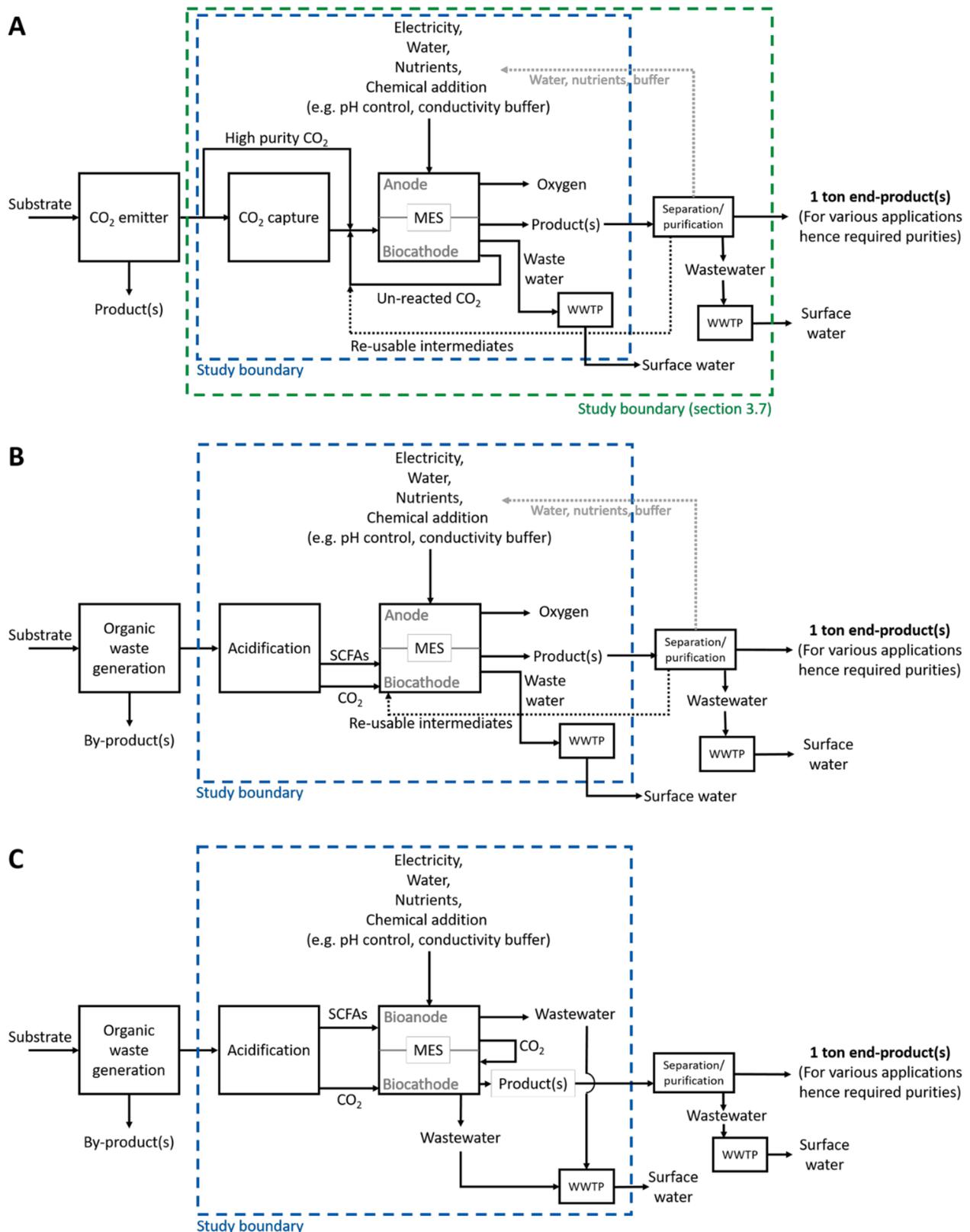


Fig. 2. Proposed integration and study boundary (blue dotted rectangular block) of (A) MES from CO₂, (B) MES from short chain carboxylic acids (SCCAs), and (C) MES-from-SCCA with the SCCA fed to a bioanode and the resulting CO₂ fed to the biocathode, for production of valuable chemicals, i.e. pure or a mixture of, n-caproate, n-butyrate, and acetate. Each block, input, and output are explained and discussed in detail in the text. The green dotted rectangular block represents the study boundary inclusive of both CAPEX and OPEX of a separation unit, as discussed in Section 3.7 for MES-from-CO₂. The recycling of water, nutrients, and buffer (dotted grey line) was not included in the models but discussed in the text. Separation units were not included in the boundary limit of scenario B and C, as economics already proved unfeasible without them (see Section 3.2).

improving the MES production performance (which are improvement achievable by continuing effort on the research and development of MES, and is independent of improvement of non-technological parameters) can be sufficient to reach feasibility targets. We also discuss the impact of electricity cost fluctuation, of the integration of separation units, and the potential complementarity with electrochemical reduction of CO₂ with heterogeneous catalysts.

2. Methodology

2.1. Process description

2.1.1. Overall process

Fig. 2A represents the MES-from-CO₂ integrated process under investigation here. The system boundary for this study includes CO₂ capture or use of high purity CO₂ (see Section 2.1.2), which is fed to the MES reactor (see Section 2.1.3). A mixture of organics (acetate, n-butyrate, and n-caproate) and O₂ are produced from MES, and unreacted CO₂ is potentially recycled to the MES to increase the overall conversion of CO₂. The mixture of organics is sent to a separation/purification unit to obtain the product(s) of interest. In the initial model, the separation unit is not included in the system boundary (blue dotted

block in Fig. 2). Caproate, as compound of main interest, can be separated. However, n-butyrate (nC4) and acetate are also products of value, and could be used for other applications, or as a mixture together with n-caproate (nC6) [10]. Therefore, either C2 and nC4 are recirculated to the MES to maximize their conversion to n-caproate, or separated from each other and sold as end-products. A third alternative is to keep all three carboxylates together and only water, cells, and nutrients are removed. Consequently, all three organics are regarded as products with value and included as such in our energy and material balances. For example, the same approach is used in the Acetone-Butanol-Ethanol (ABE) fermentation process, where each product is separated from each other and sold at their respective market values [11]. However, it must be stressed that the end-product value would largely depend on its purity. The model allows to evaluate economic feasibility with any other selling price. A one-ton-per-year production is the analysis baseline in this study. In case several products are formed, the current density and the electron recovery into each are used to calculate the production rate of each in kg m⁻³ day⁻¹ (or kg m⁻² day⁻¹), which are then summed up to obtain the total mass production rate, from which the one-ton-per-year baseline is taken from. Therefore the reason for not including the cost of a separation unit at first is that the end-product application dictates the required end-product purity, which in turn affect the choice

Table 1

Base Case (B) and Low (L) and High (H) Performance Values of Key Variables for Sensitivity Analysis of each system. Each variable is discussed in detail in the text. For convenience a complete table with the references is provided in the SI; Table S1. Numbers for which no references are provided are explained in the manuscript or SI to justify the scenarios studied for the sensitivity analysis.

Key variables	MES-from-CO ₂			MES-from-SCCA			MES-from-SCCA bioanode		
	H	B	L	H	B	L	H	B	L
Current density (A m ⁻³ (A m ⁻²))	-100000 (-1000)	-10000 (-100)	-5000 (-50)	-100000 (-1000)	-910 (-9.1)	-910 (-9.1)	-100000 (-1000)	-37 (-0.037)	-5000 (-50)
Faradaic efficiency (%)	98	88	50	98	59	59	98	45	45
e- distribution into product(s) (%)	100% C6	14.6% C6, 32.6% C4, 52.7% C2	100% C2	100% C6	25% C4, 55% C2	25% C4, 55% C2	100% C6	100% C2	100% C2
Cell voltage (V)	1.8	3	4	1.8	3	4	0.5	0.8	2
CO ₂ conversion efficiency (%)	100	100	10	-	-	-	100	100	10
Membrane H ⁺ transfer efficiency (%)	80	80	0	80	80	100	20	0	0
NaCl concentration (g L ⁻¹)	1	3	5.3	1	3	5.3	1	3	5.3
Product(s) concentration (g L ⁻¹)	10.82 C6	2 C6, 4 C4, 8 C2	18 C2	(varies)	(varies)	(varies)	10.82 C6	8 C2	8 C2
n ^o anode / cathode	-	-	-	-	-	-	1/1	1/1	10/1
Anodic coulombic efficiency (%)	-	-	-	-	-	-	100	88	25
Acetate influent conc. (g L ⁻¹)	-	-	-	20	1.8	1.8	20	4	4
Acetate conversion efficiency (%)	-	-	-	100	27	20	-	-	-
Cathode cost (€ m ⁻²)	14	155	720	14	155	720	14	155	720
Anode cost (€ m ⁻²)	100	500	1500	100	500	1500	14	155	720
Membrane cost (€ m ⁻²)	10	10	500	10	10	500	10	10	500
Reactor frame cost (€ m ⁻³)	1000	4000	15000	1000	4000	15000	1000	4000	15000
Depreciation elect-CC-memb (% CAPEX)	2.5	3.33	20	2.5	3.33	20	2.5	3.33	20
Maintenance cost (% CAPEX)	3	3	6	3	3	6	3	3	6
CAPEX side equipment (% CAPEX MES)	1	10	50	1	10	50	1	10	50
Electricity cost (€ kWh ⁻¹)	0,03	0,07	0,09	0,03	0,07	0,09	0,03	0,07	0,09
pH control - NaOH cost (€ ton ⁻¹)	150	372	500	150	372	500	150	372	500
Nutrients cost (€ ton ⁻¹)	0	1788	1788	0	1788	1788	0	1788	1788
NaCl cost (€ ton ⁻¹)	30	42	150	30	42	150	30	42	150
Water cost (€ ton ⁻¹)	0,4	0,4	1,1	0,4	0,4	1,1	0,4	0,4	1,1
CO ₂ cost or revenue (€ ton ⁻¹)	-50	29	184	-50	29	184	-50	29	184
Organic waste stream cost (€ ton ⁻¹ _{COD,SCFAs})	-	-	-	0	74	222.2	0	74	222.2
Wastewater treatment (%COD left)	2.5	5	20	2.5	5	20	2.5	5	20
Plant production capacity (ton year ⁻¹)	4000	2000	2000	4000	2000	2000	4000	2000	2000
Personnel (#)	2	2	4	3	3	6	3	3	6

