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Bioelectrochemical systems (BESs) towards conversion of carbon monoxide/syngas: A mini-review

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ABSTRACT

Microbial conversion of carbon monoxide (CO)/syngas has been extensively investigated. The microbial conversion of CO/syngas offers numerous advantages over chemically catalyzed processes *e.g.* the specificity of the biocatalysts, the operation at ambient conditions and high conversion efficiencies. Bioelectrochemical systems (BESs) exploit the capacity of electrochemically active bacteria (EAB) to use insoluble electron acceptors or donors to produce electricity or added-value compounds. Electricity production from different organic sources in BESs has been broadly demonstrated, whereas electricity production from CO/syngas has been very little reported. Acetate oxidation by a consortium of carboxydotrophic and CO-tolerant EAB has been suggested to be the main pathway responsible for indirect electricity generation from CO/syngas. Although electricity production in BESs from several organic sources has been widely investigated, the interest on BESs research is currently moving to the production of added-value compounds by electro-fermentation (EF) processes. EF allows to modify redox balances by the use of electric circuits to fine tune metabolic pathways towards obtaining products with high economic value. Although EF has been widely studied, the potential of use CO-rich gas streams as substrate has been under explored. This review presents and discusses current advances on microbial conversion of CO/syngas in BESs.

1. Context, challenges and aim

Humanity is facing unprecedented environmental concerns related to global warming and biosphere deterioration that results in an increasingly unsustainable human life in our planet. Intensive use of fossil fuels, unbalanced nutrients cycles, loss of biodiversity, water scarcity and low quality, and industrial activity, may risk the future of next generations. Microbial technology is a common element playing a central role in several Sustainable Development Goals (SDGs), contributing to our path towards sustainability. The relevance of microbial technology related to SDGs is well revised by Timmis and co-authors [1]. Although the environmental microbiology research is in expansion, more than 80%–90% of microbial diversity remains to be discovered [2]. This unknown biodiversity combined with novel and challenging biotech processes has the potential to change sectors of chemicals, pharma, energy, materials, agriculture, food and environmental protection.

Clean energy is one of the SDGs where microbial technology may play a central role. The unprecedented environmental concerns in combination with the continuous increase on utilization of fossil fuel energy, have stimulated the investigation on the production and use of alternative energy carriers such as syngas, bio-methane (CH_4) or hydrogen (H_2). Particularly, bioenergy research is increasingly looking for non-edible sources of biomass and for bio-based environmentally friendly processes. The biomass resources from agriculture [3–5], forest [6–8] and municipal waste [9–11] can be converted biologically or thermochemically. However, the biological conversion can be hindered by the presence of low-biodegradable organic matter. Furthermore, nearly any form of organic matter (industrial waste, plastics or other low biodegradable/recalcitrant materials) can be transformed through gasification processes. Biomass gasification, which is considered a way to increase the use of biomass for energy production, results in the production of a gaseous stream named syngas (or synthesis gas), mainly composed by carbon monoxide (CO), carbon dioxide (CO_2) and H_2 [12]. Depending on the biomass source and the operating conditions, syngas can contain some contaminants such as chlorine, nitrogen or sulfur compounds, among others [13,14]. CO-rich gas streams are also produced as an off gas of certain industries like steel production [15] and petroleum refining [16], among others.

Fermentation of this gas stream through the Wood-Ljungdahl pathway can produce a variety of alternative fuels and chemicals

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List of abbreviations

BESs –	Bioelectrochemical systems
DET -	direct electron transfer
MET -	Mediated electron transfer
SDGs –	Sustainable Development Goals
MFCs –	Microbial fuel cells
ORP –	Oxidation-reduction potential
EF –	Electro-fermentation
EAB –	Electrochemically active bacteria
VFAs –	Volatile fatty acids
CE –	Coulombic efficiency

List of units

kPa –	kilopascal
V –	volts
mW –	milliwatt
L –	liter
L_{Anode} –	liter of anode
d –	day
mL –	milliliter
mA –	milliampere
kJ –	kilojoule
mol –	mol

contributing at the same time to the reduction of greenhouses gases, reducing the negative impact on the environment [15,17,18]. Syngas fermentation has advantages over the chemical catalytic processes (Fischer–Tropsch process) such as, higher specificity of the biocatalysts, operation at ambient conditions and greater resistance to catalyst poisoning [19,20]. Nonetheless, the production of a specific product from syngas is still a challenge in traditional fermentations, since metabolic routes are often redox imbalanced. Furthermore, limited reducing power of Wood-Ljungdahl pathway typically results in limited microbial growth rate and conversion yields of CO strains. Therefore, it is of utmost importance to continuously explore new biotechnological alternatives for biocommodities production, using CO/syngas as substrates.

Syngas utilization in BESs appears as a versatile and innovative conversion process to produce added-value chemicals. Electro-fermentation (EF) (electrochemically-assisted fermentation) has the potential to produce compounds with higher purity and higher economic value from renewable carbon sources than traditional fermentation. The use of electrodes assembled into electric circuits to supply extra reducing power have the possibility to improve microbial growth and to prevent the use of additives for balancing redox with simultaneous production of added-value products.

In 2009, the concept of bioelectrochemical syngas conversion in BESs was proposed by Kim and Chang, thus combining the biological conversion with the electricity production [21]. More recently, in 2018, production of added-value biochemicals from syngas in BESs have also been proposed [22]. This technology could be seen as a very promising 4th generation biofuel process for upgrading waste gases treatment since it includes the concept of carbon capture and storage into chemicals and/or fuels. This review aims at presenting and discussing current advances and challenges of the electrochemically assisted microbial conversion of syngas components in BES.

