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In-line and selective phase separation of medium-chain carboxylic acids using membrane electrolysis

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Supplementary Information:

Materials and Methods

Bioreactor operating conditions. We operated a 5-L jacketed glass bioreactor for over three years to convert corn kernel-to-ethanol fermentation beer (Table S1) to medium-chain carboxylates. Based on previous experiments, the concentration of ethanol in the fermentation beer was too high for operation, requiring a four-fold dilution before it was fed to the bioreactor. The bioreactor was maintained at 30°C *via* a water jacket connected to a recirculating water heater (SC100, Thermo Scientific, USA) to maintain a temperature of 30°C, and was mixed using a peristaltic pump recirculating biogas (7554-80, Cole-Parmer, Vernon Hills, IL) on an automated timer (XT, ChronTrol, San Diego, CA). The pH was maintained to ~5.5 with an automated control system (pH 800, Eutech Instruments, Singapore), using 5 M NaOH fed with a peristaltic pump (7540, Cole- Parmer, Vernon Hills, IL). We operated the bioreactor as an anaerobic sequencing batch reactor (ASBR) on a 48-h cycle: (0 h) substrate was fed into the bioreactor; (0-47 h) the bioreactor was operated with semi-continuous medium-chain carboxylate extraction, pH control, and hourly mixing; (47-48 h) biomass settling period; and (48 h) rapid effluent removal of same volume as feed volume. We maintained a hydraulic retention time (HRT) of 15 days (666 mL of substrate fed per cycle).

Membrane liquid-liquid extraction (*i.e.* pertraction) system. Medium-chain carboxylates were continuously extracted from the bioreactor with a membrane-based liquid-liquid extraction system (pertraction; Fig. 1). The pertraction system consisted of two hollow-fiber hydrophobic membrane extraction modules featuring high-surface areas (8.1 m^2) for enhanced transfer between the solutions on either side of the membrane (4 x 13 Extra-Flow, Liqui-Cel, Charlotte, NC). The first module (forward module; F) facilitated transfer between the bioreactor broth and a mineral oil solvent. The solvent consisted of mineral oil with 3% w/v tri-n-octylphosphineoxide, which is a reactive solvent that is selective for hydrophobic molecules such as longer-chain medium-chain carboxylic acid (MCCAs). Since the bioreactor was operated at a pH of 5.5, there was a relatively high proportion (~20%) of MCCAs in their undissociated form (pKa = 4.8-4.9). The second module (backward module; B) transferred MCCAs from the mineral oil solvent to the alkaline extraction solution, which was maintained at a pH of 9.0. At this higher pH, the alkaline extraction

solution had a considerably lower proportion of MCCAs in the undissociated form, which drove the hydrophobic undissociated MCCAs through the hydrophobic membrane by diffusion.

Operationally, the bioreactor broth was pumped into the shell side (outside the fibers) of the forward module at 15 mL min^{-1}, as described previously[1]. The mineral oil solvent was pumped at 25 mL min^{-1} on the lumen side (inside the fibers) of the membrane, in parallel-flow to the bioreactor broth, and then flowed to the lumen side of the backward module. The alkaline extraction solution was continuously recirculated from a stirred 5-L reservoir at 20 mL min^{-1} in parallel-flow to the shell side of the backward module. A pH controller (pH 800, Eutech Instruments, Singapore) maintained the reservoir to 9.0 pH by automatic addition of 5 M NaOH[1].

Membrane electrolysis cell. Two rectangular Perspex frames housed the anode and cathode compartments (internal dimensions: 20 cm tall × 5 cm wide × 1.9 cm deep, 2 cm frame thickness). The compartments were separated by an anion exchange membrane (AMI-7001S, Membranes International Inc., Ringwood, NJ). The frames were bolted together between two Perspex plates, making the wet volumes 270 mL and 240 mL for the cathode and anode chambers, respectively. The anode was a titanium mesh electrode coated with Ir MMO (geometric dimensions: 18.8 cm tall × 4.8 cm wide × 0.1 cm thick; specific surface area 1.0 m^2 m^{-2}; Magneto special anodes B.V., Schiedam, The Netherlands). The cathode was a 316L stainless steel mesh (geometric dimensions: 20 cm tall × 5 cm wide; mesh width: 564 μm; wire thickness: 140 μm; Solana, Schoten, Belgium). Both the anode and cathode had projected electrode surface areas of 100 cm^2 and were placed in close contact to the membrane[2]. The DC power supply (HY6003D, Automation Technology Inc., Hoffman Estates, IL) leads were attached to the anode and cathode. The voltage drop across a 1.0 Ω resistor was used to measure current between the electrodes. An Ag/AgCl reference electrode in a glass housing (made in-house) was inserted into the cathode chamber to measure cathode potential. Cell potential difference, cathode potential, and current were measured using a digital multimeter (Keithley 2700, Keithley Instruments, Inc., Cleveland, OH). All experiments were performed at room temperature (20±3°C).