of unit operation of the downstream process (DSP). As discussed above, the applications can be various for such carboxylates hence many different DSP could be designed. Moreover, a wide range of faradaic efficiency and electron efficiency are investigated here (see Table 1), which dictate the MES outflow composition hence the choice of DSP units. Designing many different DSP for each MES outflow composition was out of the scope of this study. Additionally, there is a lack of information in the literature for the separation of such products streams [12]. Instead, as defined by Bonk et al. (2015), we introduced a maximum purification cost (MPC) that represents the maximum cost of separation (both CAPEX and OPEX) to reach a net present value of zero for the overall process (see Section 3.7) [12]. The MPC is a useful tool to assess the feasibility of carboxylic acid separation methods, allowing to reflect on the cost requirement for a separation unit so that the overall process remains profitable. Here, the MPC for a specific scenario takes into account the MES outflow composition and the cost to obtain each of the product present in their pure form. Eventually, we applied a cost of separation extracted from lactic acid fermentation industrial practices to MES-from-CO₂ and analyzed its impact on the overall economics (Section 3.7). Also included in the study boundary is the input of all main identified energy and chemical requirements including electricity, water, heat, nutrients for microbial growth, and chemical addition for pH and conductivity control (see Section 2.1.2). The cost of treating the wastewater generated from the MES was also included in our analysis. All inputs and outputs are discussed in details below. In summary, Sections 3.2–3.6 of the results and discussion section focus on the microbial electrosynthesis process itself and discuss the impact of many key parameters (see below), while Section 3.7 evaluates how much money is left to integrate a separation/purification process to MES. The DSP is not the main focus point of this manuscript, but the introduction of MPC allows to assess its integration potential/feasibility.

Fig. 2B represents the MES-from-SCCA integrated process under investigation here. The difference with the MES-from-CO₂ process is the source of carbon fed to the MES. In that case, the organic waste stream from several sources (see Section 2.1.4) is assumed to be acidified to short chain carboxylic acids (SCCA) that are fed to the cathode compartment of the MES. For simplicity, acetate was used as model SCCA in the provided model, but the model and process design are flexible and can be used to evaluate other composition of SCCAs as well. We assume here that CO₂ is still required in this MES system, but only for biomass growth, as was demonstrated for chain elongation fermentation [13]. The other inputs and outputs are the same as listed above for the MES-from-CO₂ integrated process.

An alternative to the MES-from-SCCA process was also investigated in which the SCCA stream is not fed to the cathode but to the anode compartment where microorganisms degrade it using the anode as electron acceptor. In this configuration, the CO₂ produced at the bioanode is transferred to the biocathode where it is elongated as in the MES-from-CO₂ process above (CO₂ arrow in Fig. 2C). Depending on the cathodic reactions, additional CO₂ may need to be added and is accounted for in the model.

Table 1 lists all parameters that can affect viability of the integrated processes, related to MES reactor performance, MES assets, MES inputs, and others. In the following, each parameter is discussed in more details, as well as how the model for process analysis was built and sensitivity analysis performed. As a base case, state-of-the-art performance parameters are utilized for all components of the system, with the exception of the CO₂ conversion efficiency (see explanation in Section 2.1.3). A range of values corresponding to the lower and upper bound system performances is also presented in Table 1 (see explanation in Section 2.2.2).

2.1.2. Microbial electrosynthesis (performance and assets)

MES is the new process in the integrated system investigated here. The other processes including CO₂ capture and product separation are technologies that are either commercial or demonstrated at small or

medium scales. To date, most fundamental research for MES has utilized a 3-electrode cell, and several types of bench-scale reactors have been tested [14]. Four main bioelectrochemical process parameters are of interest when investigating the practical implementation of MES: cell voltage (*V*), i.e. the used potential difference across the anode and cathode; current density (*I*), typically measured in A m⁻² or A m⁻³; the Faradaic efficiency (FE) into all desired organics, and electron distribution into each product (i.e. electron selectivity). FE is a measurement of the amount of energy input into the cell that actually ends up as chemical energy in organic products [15].

The energy required for each unit of CO₂ reduction can be calculated as

$$J = \frac{V \times C}{FE}$$

where *J* is energy in joules per unit of CO₂ reduction or organics production, *V* is voltage in volt, and *C* is charge measured in Coulombs. According to Faraday's law, *C* is directly correlated to moles of CO₂ reacted or organics produced. The result is a measurement of energy input per unit of organics produced, which is directly dependent on voltage *V*. Energy use is also dependent on FE. When FE is lower, more energy is wasted in by-product production, increasing the energy necessary to produce a given amount of product.

The base-case for MES-from-CO₂ in our model uses the MES performance, electrode materials, and reactor design reported by [3]. This study is one of three studies that quantitatively reports n-caproate production from CO₂ in MES to date, and also corresponds to the highest current density and production rates reported to date in MES. Additionally, it is one of the only MES studies that reports continuous production. Current density of −10 kA m⁻³ (ca. −100 A m⁻²), electron recoveries of 12.8, 28.6, and 46.2% into n-caproate, n-butyrate, and acetate respectively, and a cell voltage of 3 V, were hence used as base case here. Similarly, the reported products' concentration were used as base case [3], while the maximum reported concentration of each product obtained from fermentation are used as high performance case. This study assumes that MES performance on a laboratory scale can be achieved on an industrial scale. Variation to the base case on all those parameters were investigated as presented in Table 1 and discussed in the results and discussion section. So far, MES-from-SCCA has been experimentally proven at lower current densities and faradaic efficiency of −9 A m⁻² and 59%, and only produced acetate and butyrate [16]. MES using a bioanode also recorded lower current densities of ca. −0.37 A m⁻² and 25–45% faradaic efficiency, and only produced acetate [17]. Those performance were used as base-case for both configurations (see Table 1).

The costs of cathode, anode, membrane, current collectors and reactor frame are also included individually in our model (Table 1). Currently, MES exists only at the bench scale. Furthermore, there is no standard design for a MES cell with several configurations reported to date [14]. For this study, an alkaline water electrolyser stack design was assumed, similar to the lab-scale flat-plate reactor from which we obtained our experimental data [3]. However, our model is flexible and other designs could be investigated. Educated assumptions were made, as detailed cost data are hardly available at the current R&D stage. However, the sensitivity analysis to these parameters enables assessing the impact of each of these costs. Carbon felt cathode material at 155 € m⁻² (cost for lab-use given by the provider for a 1-cm thick material [3]) was used as base case. This cost would likely decrease upon ordering the material in bulk industrial amount, which is represented by the high performance value of 14 € m⁻², as used by others [18]. The low performance value of 720 € m⁻² is the lab cost of a reticulated vitreous carbon electrode modified with carbon nanotube (RVC-CNT), the electrode on which the highest MES to sole acetate performance were recorded [19]. Carbon felt was chosen as base and high performance cases because current density as high as on RVC-CNT were obtained, and

further elongation to butyrate and n-caproate were demonstrated on carbon felt [3]. A Pt/IrO₂-coated Titanium is used as anode electrode (Magneto Special Anodes, Schiedam, The Netherlands), at a market price of 1500 € m⁻². This cost was used as low performance value. It should be noted that the cost of 1500 € m⁻² is the cost of an electrode able to sustain current densities higher than 1000–5000 A m⁻² [20]. In MES, current densities are for now in the order of 100–200 A m⁻². Therefore, the cost of anode electrodes could be substantially decreased for MES application by lowering the catalyst loading, and was calculated to be around 500 € m⁻² (base case). The different anode materials, catalysts, and reactions investigated in MES systems were recently reviewed [2]. The same number of anode than cathode were assumed here (i.e. same projected surface area and same compartment volume). However, the impact of different ratio can also be investigated, e.g. in the case that the max (bio)anode current density differs from the bio-cathode current density. A cation exchange membrane at a cost of 10 € m⁻² was assumed for the base case [21], while a low performance value of 500 € m⁻² was modelled.

A reactor frame cost of 4000 € m⁻³ was used for the base case, and varied from 1000 to 15,000 € m⁻³ [21]. Current collector at 27.5 € m⁻² were assumed [18]. In the case of the bioanode, the same costs as for the cathode above are used. Additionally, given that pilot studies of MES has not been performed to date, it is difficult at this stage to make a detailed list of all needed side-equipment and their corresponding cost. Therefore, the capital investment of the side-equipment was accounted for as a percentage of the capital investment of the MES, which was varied from 1 to 50%, with 10% as base case (Table 1).

We assume here that MES off-gas treatment is not necessary. Only CO₂ and H₂ are exhausting the MES cathode compartment, and they could be recirculated into the MES until reaching the set CO₂ conversion efficiency. Similarly, we assume that the oxygen produced at the anode is simply released to the atmosphere without pre-treatment. The produced O₂ might be used for combustion or industrial purposes. However we disregarded O₂ as a valuable product in this study. With potential electrification of more industrial processes, O₂ may become a clean waste product which is simply discharged and not recoverable as valuable product.

