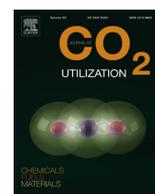




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The use of carbon dioxide in microbial electrosynthesis: Advancements, sustainability and economic feasibility



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ABSTRACT

This study examines the latest advancements in the field of Microbial ElectroSynthesis (MES) and reports a unique sustainability and economic assessment for the production of five alternative compounds (formic, acetic, propionic acids; methanol and ethanol). Different chemical production conditions were compared by modelling a 1000 t per year production plant. Three sustainability indicators; net energy consumption (NEC), energy gain (EG) and global warming ratio (GWR), were used; along with three economic indicators: production cost, pay-back period and discounted cash flow rate of return. NEC analysis revealed substantial energy requirements in the MES reactor and rectification unit. The former due to the energy required to synthesise CO₂ to longer chains and the later due to increased water molecules formed during synthesis. EG values suggested that producing formic acid and methanol using MES were lower than conventional processes. MES was shown to use more carbon dioxide for methanol, ethanol and formic acid synthesis than those produced. The economic analysis showed that formic acid and ethanol had a long pay-back period of 15 years. However, production costs were found to be competitive with the market only for formic acid (0.30 £/kg) and ethanol (0.88 £/kg). Moreover, high returns were evaluated for formic acid (21%) and ethanol (14%) compared to the minimum requirements of the industry (11.60%) making these products economically attractive. Our findings reveal insights about the use and scale up of MES for a sustainable and economically viable chemical production process.

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1. Introduction

Interest in bioelectrochemistry has peaked in the quest to determine how bacteria transfer electrons to solid state electrodes and how we can benefit from this process. According to Scopus, the period between 2005 and 2015 had a linear growth in the number of publications in this field from 100 to 1000 per year. The process occurs in so-called bioelectrochemical systems (BES); a technology that was initially aimed at converting organic and inorganic waste into energy products [1]. Traditional BES consist of an anode and a cathode which are separated by an ion exchange membrane, however membrane less reactors are also available [2]. An electrode reduction occurs in the anode compartment, the opposite, an electrode oxidation, occurs in the cathode compartment. Redox reactions are driven by electroactive biocatalysts; bacteria that interact with solid state electrodes connected through an electrical circuit that defines the cell's mode.

Novel applications of BES have emerged which can be divided into: microbial fuel cells (MFCs), microbial desalination cells, microbial solar cells and microbial electrolysis cells [3]. In microbial electrolysis cells, bacteria reduce organic or inorganic compounds with the use of external energy to produce hydrogen [4]. To assess how bacteria deal with electrical current, it is important to understand how electrons may be transported from the electrode to the cell. Electron transfer mechanisms can occur directly or indirectly and have been fully discussed in literature ([87,5]). Even that the performance of electron transfer mechanisms in bioanodes has been extensively explored ([88,6]), only recently it was found that the electron transfer mechanisms are bidirectional and are also used in biocathodes [7–9].

Even though MFCs have been the most commonly studied application, they present practical and theoretical energy production limitations. Recently, researchers have focused on microbial electrosynthesis (MES) and their ability to reduce substrates into usable chemicals [10]. MES has gained increased attention for the conversion of carbon dioxide (CO₂) to methane [11,10], acetate [12] and other higher biofuels [13,14]. Enzymes are also used to perform

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such bioproduction [15], however, enzymes are not in the scope of this article and are thus not further discussed. MES fits within the green chemistry as they operate under mild conditions (designed for energy efficiency), use bacteria as catalysts (less hazardous chemical synthesis) and CO₂ as raw material. MES is a technology with the potential of becoming a high atom economy process needed for sustainable development. Therefore, MES is a feasible solution and should be embedded to set up a framework for contributing towards meeting the CO₂ emission reduction targets; i.e. the 2050 CO₂ reduction target [16].

MES is at an early stage of development and its feasibility has not met rates close to that required for an efficient electrosynthesis [17]. In MES electrons are exclusively supplied by an external power source. These electrons are then used by the microorganisms for CO₂ reduction to e.g. acetate (reaction (1)) [18]. When this power source comes from renewable sources, the concept is also known as an ‘artificial form of photosynthesis’ [19]. Fuels and chemicals produced via MES (from CO₂) are referred to as electrobiocommodities [20].



Using CO₂ as a substrate in MES offers advantages. CO₂ is an abundant source as it is available in the atmosphere, oceans and soils. It can be considered as subsidized cost by government funding [21]. However, using such a substrate also presents disadvantages, the main one being that CO₂ requires a significant amount of electrons for synthesis of organic compounds due to its thermodynamic stability. In addition, energy is needed to activate the bacteria pathway for autotrophic growth, resulting in increased costs. Efficient electron use is a major concern, from both an economic and an environmental point of view. It can be noted that the use of renewable energy, mixed culture biofilms with varied metabolism and/or redox mediators may help solve this problem.

1.1. Empirical determination of microbial electrosynthesis

Autotrophic microorganisms that are capable of accepting electrons were initially targeted as catalysts for MES [22]. Acetogenic microorganisms were adopted based on their ability to convert CO₂ into acetyl-CoA which then can be used for biosynthesis [23]. Microorganisms that meet autotrophic requirements often do not meet electron acceptor requirements. In this

