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Removal and recovery of inhibitory volatile fatty acids from mixed acid fermentations by conventional electrodialysis

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HIGHLIGHTS

- Conventional electrodialysis used to remove VFAs from H_2 fermentation broths for the first time.
- VFA removal from fermentation broths was equal or greater than from model solutions.
- Up to 99% of VFA removal from fermentation broths was achieved within 60 min.
- Removed VFAs are recoverable for use in bioenergy systems and as raw materials.

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ABSTRACT

Hydrogen production during dark fermentation is inhibited by the co-production of volatile fatty acids (VFAs) such as acetic and n-butyric acid. In this study, the effectiveness of conventional electrodialysis (CED) in reducing VFA concentrations in model solutions and hydrogen fermentation broths is evaluated. This is the first time CED has been reported to remove VFAs from hydrogen fermentation broths. During 60 min of operation CED removed up to 99% of VFAs from model solutions, sucrose-fed and grass-fed hydrogen fermentation broths, containing up to 1200 mg l^{-1} each of acetic acid, propionic acid, i-butyric acid, n-butyric acid, i-valeric acid, and n-valeric acid. CED's ability to remove VFAs from hydrogen fermentation broths suggests that this technology is capable of improving hydrogen yields from dark fermentation.

1. Introduction

Alternative energy sources to fossil fuels must be made readily available if the problems associated with diminishing reserves, environmental damage, security of supply, and increasing demand are to be overcome (Patterson et al., 2008; Yüksel, 2010). Converting a biomass energy source to a hydrogen energy vector is attractive due to its high calorific value of 122 kJ g^{-1} (Azbar and Cetinkaya Dokgoz, 2010), and because it represents a renewable and carbon neutral fuel (Meherkotay and Das, 2008). Fossil fuels are currently more economically attractive than alternative energy vectors however and questions regarding the long term availability of biomass in sufficient volumes to establish a hydrogen economy need to be addressed before its large-scale production is feasible (Hay et al., 2013).

Dark fermentation, which uses a range of substrates from industrial waste to energy crops, is a widely researched, renewable, pathway to hydrogen. Theoretically, it is possible to produce 4 mol H_2 mol^{-1} hexose sugar when acetic acid is the only product (Guwy et al., 2011), but experimental values tend to be in the range of 2.5–3.5 mol H_2 mol^{-1} hexose sugar due to thermodynamic limitations (De Gioannis et al., 2014; Rosales-Colunga et al., 2010). Hydrogen yields are also limited by the co-production of volatile fatty acids (VFAs), in particular acetic acid and n-butyric acid, which form during fermentation. VFA formation eventually prevents hydrogen production due to end product inhibition (Hawkes et al., 2007; Hirata et al., 2005) and cell lysis of the hydrogen producing bacteria (Choudhari et al., 2014; Tang et al., 2014)

Studies have demonstrated that reducing the concentrations of acetic acid and n-butyric acid in hydrogen fermentation broths, via bipolar membrane electrodialysis, increases hydrogen yields (Redwood et al., 2012a, 2012b; Tang et al., 2014). Bipolar membrane electrodialysis is one of several electrodeionisation and

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electrodialysis processes, the majority of which were described by Huang et al. (2007). Bipolar membrane electrodialysis requires expensive, bipolar, water-splitting, membranes in order to work and reported increases in hydrogen yield using glucose as a substrate are inconsistent. For example, Tang et al. (2014) report an increase from 1.7 to 2.2 mol H_2 mol^{-1} glucose, whereas Redwood et al. (2012b) claim that the removal of organic acids via bipolar membrane electrodialysis prolongs fermentation time from 3 days to 3 weeks, tripling H_2 production in doing so from 1 to 3 mol H_2 mol^{-1} glucose. More recent work used activated carbon as a means to extract inhibitory byproducts from hydrogen reactors fed by water hyacinth, and increased hydrogen yields from 124.9 ml H_2 g^{-1} total volatile solids to 134.9 ml H_2 g^{-1} total volatile solids (Cheng et al., 2015). As will be discussed below, VFAs are valuable in a number of applications and their recovery following activated carbon treatment would be difficult.

The work reported here compares the ability of conventional electrodialysis (CED) to reduce VFA concentrations in model solutions, and post-fermentation broths that were obtained following dark fermentation of sucrose and grass pellets. CED is a versatile technology that can concentrate, dilute, and separate matter whilst producing relatively low amounts of waste (Bailly et al., 2001; Huang et al., 2007; Lameloise and Lewandowski, 2012). CED utilises less costly materials than bipolar membrane electrodialysis, as was used by Redwood et al. (2012b) and Tang et al. (2014), and so in some applications it could possess an economical advantage over bipolar membrane electrodialysis. VFAs extracted via CED would not be contaminated as they might be using Cheng et al. (2015) activated carbon method, so they can easily be used as substrates in downstream bioenergy systems such as photofermentation, microbial electrolysis, and microbial fuel cells, theoretically producing up to 12 mol H_2 mol^{-1} hexose sugar (Claassen et al., 2010; Guwy et al., 2011; Redwood et al., 2012a, 2012b; Singhania et al., 2013, 2012).