2. Types of BESs and mechanisms

BESs are a type of bioreactor in which electrochemical and biological reactions occur simultaneously. In BESs, the chemical energy stored in a compound is converted into bioenergy by a biocatalyst that can be applied at the anode (anodophiles) for electricity production catalyzing oxidation reactions [23] and/or at the cathode (cathodophiles) for valuable biochemicals production catalyzing reduction reactions [24,25]. The electrons released during redox reactions by anodophiles can be captured for direct electricity production in microbial fuel cells (MFCs) [26] or used by cathodophiles to produce added-value chemicals [27].

To date, electricity production in MFCs has been the most investigated topic in the BESs field [28]. The most common MFCs are composed by two chambers, an anode and a cathode, separated by a membrane. At the anode chamber, electrons and protons are produced by the oxidation of a biodegradable compound (electron donor), by a biocatalyst. The electrons are then transferred to the anode by different electron transfer mechanisms. Posteriorly, the electrons flow through an external electrical circuit from the anode to the cathode, producing electricity. Protons flow through the membrane from the anode chamber to the cathode chamber, thus ensuring the charge balance. At the cathode chamber, electrons and protons combine with a final suitable electron acceptor (*e.g.* oxygen) [29].

Although MFCs are the most investigated type of BESs, the current scenario and interest on BESs research is moving to the production of biochemicals. Controlling the oxidation-reduction potential (ORP) of the fermentation broth is an efficient way to direct the metabolic pathways toward the production of specific products, because intracellular redox homeostasis is influenced by the extracellular ORP [30]. The most common strategies to control extracellular ORP include gas sparging [31], pH control and chemical supplementation of the medium [32]. ORP control using an external power source has been investigated [33].

Extracellular ORP control in BESs has been used to electrochemically assist the fermentation of an energy-rich substrate in a process named EF [34]. In EF, an electrode is introduced in the fermentation broth to induce the conversion of the substrate into a specific product by imposing a potential. Compared to conventional fermentation processes, EF allowed to produce metabolites of economic interest, such as biobutanol, at higher yields [35]. The most common EF system is composed by an anode and a cathode chambers separated by a membrane. Like MFCs, the oxidation of an electron donor, at the anode, produces electrons and protons. The electrons move towards an external electrical circuit from the anode to the cathode, while protons diffuse through the membrane. In a EF system, microorganisms can be present at the anode chamber catalyzing oxidation reactions (bioanode) producing a compound more oxidized than the substrate (*e.g.* glycerol to ethanol) (anodic EF) [36] and/or at the cathode chamber catalyzing reduction reactions (biocathode) producing a compound more reduced than the substrate (*e.g.* glycerol to 1,3-propanediol) (cathodic EF) [37]. The electrons could be transferred to the anode and collected from the cathode by different electron transfer mechanisms.

2.1. Electron transfer mechanisms

In BESs, the electrons can flow from microorganisms to the anode and from the cathode to microorganisms [38]. In both cases, microorganisms can use a direct or a mediated way to exchange electrons with the electrodes.

Direct electron transfer (DET) implies the physical contact between the electrode surface and the microorganisms. In monolayer biofilms, this contact may occur through the c-type outer membrane cytochromes associated with outer membrane of the bacterial cell [39]. In multilayered biofilms, some microorganisms have the capability to develop conductive pili, known as nanowires, since only few cells have direct access to the electrode surface. Nanowires are conductive nanofilaments of proteins which enable long-range electron transfer between microorganisms and the electrode surface [40].

Microorganisms that cannot contact directly with the electrode surface and that are not capable to develop nanowires, use a mediated

electron transfer (MET) mechanism for exchange electrons with the electrode. MET involves the use of redox-active organic molecules referred as redox mediators which can be self-secreted by cells or added to the medium such as phenazines, flavins and quinones [41].

Data from literature indicate that microorganisms from all three domains of life have been identified in anodic biofilms: most often Proteobacteria, but also Firmicutes, Euryarchaeota and Ascomycota. On the other hand, only microorganisms from Bacteria and Archaea domains were identified in cathodic biofilms: most often Proteobacteria but also Firmicutes, Actinobacteria and Euryarchaeota [39]. Bacteria from the genera *Shewanella* and *Geobacter*, considered as electrochemically active bacteria (EAB), can act as anodophiles oxidizing an electron donor and transferring the electrons to the electrode but also as cathodophiles collecting electrons from the electrode to reduce an electron acceptor [24].

3. Microbiology of CO/syngas conversion

Added-value compounds can be produced from syngas during its fermentation using carboxydotrophic microorganisms. Microbial conversion of syngas by carboxydotrophic bacteria involves microbial fermentation through the Wood-Ljungdahl pathway which is also called the Acetyl-CoA pathway (Fig. 1) [42,43]. Carboxydotrophic bacteria can use CO as carbon source due to the presence of the enzyme CO-dehydrogenase [43]. Several types of carboxydotrophic microorganisms have been described, namely acetogenic, hydrogenogenic and methanogenic microorganisms, mainly producing acetate, H_2, and CH_4, respectively. Acetate production by acetogenic carboxydotrophs such as *Alkalibaculum bacchi* [44], *Clostridium ljungdahlii* [45] and *Clostridium carboxidivorans* [46] typically occurs under mesophilic conditions. H_2 is typically produced under thermophilic conditions by hydrogenogenic microorganisms such as, *Moorella stamsii* [47] and *Calderihabitans maritimus* KKC1 [48]. Regarding the ability to produce CH_4 from CO, only few species, namely, *Methanosarcina barkeri* [49], *Methanosarcina acetivorans* [50], *Methanothermobacter thermoautotrophicus* [51] and *M. marburgensis* [52] have been reported. Different added-value products, namely ethanol, butanol, 2,3-butanediol and other short- and medium-fatty acids can also be produced, *e.g.* by different members of *Clostridium* genus [19,53–55].

