# **Volatile Fatty Acid recovery**

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Volatile fatty acids (VFAs) are low-molecular-weight carboxylic acids containing two to six carbon atoms that are produced as the final product of acidogenic fermentation in anaerobic digestion process.

Keywords: biorefinery concept ; value-added ; membrane-based technology ; volatile fatty acid recovery

# 1. Introduction

VFA production by biological routes from organic waste is gaining attention because of its economic and environmental advantages. VFAs, including acetic acid, propionic acid, butyric acid, caproic acid, and valeric acid, are produced as the final products of acidogenic fermentation in the anaerobic digestion process. These compounds are reported to be the most critical precursors in the biorefinery concept. They can be directly or indirectly used as carbon sources for biological nutrient removal from wastewater <sup>[1]</sup> or as precursors to synthesize high-value-added products, such as bioplastics <sup>[2]</sup> and biodiesel <sup>[3]</sup>.

Although several studies have investigated the process and operational parameters of VFAs production, the process cannot be easily scaled up to the pilot-scale because of limitations in the recovery of the produced VFAs <sup>[4]</sup>. The challenges in VFA recovery include: 1) processing cost, which accounts for approximately 30–40% of the total production cost, 2) the mixture complexity of fermentation broth, and 3) VFAs with low concentration in the fermented stream <sup>[1][5]</sup>. Furthermore, the presence of suspended solids including cells and inorganic precipitates in real fermentation broth might hinder mass transfer coefficients of the VFA recovery step. Various techniques have been applied for VFA recovery, including liquid–liquid extraction <sup>[6]</sup>, adsorption <sup>[7][8]</sup>, membrane contactors <sup>[9]</sup>, membrane reactors <sup>[10][11]</sup>, electrodialysis <sup>[12]</sup> and membrane pervaporation <sup>[13]</sup>. Among them, membrane-based recovery appears to be a more promising technology than other techniques because of its economic and environmental potential <sup>[1][4][14]</sup>.

# 2. Membrane-Based VFA Recovery

VFA recovery can be broadly classified into non-membrane-based and membrane-based recovery. Previous studies have provided a complete explanation of the various strategies for recovery of VFAs by conventional non-membrane-based methods, including solvent extraction, distillation, chemical precipitation, adsorption, and ion exchange <sup>[4]</sup>(14)(15). However, current researchers have focused on applying membrane technology to achieve effective VFA recovery strategies because it could reduce the number of recovery steps while shortening the residence time, resulting in a more economical process <sup>[14]</sup>(16). Table 1 summarizes the advantages and disadvantages of membrane-based techniques for VFA recovery from acidogenic effluents.

Table 1. Membrane-based VFA recovery techniques.

Processes	Principle	Advantages	Disadvantages	Ref.	

