



Editorial: Microbial Synthesis, Gas-Fermentation and Bioelectroconversion of CO₂ and Other Gaseous Streams

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Editorial on the Research Topic

Microbial Synthesis, Gas-Fermentation and Bioelectroconversion of CO₂ and Other Gaseous Streams

INTRODUCTION

The ongoing climate crisis, mainly caused by the emission of greenhouse gases (GHGs), gives rise to an urgent need for solutions to re-convert industrial waste gases and emissions into useful chemicals (LaI, 2005). Concentrated streams of carbon dioxide (CO₂) are continuously generated and emitted by a variety of anthropogenic activities. These include both biogenic sources (e.g., organic waste and wastewater treatment plants, biogas plants, landfills, waste and biomass combustion facilities, etc.) and fossil-carbon sources (e.g., centralized fossil-based energy production facilities, engines, etc.) In recent years, several efforts have been undertaken globally that are directed toward CO₂ capture and converting CO₂ into storable fuels and chemicals (ElMekawy et al., 2016). This conversion can be done via living bacteria as biocatalysts (Rojas et al., 2018a), via enzymes (Chiranjeevi et al., 2019), or electrocatalytically (Gutiérrez Sánchez et al., 2019).

In light of the different possibilities for efficiently utilizing such concentrated CO₂ streams, their dispersion in the atmosphere is a waste of an otherwise potentially valuable resource. In fact, only photosynthetic organisms can utilize CO₂ at atmospheric concentrations (around 400 ppm) (González Del Campo et al., 2013). Plants and photosynthetic microorganisms are known to significantly increase their growth rates under higher CO₂ concentrations (Brown et al., 2019). CO₂ fertilization in microalgae production facilities is widely recognized as a strategy for improving biomass yields and synthesizing a variety of bioproducts and food ingredients (Eustance et al., 2016).

Alternative pathways enabling the utilization of concentrated CO₂ streams to synthesize organic molecules have recently been developed using microorganisms (bacteria and archaea) as catalysts. In gas fermentation, reducing power is provided either within the gaseous stream or in the water solution. In microbial electrochemical technologies (METs), a biocatalyst (i.e., electroactive bacteria) exchanges electrons with an external circuit through a solid electrode.

GAS FERMENTATION

Gas fermentation is a process in which microorganisms can fix CO₂ if sources of reducing power and metabolic energy are available (Liew et al., 2016). Hydrogen (H₂) generated by electrochemical water-splitting is an example of an energy-rich electron carrier that can be utilized in co-fermentation with CO₂. Bio-syngas streams coming from biomass gasification or pyrolysis are mainly rich in H₂, carbon monoxide (CO), methane (CH₄), and CO₂. Their efficient utilization by gas fermentation has already been demonstrated at pilot scale for the production of high-value biocommodities (e.g., succinate, 2,3-butanediol, lactate, and acetone; Marcellin et al., 2016).

BIOELECTROCHEMICAL CO₂ REDUCTION

More recently, METs were proposed as a new strategy for furnishing electrons and metabolic energy for carbon fixation. In microbial electrosynthesis (MES) processes such as electromethanogenesis and electrofermentation, renewable electricity stimulates the metabolism of selected electro-active microbial communities to produce organic molecules [methane, short-chain fatty acids, alcohols, etc. (Kracke and Krömer, 2014; Sharma et al., 2014; Schievano et al., 2016)]. These molecules can undergo further carbon chain-elongation by heterotrophic communities to synthesize higher value biocommodities and biopolymers (Aglar et al., 2012; Dennis et al., 2013).

The reduction of CO₂ to organics can occur through direct electron transfer (DET) or through the intermediate production of H₂, which acts as an electron transfer shuttle (as is the case with many acetogenic bacteria (Puig et al., 2017); Wenzel et al.). Until now, the main products of MES have been methane (electromethanogenesis) and acetate (homoacetogenesis), although the yield and product titers are still far from commercial application. During the last 10 years of research, several strategies have aimed at improving MES reactors and their production rates/yields. In the past 2 years, MES has been more intensively studied. Jourdin et al. proved that MES is progressing to becoming a robust clean CO₂ biorecycling process, producing higher-value chemicals at increasing rates while minimizing the cost of electrode materials. Verbeeck et al. presented a reactor setup that allowed the operation of MES reactors at higher current densities. An H₂/CO₂ gas-fermentation column was directly coupled to extraction, allowing pure product recovery in an acidic and clean liquid, achieving simultaneous stabilization of the pH in the fermentation broth.

Another key parameter affecting MES performance is the cathode material itself. Some key-properties are essential for superior cathodic performance: high conductivity, excellent chemical stability, high mechanical strength, good biocompatibility, high surface area, and low cost (Aryal et al., 2017). Aryal et al. reported the fabrication of a cathode coated with highly conductive polystyrene sulfonate polymer for acetate production in MES. This coating allowed increased acetate production while optimizing current consumption. The biofilm of *S. ovata* showed increased biomass presence

as compared with the plain carbon cloth surface. Another strategy is the use of granular activated carbon (GAC) and graphite granules (GG) in a packed bed as the cathode electrode. Liu et al. showed that both GAC and GG are suitable cathode materials for high methane production rates in methane-producing MESs.

Gas diffusion electrodes (GDEs) have also represented a breakthrough in the current state of the art of MES. Srikanth et al. (2018) evaluated the impact of GDEs in enhancing CO₂ bioavailability for its transformation to C₄-organics, especially to alcohols using selective mixed culture. A more stable current density was observed with GDE vs. submerged experiments, which significantly varied with pH and respective CO₂ solubility. An interesting synergy between METs and syngas fermentation is that the bio-char resulting from biomass pyrolysis can have interesting properties for the fabrication of bio-electrodes, such as electrical conductivity and a high surface area for microbial biofilm growth (Marzorati et al., 2018; Prado et al., 2019).

