Bioresource Technology xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

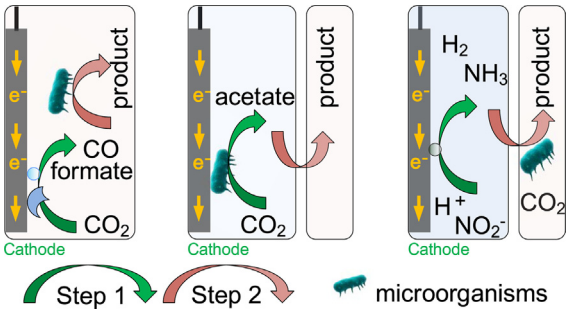
Review

Expanding the product spectrum of value added chemicals in microbial electrosynthesis through integrated process design—A review

Yong Jiang, Raymond Jianxiong Zeng*

Center of Wastewater Resource Recovery, College of Resources and Environment, Fujian Agriculture and Forestry University, Fuzhou, Fujian 350002, China

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Microbial electrosynthesis (MES)
Carbon dioxide
Value-added chemicals
Extracellular electron transfer
Electroactive microorganisms
Integrated process

ABSTRACT

Microbial electrosynthesis (MES) is a novel microbial electrochemical technology proposed for chemicals production with the storage of sustainable energy. However, the practical application of MES is currently restricted by the limited low market value of products in one-step conversion process, mostly acetate. A theme that is pervasive throughout this review is the challenges associated with the expanded product spectrum. Several recent research efforts to improve acetate production, using novel reactor configuration, renewable power supply, and various 3-D cathode are summarized. The importance of genetic modification, two-step hybrid process, as well as input substrates other than CO_2 are highlighted in this review as the future research paths for higher value chemicals production. At last, how to integrate MES with existing biochemicals processes is proposed. Definitely, more studies are encouraged to evaluate the overall performances and economic efficiency of these integrated process designs to make MES more competitive.

1. Introduction

Today's fossil-based economy has led to a rapid economic expansion, and, however is also restricted by the natural resources and environment, which cannot support the continuous growth on its current trajectory. The challenges of detrimental climate change, the rapidly depleting of fossil fuels, and the unprocessed waste disposal, all motivate the social interest to move from fossil-based economy to a more sustainable alternative (ElMekawy et al., 2016). The microbial electrochemical technology (MET) is regarded as one of these sustainable platform technologies, which employ microorganism as the catalyst to implement various functions, by utilizing the unique extracellular electron transfer (EET) process with the electrode served as the solid electron accepter or donor (Logan, 2009). Besides the electric energy recovery from wastewater using microbial fuel cell, many other derivative METs have been intensively studied and developed for a variety

* Corresponding author.
E-mail address: rzeng@ustc.edu.cn (R. Jianxiong Zeng).

https://doi.org/10.1016/j.biortech.2018.08.101
Received 21 August 2018; Received in revised form 23 August 2018; Accepted 24 August 2018

of purposes, including the microbial electrolysis cell for H_2 production (Jiang et al., 2016; Liu et al., 2005; Luo et al., 2017), microbial remediation cells for remediate contaminants (Gregory and Lovley, 2005), Microbial electrochemical biosensor for water monitoring (Jiang et al., 2015; Jiang et al., 2018b; Liao et al., 2018), microbial desalination cell for seawater desalination (Cao et al., 2009), and microbial nutrient recovery cell for nutrient ions recovery (Ge et al., 2018). The term "microbial electrosynthesis (MES)" was firstly introduced in 2010 in a study of using *Sporomusa ovata* based biochathode to reduce CO_2 into acetate (Nevin et al., 2010). Recently, the term of MES has been widened to the research field using the cathode as the sole electron donor for chemicals production from the reduction of carbon dioxide or from the process of waste biorefinery (Roy et al., 2016). The chemicals production oriented MES provides the following outstanding advantages: the MES has shown the promising to capture the renewable energy from various sources, e.g., solar, wind and wastewater, and store the energy into covalent chemical bonds (Nevin et al., 2010); the overall solar-to-chemicals efficiency of MES is expected to be much higher than that of the traditional plant-fermentation route (Claassens et al., 2016).

There have been excellent reviews on the productivity achieved and the bacterial versatility in MES (Bajracharya et al., 2017a; Geppert et al., 2016; Jadhav et al., 2017; Lovley and Nevin, 2013; May et al., 2016; Rabaey and Rozendal, 2010; Sadhukhan et al., 2016; Tremblay et al., 2017), the logical data representation and frameworks (Patil et al., 2015b; Schlager et al., 2017; Zou and He, 2018), and the economic feasibility of MES (Christodoulou et al., 2017; Christodoulou and Velasquez-Orta, 2016). However, after almost 10 years' study, the practical application of MES is still largely restricted. In this review, it highlights that the limitation of current MES technology is that the products from carbon dioxide are limited to chemicals with low market value. Thus, a basic question begs for answer currently is that how to decrease the cost of chemicals production in MES, and also employ MES for higher value chemicals production. This review summarizes the strategies to make the MES become competitive with increased acetate production, by using novel reactor configuration, renewable driving power supply, and various biocompatible 3-D cathode. The promising and challenge of using MES for higher value chemicals production, by genetic modification and hybrid two-step conversion process, are well discussed. This review also outlines future research paths to integrate MESs with existing biochemical processes to improve the overall sustainability and economic efficiency.