Membrane contactor	Hydrophobic membrane is used to separate two aqua phases. The volatile species (e.g., VFAs) from the feed side would transfer into the permeate side until the partial pressure or concentration gradient between the two sides are in equilibrium under isothermal conditions.	<ul> <li>VFAs selectivity can be improved by filling specific extractants.</li> <li>Can be directly connected to a reactor</li> </ul>	<ul> <li>The number of carbon atoms limits recovery efficiency.</li> <li>High ions and solid content negatively affect recovery.</li> <li>Extractant is needed</li> </ul>	[9] [ <u>14]</u>
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Electrodialysis	The positively charged ions (cations) in the solution move toward the cathode. Likewise, the negatively charged ions (anions) move toward the anode. The cations pass through the cation- exchange membrane into the concentrate compartments, but the anion-exchange membrane retains them. Simultaneously, the anions pass through the anion membrane into the concentrate compartments, but the cation-exchange membrane retains them. The overall result in concentrating of VFAs in concentrate compartments are depleted.	<ul> <li>No need for high pressure</li> <li>Directly connected to side stream or in situ process is possible.</li> <li>High VFA recovery rate</li> </ul>	<ul> <li>Not selective to VFAs alone, leading to loss of nutrients, such as NO<sub>3</sub><sup>-</sup> and PO<sub>4</sub><sup>3-</sup></li> <li>High energy demand</li> <li>Back diffusion</li> <li>The cost associated with membrane maintenance and replacement.</li> </ul>	[4] [15] [16] [17]
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Anaerobic membrane bioreactor	Bioreactor combined with pressure- driven microfiltration system to separate the VFA solution from the mixture (fermentation broth). VFA solution passes through a semipermeable membrane, whereas the solids, impurities, microorganisms that are too large to pass through membrane pores are retained on the membrane surface.	<ul> <li>Can be operated under high-solid loading and high- medium viscosity.</li> <li>Cell retention with minimal washout rate</li> <li>In line VFA recovery</li> <li>Easy to scale up</li> </ul>	<ul> <li>Control of membrane fouling</li> <li>Biofilm formation</li> <li>Not selective for VFAs</li> </ul>	[1] [10] [18]
Membrane pervaporation	Non-porous membrane was used to separate between VFA feed solution and vapor-permeate phase. VFAs are transferred across the membrane into a vapor-permeate phase by the difference in chemical potential gradient established by the difference in the partial pressure.	<ul> <li>High concentration of recovered VFAs</li> <li>No adverse effects on microbial growth</li> <li>Low capital cost</li> </ul>	<ul> <li>Intensive energy input</li> <li>Control of membrane fouling</li> <li>Control of pH of the feed</li> <li>Impurities hinder VFA recovery</li> </ul>	[14] [18] [19]

### 2.1 Membrane Contactor

The membrane contactor uses a hydrophobic porous membrane to separate the two aqueous phases on opposite sides of the membrane, avoiding mixing (Figure 1) <sup>[14][20]</sup>. The commonly used polymers in membrane contactors, selected based on their properties, such as mechanical stability, chemical resistance, and hydrophilic or hydrophobic

characteristics, are polypropylene (PP), polyvinylidene fluoride (PVDF), and polytetrafluoroethylene (PTFE) <sup>[21]</sup>. The transmembrane pressure is determined by the partial pressure or concentration difference between the two sides of the membrane. In most membrane contactor processes, the driving force is created by the pH gradient between the two sides of the membrane.

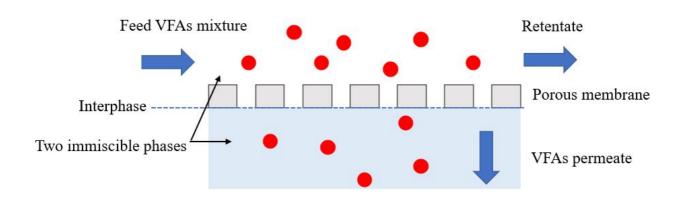


Figure 1. Operating principle of VFA recovery by membrane contactor.

#### 2.2 Electrodialysis

Electrodialysis is a membrane separation process used to transport ionic solutes from one solution to another through anion and cation-exchange membranes separated by a spacer gasket in an alternating pattern forming individual cells between two electrodes <sup>[4]</sup>, as illustrated in Figure 2.

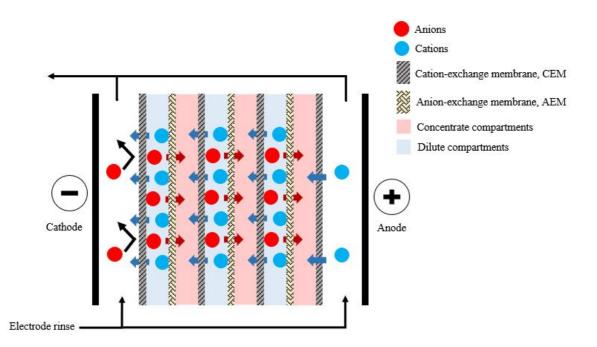


Figure 2. Schematic representation of electrodialysis.

The VFA-rich fermentation broth was transferred through the microfiltration system before feeding it into the electrodialysis stack to prevent solid particles from interfering with electrodialysis operation and to reducing the fouling tendency of the downstream process <sup>[15]</sup>. Previous studies found that, even though electrodialysis concentrated approximately 90% of the VFAs in the permeate, each acid behaved differently. The transport efficiency of small molecular weight acids was greater than that of larger molecular weight acids <sup>[12]</sup>.