The chemical energy stored in the products of MES can be seen as a potential store of renewable energy surpluses (Schievano et al., 2018). However, solar and wind energy are typically characterized by a fluctuating regime, and this may represent a threat to microbial communities in MES biocathodes that rely on continuous polarization. Mateos et al. (2020) recently showed how MES could be resilient to long-term power interruptions (6 weeks). In the same line, Rojas et al. (2018b) demonstrated that the electro-autotrophic activity of an MES system could recover after power shortages, restoring acetic acid production while recovering sufficient electron transfer at current densities of -25 A m^{-2} .

CURRENT STATE OF ART (TOWARD UPSCALING AND INDUSTRIALIZATION)

In recent years, several developments have taken place to upscale the microbial gaseous conversion technologies, and both governments and industry have taken a lead in supporting such initiatives. One of the leaders in this field is the USA-based company LanzaTech, which has made rapid strides in syngas fermentation, with several demonstration plants operating globally (LanzaTech, 2019). Their core technology is based on the acetogen *Clostridium autoethanogenum*, with an estimated volumetric productivity of around $10 \text{ g l}^{-1} \text{ h}^{-1}$ (Takors et al., 2018). Within Europe, LanzaTech is involved in the Steelanol project funded by the European Commission, which aims at building a demonstrator for ethanol production at the Arcelor Mittal steel mill in Ghent to convert the gases produced during the steel production process by using fermentation by microbes that secrete ethanol (Steelanol, 2019). The plant is expected to have a capacity of 62,000 t/a (Carus et al., 2019). Their other operations are in China, India, and South Africa.

Upgrading of biogas by converting the CO₂ fraction of the biogas into gas-grid quality methane is also gaining significant momentum, and several pilot and industrial initiatives are currently being undertaken (Aryal et al., 2018). One of the main

players in this field is the Germany-based company Electrochaea, which recently announced the commissioning of a power-to-gas demonstration facility in Foulum, Denmark, based on a 10,000-liter bioreactor (Electrochaea, 2018).

Besides these industrial applications, research on this topic is also gaining momentum, and within Europe, several projects at different technology readiness levels (TRL) are being supported by the European Commission. One of these projects is BioRECO2VER, which aims at refining biotechnological processes that can turn CO₂ from industrial point sources into valuable platform chemicals such as lactate and isobutene (<http://bioreco2ver.eu/>). Another recently started project, Bac-To-Fuel, is developing a process to transform CO₂/H₂ into fuels by mimicking the photosynthetic process of plants. This approach uses novel inorganic photocatalysts that are capable of evolving H₂ from photocatalytic water splitting in the presence of sunlight and enhanced bacterial strains to convert CO₂ and the renewable hydrogen into biofuels (i.e., ethanol and butanol) in a novel electro-biocatalytic cell (<http://bactofuel.eu/>). The CelbiCon project, also funded by the European Commission under the H2020 program, attempts to combine CO₂ capture and electrochemical and biochemical conversion technologies for CO₂ conversion into chemicals (<http://www.celbicon.org/>). Yet another recent project on this topic is BIOCON-CO₂, which is developing biological processes to transform raw waste CO₂ from the iron, steel, cement, and electric power industries into value-added chemicals and plastics (<https://biocon-co2.eu/>). The above-mentioned projects are only representative examples of the research projects that are currently going on in the EU. There are several other initiatives being undertaken globally to harvest the potential of microorganisms in converting gaseous feedstocks into valuable chemicals.

CONCLUSIONS

To summarize, microbial conversion of waste gases, industrial off-gases, and CO₂-rich streams is gaining momentum, with interest coming from the industrial users, governments giving support, and researchers working toward upscaling these systems. A multidisciplinary approach is needed to develop new metabolic pathways and to optimize existing processes. Synthetic biology and microbial community selection should play a major role in constructing strains or communities for commercial operations. Metatranscriptomics,

metabolomics, and proteomics, as well as metabolic engineering, are fundamental tools to understand and enhance microbial catalysis. Moreover, bioreactor engineering and material science are crucial for studying scalable process architectures and for optimizing microbial biofilm growth, gas solubilization, and product recovery.

This broad range of disciplines is also represented in the papers appearing on this Research Topic, which contribute toward advancing the basic research while moving to the next level of practical implementation. Theoretical and perspective insights into several possible metabolic pathways (Averesch and Kracke) and thermodynamic considerations (Scheller) have been presented regarding methane oxidation (and that of other alkanes) and toward the production of liquid biofuels or electricity. Also, fundamental experiments are being carried out, dealing with biofilm formation, microbial community structure on bioelectrodes (Jourdin et al.), and electrode materials optimization (Aryal et al., 2018; Liu et al.).

Innovative approaches are also being taken to biological CO₂ conversion, including an interesting experiment on the use of purple phototrophic bacteria for simultaneous bio-H₂ generation and carbon fixation (Vasiliadou et al.) and a mini-review on possible biocathodic CO₂-fixation pathways and applications by sulfate-reducing electroautotrophs (Agostino and Rosenbaum). Finally, practical approaches toward different configurations of reactors and process design have been reported (Ishii et al.; Lim et al.; Verbeeck et al.).

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All authors listed have made a substantial, direct and intellectual contribution to the work, and approved it for publication.

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