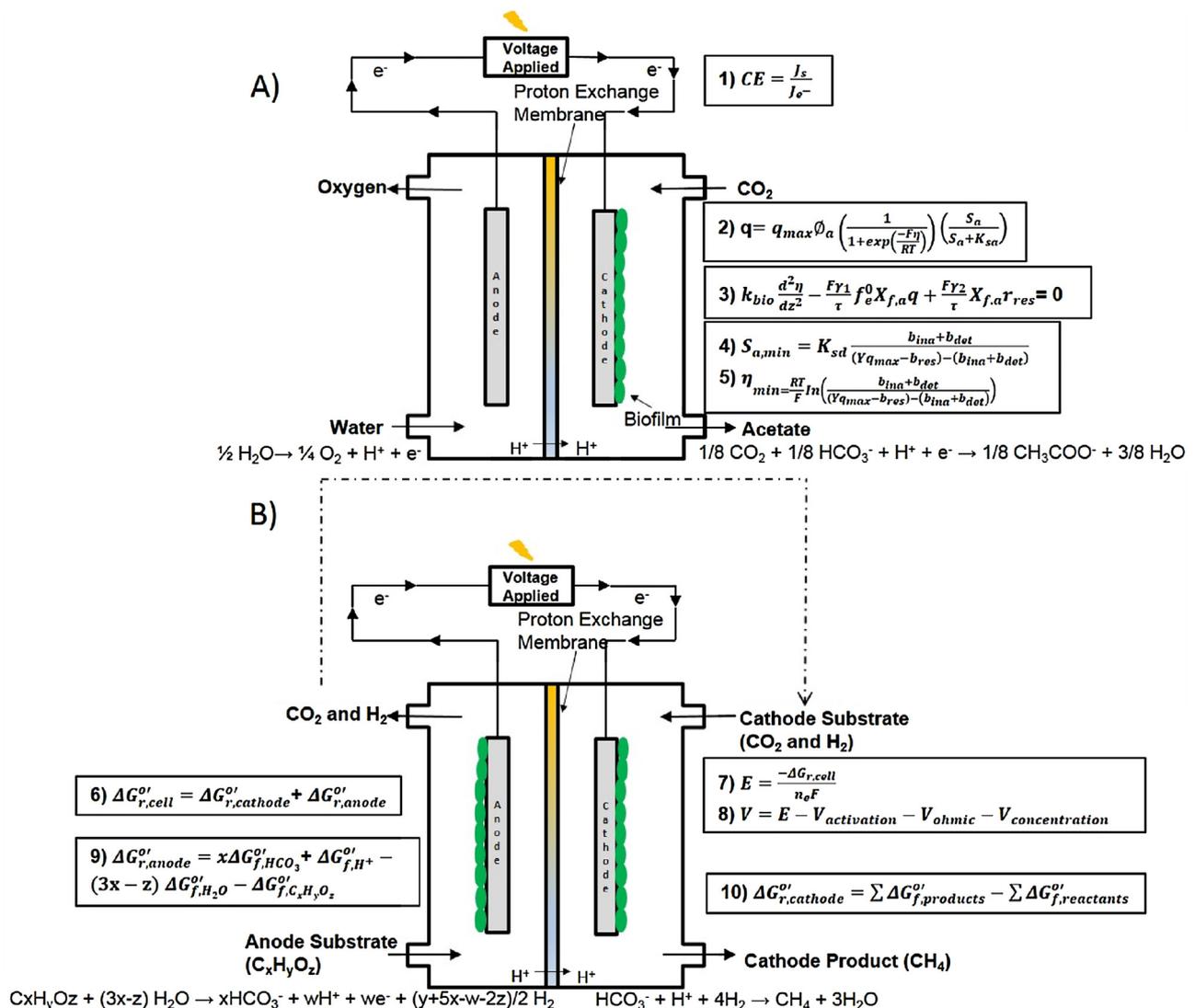


Fig. 1. Diagrams obtained from mathematical models A) Kazemi model and B) Sadhukan model [41,42].

line, genetically modified microorganisms, such as *Clostridium ljungdahlii*, are an option for optimising MES [24,25].

The most common electrobiocommodities synthesized through MES are acetate and methane, produced usually by acetogenic and methanogenic cultures [26,27]. The choice of microorganisms is essential to generate the desired product, as it can affect the quality and quantity of the end product. Pure strain cultures were initially used for producing acetate and methane [12], however, the use of mixed cultures increased production yields [28–33]. The choice of electrode material also resulted in critical improvements in production yield and conversion rates as demonstrated by Jourdin et al. [30] and Jourdin et al. [34]. The importance of hydrogen was also highlighted in MES systems confirming that higher proton availability increases product formation [35,36] leading to the influence of different polarization potentials in bioproduction [10]. MES has also been used to produce building blocks for larger molecules using intermediary biocatalyst from CO₂, i.e. formate and acetate [37]. Zhao et al. [38] observed the production of formate when MFCs were used connected in series to reduce CO₂ *in situ* using the energy generated from the degradation of carbon substances in the anodes.

Even though MES has gained a lot of attention for the conversion of CO₂ to methane, acetate and formate, nowadays researchers are not only investigating the formation of short carbohydrates but also longer chain carbohydrates and bioalcohols. Longer chain carbohydrates, i.e. butyrate, have been produced from CO₂ [14]. Li et al. [13] also demonstrated that after genetically modifying *Ralstonia eutropha* H16, were capable to obtain longer chain alcohols such as isobutanol and 3-methyl-1-butanol. Additionally, Bajracharya et al. [39] demonstrated that the use of a mixed culture inoculum along with a pure strain of *Clostridium ljungdahlii* not only produced acetate but also butyrate and ethanol. These results stimulate the opportunity of producing desired products through the manipulation of electrode potentials, proton concentration and choice of microorganisms.

1.2. Mathematical determination of microbial electrosynthesis

MES involves complex biological and electrochemical processes for achieving product formation. The amount and type of product generated depends on various parameters. The main parameters considered are quantity and/or species of microorganism, mixing and mass transfer phenomena, anodic and cathodic reactions, voltage or current supplied and performance of proton exchange [40]. Modelling of MES process, along with experimental data, could simplify experimental designs, help to identify the process limiting step and thus provide understanding for the scalability of this technology. Two detailed MES mathematical models have been reported: one developed by [41] that describes acetate production in a pure culture biofilm taking into account kinetic rate and mass balance whereas the other shown in [42] is more generic describing product formation by looking at the overall Gibbs free energy of the system.