2.1.3. Carbon dioxide sources (MES input)

Several sources of carbon dioxide can be envisioned. In a first instant that extremely pure CO₂ must be used, an option is to use commercial CO₂ at 184 € ton⁻¹ [22]. This represents the most expensive option for our system. An alternative would be to use flue gases from industrial processes. On one hand, flue gases from industries such as ethanol fermentation are almost pure in CO₂ (purity > 99%) [23]. Such high purity CO₂ flue gases could be envisioned to be fed as is in a MES reactor without any required pre-treatment. Another cheap and readily available carbon dioxide source is biogas, which could be regarded as an interesting option as it is primarily composed of methane and carbon dioxide. Biogas is produced during anaerobic digestion and can be used on-site for power generation but could also be more economically used as a transport fuel for buses, cars, etc. For the latter application, the CO₂ fraction needs to be removed to improve gas compression, storage, and combustion efficiency [19]. A biogas-fed MES process was showed to convert the CO₂ fraction to acetate and proved it could be suitable to “clean” the biogas with a higher methane purity [19]. In another study, bioelectrochemical system was also proposed as a biogas upgrading technology with conversion of the CO₂ fraction to methane [24]. In the case of a MES system installed next to such CO₂ sources, the latter would be virtually free, apart from the piping connecting the two processes and potential pumping (investment cost and maintenance). For flue gases with lower purity of CO₂, from e.g. cement, iron, steel, and incineration plants, the CO₂ can be captured e.g. using the current acid gas removal process that use chemical absorption and monoethanolamine as the solvent [25]. The capture of CO₂ from these flue gases is a mature technology commercially available, and amounts to 29 € ton⁻¹ of CO₂

[22]. CO₂ could also be captured from air before being fed to MES. The latter capture technology is under intensive development with several demonstration plant operating around the world (e.g. Climeworks in Switzerland, Carbon Engineering in the USA). To date, CO₂ capture from air remains more expensive, at about 200 € ton⁻¹ [26], while recent work has shown a pathway towards a cost of 94 \$ ton⁻¹ [27]. One advantage of direct air capture is that it represents a net-reduction in CO₂ as opposed to avoided emissions [28]. Meylan et al. (2010) assessed power-to-gas through CO₂ methanation technology and concluded that biogenic and atmospheric CO₂ are most interesting because of their low greenhouse gas emissions [29].

Moreover, many countries have now implemented carbon pricing policies [30]. For example, the European Union has implemented the Emissions Trading System (EU ETS) which puts a price on carbon and thereby gives a financial value to each ton of emissions saved [31]. However, the EU-ETS is a highly volatile system, with current values fluctuating from 6 to 70 €/ton of CO₂. A CO₂ allowance price of 50 €/ton was used as high performance value in our sensitivity analysis, while it could go up to 100 €/ton by 2030 in Europe [30]. Developments in governmental regulation to subsidize use of captured CO₂ from air can substantiate to make CO₂ utilization economic feasible.

In order to quantify the amount of CO₂ to be fed into the MES, the CO₂ conversion efficiency was introduced into the model (Table 1). The CO₂ conversion efficiency corresponds to the percentage of the inflow CO₂ that is converted to the targeted products. It must be noted that CO₂ conversion is not often reported in the literature with experiments either performed in a batch cell or single-pass flow cell, or fed with bicarbonate. For any targeted CO₂ conversion efficiency, it would be speculative to say whether this fraction of CO₂ fed would be converted after the first pass-through, or whether the off-gas would need to be recycled once or several times before achieving the target. In the latter case, a CO₂ purification unit may be required before recycling the unconverted CO₂. Though, mainly CO₂ and possibly non-converted in-situ produced H₂ are present in the off-gas, both of which could be fed to another MES as is and utilized by a MES microbial community. Optimized reactor design for high CO₂ conversion efficiency, and feeding MES off-gases to the inlet of another MES remain to be investigated. We assume here that a large-scale MES design could boost the CO₂ conversion up to 100% at the first gas pass-through (base case). We also investigated the impact of lower CO₂ conversion efficiency, down to 10%, on economic viability (low performance case).

2.1.4. Organic waste stream sources (MES input)

Generating value from organic waste is of high interest. The disposal of organic wastes into landfills has an environmental cost as well as an economic cost, ranging from 40 to 400 USD t⁻¹ [32]. Instead of creating a cost, organic residues can be valorized into bio-products and/or bio-energy, for the benefit of the society [33]. Organic waste can be classified into: food waste, agricultural waste, and municipal waste. Anaerobic digestion has been the main technology used for the treatment of complex biodegradable organic waste. Anaerobic digestion converts the organic wastes into methane-containing biogas (bioenergy) and a digestate that can be valorized e.g. as soil improver [32]. However, it was evaluated that the conversion of organic waste to bulk chemicals such as lactic, acetic, or butyric acid were 3.5–16 times more profitable than its conversion to fuels/energy [32]. The conversion of short-chain carboxylate such as acetate to longer-carbon-chain carboxylates of higher-value was proven in microbial electrosynthesis [16]. Therefore, as explained above, we envision here to couple acidogenesis fermentation of organic waste streams into a mixture of short chain carboxylic acids to their further elongation and valorization by MES up to n-caproate. The short chain carboxylic acids obtained from acidogenesis are mainly acetate, propionate, and n-butyrate [34].

Due to the lack of techno-economic assessment of acidogenesis fermentation in the literature, we derived its cost from the production of 1 m³ of methane from a typical biogas plant. About 3 kg_{COD} of organic

waste are usually required to produce 1 m³ of methane. The base case used here corresponds to the non-subsidized scenario which costs 0.2 € m⁻³ CH₄ [35]. This would correspond to a SCCAs stream of 74 € ton⁻¹ COD. The low performance case corresponds to the subsidized scenario at 0.6 € m⁻³ CH₄, which represents a SCCAs stream at 222 € ton⁻¹ COD [36]. Finally, the high performance case uses a free SCCA stream, in case of specific waste streams which already have the right characteristics and composition. An acetate conversion efficiency factor was also introduced into the model to quantify the amount of SCCA (i.e. acetate) stream to be fed to the MES, ranging from 20 to 100% conversion efficiency, with 46% as the base case as reported by Roghair et al. 2018 in ethanol-based chain elongation (Table 1) [37]. Additionally, different acetate concentration in the SCCA stream were used in the model in order to investigate its impact on the overall process feasibility (Table 1).

2.1.5. Chemicals addition (MES input)

Nutrients considered for the cost analysis of the culture medium are nitrogen (as urea), phosphorus (as triple-superphosphate) and carbon dioxide, since these are main components of biomass and have most impact on the economics compared to other elements [22]. Nutrient concentrations in the culture medium, and therefore the cost, are calculated separately for each case, based on electron recovery into biomass and biomass composition. Biomass composition used for the simulation is the following empirical formula CH_{1.71}O_{0.42}N_{0.15}P_{0.009} [38]. From our laboratory experiments an average of 2% of electron are converted into biomass [39]. Carbon, nitrogen and phosphorous losses are neglected. Future studies should quantify the amount of other nutrients required, e.g. metal-based nutrients, and the extent to which they can effectively be recycled.

Either sodium hydroxide or CO₂ are used for pH control purposes. Refer to Appendix A for the pH control requirement calculation, based on reactions' stoichiometry and ions' transport (Fig. S1). It is worth noting that pH evolution in these systems are complex and dynamic. A pilot scale study will be needed to evaluate the pH dosing requirement with more accuracy. Sodium chloride is used as conductivity buffer in our models. Additionally, the end-product and its utilization is outside the study's boundary; therefore, the products' form, i.e. carboxylate or acid form, was not considered here. However, it should be noted that this would have an influence on chemicals and downstream processing requirement.

2.1.6. Water

It is assumed here that a water-oxidizing anode is used (except for the scenario using a bioanode). The amount of water consumed at the anode is calculated from the current density and anodic coulombic efficiency. The amount of water needed at the cathode depends on the products' concentration and the desired productivity. The cost of water was assumed at 0.4 € m⁻³ [40], the cost that industries in the Netherlands are charged. Process water quality was assumed sufficient here for both the anolyte and the catholyte. However, the water quality requirement remains to be investigated. Energy expenditure for heating up and pumping the water was accounted for in the energy and economic model. The heat of reaction and heat management were disregarded at that stage.

The treatment of wastewater from the separation unit was also accounted for. We assumed a 95% separation efficiency, hence 5% of the COD produced from the MES cathode remains in the wastewater, which needs to be removed. Wastewater treatment cost was calculated based on pollution unit. According to the Dutch Water Law one pollution unit corresponds to 54.8 kg_{COD} per year, with the corresponding cost of 40 € per pollution unit [41]. The water from the chemical anode was assumed not to have to be treated, unlike the effluent from the bioanode which treatment was accounted for.

2.1.7. Electricity (MES input)

In the base case in this study, electricity is purchased from the grid. However, one of the motivation for producing valuable chemicals with microbial electrosynthesis is to reduce CO₂ emissions. Whether the integrated system will achieve the life cycle CO₂ reduction goals will depend on its performance and the carbon intensity of the electricity used, as previously discussed for electrochemical CO₂ reduction systems [15]. A follow up study will need to evaluate the life cycle of the proposed integrated systems, with different electricity sources. There have been increasing efforts to decarbonize electricity in many countries and regions around the world, e.g. with the development and deployment of renewable energy processes such as solar, wind, and hydro. Therefore, the impact of electricity costs ranging from 0.03 to 0.09 € kWh⁻¹ was assessed here. The base case electricity price of 0.07 € kWh⁻¹ is consistent with industrial electricity rates currently available in the Netherlands. In the meantime, renewable energy sources continue to become cheaper, and could get as low as 0.02 € kWh⁻¹ [28]. An optimistic case value of 0.03 € kWh⁻¹ was chosen as this could be reached as soon as 2030 [42]. Varying the cost of electricity in our model also allows to assess the effect of cost fluctuation inherent to the intermittency of renewable electricity supply.

2.1.8. Labor

Manpower cost derives from the estimated number of workers (assuming a standard workweek of 40 h), qualification and cost of working hour (from salary and number of hours per workweek). We assumed the occupation title "Installation, Maintenance, and Repair Occupations" for operators, with 3 times the minimum wage [43]. The minimum wage in the Netherlands is 18936 € Y⁻¹ [44]. The employer's contribution (18.8%) is added to the manpower cost to cover for the liability of work-related accidents and occupational illness [22]. For a plant's production capacity of 2000 ton y⁻¹ (base case), one operator per main operation unit was assumed, i.e. MES, separation unit, and organic waste stream acidification, depending on the scenario. It should be noted that minimum wages vary greatly with location, but was not considered in this study.