Despite the known advantages of syngas fermentation, the production of a specific product at high rate and high selectivity is still a challenge in the field of syngas fermentation technology [56–58]. Recent studies demonstrated that the use of increased pressure increased the gas-liquid mass transfer accelerating the conversion rates, but also influenced the distribution of metabolites [104–106], suggesting the activation of different metabolic pathways [59,60].

A recent study demonstrated an alternative method for syngas conversion, which relies on the development of a microbial consortium combining carboxydotrophic and CO-tolerant EAB [21,61] that have the ability to transfer/to accept electrons to/from an insoluble electron acceptor/donor, as explained above [62,63].

Based on the analysis of the metabolic products associated to the electricity production from syngas in BESs, two main pathways have been suggested: (1) directly, through direct transfer of electrons to the anode by Fe(III)-reducing carboxydotrophic bacteria [61] and (2) indirectly, through the conversion of CO fermentation products, such as acetate or H_2, by CO-tolerant anodophilic microorganisms [64]. Acetogenic carboxydotrophic microorganisms, such as *Alkalibaculum bacchi, C. ljungdahlii* or *C. carboxidivorans* present in the microbial consortium are responsible for CO conversion to acetate (Equation (1)), which seems to be the main direct substrate for electricity production in MFCs, by *e.g. Geobacter sulfurreducens* (Equation (2)). Mehta and coworkers demonstrated the tolerance of an enriched anodophilic community up to 70% of CO in the gas phase [61,65]. In particular, the tolerance of *G. sulfurreducens* to CO, a well-known model EAB, was confirmed up to 150 kPa in the headspace [66].

Another potential pathway involves indirect electricity production by conversion of H_2 (Equation (3)), previously produced from CO by

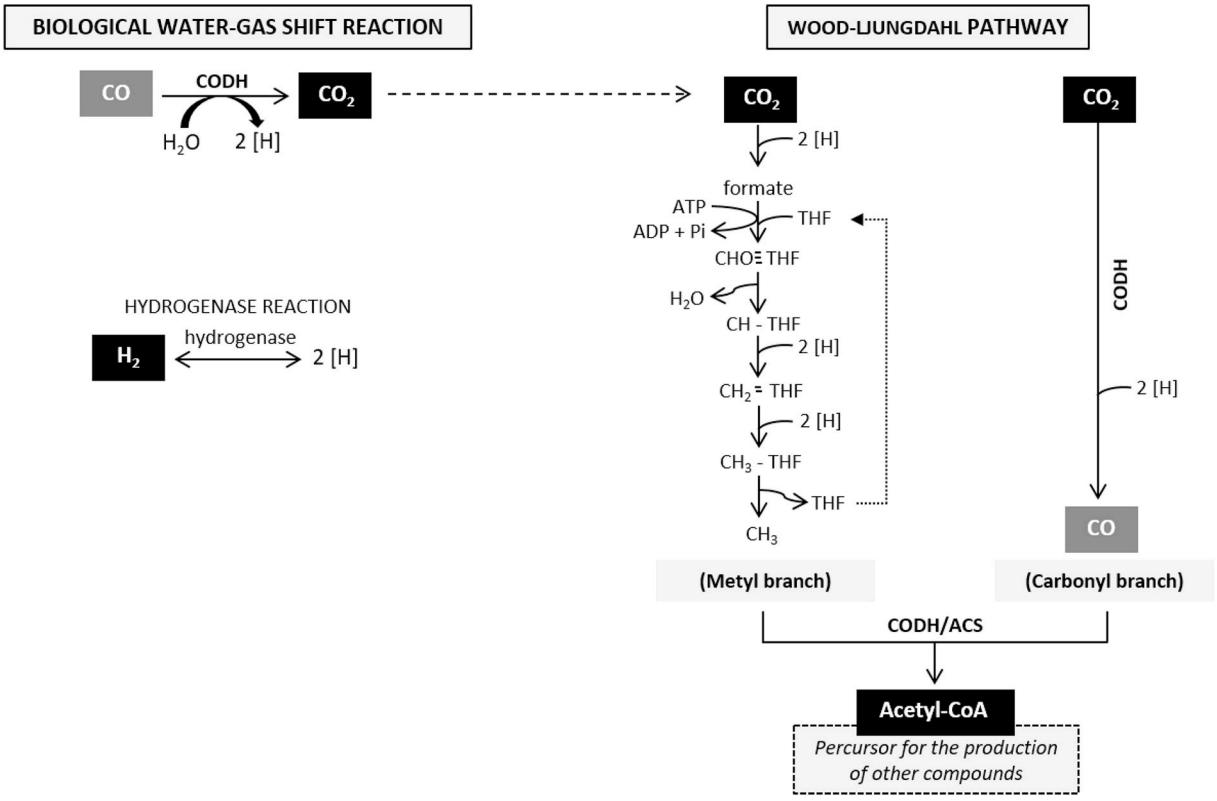

Fig. 1. Schematic representation of Wood-Ljungdahl pathway (CODH, carbon monoxide dehydrogenase; ACS, Acetyl-CoA synthase; THF, tetrahydrofolate).

