Separation of Acetate Produced from C1 Gas Fermentation Using an Electrodialysis-Based Bioelectrochemical System

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Abstract: The conversion of C1 gas feedstock, such as carbon monoxide (CO), to useful platform chemicals has attracted considerable interest in industrial biotechnology. One conversion method is electrode-based electron transfer to microorganisms using bioelectrochemical systems (BESs). In this BES system, acetate is the predominant component of various volatile fatty acids (VFAs). To appropriately separate and concentrate the acetate produced, a BES-type electrodialysis cell was constructed and evaluated under various operational conditions, such as applied external current, acetate concentration, and pH. A high acetate flux of 23.9 mmol/m²·h was observed under a −15 mA current in an electrodialysis-based bioelectrochemical system. In addition, the initial acetate concentration affected the separation efficiency and transportation rate. The maximum flux appeared at 48.6 mmol/m²·h when the acetate concentration was 100 mM, whereas the effects of the initial pH of the anolyte were negligible. The acetate flux was 14.9 mmol/m²·h when actual fermentation broth from BES-based CO fermentation was used as a catholyte. A comparison of the synthetic broth with the actual fermentation broth suggests that unknown substances and metabolites produced from the previous bioconversion process interfere with electrodialysis. These results provide information on the optimal conditions for the separation of VFAs produced by C1 gas fermentation through electrodialysis and a combination of a BES and electrodialysis.

Keywords: electrodialysis; bioelectrochemical system; microbial fuel cell; C1 gas; carbon monoxide; acetate

1. Introduction

The biological conversion of industrial waste gases containing carbon dioxide and carbon monoxide are being highlighted to reduce the emissions of greenhouse gases and simultaneously produce the building blocks of fuel and more useful commodity chemicals [1,2]. Among them, CO, which is toxic and recalcitrant to the environment, accounts for 50 to 70% of the effluent gas from steel factories. Hence, appropriate treatment technologies are anticipated. Recently, Im et al. (2018) reported that a bioelectrochemical system (BES) could compensate for the limitation of natural biological CO conversion and enhance the production of volatile fatty acids [3]. The applied potential of the BES supplies reducing power for autotrophic microorganisms and improves the yield of C1 gas conversion and cell growth [4–8].

The metabolites produced from BES-based C1 fermentation may contain acetate as well as various volatile fatty acids (VFAs) and alcohols [9,10]. Therefore, additional separation processes are needed to...
isolate and/or concentrate acetate from fermentation broth. In a conventional study, the separation of ionic metabolites was carried out using chemical and physical methods, such as acidification, ion-exchange, crystallization, and adsorption. On the other hand, these attempts may need to be moderated with the recent trends of environmentally and economically sustainable research and development [11,12]. For example, in the case of acidification or ion exchange, considerable amounts of acid and alkali are consumed during the operation, which is problematic. Regarding crystallization or adsorption, additional purification and chemical waste discharge have been a concern.

Electrodialysis (ED) is a technology to separate and enrich target substances by transferring the ionic forms through a selectively transmissible ion exchange membrane under an electrochemically induced oxidation/reduction reaction [11]. The separation of fermentation metabolites by electrodialysis was proposed to prevent the inhibition of lactic acid [13]. Im et al. reported that BES-based C1 gas conversion produced up to 8.4 g/L of acetate, which is an industrially useful intermediate chemical and a source for further biosynthesis. Recently, many research groups have attempted to separate acetate from a range of wastewater or microbial fermentation broths [14,15].

In a normal fermentation broth, the anionic form of acetate is the dominant species rather than acetic acid because the culture condition is generally near neutral pH. Therefore, acetate species can be separated using the ion exchange membrane of an electrodialysis cell. In electrodialysis, the H⁺/OH⁻ ion can be supplied continuously by electrochemical control in electrodialysis, and this can provide a driving force to separate various metabolites from the fermentation broth without the need for additional chemical reagents, such as salts. Moreover, it is capable of separating and concentrating high purity substances efficiently compared to other methods, enabling applications in a wide range of industrial processes, including food and biofuel production [16,17]. In particular, there have been many applications of electrodialysis in bioelectrochemical systems [18–20]. For example, ethyl acetate was produced through biphasic esterification, and acetic acid was separated from the fermentation broth by electrodialysis [21]. In addition, acetic acid, which was produced from carbon dioxide in a three-chamber bioelectrochemical system, was separated by electrodialysis with yields of up to 13.5 g/L over a 43 day period [5].