2.2. Model for process analysis

2.2.1. Model description

The model developed has two integrated modules: a mass and energy balance module, and a cost analysis module for the systems outlined in Fig. 2. The mass and energy module provides input for the cost analysis module which allows sizing the equipment and calculating the capital cost (CAPEX) and annual operating cost (OPEX) of the processes. Due to the direct integration of both modules in a dynamic model it is possible to directly quantify the influence of changing one or more parameters (both technical and economic) on the feasibility of the process. The model is made available in Appendix B. The main focus of this study is the microbial electrosynthesis system, the only non-commercially available process in the proposed integrated system. Therefore, we focused our model on the mass and energy inputs and outputs to and from the MES. However, the mass and energy balance of the other technologies are already included in their respective costs, e.g. in the cost of CO₂ from flue gas capture, acidification, cost of electricity, nutrients, wastewater treatment, etc. The plant is operated for 8760 h per year, the plant's lifetime is set at 30 years [30], and the plant production capacity is 2000 ton year⁻¹. The depreciation of the capital investment was calculated using the straight-line method for a 30-year lifetime with negligible salvage values, i.e. 3.3% of the capital investment [45].

Several indicators were used to evaluate the economic performance and viability of the different scenarios. The indicators included net present value (NPV), internal rate of return (IRR), payback time (PB), return on investment (ROI), annual gross profit, and annual net profit (see Appendix B for calculation explanation). The NPV determines if the scenario is profitable for the entire plant's lifetime by discounting the

future cash flows to the present value. A positive NPV indicates that the process is profitable and vice versa. The IRR is also an important indicator to reflect the investment's efficiency, essentially representing the projected annual rate of growth for that investment, i.e. the higher a project's IRR, the more desirable it is to undertake. It is the discount rate at which the NPV of all cash flows equals to zero [46]. The PB refers to the time required to recover the investment cost. The ROI describes the rate of the cash return without the consideration of cash discount in the plant's lifetime. Finally, the gross profit is a measure of profitability by subtracting the annual revenue from the annual operation cost, whereas the net profit takes income tax (16.5%) into account [45].

2.2.2. Sensitivity analysis

The integrated calculation also allows to see how the result is influenced by the uncertainties of the assumptions made. A sensitivity analysis was conducted to identify the parameters that have the largest impact on overall performance and cost and to identify the key areas of improvement. This study evaluates the MES-from-CO₂ and MES-from-SCCA, shown in Fig. 2 through case studies. For sensitivity analysis, one deviation from the base case value for one parameter while all other parameters are held at their base case value represents one case. Two deviations per parameter were investigated, namely the low and high performance cases, which values are shown in Table 1. The lower and upper performance bounds of the parameters are not arbitrary, and in general, they represent an estimate at a high confidence level. Though, some parameters such as the ones intrinsic to production performance of the MES (e.g. upper performance in terms of current, electron recoveries, and cell voltage) represent performance never reached at lab scale to date. This is done to identify how future MES performance improvement will affect the economic competitiveness of MES. Data not related to MES performance were provided by technology suppliers in the region and were validated and completed using scientific peer-reviewed literature (Table 1).

All cases are compared with a reference scenario, referred to as business as usual (BAU). This BAU is the current-day scenario in which the equivalent amount of n-caproate, n-butyrate, and acetate produced by MES is bought at the market price of each (Table 2) and combined to a final cost. Accordingly, the BAU value differs with the products distribution investigated in the different case studies. Optimistic cases are also developed in this study, to represent future scenarios where more than one parameter is improved within plausible limits, as discussed in the results and discussion section.

3. Results and discussion

3.1. Main microbial electrosynthesis products

The market price (€ ton⁻¹) of the five main chemicals produced from MES to date are listed in Table 2. The market price was also normalized to the number of mole of electrons to incorporate the electrical cost. The

Table 2

Market price and annual global production of main microbial electrosynthesis from CO₂ products.

Product	Number of required electrons	Market price (€ ton ⁻¹)	Normalized price (10 ³ × € electron ⁻¹)	Annual global production (10 ⁶ ton)
Acetic acid	8	650 [47]	4.9	3.5 [47,48]
Butyric acid	20	2000 [12,32]	8.8	0.03 [47,48]
Caproic acid	32	4400 [49] ^a	16.0	0.03 [47,48]
Ethanol	12	1000 [28]	3.8	51.0 [47]–77.0 [28]
Butanol	24	1100 [50]	3.4	2.8 [51]

^awww.alibaba.com accessed in July 2019 for quantities larger than 1 ton.

annual global production of each product was also tabulated, which reflects their current market capacity and demand.

Although n-caproate requires the highest number of electrons, it has the highest normalized market price (16.0 × 10⁻³ € electron⁻¹). However, the annual production of n-caproate is the lowest nowadays (30 kton). Similarly, n-butyrate has the second highest normalized market price but also a low annual production. Nevertheless, if n-caproate and n-butyrate could be efficiently produced through MES, it could increase their market potential. The carboxylic acid market size is expected to grow in the near future and surpass USD 20 billion by 2024 [52]. The global market is expected to rise because of their increasing use in the polymer industry, cosmetics, personal care market, and feed and food products [53]. The increasing market sizes will also likely affect the future market values. The market prices in Table 2 can be debated. However, the cost analysis performed below (Sections 3.2 and 3.3) is independent of the market values, hence every reader can make their own interpretation, e.g. in terms of return on investment. Additionally, a sensitivity analysis on the price of n-caproate is presented in Section 3.5. Ethanol and butanol were also produced in two-compartments [54] and three-compartments MES [55], though at lower faradaic efficiencies and production rates. Ethanol has the highest market capacity as well as a decent normalized market price though lower than the carboxylates, with applications e.g. as fuel additive, solvent, and chemical precursor. It should be noted that other products of interest have been produced from CO₂ in MES, such as isopropanol [56], propionate [57], and isobutyrate [54], though in so far limited number of studies. We therefore disregarded them in the above market study.

Given the current state-of-the-art of microbial electrosynthesis, the production of pure and mixed C2-C4-C6 carboxylates was selected for the detailed cost analyses presented here.

3.2. Cost distribution comparison of MES-from-CO₂ and MES-from-SCCA base cases

Three main integrated processes were analyzed for the production of short and medium-chain carboxylates by microbial electrosynthesis, either from carbon dioxide (MES-from-CO₂) or from organic waste stream (MES-from-SCCA). A mass and energy balance module, and a cost analysis module for these systems were integrated into a single model.

Fig. 3 represents the capital and operating costs distribution of the base case of each process configuration (see Table 1). The MES-from-CO₂ process presents the lowest capital cost amounting to 5061 € ton⁻¹, 18 and 250 times lower than MES-from-SCCA using a chemical and biological anode, respectively. This is mainly explained by the lower current density and lower faradaic efficiency recorded in the two latter configurations. In both configurations using a chemical anode, the anode cost represents the main cost contribution amounting to 59% of the total CAPEX for both systems. These CAPEX distributions highlight the need either to develop cheaper water-oxidizing catalyst/electrode that would match MES current density requirement, or to consider other oxidation reactions of interest possibly generating valuable products, i.e. additional revenues [58]. Comparatively, the bioanode cost accounts for 31% of the total CAPEX, due to the use of cheaper carbon-based anode.

The total operating cost of MES-from-CO₂ (1730 € ton⁻¹) is 9 and 50 times lower than MES-from-SCCA using a chemical and biological anode, respectively, which is partly explained by the lower current density and faradaic efficiency. However, some trends are noteworthy. For the two processes using a chemical anode, electricity utilization represents the largest share of the OPEX, up to 69% for MES-from-CO₂. The cost of water is also higher for MES-from-SCCA (8% of the total OPEX), mainly due to the low acetate concentration in the influent. The larger water volume also translates in a higher salt requirement for conductivity control up to 2% of the OPEX. Apart from the high maintenance cost and depreciation which are both linked to the CAPEX (see above), the main operating cost for MES-from-SCCA using a bioanode