Acetic acid, one of the VFAs that can be extracted, also has uses beyond conversion to an energy carrier. It has been called "*one of the world's most important chemicals*" (Ijmker et al., 2014) due to widespread use in manufacturing polymers, polyethylene terephthalate, and solvents. According to market forecasts, its global demand in 2013 was 10.4 mt, and by 2020 its market revenue is expected to reach $12.2 billion. There is also demand for butyric acid, which is used in the cosmetic, food, and pharmaceutical industries and along with other VFAs, it can also be used as a precursor to fuels and chemicals (Agler et al., 2011; Blahušiak et al., 2013; Choudhari et al., 2014).

The aim of this work is to establish how well conventional electrodialysis can reduce the VFA concentrations of post-fermentation broths compared to model solutions. It is important to make this comparison because post-fermentation broths are high in microbial and particulate matter, both of which are known to contribute to fouling and thus a gradual reduction of the ion flux within a CED stack (Hongo et al., 1986; Lee et al., 2003; Singhania et al., 2012; Strathmann, 2010). Fouling is reported to increase electrical resistance within CED stacks, thereby reducing current efficiency, which is widely used to quantify the performance of electrodialysis processes (Ferrer et al., 2006; Huang et al., 2007; Lameloise and Lewandowski, 2012; Wang et al., 2011, 2010). If CED is found to be capable of removing VFAs from post-fermentation broths in similar quantities to model solutions, there would be scope for further studies into the ability of CED to remove VFAs from working reactors. The possibility exists that CED may also be capable of removing VFAs from dilute aqueous solutions, which has hitherto proved problematic for the production of chemicals and fuels from the otherwise promising carboxylate platform (Agler et al., 2011), although this application falls outside of the scope of this study. This is the first time the ability of conventional electrodialysis to remove VFAs from post-fermentation broths has been reported and quantified. It is also the first study in which a comparison has been drawn between the ability of conventional electrodialysis to treat model solutions and post-fermentation broths.

2. Methods

2.1. Experimental design

Conventional electrodialysis was carried out on controls; model solutions that contained VFAs and deionised water to establish baseline VFA removal data in the absence of microbial and particulate matter. CED was then performed on hydrogen fermentation broths collected following sucrose and grass fermentations within continuously stirred batch reactors, which contained microbial and particulate matter, and the VFA removal data were compared to the baseline established by CED of model solutions. CED was carried out on two batches each of the model solution, sucrose fed reactor broth, and grass fed reactor broth.

2.2. Apparatus

The apparatus for conventional electrodialysis (Fig. 1) is typically referred to as a CED "stack" and consists of two electrodes (one anode and one cathode) across which an electrical potential is established by an external power supply, and which are housed within an anode chamber and a cathode chamber. Between the electrodes are alternating anion exchange membranes (AEMs) and cation exchange membranes (CEMs), which are separated by spacers to create diluate and concentrate chambers, through which liquids flow. A wider housing encases and supports the aforementioned components. In this study the CED stack was manufactured by PCCell GmbH (Heusweiler, Germany), and the model was an ED 64002 with 20 cell pairs (0.128 m^2 effective membrane area).

2.3. Preparation of model solutions and stock solutions

Three, distinct, solutions flow through a CED stack; concentrate, dilute, and electrolyte. In this study, the concentrate (250 ml phosphate buffer solution: 8000 mg l^{-1} NaCl; 1440 mg l^{-1} Na_2HPO_4; 240 mg l^{-1} KH_2PO_4; and 200 mg l^{-1} KCl) and electrolyte (1000 ml of Na_2SO_4 at 35,510 mg l^{-1}) remained the same throughout all experiments. The dilute varied between experiments and consisted either of 250 ml model VFA solutions (1000 mg l^{-1} each of acetic, propionic, i-butyric, n-butyric, i-valeric and n-valeric acid, and 8000 mg l^{-1} NaCl; 1440 mg l^{-1} Na_2HPO_4; 240 mg l^{-1} KH_2PO_4; and 200 mg l^{-1} KCl), or hydrogen fermentation broths, the compositions and preparations of which are outlined below. VFA concentrations in model solutions where chosen to approximate VFA levels obtained from fermentative hydrogen production using a variety of substrates such as sewage biosolids, grass and wheat co-product (Massanet-Nicolau et al., 2013, 2010; Yu et al., 2014).

2.4. Preparation of hydrogen fermentation broths

Two dark hydrogen fermentation reactors, one sucrose-fed, and one grass pellet fed continually stirred batch reactors were adapted from Reilly et al.'s (2014) method as follows. The sucrose-fed continuously stirred batch reactors contained 100 ml of 15 g l^{-1} sucrose solution, 120 ml of inoculum (sewage sludge from a sewage treatment works serving a large metropolitan area), and 280 ml of water. The grass pellet fed continuously stirred batch reactors were identical except 100 ml of 80 g l^{-1} grass pellet suspension was added instead of sucrose solution. To inactivate methanogenic organisms and to prevent their eventual