The system configuration of BES and electrodialysis have some similarity in terms of using an ion exchange membrane (or separator) and electrical input (or output) to (or from) the reactor. Thus, electrodialysis allows the direct production and isolation of the target metabolites from C1 gas fermentation. On the other hand, the most important and problematic issue of separation by electrodialysis is membrane fouling [22]. In the sludge, wastewater or fermentation broth, there are not only secondary metabolic products, but also unused growth media components and a large number of cells [23]. These undesirable substances or microbial cells attach to the surface of the membrane and/or block the functional group of the ion exchange membrane during the electrodialysis process, eventually resulting in a decrease in separation efficiency [24]. To solve these problems, pretreating the fermentation broth before introduction to electrodialysis or various modification methods of the ion exchange membrane have been suggested [23,25,26].

This study examined the operational parameters in electrodialysis to separate acetate, which is applicable to C1 gas fermentation (Figure 1). The optimal conditions in the synthetic broth were investigated and applied to the fermentation broth. The efficiency and flux of acetate separation were compared in an actual fermentation broth and synthetic solution. The aim of this study was to assess the potential of a combination of electrodialysis with BES-based C1 gas fermentation.
The electrodialysis (ED) reactor used in this experiment consisted of an acrylic anode and cathode chamber; each chamber had a working volume of 73.5 mL (7 × 7 × 1.5 cm³) (See Figure S1). Both electrodes were made of carbon paper (surface area of 42.25 cm², 120-TGP-H-120, Toray, Japan), and connected to a circuit via a carbon fiber (20 cm). An anion exchange membrane (49 cm², FKB-PK-130, Fumasep, Bietigheim-Bissingen, Germany) was used as the ion exchange membrane for the cell, and it was rinsed with a 0.5 M NaCl solution for 24 h prior to use. A potentiostat (WMPG1000, WonA Tech, Korea) in galvanostatic mode was used to apply a current to the reactor. Graphite granules (40 g) were added to the anode chamber, and 5 cm of a graphite rod connected with titanium wire was used as the current collector from the graphite granules. The cathode potential (−1.1 V vs. Ag/AgCl) was applied continuously through a multi-channel potentiostat (WMPG1000K8, Won-A tech, Seoul, Korea) during the experiment to support the BES-based biological CO conversion. A feed gas (N₂:CO:CO₂ = 50:40:10) was continuously provided into the cathode chamber at a flow rate of 10 mL/min. All experimental conditions performed were in accordance with the research reported by Im et al. [3].

The electrodialysis (ED) reactor used in this experiment consisted of an acrylic anode and cathode chamber; each chamber had a working volume of 73.5 mL (7 × 7 × 1.5 cm³) (See Figure S1). Both electrodes were made of carbon paper (surface area of 42.25 cm², 120-TGP-H-120, Toray, Japan), and connected to a circuit via a carbon fiber (20 cm). An anion exchange membrane (49 cm², FKB-PK-130, Fumasep, Bietigheim-Bissingen, Germany) was used as the ion exchange membrane for the cell, and it was rinsed with a 0.5 M NaCl solution for 24 h prior to use. A potentiostat (WMPG1000, WonA Tech, Korea) in galvanostatic mode was used to apply a current to the reactor. To examine acetate separation from a realistic fermentation broth, both BES and ED were connected, as shown in Figure 1. In some cases, centrifuged fermentation broth, as described in Section 2.2, was introduced into the electrodialysis cell to examine the effects of particulates and cells in the media.