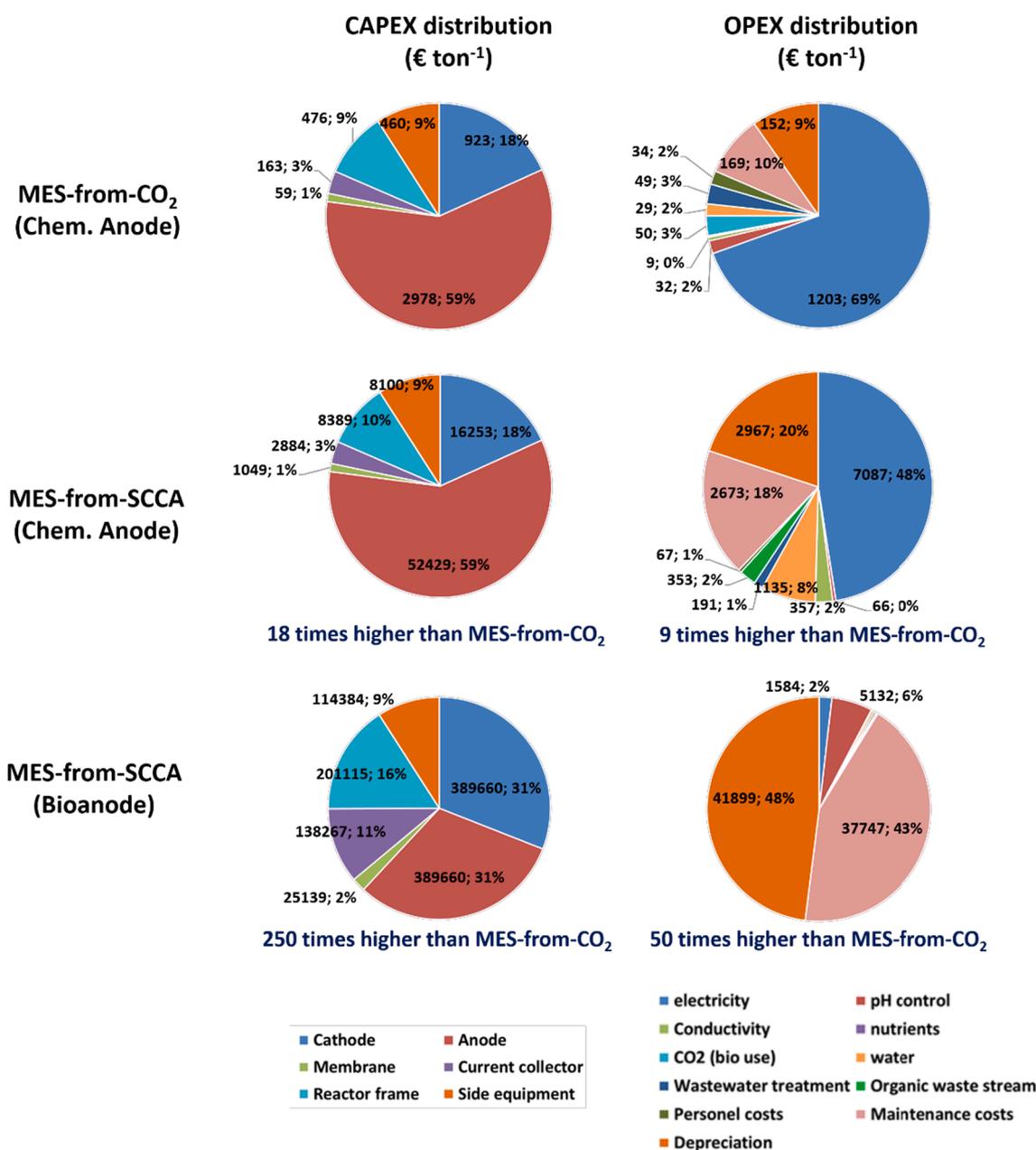


Fig. 3. Capital investment and operational costs distribution of the three base-case configurations in € ton⁻¹, i.e. MES-from-CO₂ and MES-from-SCCA using a chemical anode, and MES-from-SCCA using a bioanode with SCCA stream fed to the bioanode and the produced CO₂ at the cathode.

regards chemical addition for pH control, which is 5 times more costly than electricity in this configuration. Indeed, both redox reactions are biologically catalyzed and require around neutral pH to be maintained. Therefore, the proton concentration on the anode side is orders of magnitude lower than the concentration of the other cations, which are the ones predominantly crossing the membrane to the cathode side for charge balance [59]. Consequently, most of the protons required for the cathodic reactions must be dosed. Additionally, pH control is also required on the anode side.

Fig. S2 represents the same cost distributions as in Fig. 3, but in the case that the biocathode of both MES-from-SCCA achieve the same performance as in MES-from-CO₂ (represented as Hyp-cases in Table S1). This allows to conceptually investigate what the main differences or challenges would be if those performance were achieved in these two configurations. In brief, twice lower electricity cost is required when feeding SCCA to the biocathode compartment when compared to MES-from-CO₂, which was expected due to the lower amount of

electrons required to reduce carboxylic acids than to reduce CO₂, to the same products. Consequently this would lead to a CAPEX 70% lower than for MES-from-CO₂. And in addition to the discussion above, though electricity consumption is lower when using a bioanode vs. using a chemical anode for CO₂ reduction due to a lower cell voltage, chemical addition for pH control proves detrimental to the feasibility of this bioanode-based system. Another major challenge to this system is the synchronization of two biological conversions at high current density.

From the analysis showed in Fig. 3, it is apparent that the performance of MES-from-SCCA using a chemical anode still lags behind. Therefore, the rest of the manuscript focuses on the in-depth analysis of the MES-from-CO₂ concept. However, a sensitivity of cost of production to key parameters of the MES-from-SCCA scenario is showed in Fig. S3. Briefly, in addition of the key parameters discussed below for MES-from-CO₂, it can be seen that both the SCCA concentration in the influent and the SCCA conversion efficiency have the most significant effect on the production cost. It was modelled that a SCCA concentration above 9 g

L⁻¹ is required to make the process viable with all other parameters at their hyp-case values. The concentration of carboxylates obtained from acidogenesis fermentation are usually in the range of 2–30 g L⁻¹ [60]. Special attention must be placed on the acidogenesis fermentation stage and on the organic waste stream feedstock to guaranty sufficient SCCA concentration. Moreover, some organic waste streams already contain electron donating intermediates such as thin stillage which may contain lactate and traces of ethanol in addition of acetic acid, carbohydrates, and glycerol. With such stream, acidogenesis followed by chain elongation from SCCA to MCCA was observed without addition of exogenous electron donor, using granular fermentation [61]. The use of MES-from-SCCA may not be the most competitive route for such organic feedstock, though experimental evidence is lacking to date.

3.3. Sensitivity analysis of the MES-from-CO₂ integrated process

A sensitivity analysis can help draw an interdisciplinary roadmap for research and development, by pinpointing the major obstacles towards market penetration. Fig. 4 shows the results of the sensitivity analysis on the cost of production of all key identified parameters.

Fortunately, most parameters that have a significant effect on the cost of production are related to the MES reactor performance, which researchers can focus on improving, and which eventually can be under the operator’s control. Table 3 summarizes the effects of these main parameters. Among them, the faradaic efficiency and selectivity (electron distribution) have a large impact. Decreasing the faradaic efficiency from 88% (base case) to 50% (low-performance) increases the cost of production by 65%, to 2851 € ton⁻¹. Increasing selectivity towards the most valuable product, n-caproate, increases the production cost to 2743 € ton⁻¹ as compared to 1368 € ton⁻¹ when only acetate is produced. However, as discussed later, this does not reflect economic viability (see Section 3.4). Decreasing the cell voltage to 1.8 V (vs. SHE), as often reported in commercially available water electrolyzer [15], would decrease the electricity consumption and ultimately the cost of production by 25%.

It can also be observed that the cost of electricity has a large impact on the cost of production (Fig. 4). A decrease of electricity cost from 0.07 to 0.03 € kWh⁻¹ leads to a 40% lower production cost, down to 1043 € ton⁻¹. Prediction shows that the cost of renewable electricity could be as low as 0.03 € kWh⁻¹ by 2030 [42], which would favor feasibility and implementation of MES. Efforts should also be made to systematically

Table 3

Resulting effects of varying key MES performance parameters. The other key parameters have straight forward impact as described in Table 1 and Fig. 4.

Parameters	Main effects
Current density	Reactor sizing (production rates) -> CAPEX
Cathode faradaic efficiency	Reactor sizing (production rates) -> CAPEX
CO ₂ conversion efficiency	CO ₂ consumption for growth, nutrients, and buffer
Membrane H ⁺ permeability	Water consumption anode
Product(s) concentration	Water cathode + wastewater
Cell voltage	Nutrients
CO ₂ conversion efficiency	Electricity consumption
Membrane H ⁺ permeability	Total CO ₂ amount requirement
Product(s) concentration	pH control
	pH control
	Water cathode and wastewater
	Thermal and pumping OPEX
	OPEX (Separation unit CAPEX & OPEX)

investigate the effect of intermittent energy supply on MES microbial performance and overall economics [62], e.g. in case MES is not profitable above a certain price of electricity (see Section 3.6).

Finally, the large CO₂ feedstock requirement makes its conversion efficiency and its cost, impactful parameters (Fig. 4). However, CO₂ conversion efficiency is rarely reported in MES literature. Either a large excess of CO₂-gas is fed to MES, often leading to conversion efficiency in the order of 1% or lower [57], or MES is fed with high concentration of a bicarbonate salt, with conversion up to 100% reported in batch-mode [63]. Our latest study demonstrated that by adjusting the CO₂ feeding strategy (loading rate and partial pressure), an increased carbon (>60%) and electron (>50%) selectivity towards n-butyrate and n-caproate over acetate can be achieved in high-rate MES-from-CO₂ [39]. Different product spectra and current densities were reported when feeding either with CO₂ gas or sodium bicarbonate [57], while others have tried to feed CO₂ more locally to the (bio)catalyst using gas diffusion electrodes [64]. The actual effects of different concentration and transport rate of CO₂ on MES performance should be investigated further. Moreover, continuous operation of MES is also rarely reported, with most studies operating in batch or fed-batch. However, the source of CO₂, the nature of the gas, and the type of pre-treatment or purification needed will likely dictate the MES mode of operation in an industrial setting [65], e.g. large amount of CO₂ continuously generated and storage of CO₂ not desired would require continuous MES operation. Therefore, the source of CO₂, its required concentration, and the desired conversion efficiency must be