#### 2.3 Anaerobic Membrane Bioreactor

Anaerobic membrane technology is a hybrid system in which membranes are combined with an anaerobic bioreactor (Figure 3) <sup>[23]</sup>. Anaerobic membrane bioreactors have emerged as a promising alternative to VFA recovery technologies because of their low sludge generation and energy requirements. Moreover, it has the benefit of reducing the operating space and number of operational units <sup>[23]</sup>. Integrating a membrane recovery system with an acidogenic fermentation bioreactor would decrease cell washout from the bioreactor and the inhibition effect of the acids, thereby improving biodegradation <sup>[24]</sup>.

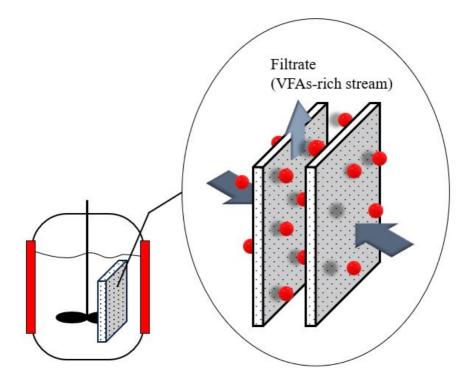


Figure 3. Anaerobic membrane bioreactor.

Long-term VFA production and recovery from acidogenic fermentation of cow manure were investigated by Jomnonkhaow et al. (2020) <sup>[10]</sup>. The authors observed that the maximum VFA yield of 0.41 g-VFAs/g-VS was obtained from heat-treated cow manure without pH control or inoculum addition. Furthermore, anaerobic membrane bioreactors can be operated at very high amounts of TSS ranging from 15 to 55 g-total suspended solid (TSS)/L by employing a routine reactor draining, backwashing, gas sparging, and chemical membrane cleaning to control the amount of TSS in the reactor. Consistent with the study by Parchami et al. (2020) <sup>[1]</sup>, they observed that even though the anaerobic membrane bioreactor was operated at a maximum suspended solid loading of 32 g/L, minimal filtration flux deterioration was observed. Other studies have shown that anaerobic membrane bioreactors have the potential to operate at high organic loading with a complex medium for a long period <sup>[24][25]</sup>.

#### 2.3 Membrane Pervaporation

The membrane pervaporation process relies on diffusing different components in the feed mixture through a dense membrane <sup>[14][21]</sup>. Pervaporation membranes can also be broadly categorized into two groups based on the target molecule to be recovered: hydrophilic pervaporation membranes ensure rapid water transport, allowing for effective dehydration, whereas organophilic pervaporation membranes provide better transport of organic compounds, making them suitable for VFA recovery <sup>[20]</sup>. The pervaporation process is also more suitable for separating VFAs from water (azeotropic mixtures) compared with other separation methods <sup>[6]</sup>. Additionally, membrane pervaporation has no adverse effects on microorganisms in the fermentation broth and can be directly integrated with an acidogenic bioreactor to continuously remove inhibitory products <sup>[5]</sup>. The driving force in membrane pervaporation is the chemical potential gradient across the membrane, which can be created by applying a vacuum or gas purge on the permeate side to keep the permeate vapor pressure lower than the partial pressure of the feed liquid <sup>[14][21]</sup>. The membrane controls the selective transport of species from the feed-liquid mixture to the vapor-permeate (Figure 4).

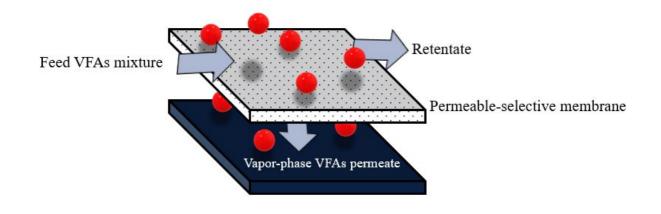


Figure 4. Schematic diagram of membrane pervaporation.

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