2.2. Composition of Electrolyte

Two types of catholytes were used to examine acetate transportation across the ion exchange membrane: synthetic broth and fermentation broth. The synthetic broth contained a CO/CO₂ fermentation medium, which was composed of the following (per liter): 1.5 g KH₂PO₄, 2.9 g K₂HPO₄, 2.0 g NaHCO₃, 0.5 g NH₄Cl, 0.09 g MgCl₂·6H₂O, 0.0225 g CaCl₂·2H₂O, and 0.5 g yeast extract. Sodium acetate (20 mM to 100 mM for each reaction condition) was added to the catholyte to examine transportation through the membrane. The fermentation medium was made by slightly modifying the synthetic broth by also adding 2.11 g of sodium-2 bromoethanesulphonate as a methanogene inhibitor, 2 ml of Pfennig’s trace element solution, and 5 mL of a vitamin solution [3]. The pH was adjusted to 6.0 with 1 M H₂SO₄ and 1 M NaOH. In some experiments, centrifugation was
conducted at 7500 RPM and 15 min to remove the cells and precipitates produced from former fermentation. Streptomycin (20 µg/mL) was added as an antibiotic to prevent acetate consumption due to contamination. The anode electrolyte consisted of the following ingredients (per liter): 0.8 g K$_2$HPO$_4$, 1.0 g NH$_4$Cl, 2.0 g KCl, 0.15 g CaCl$_2$·2H$_2$O, 2.4 g MgCl$_2$·6H$_2$O, 4.8 g NaCl, and 10.08 g NaHCO$_3$ [5].

2.3. Operation of Electrodialysis Reactor

The cathode and anode electrodes were set as the working and counter electrodes, respectively. The current applied to the cathode ranged from 0 to −15 mA using a galvanostatic method. The electrodialysis cells were located in the incubator at 25 ± 1 °C and gently shaken at 30 rpm.

2.4. Analyses

A liquid sample (<300 µL) was taken from each chamber periodically. The liquid samples were filtered through a 0.2 µm syringe filter, acidified by HCl to prevent acetate volatilization, and stored in a freezer at −80 °C. The samples were analyzed by gas chromatography (GC, 7890B, Agilent Technologies, Santa Clara, CA, USA) and high-performance liquid chromatography (HPLC, HP 1100 series, Agilent Technologies, Santa Clara, CA, USA). The experiment was conducted in duplicate, and the analyses were carried out in duplicate. The initial and final pH were measured using a pH meter (Orion 420A+, Thermo Orion, USA). The current efficiency ($\eta_A$) was estimated using the following equation:

$$\eta_A = \frac{\Delta N_A}{iA\Delta t/F} \quad (1)$$

where $\Delta N_A$ is the change in the molarity of acetate, $i$ is the current density, $A$ is the membrane area, $F$ is the faraday constant (96485 C/mol = 26.8 Ah/mol), and $\Delta t$ is the interval of time [28].

The flux ($J_A$) of acetate from the cathode to anode chamber was calculated using the following equation:

$$J_A = \frac{\Delta m_A}{A\Delta t} \quad (2)$$

where $\Delta m$ is the amount of acetate transported from the cathode to the anode chamber, $A$ is the membrane area, and $\Delta t$ is the interval of time.

3. Results and Discussion

3.1. Different Applied Current on Acetate Transportation in BES

Acetate transport across the ion exchange membrane is affected by the applied potential and current in microbial fuel cells [5,11,29,30]. Therefore, the changes in acetate concentration in both the anode and cathode chambers were examined while various currents (−5 to −15 mA) were applied to the cell (Figure 2). In the absence of an applied current, the final acetate concentration of 9.17 mM was transported to the anode chamber during 16 h of operation, indicating that acetate had diffused to the anode due to the concentration gradient. On the other hand, acetate transport was increased to 12.55 mM when a current was applied across the electrodes (−5 mA). Under −15 mA application, 24.98 mM of acetate was transported to the anode chamber. An externally applied current can drive the electrochemical reaction and actively move acetate anions against the concentration gradient between the anode and cathode chambers (Figure 2B–D) over 16 h, whereas the acetate only diffused naturally in the control (i.e., under the absence of an applied current) (Figure 2A).