hydrogenogenic carboxydotrophic microorganisms (Equation (4)). Electricity production from H_2 by *G. sulfurreducens*, has been demonstrated [67]. Additionally, conversion of H_2 and CO_2 to acetate (Equation (5)), by homoacetogenic bacteria, can also occur [61].

$$4CO + 2H_2O \rightarrow CH_3COOH + 2CO_2 \quad \text{Equation 1}$$

$$CH_3COOH + 2H_2O \rightarrow 2CO_2 + 8H^+ + 8e^- \quad \text{Equation 2}$$

$$H_2 \rightarrow 2H^+ + 2e^- \quad \text{Equation 3}$$

$$CO + H_2O \rightarrow H_2 + CO_2 \quad \text{Equation 4}$$

$$2CO_2 + 4H_2 \rightarrow CH_3COOH + 2H_2O \quad \text{Equation 5}$$

Kim and collaborators confirmed, in a two-stage reactor system, that metabolic products from CO oxidation, namely acetate, can be consumed by anodophilic microorganisms for electricity production [21]. Hussain and collaborators confirmed that electricity production from CO in mesophilic CO-fed MFCs, relies on the development of a consortium of carboxydotrophic microorganisms, which convert CO to acetate, and CO-tolerant anodophiles, which convert acetate to electricity (*e.g. G. sulfurreducens*) [68]. Homoacetogenic bacteria (*e.g. Clostridium sticklandii*), known to utilize H_2 and CO_2 for acetate formation were also identified. Methanogens responsible for CH_4 generation from H_2 and CO_2 (*e.g. Methanobacterium formicicum* and *M. beijingense*) were also identified in the microbial biofilm, as well as the acetoclastic methanogen, *Methanothrix soehngenii* [68].

On the other hand, added-value biochemicals production from syngas in BESs relies on the development of an anaerobic consortium of carboxydotrophic bacteria and CO-tolerant cathodophiles. Im and collaborators investigated the microbial community developed in the cathode of a mesophilic CO-fed BES, under cathode potential control (−1.1 V vs. Ag/AgCl) [22]. The results confirmed the development of a microbial consortium of carboxydotrophic bacteria, such as bacteria from the genus *Acetobacterium*, known as CO fermenting acetogen [69] and cathodophiles, such as bacteria from the genus *Desulfovibrio*, described to utilize electrons from a cathode to reduce H^+ to H_2. Other bacteria from the genus *Petrimonas*, known as fermentative bacteria, which can use carbohydrates and some organic acids [70] and *Alistipe*, which produce volatile fatty acids (VFAs), including succinate, acetate and propionate, were also identified [71]. Recently, Im and collaborators used zero valent iron as electron donor to isolate CO converting microorganisms [72]. The authors performed sequential batch assays using zero valent iron as electron donor under CO as headspace gas. After the 13th transfer of culture, sequencing results showed that the strains almost matched with *Clostridium* sp. (HN02) and *Fonticella* sp. (HN43). The electrochemical activity of the isolated strains was tested in a BESs under cathode potential control (−1.1 V vs. Ag/AgCl). Both strains produced acetate from CO using the electrode as electron donor, thus suggesting that both strains were electrochemically active. Nevertheless, the mechanisms involved into electrons capture from the electrode were not elucidated.

4. BESs-based systems for CO/syngas conversion

Syngas conversion in conventional fuel cells such as polymer electrolyte membrane fuel cells [73] or solid oxide fuel cells [74] has been investigated. However, the noble metal catalysts used in the fuel cells are easily poised by CO [75] and sulfur [74], compounds present in syngas. Thus, syngas should be purified before use in fuel cells [76]. CO harnessing in BESs is a sustainable alternative to syngas usage in conventional fuel cells. Contrary to the fuel cells, the biocatalysts (*e.g.* acetogens) used in BESs can use CO and are tolerant to sulfur compounds, thus not requiring syngas purification previous to its use in BESs [21].

4.1. Electricity production

MFCs allow the conversion of renewable sources (*e.g.* syngas from biomass gasification) into electricity. In MFCs, syngas is used as carbon source by a biocatalyst, thus producing protons and electrons, at the anode. Several examples of electricity production from syngas using MFCs are summarized in Table 1.

Kim and Chang were the first authors to report the production of electricity from CO in a two-stage reactor system composed by a fermenter and a MFC, in 2009 [21]. In a first stage, an enriched anaerobic community of *Acetobacterium* spp. was responsible for CO conversion to acetate. In a second stage of the process, the fermentation products were directly and continuously fed to an MFC. The combination of the two systems allowed the conversion of CO to electricity. One year later, Mehta and coworkers reported the conversion of CO into electricity in a (one-stage) single-chamber MFC [61]. The presence of soluble (*e.g.* acetate) and gaseous (*e.g.* H_2, CH_4) degradation products into the fermentation broth suggested that a consortium of carboxydotrophic and CO-tolerant anodophilic microorganisms was the responsible for the CO conversion into electricity. Although the indirect electricity production seems to be predominant, the authors also suggest the possibility of direct electron transfer to the electrode surface by Fe (III)-reducing carboxydotrophic bacteria [61].