Fig. 1 shows a descriptive diagram of each reported MES model. Fig. 1(A) illustrates acetate synthesis from CO₂ using a *Sporomusa Ovata* biofilm coated cathode while water oxidation occurred in the anode [41]. Here, the amount of energy required for acetate formation was obtained using rate equations that explain bacterial growth and substrate consumption. This included the fraction and self-oxidation ability of active bacteria cells. Mass balances were used to describe the concentration of substrate present in the biofilm and bulk electrolyte. The electric current demand to drive the reaction was estimated using ohm's law and an electron balance (Fig. 1(A) – Eq. (3)). In this model, electron active bacteria were considered to only be in a biofilm not presenting cell detachment. The transfer of electrons was based on electric conduction. Bacteria

intracellular processes involved in electron transfer, were neglected. The diffusion coefficient of substrate in biofilm was taken as 79% of that in the bulk liquid catholyte. The rate of substrate consumption and subsequent bacteria growth was described using a modified double Monod equation (Fig. 1(A) – Eq. (2)) to account for the limiting effect of both electron donors and acceptors. Mass balances were obtained assuming that CO₂ was supplied in a continuous fed mode with the rate limiting step being the diffusion of substrate in the biofilm. Fick's law was used to describe substrate diffusion into the matrix of the biofilm. The minimum substrate concentration and electric potential required to sustain a stable biofilm was calculated using equation 4 and 5, respectively (Fig. 1(A)). Performance of the system was calculated using coulombic efficiency expressed as the ratio of energy converted to the desired product in relation to the energy supplied. The final model consists of a set of partial differential equations, which were solved in combination with boundary and initial value problems using MATLAB software packages based on the finite difference and shooting methods. Upon parameter estimation it was observed that increasing substrate concentration affected coulombic efficiency negatively whilst the reverse occurred for an increased cathode potential.

On the other hand, Fig. 1(B) shows the Sadhukhan et al. [42] model as a general model that can be applied to a wider range of BESs activities as it attempts to analyse overall energy performance. For MES investigations, methane production from CO₂ was used as the model reaction. This mathematical model uses the overall Gibbs free energy of the cell to obtain the theoretical maximum potential. To utilize this model the oxidation and reduction reactions of anode and cathode substrates alongside any products formed have to be initially obtained. This can be done experimentally by isolating and characterizing responsible bacteria with reactant and product concentrations measured at the end to predict the balanced stoichiometry equation of cathodic and anodic reactions [43]. Subsequently, the Gibbs free energy for both reactions can then be derived from the Gibbs free energy of formation of each species involved in the reactions (Fig. 1(B) – Eqs. (9) and (10)). In turn, the overall Gibbs free energy of the cell can be estimated by summing the Gibbs free energies between the cathode and anode reactions (Fig. 1(B) – Eq. (6)). The Nernst equation (Eq. (7)) is used to obtain the theoretical maximum potential to drive the reaction. As the actual voltage supplied for MES is more than the theoretical voltage due to losses, the effects of activation, ohmic and concentration overpotentials are also taken into account (Eq. (8)) using a linear approximation of the Butler-Volmer equation, Nernst equation and ohm's law, respectively. Sadhukhan et al. [42] model is shown to be effective at assessing the energy efficiency of MES showing that the activation overpotential was the largest contributor to change in theoretical voltage. However, it is limited in its ability to estimate biofilm growth and calculate coulombic efficiencies of MES reactions.

Previous reviews summarize recent empirical developments of MES cells and their optimization [44,5,6,20,45,46,42]. Even though the economic assessment has been previously discussed [47,18], the sustainability assessment of MES has not and it is needed in order to reach technological maturity. This article explains the current progress in the experimental and mathematical understanding of MES and; for the first time, reports a feasibility analysis of the technology. The analysis is conducted based on the economic and sustainability analysis of a modelled full scale production process. The conversion of CO₂ into essential chemicals, such as acetic, formic/propionic acids, methanol or ethanol, using MES is explored. Environmental indicators are subsequently used to compare MES technology with conventional methods for chemical production.

2. Methods

2.1. Process description

For the sustainability evaluation all the life cycle steps were considered except the final product use (Fig. 2A) based on life cycle methodology described in the standards ISO 14040 and 14044 [48,49]. The system boundary used in this study was limited to a cradle-to-gate focus. The economic analysis only accounted the steps inside the production cycle domain: product formation (feedstock, bacteria inoculation and cultivation and energy input), separation, recycle and storage (Fig. 2B).

Acetic, formic and propionic acids, methanol and ethanol were evaluated as products using an MES plant. The MES plant was designed and assumed to be located at Newcastle Upon Tyne, UK. Large scale bioelectrochemical systems in the form of fermentation batches were considered as MES reactors which also included electrodes, reaction medium and a stable biofilm catalyst. The biofilm in the reactor was assumed to be developed prior to MES plant start-up. The MES plant is mainly operated in batch mode and runs for 8000 h per year to produce 1000 t per year (t/y) of product. A biocatalyst separator is used to remove any remaining bacteria in the effluent prior its entrance to the rectification unit. Any excess CO₂ is recycled back to the MES reactor where oxygen produced is released to the atmosphere. The main unit operations are further described below, detailed description of all unit operations and parameters used are shown in Supplementary information S1 and S2.

2.1.1. Mixer

An industrial mixer was used to prepare the reaction medium which consisted of a number of minerals, salts (Supplementary information S3) and CO₂. Mixing would last approximately 20 min per batch. CO₂ used was captured and provided from a coal fired power plant placed 30 km away from the MES plant, transported, pressurized and stored onsite. It was assumed that CO₂ was

captured from flue gas consisting of 13 mol% CO₂ at 0.1758 GJ per tonne of CO₂ [50]. This reaction medium was subsequently pumped into reactors which consisted of steady state biofilms.

For the purpose of the sustainability analysis, the energy required to produce all chemicals used in medium preparation was obtained using the average energy in gigajoules per tonne (GJ/t) to manufacture chemicals in Europe [51,52]. For the economic analysis these chemicals were included as a small percentage of raw material cost.

2.1.2. MES reactor

It was assumed that steady state biofilms were developed prior to the MES plant start-up. Some biofilm development procedures, parameters and assumptions were made based on data obtained experimentally [29]. Biofilms were derived from wastewater obtained from the Clarence Town Waste Water treatment works (UK), 50 km away from the plant site. For the production of acetic acid, the biofilm consisted mainly of bacteria from *Acetobacterium* species (51–60%), *Rhodobacteraceae* family (15.9–18.7%) and *Sulfurospirillum* genus (18.9–26.9%). For the production of other evaluated products mixed cultures or pure cultures obtained from [53] were used. The biofilms were developed in batches using 2-bromoethanesulfonate to help inhibit methanogenic bacterial growth [54]. Key properties of the wastewater source used included nutrients in composition of chemicals, vitamins and minerals (Supplementary information S3). Optimal growth temperature was assumed to be between 25 ± 2 °C. Table 1 presents the reaction balances that take place in the MES reactor alongside their activation energies and targeted flowrate. The energy values for acetic and formic acids were taken from experimental data which derived their activation energy to calculate energy balances. However, for propionic acid, methanol and ethanol values, the theoretical electrochemical data was used as none of these products formation has yet been investigated directly from CO₂.