The amount of acetate transportation increased with increasing current in BES. On the other hand, the estimated current efficiency on the applied potential decreased at a higher current (Table 1). The current efficiency estimated by Equation (1) was higher (54.4 ± 0.2%) under a lower applied current (−5 mA), whereas it decreased at a higher current (36.1 ± 1.2% at −15 mA) (Table 1). On the other hand, the acetate flux across the membrane was 23.9 ± 0.8 mmol/m$^2$·h at −15 mA, whereas it
decreased at a lower applied current (8.8 ± 0.4 mmol/m²·h at −5 mA) (Table 1). The driving force for acetate anion transportation by electrodialysis is lost under a higher current in electrodialysis. These results are consistent with the previous observation that the selectivity for ions at a low current density was higher than that at a high current density [31]. At a high current density, the current efficiency was reduced because the driving force was dissipated by the movement of other ions in addition to the target acetate, and resistance in the ion exchange membrane.

![Graph showing acetate transfer from the cathode to the anode chamber under different current conditions.](image)

**Figure 2.** Acetate transfer from the cathode to the anode chamber under different current conditions. Without current application (A,E); −5 mA (B,F); −10 mA (C,G); −15 mA (D,H) during 16 h of operation.

**Table 1.** Entire migration amount of acetate in the cathode chamber, total applied current, current efficiency, and acetate flux.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Acetate Migration from the Cathode (mM)</th>
<th>Total Applied Current (C)</th>
<th>Current Efficiency (%)</th>
<th>Acetate Flux (mmol/m²·h)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Applied current</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 mA</td>
<td>14.7 ± 4.9</td>
<td>-</td>
<td>-</td>
<td>8.8 ± 0.4</td>
</tr>
<tr>
<td>−5 mA</td>
<td>18.8 ± 5.2</td>
<td>288.0</td>
<td>54.4 ± 0.2</td>
<td>12.0 ± 0.0</td>
</tr>
<tr>
<td>−10 mA</td>
<td>24.4 ± 7.9</td>
<td>576.0</td>
<td>40.4 ± 0.6</td>
<td>17.8 ± 0.3</td>
</tr>
<tr>
<td>−15 mA</td>
<td>28.5 ± 3.6</td>
<td>864.0</td>
<td>36.1 ± 1.2</td>
<td>23.9 ± 0.8</td>
</tr>
<tr>
<td><strong>Acetate concentration</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 mM</td>
<td>16.3 ± 2.1</td>
<td>864.0</td>
<td>23.8 ± 0.6</td>
<td>15.8 ± 0.4</td>
</tr>
<tr>
<td>40 mM</td>
<td>30.1 ± 4.5</td>
<td>864.0</td>
<td>40.2 ± 1.2</td>
<td>26.6 ± 0.8</td>
</tr>
<tr>
<td>80 mM</td>
<td>44.2 ± 9.3</td>
<td>864.0</td>
<td>63.1 ± 2.6</td>
<td>41.8 ± 1.7</td>
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<tr>
<td>100 mM</td>
<td>55.9 ± 11.3</td>
<td>864.0</td>
<td>73.4 ± 4.6</td>
<td>48.6 ± 3.0</td>
</tr>
<tr>
<td><strong>pH test</strong></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>2.0</td>
<td>31.2 ± 3.1</td>
<td>864.0</td>
<td>43.4 ± 2.8</td>
<td>28.2 ± 1.8</td>
</tr>
<tr>
<td>4.0</td>
<td>30.6 ± 6.3</td>
<td>864.0</td>
<td>42.8 ± 3.4</td>
<td>28.4 ± 2.2</td>
</tr>
<tr>
<td>6.0</td>
<td>28.9 ± 3.9</td>
<td>864.0</td>
<td>40.1 ± 4.1</td>
<td>26.6 ± 2.7</td>
</tr>
<tr>
<td><strong>Catholyte composition</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Synthetic</td>
<td>25.3 ± 0.9</td>
<td>864.0</td>
<td>34.5 ± 1.2</td>
<td>22.9 ± 0.8</td>
</tr>
<tr>
<td>Fermented with centrifuge</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>11.4 ± 1.2</td>
<td>864.0</td>
<td>22.5 ± 1.5</td>
<td>14.9 ± 1.0</td>
<td></td>
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<tr>
<td>Fermented without centrifuge</td>
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</tr>
<tr>
<td>11.1 ± 0.3</td>
<td>18.6 ± 0.7</td>
<td></td>
<td>12.3 ± 0.4</td>
<td></td>
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</tbody>
</table>