Gas-liquid mass transfer limitations have been reported as a major concern in biological CO conversion [77]. Hussain and collaborators tested the use of a polymer silicone membrane and thin wall silicone tubing to improve CO transfer efficiency [78]. A significant enhancement of CO gas-liquid mass transfer was obtained, which increased the power output, leading to an increase in CO conversion efficiency.

Carbon paper containing platinum (Pt) or cobalt tetramethoxyphenyl-porphyrin (CoTMPP) as catalyst were used, at the cathode, in the previous works. However, only in 2011, Neburchilov and collaborators studied the potential inhibition of the cathode activity by CO [65]. CoTMPP, FeTMPP, and Co/FeTMPP gas diffusion cathodes were tested in comparison of a carbon cloth gas diffusion Pt cathode. The best performance in terms of power output was obtained using a Co/FeTMPP cathode with a Co:Fe ratio of 3:1, in comparison to CoTMPP and Pt cathode, demonstrating that MFCs with non-noble metal cathode catalysts can produce more power than that obtained with a Pt-containing cathode.

In 2012, Hussain and coworkers studied the effect of a moderately thermophilic temperature on CO conversion in MFCs [79]. In comparison to a similar MFC operated under mesophilic conditions, the thermophilic conditions led to a higher power density, higher syngas conversion efficiency as well as an improved Coulombic efficiency (CE). Similarly, to the previous results obtained, the presence of *Geobacter* species, *Acetobacter* species and methanogens suggested that syngas conversion to electricity takes place by a two-step process.

Hussain and collaborators further investigate, in 2014, the potential of use a multi-anode/cathode MFC to improve the efficiency of the process [80]. Different operating temperatures and anode/cathode electrodes configurations were tested. The adoption of a multi-electrode design consisting of 3 anodes and 2 cathodes, allowed to improve the power output as well as the CE in comparison to any mesophilic syngas-fed MFC. However, according to the authors, an improvement in the gas-liquid mass transfer in combination with methanogenic activity inhibition may further enhance the performance of the system.

4.2. Added-value biochemicals production

Although, the use of BES for sustainable electricity production has been widely investigated over the years, BESs research is currently moving to the conversion of electrical current into added-value biochemicals and fuels (*e.g.* acetate, CH_4 and H_2) [81]. BESs have been used to modify the extracellular ORP by imposing a potential to electrochemically assist the conversion of a renewable source (*e.g.* glucose,

Table 1
Reported examples of electricity production from syngas/carbon monoxide in bioelectrochemical systems.

Substrate	Flow rate (L L_{Anode}^{-1} d^{-1})	Biocatalyst	Setup	Anode	Cathode	Power output (mW L^{-1})	CO removal (%)	CE (%)	Reference
CO	2	Anaerobic	Air-cathode	Graphite	CoTMPP	1.35	21	9	[61]
CO + H_2	4.8	sludge	MFC	felt		6.4	53	9	
	7.5					5.75	47	6	
	10.2					0.02	3	1	
	11.6					5.13	61	5	
	4.8					4.52	53	9	
CO	2	Anaerobic	Air-cathode	Graphite	Pt-carbon paper	4	98	7	[78]
	3	sludge	MFC[b]	felt		14	92	16	
	4					12.2	88	9	
	4		Air-cathode			19.3	74	11	
	6		MFC[c]			11.2	68	7	
CO + H_2	3		Air-cathode MFC[b]			6.3	41	9	
	4		Air-cathode MFC[c]			8	57	7	
CO	477[a]	Anaerobic	Air-cathode	Graphite	Pt-carbon cloth	12	n.a.	n.a.	[65]
	477[a]	sludge	MFC	felt	CoTMPP	12.8	n.a.	n.a.	
	477[a]				CoTMPP:FeTMPP (3:1)	16.	n.a.	n.a.	
CO + H_2	4	Anaerobic	Air-cathode	Carbon felt	CO/FeTMPP	11	97	9	[79]
	6	sludge	MFC[b]			34	92	26	
	8					33	88	20	
	10					16	73	12	
CO + H_2	1.2	Anaerobic	Multi-anode	Carbon felt	MnO_2-gas diffusion	17 (37 °C)	91	26	[80]
	2	sludge	MFC			33 (37 °C)	90	43	
	3					12 (37 °C)	77	21	
	2					15 (45 °C)	69	23	
	2					10 (50 °C)	53	15	

n.a. Not available.
[a] ml of CO per day (mL d^{-1}).
[b] MFC equipped with a silicone tubing membrane for CO transfer to the anodic liquid.
[c] MFC equipped with a silicone membrane for CO transfer to the anodic liquid.

glycerol, syngas) into valuable compounds in a EF process [58,82]. The application of EF processes for added-value compounds production has been investigated to modify the extracellular ORP in mixed microbial communities as well as to deviate the microbial metabolism of pure cultures.