A total number of four reactors were assumed to work in batches. The limiting unit operation was considered to be the MES

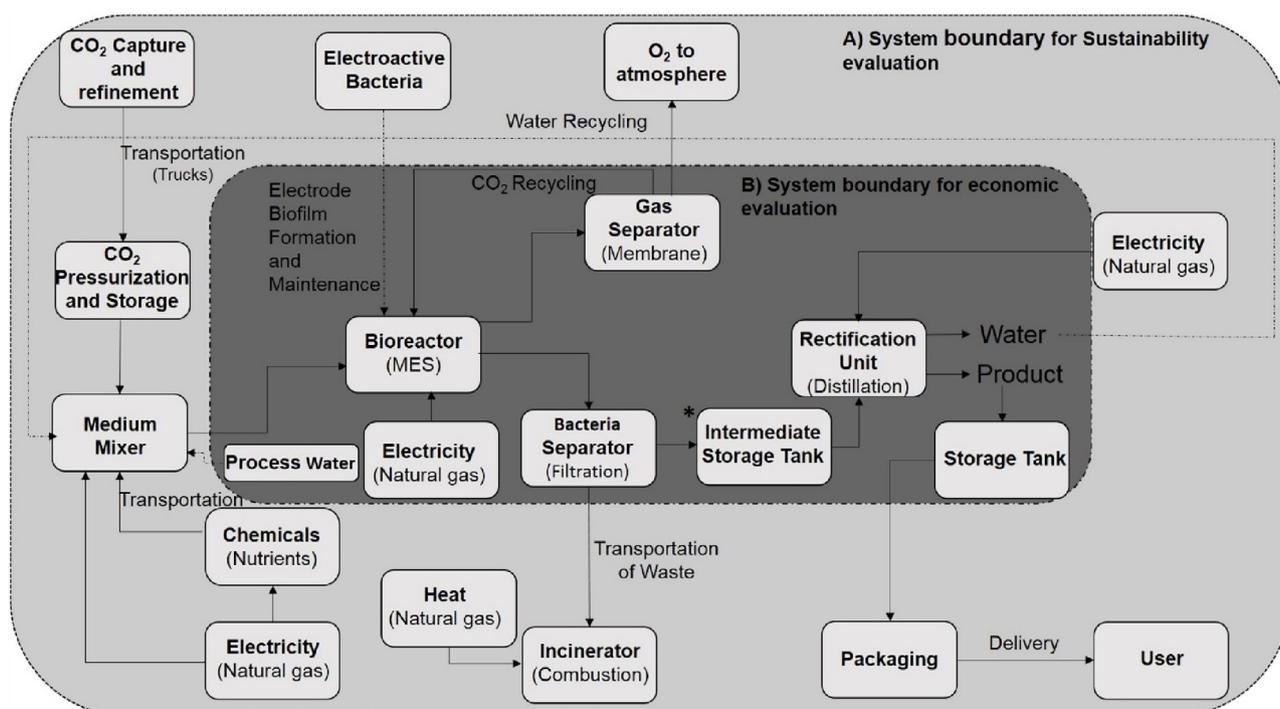


Fig. 2. Schematic representation of a 1000 t per year microbial electrosynthesis plant for formic, acetic and propionic acids, methanol and ethanol production, showing the system boundaries defined for the economic (B) and sustainability evaluation (A). *Before this unit operation all processes are batch, the distillation process runs continuously.

Table 1
Reaction balances for CO₂ reduction into acetic, formic and propionic acids, methanol and ethanol MES plants.

Product	Main reaction	Targeted flowrate (Moles per batch)	Theoretical potential (V vs. SHE)	$\Delta G^{\circ}_{25^{\circ}\text{C}}$ (kJ/mol)	Empirical potential (V vs. SHE)	Biocatalysts	Ref.
Acetic acid	$2\text{CO}_2 + 6\text{H}_2\text{O} + 8e^- \xrightarrow{\text{Biocatalyst}} \text{CH}_3\text{COOH} + 4\text{H}_2\text{O} + 2\text{O}_2$	166528	-0.290	874.82	-0.393	Mixed culture (Mainly acetogens)	[29]
Formic acid	$\text{CO}_2 + 2\text{H}_2\text{O} + 2e^- \xrightarrow{\text{Biocatalyst}} \text{HCOOH} + \text{H}_2\text{O} + 0.5\text{O}_2$	217273	-0.430	269	-0.203	Mixed culture	[55,29,15]
Propionic acid	$3\text{CO}_2 + 10\text{H}_2\text{O} + 6e^- \xrightarrow{\text{Biocatalyst}} \text{CH}_3\text{CH}_2\text{COOH} + 7\text{H}_2\text{O} + 3.5\text{O}_2$	134993	-0.290	1509	NA	Mixed culture	[29,56]
Methanol	$\text{CO}_2 + 3\text{H}_2\text{O} + 6e^- \xrightarrow{\text{Biocatalyst}} \text{CH}_3\text{OH} + \text{H}_2\text{O} + 1.5\text{O}_2$	312110	-0.390	702.45	NA	Mixed culture	[57,56]
Ethanol	$2\text{CO}_2 + 9\text{H}_2\text{O} + 18e^- \xrightarrow{\text{Biocatalyst}} \text{CH}_3\text{CH}_2\text{OH} + 6\text{H}_2\text{O} + 3\text{O}_2$	217070	-0.335	1325	NA	<i>Sporomusa ovata</i>	[35]

reactor requiring 3.66 days (88 h) per batch with coulombic efficiency for product formation estimated at 69% [29]. The conversion rate of CO₂ was set at 58.8% with the remaining gas recycled back to the mixer. The targeted flowrate for all evaluated products considered are shown in Table 1.

2.1.3. Gas separator (membrane)

A vacuum pump was used to draw the output gas mixture from the reactor to a gas separating membrane. The gas consisted of mostly CO₂ and O₂ which differed based on product produced (i.e. 44.33 mol% CO₂ and 55.67 mol% O₂ for acetic acid). The CO₂/O₂ selectivity of the membrane was assumed to be 50 with a capture efficiency of 99%. Recycled CO₂ would enter the mixer to supplement CO₂ concentration requirements for the next batch with the remaining gas supplied by CO₂ stored onsite. O₂ separated would be released to the atmosphere.