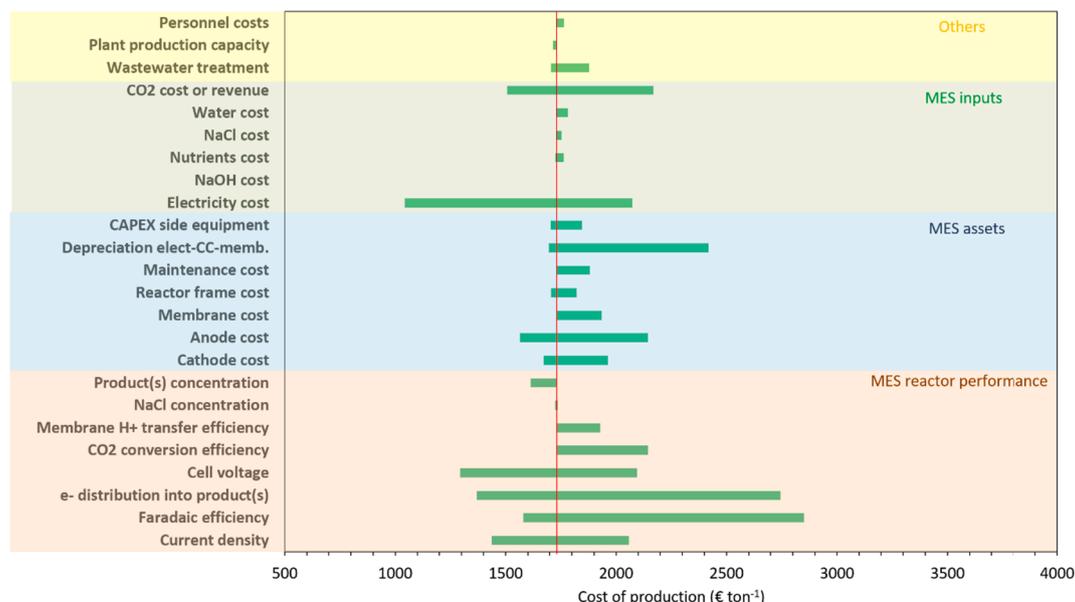


Fig. 4. Sensitivity of cost of production to key parameters of the MES-from-CO₂ scenario without a separation unit. The vertical red line represents the base-case.

considered carefully when designing a microbial electrosynthesis plant, as well as when operating lab-scale systems. Moreover, significant efforts are currently being made towards lowering the cost of CO₂ capture technologies as well (e.g. Climeworks [66], Carbon Engineering [67]).

Fig. 5 shows the sensitivity on the capital cost of key parameters. Only three parameters from MES performance and five from MES assets actually impact the sizing and capital cost of the integrated process.

As previously discussed, the cost of the anode material is the asset with the highest impact on the CAPEX. The current density, together with the faradaic efficiency directly relates to production rate and to the sizing of the reactor. Therefore, at fixed faradaic efficiency, the CAPEX is linearly proportional to the current density (Fig. 5), which justifies the intense efforts towards improving this parameter [63]. However, it should be stressed that economy of scale by size or by number was not accounted for here.

3.4. Improving selectivity to n-caproate allows profitability

Fig. 6 represents the effects on net present value of solely changing the electron distribution over the three carboxylates while all other parameters are fixed at their base case values (Table 1). For the process to be profitable, the NPV must be positive.

First of all, it can be seen that the base case has a negative NPV (−82 k€), showing that in those conditions the process is not profitable. Therefore, one or more of the most impactful parameters discussed above (Fig. 4) must be improved, preferably related to MES performance. Here we discuss the impact of production selectivity. Increasing the share of electrons above 36% into n-caproate at the expense of acetate, while keeping the share into n-butyrate to 33% leads to positive NPV. However, it also shows that solely increasing the selectivity to n-butyrate at the expense of acetate does not lead to sufficient improvement (NPV still slightly negative). Therefore, the key to economic viability in these conditions is to increase the electron selectivity to n-caproate.

3.5. MES performance improvement alone can lead to profitability

Interestingly, solely increasing the current density up to 10 fold (−1000 A m^{−2}) while keeping all other parameters at the base case does not lead to positive NPV (−22 k€). Similarly, reducing overpotentials up to obtaining a cell voltage of 1.8 V results in a NPV only slightly negative of 700 €. Profitability of MES is possible, and will likely be achievable by a combination of process performance enhancement, without the need to rely on favorable external parameters/non-technological parameters

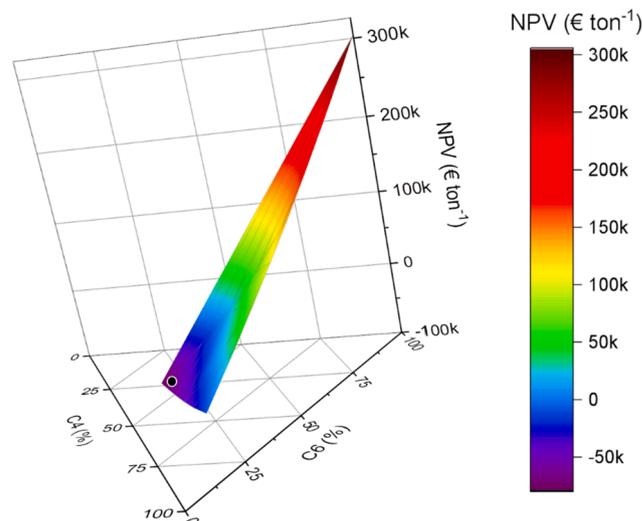


Fig. 6. Contour plot showing the dependence of end-of-life NPV on electron distribution into C2, nC4, and nC6 under otherwise state-of-the-art base case conditions at a plant's lifetime of 30 years and 5% discount rate. The black dot represents the base case conditions. (Other angles of the same graph is showed in Appendix A, Figure S3).

which are hardly in the operator control. Process performance enhancement can be achieved by continuing effort on the research and development of MES. An example of such combination of improvement is depicted in Fig. 7.

In addition of electron distribution as discussed above, cell voltage is the second most impactful MES performance parameter, together with faradaic efficiency (Fig. 4). Fig. 8 shows cell voltage/faradaic efficiency contour plots with the calculated end-of-life NPV with either n-butyrate or n-caproate as sole product or with a reversed electron selectivity as compared to the base case, i.e. with 52-33-15% electron into nC6, nC4, and C2, respectively, as these scenarios were showed to be potential profitability targets (Fig. 6).

The production of n-caproate can be done profitably under base case conditions with relatively poor MES performance, requiring faradaic efficiency over 50% at a conservative cell voltage of 3 V. Decreasing the system's overpotentials (i.e. cell voltage) at a constant faradaic efficiency logically increases the NPV. Additionally, sensitivity analyses on the selling price of n-caproate in these conditions were also performed (see Fig. S4). We show that a selling price as low as 2500 € ton^{−1} and

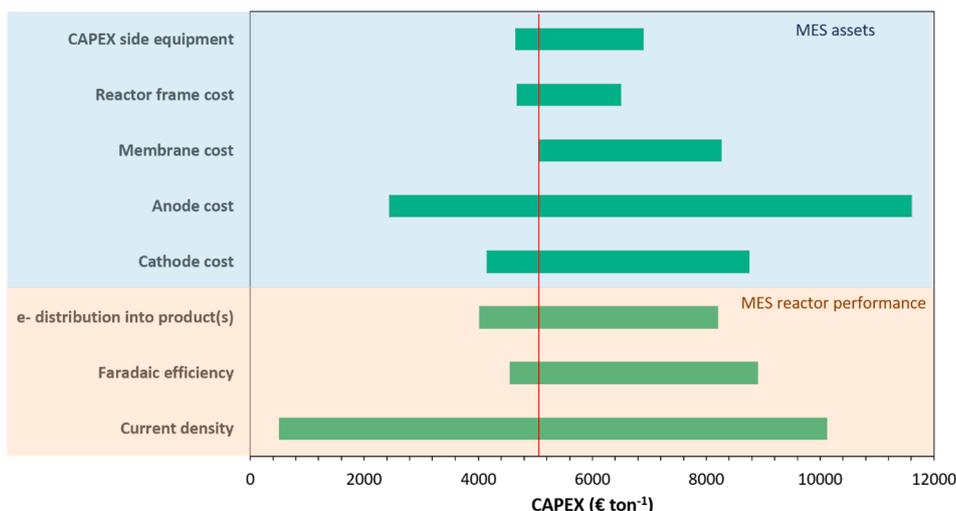


Fig. 5. Sensitivity of CAPEX to key parameters of the MES-from-CO₂ scenario without a separation unit.

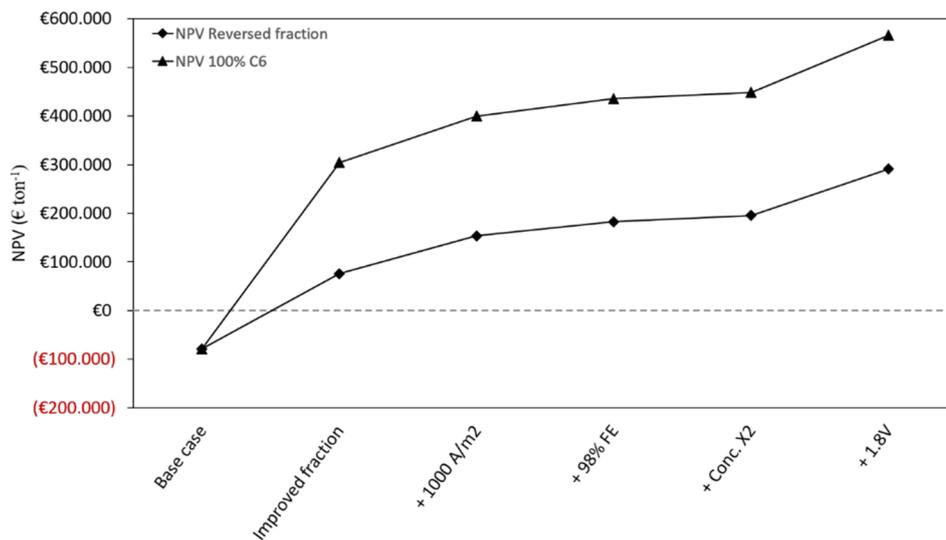


Fig. 7. Sensitivity of net present value on consecutive MES performance improvement of the MES-from-CO₂ scenario without a separation unit (improvements added from left to right on the x-axis) at a plant's lifetime of 30 years and 5% discount rate. Reverse fraction refers to 52-33-15% electron into nC6, nC4, and C2, respectively. A scenario at 100% electron recovery into n-caproate is also depicted. "+ Conc. X2" refers to an increase of products' concentration of a factor 2. FE: faradaic efficiency.

