1. Calculations for Electrolysis Reaction

To model the electrolysis reaction in Aspen, the faradaic efficiency of each reaction rates must be converted to a molar conversion rate and then adjusted for the single-pass conversion of the reaction.

Reaction chemistry:

$$2\ CO_2 + 2\ H_2O \rightarrow 1\ C_2H_4 + 3\ O_2 \qquad (1)$$

$$2\ CO_2 + 0\ H_2O \rightarrow 2\ CO + 1\ O_2 \qquad (2)$$

$$0\ CO_2 + 2\ H_2O \rightarrow 2\ H_2 + 1\ O_2 \qquad (3)$$

$$2\ CO_2 + 3\ H_2O \rightarrow 1\ C_2H_5OH + 3.5\ O_2 \quad (4)$$

Electrochemical half reactions on cathode side:

$$2\ CO_2 + 2\ H_2O + 12\ e^- \rightarrow 1\ C_2H_4 + 6\ O^{2-} \qquad (1c)$$

$$2\ CO_2 + 0\ H_2O + 2\ e^- \rightarrow 2\ CO + 2\ O^{2-} \qquad (2c)$$

$$0\ CO_2 + 2\ H_2O + 2\ e^- \rightarrow 2\ H_2 + 2\ O^{2-} \qquad (3c)$$

$$2\ CO_2 + 3\ H_2O + 14\ e^- \rightarrow 1\ C_2H_5OH + 7\ O^{2-} \quad (4c)$$

Faradaic efficiencies for components (Chen, 2020):

$$FE_{C_2H_4} = 87\ \%$$

$$FE_{CO} = 5.5\ \%$$

$$FE_{H_2} = 2\ \%$$

$$FE_{C_2H_5OH} = 5.5\ \%$$

Conversion rate total $X = 16.5\ \%$ of CO_2 (Ma, 2020)

The conversions of CO_2 for each reaction are: $X_i = X \cdot \frac{FE_i}{n_i e^-} \Big/ \sum \frac{FE_i}{n_i e^-}$

$$X_{C_2H_4} = 0.105$$

$$X_{CO} = 0.0398$$

$$X_{H_2} = 0.0145$$

$$X_{C_2H_5OH} = 0.0057$$

2. Energy Demand of Electrolysis Reaction

To calculate the energy demand for the electrolysis cell, the heat of reaction for every reaction needs to be calculated and then combined with the flow rates and efficiency to find the electricity and cooling necessary.

Heat of formation of components:

$\Delta_f H^o_{CO_2} = -393.52 \frac{kJ}{mol}$ from NIST-Webbook

$\Delta_f H^o_{H_2O} = -285.83 \frac{kJ}{mol}$ from NIST-Webbook

$\Delta_f H^o_{C_2H_4} = 52.47 \frac{kJ}{mol}$ from NIST-Webbook

$\Delta_f H^o_{O_2} = 0 \frac{kJ}{mol}$ Per definition

$\Delta_f H^o_{CO} = -110.53 \frac{kJ}{mol}$ from NIST-Webbook

$\Delta_f H^o_{H_2} = 0 \frac{kJ}{mol}$ Per definition

$\Delta_f H^o_{C_2H_5OH} = -277.05 \frac{kJ}{mol}$ from Argonne National Laboratory

Enthalpies of reaction:

(1) $\Delta H_{reac,1} = 705.585 \frac{kJ}{mol_{CO_2}}$

(2) $\Delta H_{reac,2} = 282.99 \frac{kJ}{mol_{CO_2}}$

(3) $\Delta H_{reac,3} = 285.83 \frac{kJ}{mol_{H_2O}}$

(4) $\Delta H_{reac,4} = 683.74 \frac{kJ}{mol_{CO_2}}$

$$\Delta E = \Delta H_{reac,1} \cdot 2 \cdot \Delta n_{C_2H_4} + \Delta H_{reac,2} \cdot \Delta n_{CO} + \Delta H_{reac,3} \cdot \Delta n_{H_2} + \Delta H_{reac,4} \cdot 2 \cdot \Delta n_{C_2H_5OH}$$

$$\Delta n_{C_2H_4} = 23.551 \frac{mol}{s}$$

$$\Delta n_{CO} = 17.866 \frac{mol}{s}$$

$$\Delta n_{H_2} = 6.864 \frac{mol}{s}$$

$$\Delta n_{C_2H_5OH} = 3.248 \frac{mol}{s}$$

$$\Delta E = 44.694\ MW$$

Full cell electrical efficiency (Chen, 2020): $eta_c = 0.5$

Other losses: $eta_r = 0.9$ (estimated)

Electricity required:

$$W = \frac{\Delta E}{eta_c \cdot eta_r} = 99.321\ MW$$

Cooling required:

$$Q = W - \Delta E = 54.627\ MW$$

3. Heat of Combustion Vent Streams

The ethanol and off-gas streams are burned with the heat used in the process and excess heat sold to other facilities. For that, the heat of combustion of these streams must be calculated:

Ethanol:

$$\Delta H_{C,EtOH} = x_{C_2H_5OH} * \Delta_c H^o_{C_2H_5OH} = 1133.94\ \frac{kJ}{mol}$$

$\Delta_c H^o_{C_2H_5OH} = 1367\ \frac{kJ}{mol}$

$$E_{c,EtOH} = \dot{n}_{EtOH} * \Delta H_{c,EtOH} = 4040\ kW$$

Off-Gas:

$$\Delta H_{C,Off} = x_{C_2H_4} * \Delta_c H^o_{C_2H_4} + x_{CO} * \Delta_c H^o_{CO} + x_{H_2} * \Delta_c H^o_{H_2} + x_{CH_4} * \Delta_c H^o_{CH_4} = 285.6\ \frac{kJ}{mol}$$

$\Delta_c H^o_{C_2H_4} = 1411 \frac{kJ}{mol}$

$\Delta_c H^o_{CH_4} = 891 \frac{kJ}{mol}$

$\Delta_c H^o_{H_2} = 286 \frac{kJ}{mol}$

$\Delta_c H^o_{CO} = 283 \frac{kJ}{mol}$

$$E_{c,Off} = \dot{n}_{Off} * \Delta H_{c,Off} = 8171\ kW$$

Heat of Combustion data from the Engineering Toolbox

4. Coefficient of Performance Estimations

For the condensers in the cryogenic distillation columns, refrigeration in necessary. To estimate the electricity needed to produce a cooling duty of refrigeration at different temperatures, a coefficient of performance is calculated. Here, it is estimated using the prices of electricity supplied and refrigeration (see Section 6).

Electrical Energy Demand for Refrigeration (Coefficient of Performance estimated using utility cost):

$$COP_{ref,est} = \frac{0.1219\,\frac{€}{kWh}}{0.0436\,\frac{€}{kWh}} = 2.796$$

Electrical Energy Demand for Liquid Nitrogen (Coefficient of Performance estimated using utility cost):

$$COP_{N_2,est} = \frac{0.1219\,\frac{€}{kWh}}{0.449\,\frac{€}{kWh}} = 0.271$$

5. Full Process Thermodynamic Key Performance Indicators

Specific Energy Demand

Before Heat Integration:

$$E_{Spec} = \frac{P_{before}}{\dot{m}_{Ethylene}} = 260\ \frac{MJ}{kg}$$

After Heat Integration:

$$E_{Spec} = \frac{P_{after}}{\dot{m}_{Ethylene}} = 192\ \frac{MJ}{kg}$$

Energy converted to chemical energy inside ethylene:

$$\Delta E_{PC2H4} = 2 \cdot \Delta H_{reac,1} \cdot \dot{n}_{C_2H_4,PC2H4} = 32.342\ MW$$

Electric Power Steady State Process:

$$P = 124\ MW$$

Full Process Electrical Efficiency:

$$\frac{\Delta E_{PC2H4}}{P} = 26.1\ \%$$

6. Cost of Streams and Utilities

All costs found in USD were converted to Euro using the exchange rate as stated by the European Central Bank on 03/20/2025: 1.083 $/€

Cost of carbon dioxide emission: 100 €/t (avrg. of 2030-2040 prediction of EU ETS system emissions)

Inlet Streams

Carbon dioxide from pipeline: -0.1 €/kgCO2 (from carbon price)

KOH: 0.54 €/kg (0.59 $/kg) (Business Analytiq Pte Ltd)

Distilled water: 0.602 €/m^3 (Cooling water x10 for preprocessing)

Outlet Streams

Carbon dioxide vent: 0.1 €/kgCO2 (from carbon price)

Electrolyte vent: 0.3013 €/kg (Ulrich 2007)

Off-gas: Cost of Electricity *0.3 -> 0.01975 €/kWh – cost of CO2

Ethanol: Cost of Electricity *0.3 -> 0.01975 €/kWh – cost of CO2

Ethylene: 0.827 €/kg (0.896 $/kg) (Statista)

Oxygen: 0.148 €/kg (Business Analytiq)

Utilities

Cooling water: 0.0602 €/m^3 (0.0652 $/m^3) (Intratec Solutions, L. L.C.) -> 0.005185 €/kWh

Low pressure steam: Cost of Electricity *1.1 -> 0.07243 €/kWh

Refrigerant -40 C: 0.0436 €/kWh (13.11 $/GJ) (Turton)

Liquid Nitrogen: 0.449 €/kWh (135 $/GJ) (Luyben 2017)

Electricity: 0.1219 €/kWh (Average 2023) (Eurostat)

Cooling/Heating Capacity Water

Cooling Water Stats: $\Delta T = 10\ K$

Specific heat: $C_p = 4.18\ \frac{kJ}{kg \cdot K}$

Cooling Capacity: $41.8\ \frac{kJ}{kg}$

7. Ecological Assessment

We perform a gate-to-gate life cycle assessment of the process by calculating the amount of carbon dioxide emitted or removed in the streams containing carbon and the electricity used to power the plant. Cooling water is assumed to not have any greenhouse gas potential. We then calculate the specific emissions per weight of ethylene in each case and the cost of carbon removal for the two cases with negative carbon emissions.