2.1.4. Filtration system

The liquid effluent from the reactor, which contains the desired product alongside any other by-products, would be pumped through a cartridge filtration system to separate any remaining bacterial cells prior to entrance to the rectification unit. Removed bacterial cells would be transported 50 km for incineration, whilst filtrate would be kept in a storage tank prior to it being pumped through the unit. The storage tank is used because thereafter all unit operations becomes continuous instead of batch.

2.1.5. Rectification unit

Bacteria-free liquid product would be supplied to the rectification unit for purification. Equipment in the rectification unit would vary depending on properties of mixture from the MES reactor (Supplementary information S7 for flowsheets). The mixture gets separated by distillation in single or multiple columns to achieve the desired product in high concentrations and water. The separated water is recycled back to the process whilst pure products are stored and packaged onsite. Tight head steel drum containers (208 L) would be used for packaging before transportation to the end user.

2.2. Sustainability and economic analyses: methodology and indicators

Three sustainability indicators were selected for this study: the net energy consumption (NEC), energy gain (EG) and global warming ratio (GWR) calculated as Eqs. (1)–(3), respectively.

NEC is the summation of the difference between the energy used and energy produced per unit operation expressed in gigajoules per year (GJ/year). EG is the ratio of the energy consumed to generate certain amounts of a product conventionally to the net energy consumption of that same product manufactured

through MES. Conventionally, 5.28GJ is required to produce one tonne of acetic acid [60], 12.60 GJ for formic acid [61], 19.00 GJ for propionic acid [62], 14.76 GJ for ethanol [63] and 33.00 GJ for methanol [64]. Concerning NEC, the energy consumption of each process was calculated based on energy data and technical information available from contractors or open literature (Supplementary information S1 and S6). Data for ethanol rectification was obtained from simulations done by Li and Bai [65]. For the remaining four product streams, the rectification unit was simulated using Aspen Plus V86 with non-random two-liquid (NRTL) activity and Hayden-O'Connell second virial coefficient models (Supplementary information S7, S8 and S9).

$$\text{Net energy consumption (NEC)} = \sum \text{energy input per process unit} - \sum \text{energy output per process unit} \quad (1)$$

$$\text{Energy Gain (EG)} = \frac{\text{Net energy consumption of conventional process}}{\text{Net energy consumption of process}} \quad (2)$$

GWR is the ratio of the contribution to global warming when a certain amount of product is generated using conventional methods to that when it is made through MES. In general, GWR measures the contribution of different greenhouse gases to global warming, expressed as equivalent CO₂ emission per unit energy (Tonne CO₂-eq/GJ). Here, only total CO₂ emissions were considered and derived from the calculated energy consumption. CO₂ captured in the MES reaction was subtracted from the overall CO₂ released. The CO₂ released was considered to be derived from the processing of natural gas used to generate electrical energy. According to this, it was considered that 0.05 t of CO₂-equivalent were emitted per GJ of electricity [59]. GWR was used alongside EG to compare the efficiency of manufacturing a product using MES to methods widely used industrially.

Global warming ratio (GWR)

$$= \frac{\text{Contribution to global warming of conventional process}}{\text{Contribution to global warming of MES process}} \quad (3)$$

The global warming contribution for each unit operation was calculated using Eq. (4).

$$\text{Global warming contribution} = \sum_i \text{GWP}_i \times E_i \quad (4)$$

where E_i is the mass of compound i emitted to the air and GWP_i is the global warming potential of the compound i , calculated as the net GHG emissions through the life cycle.

Regarding the economic analysis, several items were taken into account. Two main types of products are generated from the processes: desired products (formic, acetic and propionic acids, methanol or ethanol) and by-products; water. The desired products will represent the process source of revenue. The capital investment for the acquisition and construction of unit operations and other fixed assets were considered, Lang factors are used for a gas-fluid plant (Supplementary information S4 and S5) as demonstrated in [47]. Regarding costs, the main items are the acquisition and construction costs of the unit operations, and the operating (labour and maintenance) costs.

Following the methodology described before [47] with a few modifications and the main assumptions listed above, three economic indicators were considered for the economic analysis: production cost (per Kg), pay-back period and discounted cash flow rate of return. These indicators were chosen to evaluate the economic return and financial risk of the bioprocesses' scale up.

The total investment cost was calculated as the sum of fixed and working capital costs. The operating cost included raw material, utilities costs (i.e. energy for product formation only), maintenance, operating labour, supervision, plant overheads, capital charges, taxes, insurance and licence fees. Production costs were calculated as shown in Eq. (5).

$$\text{Production cost} (\text{£/Kg}) = \frac{\text{Operating costs} (\text{£/year})}{\text{Total amount of product} (\text{Kg/year})} \quad (5)$$

Payback period was calculated using discounted net cash flow for each year. The discounted cash flow rate of return was calculated as follows:

$$\sum_{n=15}^{n=0} \frac{\text{Estimated net cash flow in year } n}{(1+r)^n} = 0 \quad (6)$$

The life of the project was estimated as 15 years as a standard measurement for the purposes of the rate of return calculations. Reaction balances used for the design of plants are described in Table 1.

3. Results and discussion

Within the several factors that can decrease the sustainability and economic viability of producing chemicals from bioprocesses, it has been shown that the most important ones are: production rates and energy use [47]. Fig. 3 shows the energy, global warming and capital investment values for different products derived from

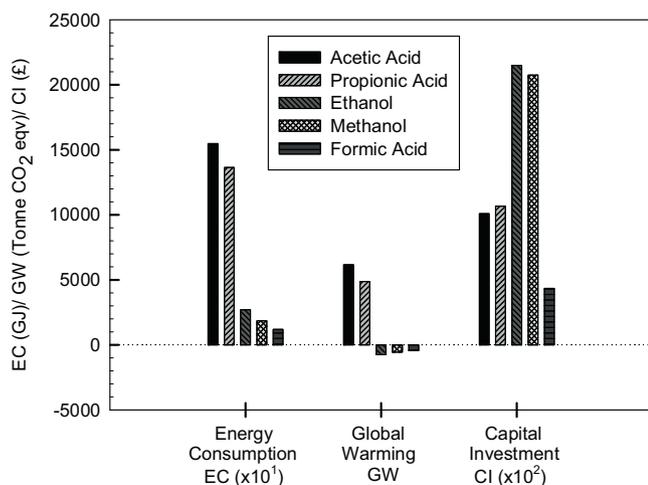


Fig. 3. Energy used, Global warming yield and Capital Investment of MES for the production of formic, acetic and propionic acids, methanol and ethanol.

