In-situ extraction of microbial electrosynthesis products

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In recent years, microbial electrosynthesis (MES) has emerged as an intriguing new process to produce valuable biochemicals from renewable and sustainable carbon sources such as carbon dioxide. This process uses electrical power to drive electro-active microorganisms to catalyse the synthesis of organic compounds. MES has the potential to drive a biorefinery process without agricultural biomass, and therefore without the vast water, energy and arable land requirements that biorefineries are beholden to (Rabaey et al., 2011; Rabaey & Rozendal, 2010). Several different homoacetogenic strains have been proven to form biofilms on cathodes and produce organics (*e.g.* acetate, butyrate, and succinate) using carbon dioxide as carbon source and electricity as reducing power (Nevin et al., 2011). However, this process is still in its infancy and many challenges remain including achieving higher product concentration and production rates, separation of the produced chemicals from the electrolyte and decreasing of the start-up time of the MES cells (Desloover et al., 2012). In this study, we aimed to achieve a faster and higher acetate production rate using a defined mixture of homoacetogens and in-situ extraction of acetate by combining production and efficient separation in a single system. Combining production and separation would result in a process where the microorganisms are not hampered by product inhibition and deliver a more concentrated product for downstream processing.

Two fed-batch electrochemical cell reactors were constructed. The defined mixture of homoacetogens comprised of *Acetobacterium woodii*, *Clostridium acetobutylicum*, *Clostridium butyricum*, *Clostridium autoethanogenum*, *Clostridium carboxidivorans,* and *Clostridium ljungdahlii*. The anodic chamber (16 mL) and cathodic chamber (16 mL) were separated by a cation exchange membrane. Carbon felts were used as the working electrode (cathode) and glassy carbon plates were used as counter electrode (anode). The anolyte (pH 2 H_2SO_4,) was continuously pumped into the anode at 30 mL/h. 100 mL of catholyte was recirculated in the cathode with an external recirculation bottle at the same flow rate. The reactors were operated under anaerobic conditions and HCO_3^- was added as carbon source in the catholyte. By applying a fixed current of 1.5 A/m², water was electrolysed to oxygen at the anode and hydrogen gas and acetate were produced at the cathode.

During the 20 days batch test, the mixed microbial culture produced up to 3.3 g/L acetate (Figure 1.1) with a start-up time of 5 days and a production rate of 0.6 g/Ld^{-1} before bicarbonate depletion. At the end of the batch experiment, no further increase in acetate concentration was measured, but other volatile fatty acids (VFA; propionate and butyrate) were formed by the homoacetogens at up to 35 mg/L. It is known that the strains used for this experiment can produce VFAs other than acetate (KEGG). Although direct electron transfer cannot be excluded, VFA production is

likely due to hydrogen evolution at the cathode resulting in a readily available source of reducing power for the microorganisms. This contrasts to most of the works on microbial electrosynthesis which focus on biofilm formation and direct electron transfer between the electrode and the microorganisms (Marshall et al., 2012; Nevin et al., 2011). To obtain cathodic biofilms, a long period of continuous supply of hydrogen gas and carbon dioxide is necessary (Nevin et al., 2010). The work presented here indicates that high production rates and short start-up times, two important characteristics for up-scaling, can easily be achieved by applying a chronopotentiometry method. A further increase of the production rate can be expected if a continuous supply of CO_2 was ensured (Marshall et al., 2013).

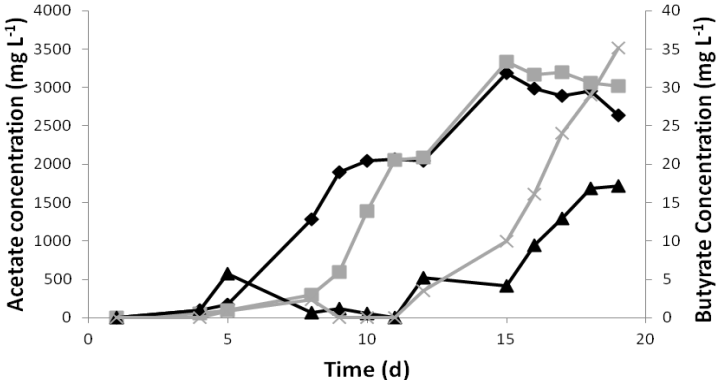

Figure 1.1 Acetate (Reactor 1♦; Reactor 2 ■) and butyrate (Reactor 1 ▲; Reactor 2 ✕) concentration in the two fed-batch reactors.

A three-compartment electrochemical reactor was used for the in-situ extraction of acetate. The anode and middle compartment had a volume of 200 mL, while the cathode compartment had a volume of 20 mL, with a recirculation buffer vessel. The middle compartment contained a low pH solute with a higher salt concentration than the catholyte and no electrode. This chamber was used to concentrate the acetate generated by the microbes in the cathode. The cathode and anode compartment of this reactor were similarly constructed as the fed-batch reactors. A current of 10 A/m² was applied to drive the acetate production and extraction.

Acetate was extracted through an anion exchange membrane as driven by the charge balance from the applied current, which is also used for the reducing power for bioproduction based on CO_2. In the middle compartment, the extracted acetate was protonated to acetic acid at pH 2, a consequence of the diffusion of protons from the anode to the middle compartment. The resulting acetic acid, an electrically neutral molecule, did not migrate back to the cathode, thus resulting in a net flux of acetate out of the catholyte. As such, acetic acid concentration in the middle compartment was four times greater than the concentration of acetate in the catholyte. As the characteristics of the membrane highly influence the extraction a better performance of the reactor system can be expected if the type of AEM was rigorously selected. This is an important step in the further development of production processes, as it can promote the continuous production of acetate at the cathode, and facilitate the further processing of the biochemicals.

Perspectives

Microbial electrosynthesis can generate biochemicals directly from CO_2, avoiding the resource intensive cultivation of energy crops. In this work we obtained a fast-working production of acetate from CO_2 in an electrolysis cell. By focussing on

process design, high-efficiency extraction of the organics was achieved. Strategies to further increase the productivity were proposed. This creates possibilities for further research on the combination of production and extraction in one efficient system.

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KEGG. Kyoto Encyclopedia of Genes and Genomes.

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