3.2. Effect of Different Acetate Concentration

The effects of the initial acetate concentration (20 to 100 mM) on electrodialysis were investigated at an applied current of −15 mA (Figure 3). The acetate flux was estimated to be 48.6 ± 3.0 mmol/m²·h at an initial acetate concentration of 100 mM, whereas it decreased proportionally to 15.8 ± 0.4 mmol/m²·h with 20 mM (Figure 3 and Table 1). At the highest acetate concentration (100 mM), the current efficiency (73.4%) was much higher than that at a lower
current efficiency (73.4%) was much higher than that at a lower concentration (20 mM vs. 23.8%) (Table 1). These results suggest that a higher efficiency of acetate separation can be obtained at a higher acetate concentration. When no current was applied to the cell, separation was carried out by diffusion depending on the acetate concentration. This indicates that, in addition to the applied current, diffusion plays an important role in the transport of acetate [29]. Accordingly, a higher acetate concentration is required for optimal process efficiency, even though the performance of electrodialysis is also related to the reactor configuration. Im et al. examined the fermentation of acetate production from CO by electrosynthesis and revealed the productivity of acetate at a maximum of 8.4 g L\(^{-1}\) in a BES [3]. Therefore, electrodialysis-driven acetate separation around the maximum was examined in the electrodialysis cell. The separation of acetate at this point is expected to increase both the growth of microorganisms and the acetate productivity from CO conversion.

![Figure 3. Change in acetate concentration by electrodialysis under various initial acetate concentrations in the cathode chamber, 20 mM (A,E), 40 mM (B,F), 80 mM (C,G), and 100 mM (D,H). The applied potential was fixed to –15 mA.](image)

### 3.3. Effect of Different Initial Anodic pH

The pH of the anode chamber can also be an important factor for the efficient separation of acetate. The pK\(_a\) of acetate is 4.76. Hence, acetate exists mainly as an ionized form in the catholyte in the cathode chamber (pH 6.0), which is provided from the former BES reactor. To examine the effects of the anodic pH in electrodialysis, the anodic pH was adjusted from 2.0 to 6.0 while the cathodic pH was fixed to 6.0 because the pH from the effluent from the former C1 gas fermentation is approximately 6.0. As shown in Figure 4, the pH effect on acetate separation was negligible, and the current efficiencies were estimated to be approximately 40–43% under these pH conditions (Table 1). In electrodialysis cells, the following oxidation and reduction reactions take place in the anode (3) and cathode chamber (4):

\[
\begin{align*}
\text{H}_2\text{O} & \rightarrow 2\text{H}^+ + 1/2\text{O}_2 + 2\text{e}^- \\
2\text{H}_2\text{O} + 2\text{e}^- & \rightarrow 2\text{OH}^- + \text{H}_2
\end{align*}
\]  

(3)  

(4)

The H\(^+\) produced by water electrolysis reaction (3) reduces the pH in the anode chamber continuously, which eventually approaches pH 2.0, even if the initial pH of the anode chamber is higher than pH 2.0. The final pH of the anode chamber in the tested reactors was pH 1.9 to 2.0, which converged from a varied initial pH 2.0 to 6.0. This suggests that proton transport from the anode to the cathode in the reverse direction of acetate anion species separation might be limited by the ion exchange membrane [32].
Figure 4. Changes in the acetate concentration by electrodialysis when the initial pH of the anode was varied. Initial anode pH 2.0 (A,D); pH 4.0 (B,E); pH 6.0 (C,F).