MES. Acetic acid production was observed to require the highest amount of energy (154,747 GJ) of all the products assessed (Fig. 3). In contrast, formic acid production required the lowest energy; thirteen times (8158 GJ) lower than acetic acid production. These findings were partially based on energy balances and the amount of electrons needed for synthesizing the desired product (Table 1). The electrochemical reaction for acetic acid production uses four times ($8 e^-$) more electrons than formic acid ($2 e^-$) and thus results to a higher energy demand (Table 1). Thermodynamically, producing acetic acid (874.82 kJ/mol) would require higher energy than formic acid (269 kJ/mol). Another major factor affecting the energy consumption is the amount of water molecules produced, which tend to dilute the desired chemicals leading to energy intensive separation processes. Global warming contributions are highly linked to energy requirements when fossil fuels are used for energy generation. Ethanol, methanol and formic acid were shown to consume more greenhouse gas (CO₂) mass during production than the mass released to the atmosphere, resulting in a negative global warming potential. Acetic and propionic acid however released more CO₂ than it used. This shows that using an MES system is dependant on the product synthesized ability to act as a carbon sink. Ethanol had the most positive effect on the environment in terms of global warming as it had the smallest GW yield (-753 t CO₂ equivalent) around nine times lower than acetic acid (6164 t CO₂ equivalent). The economic evaluation showed that the investment cost for producing formic acid was the lowest (£434,700 per annum (p.a.)) compared to methanol (£2.07M p.a.) and ethanol (£2.15M p.a.) investment costs (Fig. 3). This suggests that formic acid should be favoured for synthesis over other evaluated products in order to maximise contributions to the sustainable and economic feasibility of the MES process.

3.1. Sustainability analysis

It was observed that the overall energy requirements were mainly influenced by three unit operations; rectification, MES reactor and gas separator (see Supplementary information S6) presented in Fig. 4. Rectification units and MES reactors were found more energy intensive than gas separators. Industrially, product rectification is seen as one of the highest energy consuming unit operations [66]. Rectification of acetic acid (144,040 GJ) and propionic acid (128,932 GJ) required the most energy; significantly higher than for formic acid (7598 GJ), ethanol (4850 GJ) or methanol (4793 GJ). This can be attributed to the amount of water

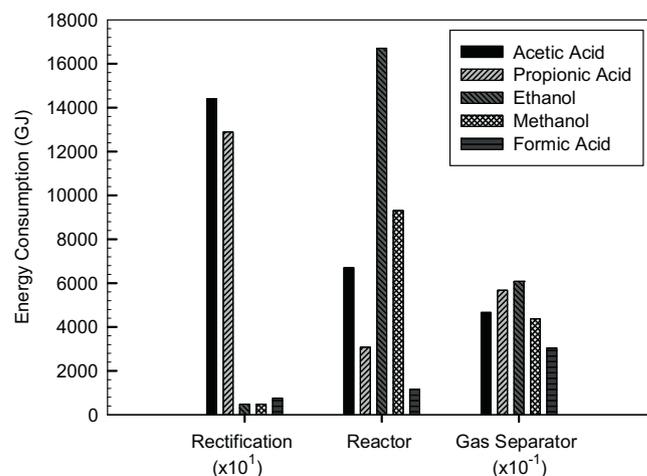


Fig. 4. Energy requirement of MES' different process units for 1000t per year production.

mixed with the desired product and the use of an entrainer for most cases. Rectification of acetic and propionic acid required intensive energy due to a large water content (1:5 and 1:4 ratio of acid to water molecules, respectively) and addition of an entrainer to overcome a water formed azeotrope [67]. Formic acid and ethanol also formed azeotropes with water [68,65,69,70,71] methanol did not. For this reason, along with the fact that methanol synthesis produces low amounts of water (1:1 ratio of methanol to water molecules), methanol rectification was the least energy consumer. Comparing MES reactors, ethanol (16,707 GJ) and methanol (9310 GJ) synthesis used the most energy. This can be attributed to the comparably large number of electrons needed (Table 1). The MES reactor for acetic acid production was shown to be the third most energy intensive reactor (6702 GJ) while that of formic and propionic acid were fourteen (1151 GJ) and five (3082 GJ) times less energy intensive when compared to ethanol synthesis (16,707 GJ). This showed that MES reactors as a standalone unit operation could potentially be a contributor to carbon emissions if its high energy requirement is supplied through fossil fuels. However, this drawback could be offset by the amount of CO₂ consumed for synthesis. Regarding gas separation, the ethanol production process (608 GJ) had the highest energy demand followed by propionic acid (568 GJ), acetic acid (467 GJ) and methanol (437 GJ) processes. Based on reaction balances (Table 1), a higher flow of oxygen is produced during ethanol synthesis than for any other MES products. Ethanol production requires two moles of CO₂ which are not fully converted to products and hence releases three moles of oxygen, more than any other products synthesized. On the other hand, formic acid requires the least energy (304 GJ) for gas separation as it produces less oxygen (0.5 mol) compared to other products.

Another indirect energy consumer is derived from the energy required to produce steel used in the process vessels, such as steel drums (208 L; 16.6 kg) employed for packaging. Studies have shown that production of stainless steel and standard steel drums requires considerable energy input [72,73]. Energy associated with steel drum fabrication accounted to around 5% of the total energy requirement for most cases. However, in the case of formic acid it increased to 11% of all energy input which was higher than the energy needed for synthesis.