Moscoviz and coworkers investigated the effect of imposing a cathodic potential on glycerol EF using a mixed-culture bioaugmented with *G. sulfurreducens* [83]. The authors obtained an increase of 10% (91 mM–101 mM) on 1,3-propanediol production under EF conditions, when compared with conventional fermentation process. The production of other metabolic products such as succinate, ethanol and propionate was negatively affected. Interestingly, the authors demonstrated that the difference in the product yields was supported by bacterial population selection rather than a shift in individual metabolic behavior. The exact way of how the cells metabolism is influenced by EF is not well known. However, it is known that various metabolic processes that compete for reducing power from the $NADH/NAD^+$ pool, can adversely affect the 1,3-propanediol production yield in glycerol fermentation [84]. Zhou and coworkers demonstrated that the use of an electrode to provide additional reducing equivalents resulted in an improvement of 25% (1 mM–4 mM) on 1,3-propanediol production possibly due to the enhance of NADH generation routes [85]. The applied potential can impact the microbial population structure and also selects the microbial community composition on the electrode's surfaces influencing the intracellular redox regulations [83,84].

The applied potential in EF processes, could also shift the products spectrum in pure cultures. A recombinant *Klebsiella pneumoniae* was investigated for 3-hydroxypropionic acid (3-HP) production from glycerol in a BES. In comparison to conventional fermentation, glycerol EF resulted in an increment of 1.7-fold (12.9 mM–21.5 mM) on 3-HP production [86]. In another study, the EF of fructose was investigated using *Clostridium autoethanogenum* as biocatalyst. The results showed a decrease on acetate production as a consequence of *C. autoethanogenum* metabolism modification [87]. An enhancement of 35-fold (0.28 mM–9.87 mM) and 3-fold (0.73 mM–2.21 mM) on lactate and 2,3-butanediol production, respectively, was observed in comparison to conventional fermentation. Choi and coauthors, evidenced a metabolic shift in *C. pasteurianum* metabolism during glucose and glycerol EF [88]. Using glucose and at a cathode potential poised at +0.045 V vs. SHE, acetate and butyrate production decreased, whereas the production of butanol increased 10 mM (2.1 mM–12.2 mM) when compared with a conventional fermentation (without electricity). On the other hand, using glycerol and at a cathode potential poised at +0.045 V vs. SHE, butanol production decreased whereas 1,3-propanediol production increased almost 30 mM (60 mM–95 mM) [88]. The authors demonstrated that the use of an electrode to supply reducing equivalents induce a metabolic shift toward NADH-consuming pathways for more reduced compounds production over the stoichiometric contribution of the electrons. Recently, Arunasri and collaborators used *Escherichia coli,* as a model organism, and pyruvate, as substrate, to provide insights into metabolic shifts as a result of potential application [89]. The authors demonstrated that applied potential modified the expression of genes encoding key enzymes in the pyruvate metabolic pathway namely lactate dehydrogenase (ldhA), pyruvate formate lyase (pflB), pyruvate dehydrogenase (aceF), hydrogenase (hycE) and NADH: oxidoreductase (nuoB). H_2 production was improved by 7.9-fold and 5.3-fold at cathode potential controlled at −0.8 V and −0.2 V, respectively, whereas applied potential of +0.8 V enhanced the production of lactate by 1.9-fold when compared to the control. At −0.8 V, the key genes involved in the pathway for H_2 production were all significantly up-regulated [89]. The electroactivity of some carboxydotrophic microorganisms has been demonstrated. *C. ljungdahlii* was applied in a BES to harvest electrons from a cathode to reduce CO_2 to multicarbon chemical commodities [90].

EF of CO/syngas represents a new approach that has not yet been reviewed so far. In a EF system, an electron donor is oxidized at the (bio)

anode producing electrons and protons. At the cathode, cathodophiles are responsible for draw, directly or indirectly, electrons from the electrode to convert syngas into more reduced compounds.

Im and collaborators investigated the production of VFAs from syngas in BESs using a mixed microbial community [22]. Since CO conversion is typically limited by the reducing power, the authors tested and confirmed that the applied potential (−1.1 V vs. Ag/AgCl) provided the additional reducing equivalents, improving the yield of syngas conversion. Among other VFAs, acetate was the main product.

Based on the previous work, Baek and collaborators investigated the potential of a combination of electrodialysis with syngas-fed BESs to recover acetate [91]. Since acetate transport trough the membrane is affected by the applied potential and current in MFCs, various currents (−5 mA, −10 mA and −15 mA) were applied to the BESs. The results showed that the amount of acetate transported increased with the increase of current applied. Although, the authors demonstrated the in-situ production and separation of acetate using an electrodialysis-based bioelectrochemical system, there are still challenges, for example related to the ion-exchange membrane fouling, that need to be solved.

Recently, Chu and coauthors, studied different CO/CO_2 fractions as alternative to pure CO_2 to improve the microbial electrosynthesis of C2–C6 carboxylates [92]. The best performance was obtained in terms of C4 and C6 carboxylates production at a CO fraction of 50%. The electrons deviation for CH_4 production and biomass growth decrease with the increase of CO fraction. Microbial diversity analysis demonstrated that the relative abundance of *Acetobacterium* sp. and *Clostridium* sp. increased by increasing the CO fraction. In EF of CO, mixed cultures were less sensitive to the increase of CO concentration than the pure cultures.

Although acetate is the main product detected reported in the literature, several other added-value compounds could be produced from CO. Table 2 summarizes the reactions of some possible products obtained from CO as well as the correspondent standard cell potential ($\Delta E^{0'}$). According to literature, the products of CO/syngas EF and rates of production may vary depending on applied potentials, observed current densities, cathodic communities and CO fraction. Thus, redirecting the microbial metabolism by imposing different potentials to the cell, is a promising strategy to obtain a selected compound of interest.

