Supplementary Information

Achieving Order of Magnitude Increases in CO$_2$ Reduction Reaction Efficiency by Product Separations and Recycling

Akriti Sarswat[1], David S. Sholl[1,2]*, and Ryan P. Lively[1]*

[1]School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0100, USA

[2]Oak Ridge National Laboratory, Oak Ridge, TN 37830, USA

Table of Contents

Details of Mass and Energy calculations of each unit operation have been described in detail for the following unit operations:

Reactor

The cathodic efficiency and conversion is based on the work by Gabardo et al. [1] and Alerte et al. [2]. The reaction assumes 63% cathodic conversion and ~25.56% overall conversion of carbon dioxide. The composition has been slightly modified to include CH_4 and C_2H_6

Table S1: Faradic efficiencies and corresponding mole fractions for the cathodic effluent stream

Product	Faradic Efficiency	Mole Fraction
C_2H_4	47	0.13
CH_4	5	0.02
CO	16	0.26
C_2H_6	1	2.30×10^{-3}
H_2	5	0.08
C_2H_5OH	17	0.04
CH_3COOH	7	0.03
C_3H_7OH	2	3.60×10^{-3}
CO_2	--	0.41
H_2O	--	0.03

Anode compositions have been calculated assuming 100% Faradic Efficiency of Oxygen Evolution Reaction, 0.5 mol CO_2/e^- crossover and 100% RH. The mole fractions are listed in Table S2.

Table S2: Mole fractions for the anodic effluent stream

Product	Mole Fraction
CO_2	0.65
O_2	0.32
H_2O	0.03

All calculations have been reported for product composition and flow rates such that 1 kg-mol/time of ethylene as product is obtained. All temperatures and pressures are assumed to be 25 °C and 1 bar unless reported otherwise. Energy Calculations for the various unit operations was done using the ASPEN HYSYS software.

Flash Tanks

The product streams from the cathode and anode are each fed to a separate flash tank.
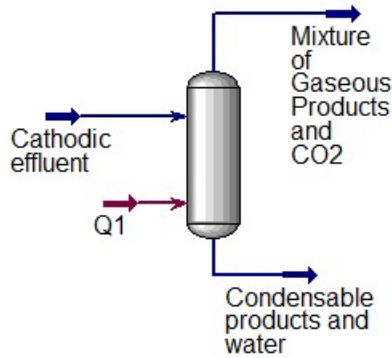
Flash tank 1

Figure S1: Flash tank which separates effluent cathodic stream as modelled in ASPEN HYSYS

Inlet stream: Product stream exiting cathode

Temperature at which flash tank is operated: -14.06 °C

Energy Requirement: 2.7860x10⁴ kJ

Table S3 (a): Effluent Mole fractions: Vapor Stream (b) Liquid Stream

(a)

	Mole Fraction
C_2H_4	0.14
CH_4	0.02
CO	0.29
C_2H_6	2.6 x10^{-3}
H_2	0.09
EtOH	2.4 x10^{-3}
CH_3COOH	0.4 x10^{-3}
C_3H_7OH	0.1 x10^{-3}
CO_2	0.45
H_2O	1.1 x10^{-3}

(b)

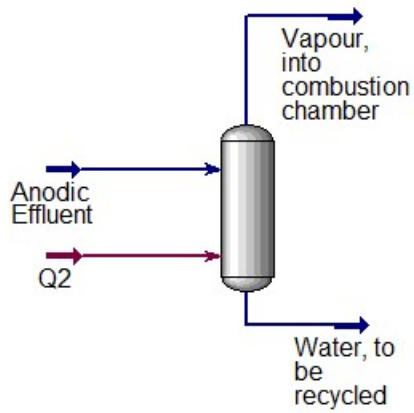|	Mole Fraction
EtOH	0.41
CH_3COOH	0.26
C_3H_7OH	0.03
H_2O	0.29

Flash tank 2

Figure S2: Flash tank which separates effluent anodic stream as modelled in ASPEN HYSYS

Inlet stream: Product stream exiting anode

Temperature at which flash tank is operated: 4.08 °C

Energy Requirement: 3.52×10^4 kJ

Table S4: Vapor stream mole fractions

	Mole Fraction
H_2O	8.2×10^{-3}
O_2	0.33
CO_2	0.66

Adsorbents

The adsorbents for the purpose of this work were taken from the work of Bachman, J.E. et al. [3] We estimate selectivities and uptakes for our mixtures by fitting the single adsorption isotherms from the work of Bachman et al. [3] to Dual-Site Langmuir-Freundlich Isotherm equation (equation S1) and then employ the Ideal Adsorbed Solution Theory model[4]. The parameters for the isotherms for CaX and Ni_2(m-dobdc) are given in Table S5 and S8 respectively.