To further assess the sustainability of using MES technology two indicators were used, namely EG and GWR. Fig. 5 represents the EG and GWR from MES for the production of formic, acetic or

propionic acids, methanol or ethanol compared to conventional routes. Industrially, acetic acid is produced by methanol carbonylation [74], formic acid through hydrolysis of methyl formate [75], propionic acid by carbonylation of ethylene [76], ethanol from fermentation of corn [77] and methanol from synthesis gas [78]. The EG obtained for methanol (2.0) and formic acid (1.2) suggested that using MES would require less energy than the existing chemical processes. On the other hand, using MES for ethanol (0.6), propionic acid (0.1) and acetic acid (0.03) production resulted in an EG lower than 1 indicating that already established routes would require less energy than MES [60,63]. GWR analysis is an important indicator for evaluating the sustainability of new or existing processes. GWR values showed that using MES to synthesize methanol (-2.2), ethanol (-1.8) and formic acid (-1.1) presented a reduction of CO₂ emission suggesting that MES processes used more carbon emissions than it produced. On the contrary, conventional methods for methanol, ethanol and formic acid production yielded positive carbon emissions. The amount of CO₂ emissions from the conventional methanol production process was twice the amount of carbon consumed when using the MES process Fig. 5. Regarding ethanol, DeCicco et al. [79] showed that using a fermentation production process emitted more CO₂ than the one used. It was shown that for a 7 year period this would result to 27% more carbon emissions than gasoline [79]. This study suggested that producing ethanol from CO₂ using MES could be more beneficial as there was no production of major carbon hiding co-products (e.g. carbon remaining in a corn plant). For formic acid, a MES process will consume similar amounts of CO₂ released by a conventional process. Producing propionic (0.7) and acetic (0.04) acids yielded a positive global warming potential, a consequence of the energy required for their purification. Results from this paper were limited to only the consideration of CO₂ emissions from energy use. Future research should evaluate other potential greenhouse gases released during the MES process to determine the GW potential. Although this could increase the amount of CO₂ equivalent, the same ranking order for the different products would be expected as emissions would proportionally increase for unit operations.

3.2. Economic analysis

Financial risk and return of MES were evaluated based on three economic indicators: production cost per kg, pay-back period and discounted cash flow rate of return. Production costs and discounted cash flow rate of return are presented in Table 2 whereas the pay-back period is discussed later. Formic, acetic and propionic acids are currently produced from biological and chemical production routes using a diversity of raw materials. Examples are the use of carbon monoxide and methanol for acetic acid production or methyl formate for formic acid production [81,75] achieving a maximum cost of 380 £ per tonne of raw material. In the case of formic acid synthesis, the cost can be lowered significantly if the raw materials (methanol) are produced in house or recovered from the processes. Using CO₂ as a raw material for MES in the production of biocarboxylates and bioalcohols can be considered to be negligible. The cost of buying CO₂ starts from as low as 3\$ per metric tonne according to Global CCS Institute; with small changes based on its source (ammonia producers, pipelined CO₂, power, steel and cement plants) and thus can be considered negligible or as a cost subsidized by government [21]. In fact, the cost of releasing CO₂ to the atmosphere (12–22 £ per metric tonne by 2020 and reached up to 29–88 £ per metric tonne) should be included in the future as a utility cost in projects to support incoming legislation [82]. Therefore, companies producing CO₂ should directly absorb the costs of using it in processes such as the MES. Here, since all

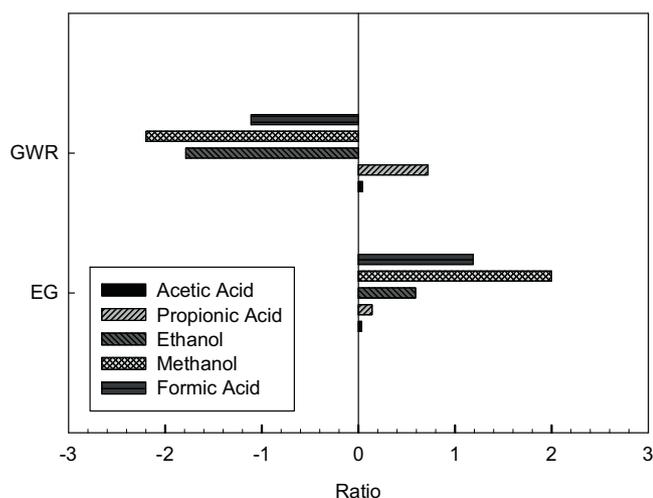


Fig. 5. EG and GWR values of formic, acetic and propionic acids, methanol and ethanol from MES.

Table 2

Investment, operating and production costs and rate of return of formic and propionic acids and methanol and alcohol using MES (1000 t/y). Chemical such as: acetic, formic and propionic acids, and alcohols; methanol and ethanol were assessed for plant capacities of 1000 t/y.

Products	Total investment cost (£)	Operating cost (£ p.a.)	Production costs (£/kg)	Production cost using renewable energy (£/kg)	Market price (£/kg) [80]	Discounted cash flow rate of return (%)
Acetic acid	1,009,300	5,743,200	5.74	3.84	0.48	NA
Formic acid	434,700	493,170	0.49	0.30	0.38	21
Propionic acid	1,066,500	5,167,000	5.16	3.46	1.01	NA
Methanol	2,074,100	1,153,300	1.15	0.77	0.23	NA
Ethanol	2,149,200	1,318,300	1.31	0.88	1.09	14

NA: Not Applicable as production costs are higher than the market price.

evaluated processes used CO₂; water, energy and fixed operating costs became the main cost elements.

An inspection of the thermodynamic properties of CO₂ reduction to organic acids and bioalcohols in Table 1 gives a rough indication on the energetic feasibility of the proposed routes. Reaction balances (Table 1) give specific energy requirements, showing that ethanol, methanol, acetic and propionic acids would incur in high operating costs. Ethanol production was shown to be the highest energy consuming process as it was 93% and 82% higher than formic and propionic acid. Acetic acid was also shown to use more energy than formic and propionic acid making these two the most desirable products evaluated. These results indicate that producing bioalcohols using MES is less economically feasible than producing organic acids which is in line with the literature [18]. Apart from the MES reactor, as discussed in the sustainability analysis, the rectification and gas separator units were energy intensive (Supplementary information Table S6). From the production cost analysis, none of the investigated products showed to be economically feasible to compete with the current market. To optimise all production costs and also to make the bioalcohol production via MES attractive, renewable energy (i.e. wind energy or energy derived from wastewater) can be used to cover energy costs, and therefore reduce production costs as previously discussed in Christodoulou and Velasquez-Orta [47] and shown in Table 2. After using wastewater to cover energy costs, only formic acid (0.30 £/kg) and ethanol (0.88 £/kg) showed economic feasibility, at the targeted production rate, to compete with the current market as the price is presently set at 0.38 and 1.09 £/kg, respectively.