The extraction solution was recirculated through the cathode of the membrane electrolysis cell at a rate of 50 mL min^{-1} (Fig. 1). The anode compartment was also recirculated at a rate of 50 mL min^{-1} in the upflow direction; liquid was drawn from the compartment from about two-thirds

of the height of the chamber and fed to the bottom for recirculation and to scour any phase-separated MCCAs to the top of the chamber. The anode was also outfitted with an overflow trap so that phase-separated MCCA oils could freely leave the system on the top into a bottle as they were produced and settled at the top of the anolyte.

Chemical analysis. MCCA and short-chain carboxylic acid (SCCA) composition was measured using a gas chromatograph (6890 Series, Agilent Technologies Inc., Santa Clara, CA) equipped with a fused silica column (15 m × 0.35 mm × 0.5 μm; Sigma-Aldrich Co. LLC., St. Louis, MO) at a gradient temperature from 70°C to 190°C, and a flame ionization detector at a temperature of 275°C.

Calculations

MCCA flux (transfer rate through membrane in electrolysis system)

$$\mathrm{MF} = \frac{m \cdot \lambda}{\mathrm{A}} \quad \text{(Eq. S1)}$$

Where:

MF = MCCA flux, g m^{-2} d^{-1}

m = total mass of MCCA oil produced per day, g d^{-1}

λ = percentage of MCCA in the oil, % (w/w)

A = projected membrane area, m^2

MCCA transfer efficiency

$$\mathrm{I_{MCCA}} = \frac{\mathrm{F}}{86400 \cdot \mathrm{A}} \cdot \sum_{\mathrm{i}=1}^{\mathrm{n}} \frac{\mathrm{m} \cdot \eta_{\mathrm{i}}}{\mathrm{M_i}} \quad \text{(Eq. S2)}$$

$$\mathrm{TE} = \frac{\mathrm{I_{MCCA}}}{\mathrm{I_{Applied}}} \cdot 100 \quad \text{(Eq. S3)}$$

Where:

I_{MCCA} = current (density) accounted for by the MCCA flux, A m^{-2}

TE = MCCA transfer efficiency, %

F = Faraday constant, 96485 C mol^{-1}

86400 = seconds per day, s d^{-1}

A = projected membrane area, m^2

m = total mass of MCCA oil produced per day, g d^{-1}

η_i = percentage of specific MCCA, % (w/w)

M_i = molecular weight of specific MCCA, g mol^{-1}

$I_{Applied}$ = applied current density, A m^{-2}

MCCA recovery (percentage of MCCA-COD in oil product from bioreactor broth)

$$\delta = \frac{COD_{C6,oil} + COD_{C8,oil}}{(COD_{C6,oil} + COD_{C8,oil}) + (COD_{C6,effluent} + COD_{C8,effluent})} \quad \text{(Eq. S4)}$$

Where:

δ = MCCA recovery, % (w/w)

$COD_{C6,oil}$ = grams of COD of *n*-caproic acid present in oil product produced per day, g d^{-1}

$COD_{C8,oil}$ = grams of COD of *n*-caprylic acid present in oil product produced per day, g d^{-1}

$COD_{C6,effluent}$ = grams of COD of *n*-caproic acid present in bioreactor effluent per day, g d^{-1}

$COD_{C8,effluent}$ = grams of COD of *n*-caprylic acid present in bioreactor effluent per day, g d^{-1}

COD yield of extracted MCCA oil from fermentation beer influent

$$\varepsilon = \frac{COD_{C6,oil} + COD_{C8,oil}}{COD_{influent}} \quad \text{(Eq. S5)}$$

Where:

ε = COD yield for the separated MCCA oil from fermentation beer, % (w/w)

$COD_{C6,oil}$ = grams of COD of *n*-caproic acid present in oil product produced per day, g d^{-1}

$COD_{C8,oil}$ = grams of COD of *n*-caprylic acid present in oil product produced per day, g d^{-1}

$COD_{influent}$ = grams of COD of influent per day, g d^{-1}

MCCA composition (percentage of MCCA in oil product)

$$\lambda = \frac{(C_{C6} \cdot 116.16 + C_{C8} \cdot 144.21) \cdot V}{m} \quad \text{(Eq. S6)}$$

Where:

λ = percentage of MCCA in oil product, % (w/w)

C_{C6} = concentration of *n*-caproic acid, mol L^{-1}

C_{C8} = concentration of *n*-caprylic acid, mol L^{-1}

V = volume of MCCA oil, L

m = mass of MCCA oil, g

116.16 = molar mass of the *n*-caproic acid, g mol^{-1}

144.21 = molar mass of the *n*-caprylic acid, g mol^{-1}

Tables S1-S4

Table S1. Corn kernel-to-ethanol fermentation beer composition.