$$n(P) = q1 * \frac{(k1 * P)^{n1}}{1 + (k1 * P)^{n1}} + q2 * \frac{(k2 * P)^{n2}}{1 + (k2 * P)^{n2}}$$

(S1)

where n is the uptake in mmol/g, P is pressure in mbar, q1, k1, n1, q2, k2 and n2 are constants

The heats of adsorption have been used as an estimate of energy requirements for regeneration of adsorbent. **Heats of adsorption provide minimum thermodynamic estimate of the process. Here, we assume the actual energy required to be 1.5 times this thermodynamic minimum.** The values for CaX and Ni_2(m-dobdc) are used as reported by Bachman et al. [3] and are reported in Table S7 and S9 respectively.
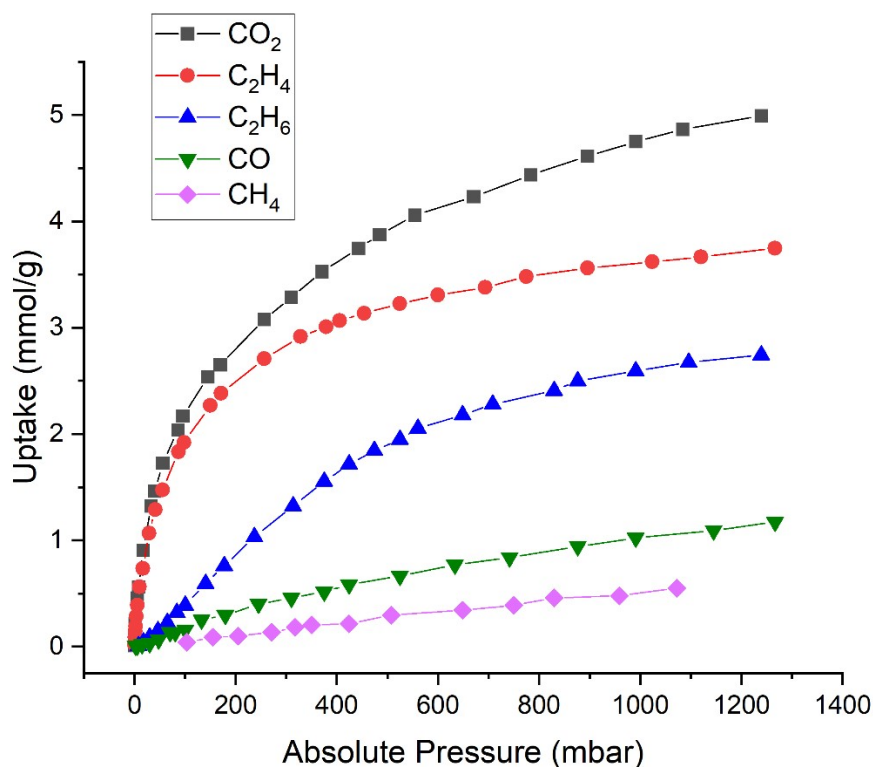
Zeolite CaX

Figure S3: Isotherms of CO_2, C_2H_4, C_2H_6, CO, CH_4 in Zeolite CaX at 25 ° C [3]

Table S5: Fitted parameters for Dual-Site Langmuir-Freundlich Isotherm equation for CaX

Constants	Gases				
	CO_2	C_2H_4	C_2H_6	CO	CH_4
q1 (mmol/g)	3.06	4.36	3.33	7.09×10^{-17}	1.59
k1 (mbar^{-1})	0.02	7.6×10^{-3}	2.4×10^{-3}	4.5×10^{-12}	5.37×10^{-4}
n1	0.81	0.76	1.43	8.18×10^{-5}	1.19
q2 (mmol/g)	3.27	1.92×10^{-14}	7.2×10^{-3}	2.25	9.32×10^{-9}
k2 (mbar^{-1})	1.4×10^{-3}	0.34	9574.79	0.8×10^{-3}	2.66×10^{-11}
n2	1.26	2.41	0.11	1.00	0.99

Here we use 2 CaX beds for the effluent cathode mixture to separate CO_2 and C_2H_4 totally remove any CO

$$\alpha_{A/B} = \frac{x_A/y_A}{x_B/y_B}$$

IAST selectivities for CaX are calculated as , where x_i refers to adsorbed mole fraction and y_i refers to initial mixture mole fraction. Here, component A is CO_2 + C_2H_4 and component B is CO + H_2 + CH_4 + C_2H_6. Selectivity for the 1st bed is ~44 and 2nd bed is ~16.