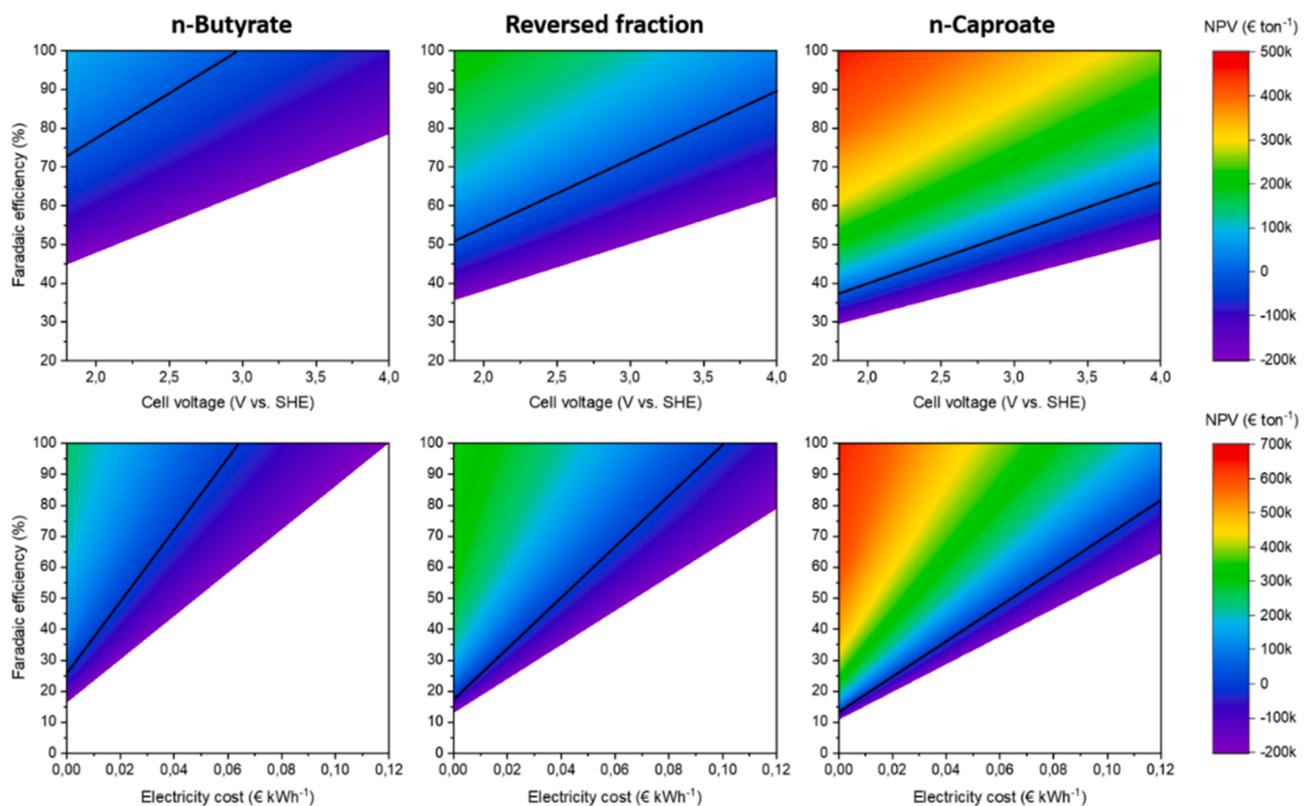


Fig. 8. Contour plots showing the dependence of end-of-life NPV on cell voltage and faradaic efficiency (top), and on electricity cost and faradaic efficiency (bottom), in the cases that either n-butyrate or n-caproate are the sole product or that the electron selectivity is reversed vs. the base case (i.e. 52-33-15% electron into n-C6, n-C4, and C2, respectively). All other parameters are fixed at base case condition at a plant's lifetime of 30 years and 5% discount rate. The solid lines depict the performance needed for an NPV of 0€.

2080 € ton⁻¹ could warrant profitability of this system at 100% faradaic efficiency and 1.8 V cell voltage, respectively, and otherwise base case conditions. It should be stressed that further decrease of the cost of production (i.e. selling price) of n-caproate can be achieved upon improving other key parameters, e.g. down to 880 € ton⁻¹ at -500 A m⁻², 1.8 V cell voltage, and electricity cost of 0.03 € kWh⁻¹. n-Butyrate requires a cell voltage lower than 2.9 V and high faradaic efficiency (>73%) for the process to be profitable. In the case of reversed electron selectivity, a wide range of cell voltage and faradaic efficiency warrants

profitability, with a minimum faradaic efficiency of 72% at a cell voltage of 3 V. Altogether, it is promising that the performance targets for the profitable production of these carboxylates are technologically feasible, though, as shown by the current state-of-art, improvements in MES performance are still needed. Prévotau et al. (2019) recently discussed some relevant strategies to decrease internal resistances in microbial electrosynthesis, such as using more saline electrolytes together with natural halophilic or adapted microorganisms, decreasing the distance between cathode and membrane while still allowing efficient mass

transfer of CO₂, organic products, alkalinity, and nutrients, and improving the cathode design such as it must be highly conductive and maximize the amount of microorganisms immobilized on its surface [68]. Downstream processes usually suffers from high salt concentration, therefore a trade-off may have to be found when investigating high salinity MES integrated to separation processes. Clever designs of highly conductive current collector with less conductive cathode material may also allow to reach internal resistance targets. Moreover, it must be added that elucidating the extracellular electron transfer mechanisms in high current density MES will give insights in the reactor design and configuration to be adopted. Testing MES in industrially-relevant conditions must also be done.

3.6. Impact of electricity cost on economic viability

In addition of determining the minimum cost of electricity for profitability, varying the cost of electricity in our techno-economic model allows to assess the effect of cost fluctuation inherent to the intermittency of renewable electricity supply. Fig. 8 shows the dependence of end-of-life NPV on electricity cost and faradaic efficiency in the same three scenarios as presented above with the other parameters at their base-case (Section 3.5). Evidently, at any electricity cost, a lower faradaic efficiency warrants profitability with n-caproate as sole product, when compared to reversed selectivity scenario, and n-butyrate as sole product, with the highest required faradaic efficiency for the latter. At 0.07 € kWh⁻¹, a faradaic efficiency (FE) higher than 52% results in a positive NPV for n-caproate production, whereas FE must exceeds 75% for the reversed selectivity. A cost of electricity lower than 0.063 € kWh⁻¹ is required for sole n-butyrate production to be profitable. In the scenario of sole n-caproate production, a constant faradaic efficiency above 80% warrants profitability (positive NPV) even if electricity cost varies from 0 to 0.12 € kWh⁻¹, whereas such FE would allow economic viability if electricity cost varies from 0 to 0.08 € kWh⁻¹ for the production of the mixture of carboxylates. Interestingly, we also show that an electricity cost of 0.045 € kWh⁻¹ or lower results in a positive NPV for the base case investigated here (Fig. S5). Nevertheless, an intermittent electricity supply not compensated by another (renewable) energy source when the primary source is not available would result in a situation where the plant will be part of the time turned off, which leads to higher capital investment per ton of product. Assuming a plant turned off half of the time (modelled as a twice lower yearly productivity) and a renewable electricity cost of 0.03 € kWh⁻¹ for the scenario of sole n-caproate production, a NPV 33% higher than for a plant turned on all year long and an electricity cost of 0.07 € kWh⁻¹ was determined, while the NPV is 21% lower, but still positive, when compared with a year-long operational plant at 0.03 kWh⁻¹ electricity cost. This shows the predominance of the operational cost over the capital investment on the overall economics for this particular scenario. A more in-depth economic and system analysis should be performed to fully understand the implication of intermittent electricity supply on electrochemical production of chemicals and fuels.

3.7. How much money is left for integrating a separation/purification unit?

Due to the lack of information in the literature about the (cost of) separation/purification of such carboxylate streams, the separation cost was omitted in the analyses presented above. Moreover, each product could be either purified and sold separately (either in their salt or acid form), or the carboxylate mixture could be sold as is after water, suspended microorganisms, and inorganic salts are removed, e.g. as feed additives [10]. The desired end-product will dictate the choice of separation unit(s) and the associated cost (out of the scope of the current study). However, we determined the maximum purification cost (MPC) to reach a NPV of zero for the scenario with 100% of the electron recovered into n-caproate with all the other parameters at their base

case values (see Table 1). At a separation unit operating cost fixed at 30% of its capital cost, MPC CAPEX of 4711 € ton⁻¹ and OPEX of 1414 € ton⁻¹ would be available for the separation unit and for the overall system to remain profitable.

These MPCs seem feasible when compared to the purification costs in other relevant sectors such as fermentation of lactic acid (LA). Kwan et al. (2018) assessed the techno-economic performance of a food waste valorization process for lactic acid production and found a CAPEX of 268 € ton_{LA}⁻¹ and an OPEX of 970 € ton_{LA}⁻¹ for the purification of lactic acid using filtration, acidulation, GAC column, evaporator, and distillation units [45]. Similarly, Demichelis et al. (2018) investigated the technical and economic assessment of food waste valorization to lactic acid and biogas and reported a CAPEX of 353 € ton_{LA}⁻¹ and an OPEX of 164 € ton_{LA}⁻¹ for the purification of lactic acid [69]. Gonzalez et al. (2007) estimated a higher LA purification costs from their fermentative process from ultrafiltered whey, with a CAPEX and OPEX amounting 1205 € ton_{LA}⁻¹ and 603 € ton_{LA}⁻¹, respectively for their separation units [70]. All the reported costs are substantially lower than our calculated MPCs. However, it should be stressed that the lactic acid fermentation and purification processes investigated above by others are more mature and already proven at large scale. Moreover, the concentration of lactic acid obtained by fermentation is usually higher (>100 g/L) than the carboxylates concentration thus far achieved in MES, which decreases the separation cost. Up to now, the maximum carboxylate concentration recorded in the catholyte of continuously-operated MES are 17.5 g L⁻¹ acetate, 9.4 g L⁻¹ n-butyrate, and 3.1 g L⁻¹ n-caproate [39]. Higher carboxylates concentration should also be a target in MES development, e.g. by optimizing the reactor design and the electrolyte/electrode surface ratio, while preventing product toxicity. In order to get a first impression of the impact on economic feasibility of incorporating a separation unit to the MES process described above, a CAPEX of 1000 € ton⁻¹ was assumed for the separation unit and its operating cost was calculated based on total water removal at a steam requirement of 0.5 kg steam per kg of water evaporated. The key economic performance indicators of the MES process with and without separation unit are presented in Table 4.