2. Current MES limited by low value chemicals production

MES is a rapidly growing bioelectrochemical technology, wherein the electrochemical process takes place mainly at the biocathode using the microorganism catalyst to generate chemicals (Su et al., 2013). Here, the principle of MES, the inward extracellular electron transfer (EET), and the limited chemicals achieved are reviewed.

2.1. The principle of MES

The core mechanism of classical MES is that microbes utilize a solid cathode as the sole electron donor to reduce CO_2 or oxidized compounds (e.g., volatile fatty acids, VFA) into reduced organic products (Fig. 1). In an MES reactor, the cathode is the reducing power even though electron transfer mechanisms from the electrode to the microbes can be different. The anode could be used for catalyzing abiotic oxygen evolution or biotic oxidization of the pollutants. An external driving power supply is required to overcome the thermodynamic barrier as the chemicals production in MES is a thermodynamically non-spontaneous process.

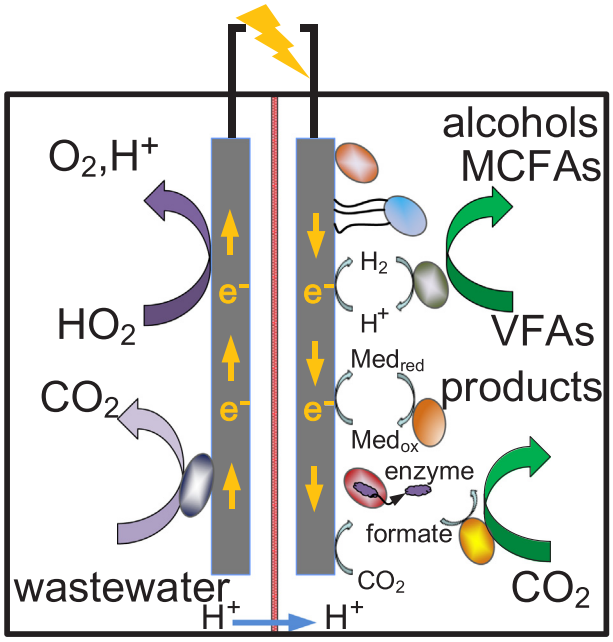


Fig. 1. Value-added chemicals production and associated extracellular electron transfer (EET) processes in microbial electrosynthesis (MES). VFAs: volatile fatty acids; MCFAs: medium-chain fatty acids.

2.2. The inward EET

Currently, little is known about the inward extracellular electron transfer (EET) from cathode to microorganisms when compared with the outward EET, and many processes remain unclear and controversial (Nealson and Rowe, 2016). Recently, whether direct electron transfer (DET) is conducted during inward EET or it is actually mediated by H_2 becomes a big and thorny issue (Deutzmann et al., 2015; Kumar et al., 2017). To understand this, one needs to consider the following essentials. First, the H_2 evolution potential depends on the pH, temperature, and H_2 partial pressure (May et al., 2016), and most of the MES reactors were not consistently operated at the standard conditions (pH 7, 25 °C and 1 bar, corresponding to −0.42 V for H_2 evolution). Second, the actual working potential might gravely deviate from the setting value by a potentiostat due to the uncompensated resistance and junction potential (Madjarov et al., 2017). The junction potential cause inaccuracy when converting the measured potentials value to SHE, and it is almost inevitable in MES studies, because the solution inside a reference electrode (Ag/AgCl electrode or saturated calomel electrode) and the cathodic medium generally have different ionic strengths and/or different ratio of the mobility of ions (Madjarov et al., 2017). Third, extra special attention should be paid to the H_2 detection in case of its leakage, and thus new type of gas analysis sensor is needed (Jourdin et al., 2016b). Last, the biofilm could induce the surface modification of the cathode martial, and thus lower the overpotential of H_2 evolution (Jourdin et al., 2016b). Thus the amount of H_2 at the abiotic cathode cannot be used for data interpretation, to calculate the contribution of H_2 mediated route to the inward EET of the biocathode (Deutzmann et al., 2015). Actually, there is almost no linear relevance between the methane/acetic acid production rates and the apparent hydrogen production rates in MES, regardless the importance of H_2 route, because of the rapid conversion of hydrogen by microorganisms (Fig. 2). A recent study using different *Sporomusa* species indicated that no relation could be established between their acetic acid production capacities under a H_2: CO_2 atmosphere without the presence of electrode and their MES performance at a cathode potential of −0.69 V vs. SHE, which was negative enough to trigger in situ hydrogen evolution (Aryal et al., 2017).