Table S6: Mole Fractions (a) CO_2 and C_2H_4 stream adsorbed by CaX beds (b) rejected mixture of gases after passing over CaX

(a)

	Mole Fraction
CO_2	0.24
C_2H_4	0.76

(b)

	Mole Fraction
CH_4	0.06
C_2H_6	6.3×10^{-3}
CO	0.71
H_2	0.22

Table S7: Heats of adsorption (kJ/mol) for gases for zeolite CaX [3]

	Heat of ad. (kJ/mol)
C_2H_4	48.29
CH_4	35.10
C_2H_6	35.16
CO	28.32
CO_2	54.94

Total Energy Requirement: $1.5 \times (4.533 \times 10^5 \text{ kJ}) = 6.800 \times 10^5 \text{ kJ}$

Metal Organic Framework Ni$_2$(m-dobdc)
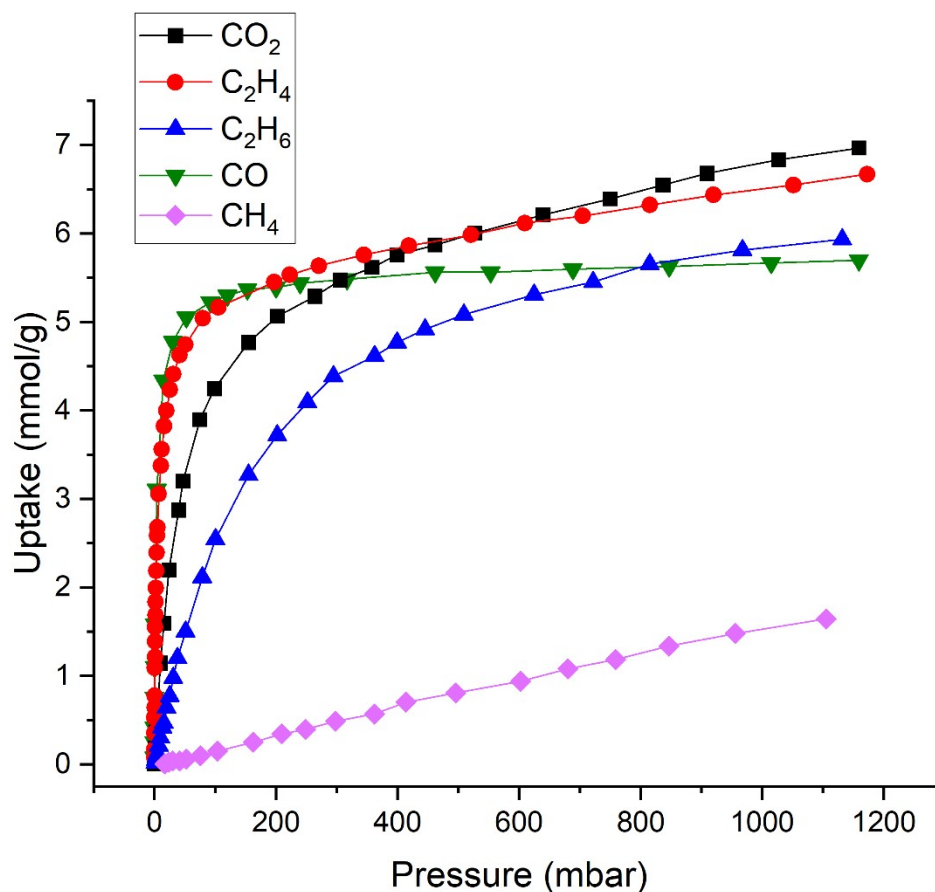
Figure S4: Isotherms of CO$_2$, C$_2$H$_4$, C$_2$H$_6$, CO, CH$_4$ in Ni$_2$(m-dobdc) at 25 ° C [3]

Table S8: Fitted parameters for Dual-Site Langmuir-Freundlich Isotherm equation for Ni$_2$(m-dobdc)

Constants	Gases	
	CO$_2$	C$_2$H$_4$
q1 (mmol/g)	3.09	4.55
k1 (mbar^{-1})	7.24x10^{-4}	0.27
n1	1.56	0.86
q2 (mmol/g)	5.81	3.58
k2 (mbar^{-1})	0.03	1.3 x10^{-3}
n2	1.04	0.64

We used 3 beds of Ni$_2$(m-dobdc) to obtain > 95% purity based on IAST calculations. As mentioned in the paper, materials with greater selectivity need to be developed here.