3.4. Acetate Separation from the Actual Fermentation Broth

The combination of acetate fermentation followed by electrodialysis-based acetate separation has been highlighted for biological C1 gas conversion. Based on the results of the above experiments, synthetic and fermentation broths containing acetate were compared for the separation of acetate in the electrodialysis cell. First, the cell and precipitate in the former fermentation broth were removed by centrifugation to exclude the effects of particulates in the broth. The final acetate concentrations with the fermentation and synthetic broth were 15.6 mM and 23.9 mM, respectively (Figure 5). The results show that approximately 20% less acetate in the fermentation broth (i.e., effluent from the former electrosynthesis process) is transported to the anode chamber than the synthetic solution, even when the particulates were removed by centrifugation (Figure 5B). A similar but slightly lower acetate separation was obtained using a non-centrifuged fermentation broth (i.e., realistic cultivation broth from BES) (13.30 mM) during the 16 h of operation (Figure 5C). The other metabolites from C1 gas fermentation in BES, such as butyrate, propionate and iso-butyrate [3], hinder acetate separation significantly. As observed in the GC analysis results, unlike the synthetic medium, the fermentation broth contains various volatile fatty acids as well as acetate (Figure S2C,D). Among these metabolites, the longer chain VFAs, such as propionate, may pass through the membrane competitively with acetate, which might reduce the rate and efficiency of acetate separation. The GC results also show clearly that propionate has passed through the anion exchange membrane used in this study (Figure S2A,B). The competitive flux of these other anions is considered to be the cause of the relatively low current efficiency for acetate separation [21]. Because the former BES process was usually inoculated with inoculum, including sludge and isolated microorganisms, it contained a variety of particulates, colloidal and dissolved fractions, all of which can act as inhibitors and potential foulants. Microorganisms and soluble substances potentially cause membrane fouling, which decreases the electrodialysis performance [24,33,34]. Ghasemi et al. reported that the microorganisms attached to the membrane surface and the biofilm formation are major factors reducing the separation efficiency in the electrodialysis cell [22]. After the operation of the electrodialysis cell with a non-centrifuged fermentation broth, contamination by unknown substances was observed on
the cathodic electrode, which was different from the synthetic and centrifuged fermentation broth (Figure S3D–F). These contaminants on the electrode and membrane may lower the current efficiency of acetate separation from the non-centrifuged fermentation broth in the electrodialysis cell.

![Figure 5. Comparison of acetate transportation in an electrodialysis cell with synthetic media containing acetate (A,D), and centrifuged C1 gas fermentation broth (B,E) and non-centrifuged C1 gas fermentation broth (C,F).](image)

4. Implication and Conclusions

Acetate is one of the primary metabolites from C1 gas fermentation and is a useful intermediate chemical for further biosynthesis [35]. On the other hand, this fermentation broth contains a variety of components, such as ion species, VFAs, and microorganisms as well as acetate. Therefore, the development of appropriate acetate separation is essential, which accounts for between 30% and 40% of the total process cost [36]. In this respect, the production of acetate through BES and the separation of the produced acetate by electrodialysis may provide an appropriate platform for the in-situ processing and separation of acetate. Through these experiments, it was confirmed that a maximum acetate flux of 48.6 ± 3.0 mmol/m²·h can be achieved using the synthetic broth. When the C1 fermentation broth was applied, the flux was 14.9 ± 1.0 mmol/m²·h, which was approximately half that of the synthetic broth (22.9 ± 0.8 mmol/m²·h) under the same conditions, probably due to the various substances and other longer chain VFAs in the fermentation broth. The obtained separation rate and efficiency are comparable to the previous results of electrodialysis (Table 2).