Carbon dioxide emissions by energy type

Grid electricity Belgium: 106.32 gCO2/kWh (European Residual Mixes 2023)

Offshore wind electricity: 13 gCO2/kWh (UNECE)

All carbon that is bound inside the ethylene product stream is removed carbon dioxide from the atmosphere, all other carbon returns back to the atmosphere as carbon dioxide either via direct venting (V-CO2) or as streams burned for heat generation (P-ETOH and OFF-GAS).

Ethylene product: $\dot{n}_{C_2H_4,PC2H4} = 82.50597 \frac{kmol}{hr}$, 1 mole of ethylene turns into 2 moles of CO2 during combustion

$$\dot{m}_{CO_2,removed} = 2 \cdot \dot{n}_{C_2H_4,PC2H4} \cdot M_{CO_2} = 7262.01 \frac{kg_{CO_2}}{hr}$$

$$\dot{m}_{C_2H_4} = 2318.19 \frac{kg}{hr}$$

$$m_{CO_2,removed} = 63{,}615{,}207.6\ kg_{CO_2}$$

Carbon dioxide emitted by electricity

Case A: Grid electricity only

$$m_{CO_2,emitted} = 1{,}083{,}391.124\ MWh \cdot 106.32\ \frac{kg_{CO_2}}{MWh} = 115{,}186{,}144.3\ kg_{CO_2}$$

$$\Delta m_{CO_2} = 51{,}570{,}936.7\ kg$$

$$\Delta m_{CO_2,Ethylene} = 2.54 \frac{kg_{CO_2}}{kg_{Ethylene}}$$

Case B: Wind energy prioritized, grid electricity until base case

$$m_{CO_2,emitted} = 183{,}393.831\ MWh \cdot 106.32\ \frac{kg_{CO_2}}{MWh} + 899{,}997.29\ MWh \cdot 13\ \frac{kg_{CO_2}}{MWh} = 31{,}198{,}396.9\ kg_{CO_2}$$

$$\Delta m_{CO_2} = -32{,}416{,}810.7\ kg$$

$$\Delta m_{CO_2,Ethylene} = -1.60 \frac{kg_{CO_2}}{kg_{Ethylene}}$$

Case C: Wind energy prioritized, grid electricity only for separation

$$m_{CO_2,emitted} = 9{,}409.737\ MWh \cdot 106.32\ \frac{kg_{CO_2}}{MWh} + 1{,}073{,}881.603\ MWh \cdot 13\ \frac{kg_{CO_2}}{MWh} = 14{,}960{,}904.1\ kg_{CO_2}$$

$$\Delta m_{CO_2} = -48{,}654{,}303.5\ kg$$

$$\Delta m_{CO_2,Ethylene} = -2.40 \frac{kg_{CO_2}}{kg_{Ethylene}}$$

Cost of CO2 removal $COR = \frac{NPV}{\Delta m_{CO_2}}$

Case 2: $COR = 1461\ €/Tonne$

Case 3: $COR = 1218\ €/Tonne$

8. Sources

NIST-Webbook pages

Carbon dioxide: https://webbook.nist.gov/cgi/cbook.cgi?ID=C124389&Mask=1

Water: https://webbook.nist.gov/cgi/cbook.cgi?ID=C7732185&Mask=2

Ethylene: https://webbook.nist.gov/cgi/cbook.cgi?ID=C74851&Mask=1

Carbon monoxide: https://webbook.nist.gov/cgi/cbook.cgi?ID=C630080&Mask=1F

Argonne National Laboratory Ethanol: https://atct.anl.gov/Thermochemical%20Data/version%201.118/species/?species_number=624

Chen, X., Chen, J., Alghoraibi, N.M. *et al.* Electrochemical CO_2-to-ethylene conversion on polyamine-incorporated Cu electrodes. *Nat Catal* **4**, 20–27 (2021). https://doi.org/10.1038/s41929-020-00547-0

Ma, W., Xie, S., Liu, T. *et al.* Electrocatalytic reduction of CO_2 to ethylene and ethanol through hydrogen-assisted C–C coupling over fluorine-modified copper. *Nat Catal* **3**, 478–487 (2020). https://doi.org/10.1038/s41929-020-0450-0

https://www.engineeringtoolbox.com/standard-heat-of-combustion-energy-content-d_1987.html