Table S9: Heats of adsorption (kJ/mol) for gases for MOF Ni_2(m-dobdc) [3]

	Heat of ad. (kJ/mol)
C_2H_4	52.27
CO_2	37.89

Table S10: Adsorbed phase mole fraction for the suggested 3 beds of Ni_2(m-dodbc) based on IAST

	Effluent stream from CaX	Bed 1	Bed 2	Bed 3
C2H4	0.24	0.59	0.85	0.96
CO2	0.76	0.41	0.15	0.04

Total Energy Requirement: $1.5*(1.918 \times 10^5 \text{ kJ}) = 2.877 \times 10^5 \text{ kJ}$

Membrane

Here the calculations are based on a cellulose acetate (CA) membrane [5] to produce Syn Gas. The upstream of the membrane is at 30 bar and 35 °C.

Separation factor for component A relative to component B, $\beta_{A/B}$ can be defined by equation S2

$$\beta_{A/B} = \frac{\left(\dfrac{y_A}{y_B}\right)}{\left(\dfrac{x_A}{x_B}\right)}$$

(S2)

Where y_i and x_i are gas phase compositions of downstream and upstream of the membrane respectively.

The separation factors for this membrane are given in Table S11. Since ethane and methane are very dilute in the upstream, perfect separation is assumed.

Table S11: Separation factor for CA membrane

	Separation Factor
H_2/CO	21
H_2/CH_4	26

Total energy required (for compressor and cooler): 1.1×10^5 kJ

We obtain Syngas with H_2/CO ratio of ~ 6.5. Note that this ratio depends on the membrane used and can be varied as required by using a different membrane or operating at different temperatures and pressure ratios.

The retentate is later combusted.
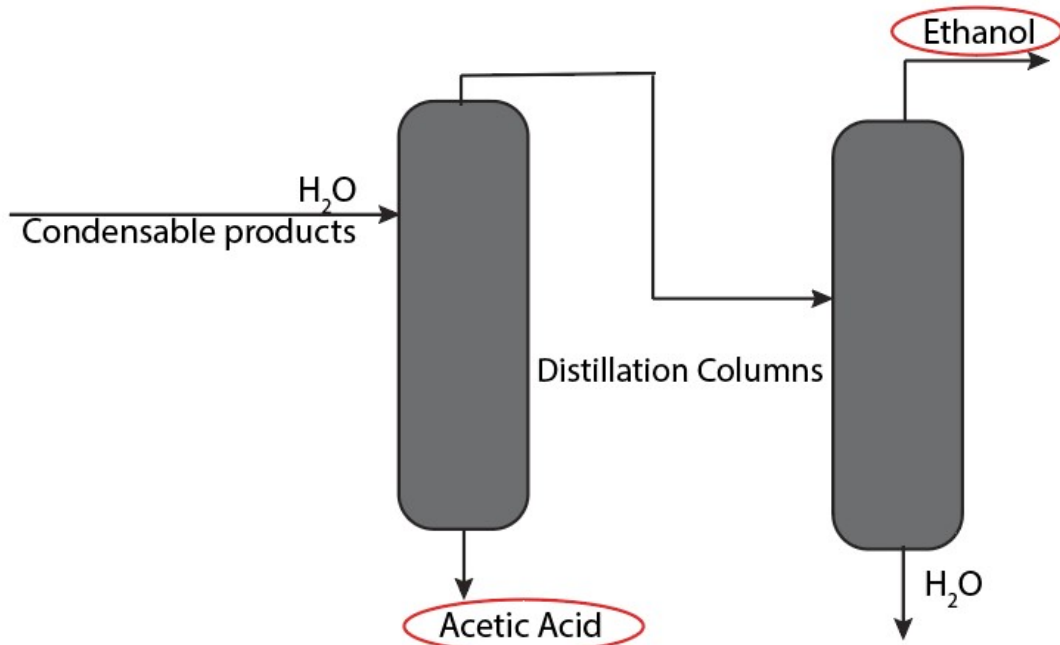
Distillation Columns

Figure S5: Separation of aqueous mixture of condensable products using distillation. Products are encircled in red

We use 2 columns to obtain acetic acid of greater than 99% purity and an azeotrope of ethanol and water. (~90% alcohol).