5. Performance of BESs-based systems for CO/syngas conversion

The performance of CO/syngas fed-MFCs could be assessed by the CO removal efficiency (%) which represents the fraction of the initial CO that was used and the CE (%) which represents the fraction of electrons recovered as current. According to the literature, CO removal efficiency in MFCs varied between 3% and 98% whereas CE varied between 1% and 43% (Table 1). Improved gas transfer systems to increase the CO transfer to the anodic medium resulted in high CO removal efficiency (98%) at a CO flow rate of 2 L L_{Anode}^{-1} d^{-1} [78]. A lower CO removal efficiency was observed at higher CO flow rate (10 L L_{Anode}^{-1} d^{-1}) indicating a possible inhibition of the microbial community at high levels of fluxes of CO [61]. Although high CO removal efficiency was reported at a CO flow rate of 2 L L_{Anode}^{-1} d^{-1}, a CE of only 7% was obtained [78]. Low CE (43% in maximum) described for CO/syngas-fed MFCs is a result of the use of mixed microbial communities. This CE is comparable to CE reported for wastewater-fed MFCs, which are in the range of 15% with winery wastewater [94], 26% with swine wastewater [95], 22% with hospital wastewater [96] and 25% with municipal wastewater [97], among others.

As mentioned above, CO conversion in MFCs with a mixed microbial community results in some concurrent pathways (Equations (1)–(5)). A two-step process in which CO is first converted to acetate and then to electricity has been hypothesized as the main pathway for indirect electricity production. Beyond direct electricity production from CO, indirect electricity production from H_2 has also been suggested. Furthermore, the use of complex microbial communities involves the substrate consumption via other competing metabolic pathways, resulting in the presence of other metabolites in the off gas and effluent. Several soluble and gaseous metabolic products such as CH_4, H_2 and acetate were identified during the study of the metabolic products [61,78,80]. According to the literature, the percentage of CH_4 in the CO/syngas-fed MFCs off-gas varied between 3% and 22%, whereas the percentage of H_2 varied between 1% and 37% (Table S1). Acetate in the effluent varied between 6 mg L^{-1} to 220 mg L^{-1}.

CE (%) could also be used to assess the performance of CO/syngas fed-BESs for added-value compounds. CE represents the fraction of consumed electrons recovered into products. Low electron recovery efficiency was reported for a CO-fed BES showing that there is an imbalance between the electrons supply and their incorporation into desired compounds, possibly due to the deviation of electron for non-target chemicals production and/or proton reduction to H_2 [22]. Among other compounds such as propionate and butyrate, acetate was the main metabolic product obtained (~2 g L^{-1}). Im and coworkers demonstrated that higher CE could be obtained by using neutral red as electron mediator, achieving a maximum acetate concentration of 8.5 g L^{-1} [22]. As mentioned above, the electro-stimulation of the metabolism of pure cultures could be a sustainable alternative toward the optimization of fermentation process to improve microbial growth and produce valuable metabolites.

Besides electrons deviation for non-target chemicals production, electrons are also used for microbial growth and maintenance. Comparable microbial growth is observed on conventional fermentation and EF [83].

Table 2
Thermodynamics of chemical reactions involved in CO conversion into added-value products.

Products	Reaction	$\Delta G^{\circ\prime}$ (kJ mol^{-1})[a]	n[b]	$\Delta E^{\circ\prime}$ (V)[c]
Hydrogen	$CO + H_2O \leftrightarrow CO_2 + H_2$	−20	2	0.104
Methane	$CO + 3H_2 \leftrightarrow CH_4 + H_2O$	−151	6	0.261
Acetate	$4CO + 2H_2O \rightarrow CH_3COOH + 2CO_2$	−175	4	0.453
	$2CO + 2H_2 \rightarrow CH_3COOH$	−135	4	0.350
Ethanol	$6CO + 3H_2O \rightarrow CH_3CH_2OH + 4CO_2$	−224	8	0.290
	$3CO + 3H_2 \rightarrow CH_3CH_2OH + CO_2$	−164	8	0.212
	$2CO + 4H_2 \rightarrow CH_3CH_2OH + H_2O$	−144	8	0.187
Butanol	$12CO + 5H_2O \rightarrow CH_3CH_2CH_2CH_2OH + 8CO_2$	−494	16	0.320
2,3-butanediol	$11CO + 5H_2O \rightarrow CH_3CHOHCHOHCH_3 + 7CO_2$	−388	14	0.287
Butyrate	$10CO + 4H_2O \rightarrow CH_3CH_2CH_2COOH + 6CO_2$	−398	12	0.343
Acetone	$8CO + 3H_2O \rightarrow CH_3COCH_3 + 5CO_2$	−322	10	0.334

[a] $\Delta G^{\circ\prime}$ was obtained from [42,93].
[b] n - number of electrons transferred in the balanced equation.
[c] $\Delta E^{\circ\prime}$ was calculated according to the equation $\Delta G^{\circ\prime} = - n F \Delta E^{\circ\prime}$ (where F is Faraday's constant = 96,485 C mol^{-1}).

6. Current bottlenecks of CO/syngas conversion in BESs and future trends

Gas streams treatment and valorization with simultaneous electricity and/or added-value biochemicals production in BESs is as a feasible strategy to increase the productivity, and/or to expand the product scope of gas fermentation processes. Conversion of other gaseous carbon sources (*e.g.* CO_2) in BESs has been extensively presented [93,98–100], whereas a syngas-fed BESs represents a novel approach.