Incorporating product's purification did not impede profitability, with a NPV still largely positive, a IRR slightly lowered to 14% and a risen payback time to 7 years. We obtained a similar operating cost of 344 € ton⁻¹ for the separation of n-caproate (including depreciation) than calculated for lactic acid purification. It should be noted that some work has focused on product recovery from lab-scale microbial electrosynthesis, mostly producing acetate as sole soluble organics, either using membrane electrolysis [72], liquid membrane extraction [73], or ion-exchange resins [74]. Future research should focus on product's recovery from MES producing a mixture of carboxylates in order to better evaluate its feasibility, impact on MES performance, and economic viability. The MPC presented here gives an economic range which

Table 4

Key economic performance indicators of the scenario with n-caproate as sole product with all the other parameters at their base case values, without separation unit and with a separation unit CAPEX of 1000 € ton⁻¹ and an OPEX calculated based on total water removal at a steam requirement of 0.5 kg steam per kg of water evaporated, and a steam cost of 6 € ton⁻¹ [71].

Economic indicators	Without separation unit	With separation unit
CAPEX (€ ton ⁻¹)	8209	9209
OPEX (€ ton ⁻¹)	2743	3087
Net present value (€ ton ⁻¹)	296,615	232,265
Internal rate of return (%)	20	14
Payback time (years)	5	7
Annual gross profit without separation unit (€)	1656	1312
Annual net profit without separation unit (€)	930	586
Return on investment (%)	7.2	6.4

the separation unit to be developed/used must fall within. Moreover, due to the early stage of research and development of MES, the estimated MES CAPEX is fairly high. It should be noted that an economy of scale by size or number was not accounted for here, which if applied could substantially decrease the CAPEX with scale, as showed by others e.g. for LA fermentation [69]. However, the reactor design and configuration will dictate whether an economy of scale is applicable, and if so to what extent.

3.8. How does MES compare to CO₂ electrolyzer?

Recently, several techno-economic assessment of CO₂ electrosynthesis systems (using chemical heterogeneous catalysts) have been published, such as to determine which products are the most economically viable [75], or to explore viability of CO production [15]. Most of them assume a CO₂ electrolyzer resembles an alkaline water electrolyzer and applies the capital cost of a water electrolyzer to that of a CO₂ electrolyzer. For example, De Luna et al. (2019) [30] and Jouny et al. (2018) [28] assumed the CO₂ electrolyzer CAPEX at 300 and 250 \$ kW⁻¹, respectively. In comparison, the n-caproate-producing MES system discussed above (Table 4) has a normalized capital cost of 2488 € kW⁻¹. Though this MES system was showed to be profitable, its CAPEX remains substantially higher than assumed by others for CO₂ electrolyzers. We could also expect that MES resembles an alkaline water electrolyzer, though the cathode electrode/catalyst in MES (i.e. carbon-based electrode and microbiome) could be cheaper than the electrocatalysts (e.g. noble metals, alloys, transition metal oxide) used in CO₂ or water electrolyzers, which could in theory lead to lower capital cost for MES, though other key parameters must be considered as detailed above. One main reason for cheaper capital cost of CO₂ electrolyzer when normalized to kW is that those studies assume optimistic scenarios at high current densities ($\geq -1000 \text{ A m}^{-2}$), high faradaic efficiencies, and long-term stability of the catalysts. The latter remains one of the biggest challenge for most CO₂ electrocatalytic reduction reactions [30]. Most studies report hours or days of stability up to now, though companies such as Dioxide Materials reported stable performance over 6 months for CO₂ to CO conversion using their Sustainion™ imidazolium-functionalized polymer as membrane [76]. Microbial catalysts have already demonstrated robust long-term continuous operation for over 1 year in MES [3], though it must still be proven on real scale and industrial conditions. Increasing the current density to -1000 A m^{-2} of the n-caproate-producing MES decreases its capital cost down to 250 € kW⁻¹, in the same range than mature water electrolyzer. However, only discussing current density and faradaic efficiency when comparing, and discussing viability of, CO₂ electrolyzer versus MES is not sufficient [77]; the targeted product and its value must be considered, as demonstrated in this study. Largely different products can be produced from both systems, with electrocatalysts mostly producing small C1 or C2 molecules such as formic acid and carbon monoxide which requires only a few electrons [30], whereas MES has moved away from sole acetate production to production of longer carbon-chain molecules such as n-butyrate, butanol, iso-butyrate, n-caproate, and hexanol. The latter products generally have higher market values than the smaller molecules (Table 2). As seen in our analysis, and as can be extracted from the other techno-economic analyses [28], the lower the value of the product, the higher the current densities and faradaic efficiencies required to meet profitability targets. We showed above that relatively lower current density of -100 A m^{-2} can prove profitable provided e.g. that electron selectivity to n-caproate is increased (see Fig. 6). Additional advantages of CO₂ electroreduction vs. MES could be that e.g. the electrocatalysts could be thermally activated (e.g. solid oxide approaches) and non-aqueous electrolytes could be used, such as methanol, acetonitrile, propylene carbonate, or dimethyl sulfoxide [78]. The aim of the latter approach is mainly to increase the solubility of CO₂ compared with water, though water must still be present in the system or else the products will differ drastically from the aqueous case [79].

Therefore, both CO₂ electrolysis and MES technologies are relevant, and could target different markets based on their respective strengths.

Finally, it must be highlighted that considerable progress has recently been achieved towards obtaining high biocatalyst density/thick biofilm (catalyst) in MES (e.g. biofilm covering 1.2 cm thick 3D graphite felt of 19.8 cm² projected surface area) [3] which in turn allowed to reach current density of -175 A m^{-2} , only a factor 5.7 lower than the current density often referred to as target in CO₂ electrolysis. Further research must investigate electron and carbon fluxes as well as mass transfer mechanisms that are at play within thick biofilms and 3D electrodes, and whether it could be further improved. As discussed above, reaching higher current densities could allow to target lower value products with potentially larger markets (e.g. ethanol, see Table 2). Moreover, higher current densities entails that larger amount of electricity is stored into chemicals bonds, which is particularly important in case the target product is used as a fuel.

Though likely useful for future long-term projection, using water electrolyzer capital costs do not allow to assess the parameters inherent to CO₂ electrolyzer which differ from water electrolyzer, such as the catalyst used for the cathodic reaction. Here, we broke down the costs of a CO₂ microbial electrosynthesis systems into 28 key parameters and investigated their impact on economic viability. This allowed to target and prioritize the key parameters research and development should focus on. The presented model should be updated and completed in the future. Ideally, pilot studies will be carried out and values for the parameters discussed above can be obtained with higher accuracies. Moreover, data on e.g. heat, water, salts, and nutrient management (e.g. possible recycling) could be deducted from pilot studies and added to the model. Other revenues could also be generated from the proposed integrated processes and added to the model, e.g. biogas upgrading, biomass, H₂, O₂, products from alternative anodic reaction, but were not accounted for in the present study. However, our aim here was to provide a detailed (sensitivity) analysis which allowed to lay down an interdisciplinary roadmap towards future research and development of MES.

4. Conclusions

Microbial electrosynthesis allows carbon-waste valorization while using renewable electricity as energy source. In this work, we developed a techno-economic model consisting of integrated engineering and economic modules for the detailed assessment of microbial electrosynthesis systems. Sensitivity analyses on twenty eight identified key parameters were performed to establish performance and non-technological targets such that if these targets are achieved, microbial electrochemical CO₂ and/or organics reduction for chemicals production can become a profitable option. The anode material cost and electricity consumption were identified as the main capital and operating costs in both MES-from-CO₂ and MES-from-SCCAs systems. Though not viable in current state-of-the-art performance and economic conditions, solely improving performance of MES can result in positive net present value and profitability of these systems. Remarkably, only increasing the share of electrons into n-caproate ($\geq 36\%$) allows to reach profitability targets, especially at the expense of electron recovery into acetate. Three main scenarios were investigated in more details, (1) sole n-butyrate production, (2) production of a mixture of acetate, nC4, and nC6 at improved electron recovery of 15-33-55%, respectively, and (3) sole n-caproate production, in the order of increasing revenues. The effects of faradaic efficiency, cell voltage, and electricity costs on the net present value of these three scenarios were assessed. It was showed that n-caproate production is economically feasible at faradaic efficiencies above 52% at a conservative 3 V cell voltage, and that at faradaic efficiency higher than 80%, a fluctuation in electricity cost from 0 to 0.12 € kWh⁻¹ does not impede profitability. The latter simulation allows to mimic the impact of daily electricity cost fluctuation and intermittency of renewable electricity generation. At a separation unit operating cost

fixed at 30% of its capital cost, a maximum purification capital cost of 4711 € ton⁻¹ and operating cost of 1414 € ton⁻¹ were determined. These allow to set a maximum economic target for future integration of separation unit(s) to a MES system. Finally it was discussed that both MES and electrochemical reduction of CO₂ are relevant, non-competitive processes, which target different markets. Moreover, both fields of research can benefit from each other, and increased cooperation is encouraged.

CRedit authorship contribution statement

Ludovic Jourdin: Conceptualization, Methodology, Validation, Investigation, Writing - original draft, Visualization, Funding acquisition. **João Sousa:** Validation, Writing - review & editing. **Niels van Stralen:** Validation, Writing - review & editing. **David P.B.T.B. Strik:** Conceptualization, Validation, Writing - review & editing, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apenergy.2020.115775>.

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