For the investment to be financially viable, the return over the life of the plant must exceed the original capital investment. This return was measured in terms of pay-back period and discounted cash flow rate of return. Both of these measures are directly impacted by the level of investment costs. The investment costs needed for producing formic acid were found to be the lowest (£434,700 p.a.) due to the use of a smaller reactor size (total size: 7.8 m³) when compared to methanol (total reactor size: 50 m³), and ethanol (total reactor size: 36 m³) which had the largest investment costs of £2,074,100 and £2,149,200 p.a., respectively. Consequently, the purchased equipment cost was highly dependent upon reactor size. The larger the reactor, the higher the cost and thus the overall purchased equipment cost increases. Methanol and ethanol used both, more and larger reactors due to product accumulation allowance of only 10% to prevent biocatalyst's death.

MES for the production of methanol, acetic and propionic acids produced no positive return across 15 years of operation, mainly due to the high operating costs and low revenue (see Table 2). These were calculated based upon current market prices of each product. The results suggested that the capital outlay would not be paid back as the process would not generate any net positive revenue streams across a 15-year period. A long pay-back period of

15 years was estimated only for formic acid and ethanol MES projects.

The discounted cash flow rate of return of the MES plants for formic acid and ethanol was also evaluated and results suggested that the plants would generate a maximum rate of ca. 21% and 14%, respectively. This indicates that these two processes could be economically viable. Based on the chemical manufacturing sector of [83] this offer returns far in excess of the requirements of the industry (11.60%). This makes the process economically attractive for the two products. Using the same assumptions for acetic acid, propionic acid and methanol production plants; it showed a negative rate of return as the earnings were lower than the operating costs (Table 2).

The results suggested that MES as a production route using bioelectrochemical conversions would become more attractive if high-energy value molecules with high market value are targeted. The market of the assessed chemicals is in scale of 100 thousand to million tonnes with acetic acid having the largest market volume as it is used as a raw material for many petrochemical intermediates [84]. Market saturation is an important limitation in establishing a business case and in defining the production strategy for a targeted chemical. Propionic and formic acids showed to be the most interesting assessed chemicals from both their use and economic point of view. However, their global production stands at 350 thousand [85] and 610 thousand [86] tonnes per year, respectively. A strategy that can be applied in order for MES to become part of industry as a production route is to achieve a full atom economy. The produced water and oxygen from these processes already contribute to a better atom economy and they can also be sold to contribute to the process revenue.

4. Conclusions

Comprehensive sustainability and economic analyses of MES have been presented. The sustainability assessment showed that using gaseous CO₂ as a substrate offers environmental benefits when methanol, ethanol and formic acid are synthesized. Product formation and purification have high energy demand due to CO₂ thermodynamic properties and formation of water molecules during synthesis. EG values for methanol and formic acid suggested their advancement over conventional processes. The economic evaluation showed that MES plants for methanol and ethanol incurred high investment costs due to the product concentration allowance. On the other hand, formic acids and propionic acids resulted to be the cheapest products derived from MES. Moreover, the return of formic acid and ethanol production plants showed a high discounted cash flow rate of return suggesting their high economic viability. This reveals that focusing on the production of high value products with small demand would lead MES to become an appropriate compatible process. MES as a technology not only helps decrease green-house gas emissions but can also result in low production costs and

strengthen the economy. This offers a bright opportunity towards the use and scale up of MES for industrial intake.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jcou.2017.01.027>.

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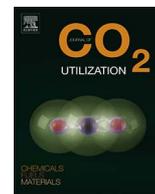


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Corrigendum to “The use of carbon dioxide in microbial electrosynthesis: Advancements, sustainability and economic feasibility” [Journal of CO₂ Utilization 18 (2017) 390-399]



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The table on page 394 (Table 1 ‘Reaction balances for CO₂ reduction into acetic, formic and propionic acids, methanol and ethanol MES plants’) is deleted.

The new table is:

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Table 1
Overall reaction balances for CO₂ synthesis into acetic, formic and propionic acids, methanol and ethanol in MES plants.

Product	Overall reaction	Targeted flowrate (Moles per batch)	Theoretical potential (V vs. SHE)	$\Delta G_{25^\circ\text{C}}^{\circ}$ (kJ/mol)	Empirical potential (V vs. SHE)	Biocatalysts	Ref.
Acetic acid	$2\text{CO}_2 + 4\text{H}_2\text{O} \xrightarrow{\text{Biocatalyst}} \text{CH}_3\text{COOH} + 2\text{H}_2\text{O} + 2\text{O}_2$	166528	-0.290	874.825	-0.393	Mixed culture (Mainly <i>acetogens</i>)	(Marshall et al., 2013)
Formic acid	$\text{CO}_2 + \text{H}_2\text{O} \xrightarrow{\text{Biocatalyst}} \text{HCOOH} + 0.5\text{O}_2$	217273	-0.430	268.998	-0.203	Mixed culture	(Reda et al., 2008; Marshall et al., 2013; Srikanth et al., 2014)
Propionic acid	$3\text{CO}_2 + 7\text{H}_2\text{O} \xrightarrow{\text{Biocatalyst}} \text{CH}_3\text{CH}_2\text{COOH} + 4\text{H}_2\text{O} + 3.5\text{O}_2$	134993	-0.290	1509.800	NA	Mixed culture	(Marshall et al., 2013; CEAE, 2014)
Methanol	$\text{CO}_2 + 3\text{H}_2\text{O} \xrightarrow{\text{Biocatalyst}} \text{CH}_3\text{OH} + \text{H}_2\text{O} + 1.5\text{O}_2$	312110	-0.390	702.457	NA	Mixed culture	(Xu et al., 2006; CEAE, 2014)
Ethanol	$2\text{CO}_2 + 6\text{H}_2\text{O} \xrightarrow{\text{Biocatalyst}} \text{CH}_3\text{CH}_2\text{OH} + 3\text{H}_2\text{O} + 3\text{O}_2$	217070	-0.335	1325.500	NA	<i>Sporomusa ovata</i>	(Blanchet et al., 2015)

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