Electricity production in an MFC has been proposed for microbial conversion of syngas, contributing at the same time to the reduction of greenhouses gases emission, lowering the negative impact on the environment. Although MFCs are the most investigated type of BESs, the potential of BESs to produce added-value compounds has attracted the interest of the industrial world. The potential to produce building blocks, namely acetate, from CO/syngas through EF is already proved.

However, a few practical challenges need to be overcome to approach this technology to the commercial level. Technical hitches related to gas-liquid mass transfer limitations have been reported as the main issue associated to syngas fermentation. The selection of an adequate electrode with an adequate porosity should be considered since, high porosity results in a high specific surface area maximizing the microbial attachment thus favoring their contact with the gas. The use of gas diffusion electrodes has demonstrated encouraging results [101]. Moreover, the selection of a CO-poisoning resistant electrode is of utmost importance since common catalysts used (*e.g.* Pt) suffer from high toxicity by CO, in addition to their environmental impact and high cost. Preliminary results demonstrated that promising results could be obtained by using gas diffusion electrodes containing non-noble metal catalysts (*e.g.* Co or Fe) [65]. The low electron transfer rate between electrodes and biocatalysts is another challenge that should be further investigated. Genetic engineering, recently considered in BES research, can contribute to optimize the electron transfer rates, to either increase productivities or to produce a new product at interesting titres [102]. Consortia of carboxydotrophic and CO-tolerant EAB have been reported as fundamental for syngas conversion in BES. However, the presence of different microorganisms could lead to the diversion of electrons to other metabolic pathways, thus resulting in a low CE which is also an aspect that should be further investigated. The use of pure cultures could be an alternative to target formation of a specific target product. Selected microorganisms should be able to use the electrode as electron acceptor/donor for syngas conversion into electricity/added-value compounds, respectively. Data from literature demonstrated that some carboxydotrophs such as *Clostridium ljungdahlii* [90] and *Moorella thermoacetica* [98] are capable to draw electrons from an electrode.

As reported before by several authors it is not only highly important to improve product formation and increase productivities, but also reduce energy/operating costs, before scaling-up EF processes [100–103]. A techno-economical evaluation has to be developed to evaluate if the gains (value of the products generated) in process compensate the additional costs of the EF (energy application). In this context, there are several examples showing that EF allows to increase products formation rates and titres, making EF more attractive, even from an economic point of view, when compared to non-electrochemically assisted fermentation [85,107,108]. In an example, Harnisch and co-workers reviewed, in 2015, the technical parameters and hurdles that should be taken into account before scaling-up EF [109]. Based on bulk electricity prices, the authors anticipated that EF of sucrose for lysine production would be able to provide significant cost savings (8% in EU and 18% in US) in comparison with traditional process. The authors also stated that more economic systems should be developed, mainly for production of specialty chemicals that are not competitively produced by existing industrial fermentation processes [109].

Nevertheless, EF can use renewable current mainly from intermittent solar and wind sources. Furthermore, it was demonstrated that microbial community on BES revealed to be resilient to current fluctuations and capable to restore the electrochemical activity regardless the duration of power interruptions [110,111]. Thus, EF could be a relevant process using intermittent and fluctuating renewable energy for syngas EF, allowing its conversion into storable chemicals and/or gaseous fuels.

From the economic perspective, the cost of the process should be compensated by the value of the products generated. However, it is imperative to improve cost-effective electrodes and cells configurations to increase the general process performance. Scale-up is also an important issue to consider in order to bring the technology to higher levels of readiness. Although further studies are needed before these systems can be applied to industrial environment, the proof-of-principle of syngas conversion in BESs is proved to be technologically feasible. Further, the results obtained for added-value compounds production are quite encouraging, thus, motivating further novel research opportunities. The understanding as the applied potentials could influence the metabolic pathways towards the formation of a specific product from syngas is an inspiring scientific challenge. In conclusion, electrochemical bioconversion of syngas is seen as a very promising 4th generation biofuel process substituting fossil fuels, thus contributing to the reduction of greenhouse gas emissions. Research on electrochemical bioconversion of syngas will contribute to design new eco-innovative and green processes for gas streams valorization.

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 data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.rser.2020.110358.

Table S1
Reported examples of electricity production from syngas/carbon monoxide in bioelectrochemical systems.

Substrate	Flow rate (L L_{Anode}^{-1} d^{-1})	Acetate mg L^{-1}	CH_4%	H_2%	Reference
CO	2	172	5.2	7.6	[61]
CO + H_2	4.8	18	4.5	0.1	

(*continued on next page*)

Table S1 (*continued*)

Substrate	Flow rate (L L_{Anode}^{-1} d^{-1})	Acetate mg L^{-1}	CH_4%	H_2%	Reference
	7.5	66	5.5	0.6	
	10.2	70	0.1	0.0	
	11.6	220	4.2	1.4	
	4.8	49	22.1	22.1	
CO	2	6	15	5.3	[78]
	3	58	9.3	2.1	
	4	74	9.4	4.7	
	4	18	11.1	3.1	
	6	46	15.3	4.8	
CO + H_2	3	51	3.3	26.0	
	4	35	11.5	22	
CO + H_2	1.2	26	13	14	[80]
	2	61	15	14	
	3	44	10	9	
	2	31	13	20	
	2	19	7	37	

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