Fluid Package used: NRTL-ideal

Table S12: Column design specifications

	Column 1	Column 2
Number of trays	15	100
Reflux Ratio	2	6.28
Distillate amount per kg-mol C2H4 produced (kg-mol)	0.62	0.32
Bottoms Product per kg-mol C2H4 produced (kg-mol)	0.22	0.30

Total energy requirement: 3.34×10^5 kJ

Combustion Chamber

Table S13: Heats of Combustion at 25 °C and 1 bar

	Heat of Combustion (kJ/mol)	Reference
CO	-282.38*	[6]
CH_4	-890.71	[7]
C_2H_6	-1560.69	[7]

*Corrected to 25 °C

We add 2.52 kg-mol Methane (per kg mol ethylene produced) to consume all oxygen in the combustion chamber

Table S14: Final composition of the fuel in combustion chamber (per kg mol ethylene produced)

	Amount (kg-mols)	Mole Fraction
CO	1.94	0.08
CH_4	2.68	0.11
C_2H_6	0.01	0.6×10^{-3}
O_2	6.38	0.27
CO_2	12.77	0.53
H_2O	0.16	6.6×10^{-3}

Total energy produced: 2.95×10^6 kJ

Adiabatic flame temperature of this mixture is 2244 °C

Flash tank 3

Inlet stream: Effluent mixture of CO_2 and H_2O from the combustion chamber

Temperature at which flash tank is operated: 3.6 °C

Energy Requirement: 1.75×10^4 kJ

Carbon Footprint Analysis

DAC carbon footprint: 16 g eq. CO_2/ kg captured [8]

CH_4 supply chain emissions: 10.5 g eq./ MJ HHV (= 582.75 g eq./kg CH_4 delivered) [9]

Overall footprint associated with ethylene production is given by

$$\frac{-CO_{2consumed} + CO_{2DAC\ footprint} + CO_{2CH_4\ supply\ chain\ footprint}}{m_{C_2H_4}}$$

= -0.46 g eq. CO_2/g C_2H_4

produced

References:

1. Gabardo, C.M., et al., *Continuous Carbon Dioxide Electroreduction to Concentrated Multi-carbon Products Using a Membrane Electrode Assembly.* Joule, 2019. **3**(11): p. 2777-2791.
2. Alerte, T., et al., *Downstream of the CO_2 Electrolyzer: Assessing the Energy Intensity of Product Separation.* ACS Energy Letters, 2021. **6**(12): p. 4405-4412.
3. Bachman, J.E., et al., *Enabling alternative ethylene production through its selective adsorption in the metal–organic framework $Mn_2(m\text{-}dobdc)$.* Energy & Environmental Science, 2018. **11**(9): p. 2423-2431.
4. Myers, A.L. and J.M. Prausnitz, *Thermodynamics of mixed-gas adsorption.* AIChE Journal, 1965. **11**(1): p. 121-127.
5. Perry, J.D., K. Nagai, and W.J. Koros, *Polymer Membranes for Hydrogen Separations.* MRS Bulletin, 2006. **31**(10): p. 745-749.
6. Awbery, J.H. and E. Griffiths, *The heats of combustion of carbon monoxide in oxygen and of nitrous oxide in carbon monoxide at constant pressure.* Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character, 1933. **141**(843): p. 1-16.
7. Pittam, D.A. and G. Pilcher, *Measurements of heats of combustion by flame calorimetry. Part 8.— Methane, ethane, propane, n-butane and 2-methylpropane.* Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases, 1972. **68**(0): p. 2224-2229.
8. Terlouw, T., et al., *Life Cycle Assessment of Direct Air Carbon Capture and Storage with Low-Carbon Energy Sources.* Environmental Science & Technology, 2021. **55**(16): p. 11397-11411.
9. Balcombe, P., et al., *The Natural Gas Supply Chain: The Importance of Methane and Carbon Dioxide Emissions.* ACS Sustainable Chemistry & Engineering, 2017. **5**(1): p. 3-20.