The ethanol fermentation beer fed to the bioreactor was obtained from Western New York Energy in Medina, NY.

	TS ($g\ L^{-1}$)	VS ($g\ L^{-1}$)	TCOD ($g\ L^{-1}$)	Ethanol ($g\ L^{-1}$)
Fermentation beer	125.73 ± 0.14 (n=6)	117.19 ± 0.15 (n=6)	450.50 ± 51.12 (n=6)	152.7 ± 3.4 (n=4)

Table S2. Electrode reactions in the membrane electrolysis cell and standard electrode potentials.

Electrode	Electrode reactions	Standard electrode potential（V）
Cathode	$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	E_0 = -0.827
Anode	$4OH^- \rightleftharpoons O_2(g) + 2H_2O(l) + 4e^-$	E_0 = -0.402
Overall	$2H_2O(l) \rightleftharpoons 2H_2(g) + O_2(g)$	E_0 = -1.229

Table S3. Purity of carboxylic acid oil product.

	n-butyric acid	*n*-caproic acid	*n*-caprylic acid	Total
Percentage (%)	2.62 ± 0.21	53.30 ± 1.07	36.97 ± 0.77	92.89 ± 0.09

Table S4. Molar percentage of total carboxylic acids in system streams.

Factor change indicates change in process stream compared to the one above it.

	n-butyric acid (%)	*n*-caproic acid (%)	*n*-caprylic acid (%)
Bioreactor broth	67.30	32.45	0.24
Alkaline extraction solution	23.80	61.20	14.99
Factor change	0.5x	2x	60x
Anodic oil product	7.69	59.22	33.09
Factor change	0.25x	0.9x	2x

Figure S1

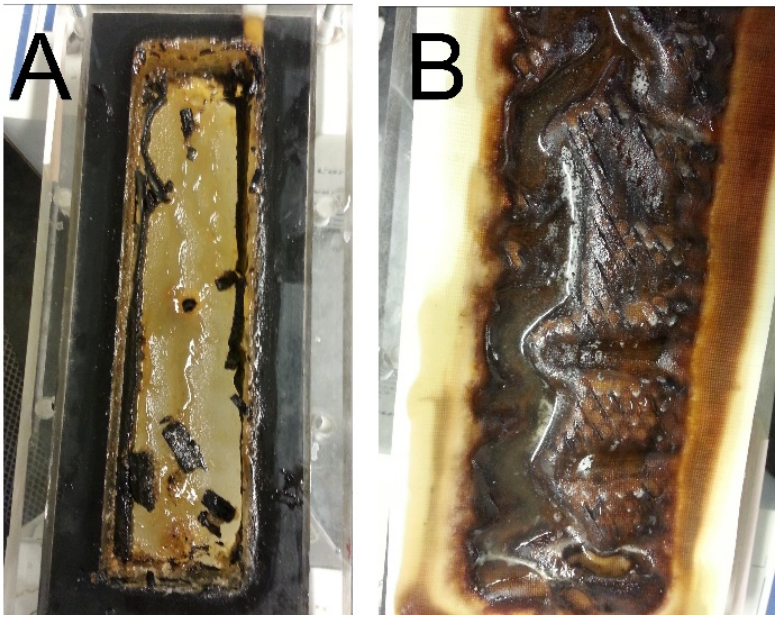

Fig. S1. Images of disassembled membrane electrolysis cell at the end of Phase 2 when the membrane was replaced. A: The cathode side of the membrane shows significant solids and oil buildup. B: Close-up of the anode side of the membrane also shows buildup and an oil residue.

References:

1 M. T. Agler, C. M. Spirito, J. G. Usack, J. J. Werner and L. T. Angenent, *Energy Environ. Sci.*, 2012, **5**, 8189-8192.

2 J. Desloover, A. Abate Woldeyohannis, W. Verstraete, N. Boon and K. Rabaey, *Environ. Sci. Technol.*, 2012, **46**, 12209-12216.