There are still challenges that need to be overcome before this system can be applied to an actual industrial environment; several studies to solve these problems are underway. To solve the fouling of an ion-exchange membrane, some research groups have focused on modifying the membrane by a treatment with polymer compounds, such as poly (sodium 4-styrene sulfonate) (PSS)/poly(diallyldimethylammonium chloride) (PDADMAC) [34]. An ultra-low voltage customized DC–DC booster circuit [37] and maximum power point tracking (MPPT) [38] may provide an affordable voltage and current for self-sustained electrodialysis applications. Although further studies will be needed in the future, these results may provide a basis for techniques to isolate acetate from actual fermentation end products and culture broth from bioelectrochemical systems.
Table 2. Volatile fatty acid separation using various ion exchange membranes and resins.

<table>
<thead>
<tr>
<th>Volatile Fatty Acids</th>
<th>Separated Acetate Titer</th>
<th>Separation Material &amp; Membrane</th>
<th>Applied Potential or Current</th>
<th>Current Efficiency (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetate</td>
<td>1.21 mol/m$^3$ during 32 days</td>
<td>Anion exchange membrane (1.77 cm$^2$, AMI-7001)</td>
<td>$-800$ mV (vs. SHE)</td>
<td>-</td>
<td>[39]</td>
</tr>
<tr>
<td>Acetate</td>
<td>0.379 kg/m$^2$·d</td>
<td>Anion exchange membrane (64 cm$^2$, AM-7001)</td>
<td>$20$ Am$^{-2}$ (vs. Ag/AgCl)</td>
<td>36% (coulombic efficiency)</td>
<td>[21]</td>
</tr>
<tr>
<td>Acetate</td>
<td>225 mM during 43 days</td>
<td>Anion exchange membrane (Fumatech FAB)</td>
<td>$-50$ mA (vs. SHE)</td>
<td>-</td>
<td>[5]</td>
</tr>
<tr>
<td>Acetate</td>
<td>100 mg/g (acetate sorption)</td>
<td>Anion exchange resin (35 g, Amberlite TM FPA53)</td>
<td>-</td>
<td>-</td>
<td>[40]</td>
</tr>
<tr>
<td>Succinic acid</td>
<td>15.7 g/dm$^3$ during 180 min</td>
<td>EDMB stack: 10 Bipolar (PC 200bip), 10 Anion exchange (PC 200D), Cation exchange(PC-SK), (207 cm$^2$ each)</td>
<td>120 A/m$^2$</td>
<td>14.3%</td>
<td>[41]</td>
</tr>
<tr>
<td>Lactic acid</td>
<td>1.46 mol/L during 15 h</td>
<td>EDMB stack: Bipolar (40 cm$^2$, BMP-1), Anion exchange (40 cm$^2$, FAS-PET-130), Cation exchange (40 cm$^2$, JCM-II-05)</td>
<td>40 mA/cm$^2$</td>
<td>-</td>
<td>[42]</td>
</tr>
<tr>
<td>Acetate</td>
<td>12.3 ± 0.4 mmol/m$^2$·h</td>
<td>Anion exchange membrane (49 cm$^2$, FKB-PK-130)</td>
<td>$-15$ mA</td>
<td>18.6 ± 0.7%</td>
<td>This study</td>
</tr>
</tbody>
</table>
**Supplementary Materials:** The following are available online at http://www.mdpi.com/1996-1073/11/10/2770/s1.

Figure S1. Schematic diagram of the electrodialysis reactor used in this study and a photograph. Figure S2. Comparison of propionate transfer through an anion exchange membrane. (A) Amount of propionate transferred to the anodic chamber, (B) applied current in the reactor for 16 h, (C) GC analysis results of the fermentation broth, (D) GC analysis results of the synthetic medium. Figure S3. Membrane and cathodic electrode surface after the completion of electrodialysis for acetate separation. (A) Anodic chamber, (B) applied current in the reactor for 16 h, (C) GC analysis results of the fermentation broth. Figure S4. Estimated current efficiency on different parameters tested. (A) Current efficiency of different currents from −5 mA to −20 mA, (B) Effects of the initial acetate concentration, (C) Effects of different initial anodic pH, (D) Effects of different catholytes with synthetic media (a), centrifuged fermentation broth (b) and non-centrifuged fermentation broth (c).

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**References**


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