Electronic Supporting Information for:

Is Electrochemical CO₂ Reduction the Future Technology for Power-to-Chemicals?

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1. Background Processes

Table 1: Summary of background processes and their global warming potentials.

<table>
<thead>
<tr>
<th>process</th>
<th>reference unit</th>
<th>database process / ecoinvent 3.7 cut-off</th>
<th>global warming potential / kg CO₂-eq.</th>
</tr>
</thead>
<tbody>
<tr>
<td>wind power</td>
<td>kWh</td>
<td>electricity, high voltage/DE electricity production, wind, 1-3MW turbine, onshore</td>
<td>0.017</td>
</tr>
<tr>
<td>photovoltaic</td>
<td>kWh</td>
<td>electricity, low voltage/DE electricity production, photovoltaic, 570kWp open ground installation, multi-Si</td>
<td>0.095</td>
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<tr>
<td>current German grid mix</td>
<td>kWh</td>
<td>electricity, high voltage/DE market for electricity, high voltage</td>
<td>0.580</td>
</tr>
<tr>
<td>dionized water</td>
<td>kg</td>
<td>water, deionised/RoW market for water, deionised</td>
<td>0.000</td>
</tr>
<tr>
<td>methanol fossil state-of-the-art</td>
<td>kg</td>
<td>methanol/GLO market for methanol</td>
<td>0.625</td>
</tr>
<tr>
<td>ethylene fossil state-of-the-art</td>
<td>kg</td>
<td>ethylene, average/RER market for ethylene, average</td>
<td>1.396</td>
</tr>
<tr>
<td>methanol end-of-life</td>
<td>kg</td>
<td>own calculation</td>
<td>1.375</td>
</tr>
<tr>
<td>ethylene end-of-life</td>
<td>kg</td>
<td>own calculation</td>
<td>3.143</td>
</tr>
</tbody>
</table>

Table 2: Summary of background processes and their levelized costs.

<table>
<thead>
<tr>
<th>process</th>
<th>reference unit</th>
<th>database</th>
<th>levelized costs / USD</th>
</tr>
</thead>
<tbody>
<tr>
<td>wind power</td>
<td>kWh</td>
<td>IEA Levelized Costs of Electricity²</td>
<td>0.04</td>
</tr>
<tr>
<td>photovoltaic</td>
<td>kWh</td>
<td>IEA Levelized Costs of Electricity²</td>
<td>0.08</td>
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<tr>
<td>methanol fossil state-of-the-art</td>
<td>kg</td>
<td>Thomson Reuters, Global Data Petrochemical³</td>
<td>0.350</td>
</tr>
<tr>
<td>ethylene fossil state-of-the-art</td>
<td>kg</td>
<td>Thomson Reuters, Global Data Petrochemical³</td>
<td>0.800</td>
</tr>
</tbody>
</table>
2. Correlation CO₂ conversion and Current Density

Figure 1 shows the current status of eCO₂R development. The laboratory experiments are sorted by the current density on the horizontal axis and the single-pass CO₂ conversion on the vertical axis. Increasing current density correlates with increasing single-pass CO₂ conversion. Thus, with further development toward economically feasible current density⁴ of ≥ 300 mA/cm², we expect the CO₂ conversion to increase.

![Figure 1: Correlation of single-pass CO₂ conversion and current density in experimental studies. The marker size represents the current density.](image)
3. ECO$_2$R Model

The mass-specific electricity demand of the eCO$_2$R system is the sum of the energy demand from the electrochemical cell $w_{cell}$ and the separation duty $w_{SU}$ (cf. Eq. 1). The electricity demand of the cell depends on the cell voltage $U_{cell}$ and the faradaic efficiency $\eta_{FE}$ (cf. Eq. 2) since the electric current $I_{cell}$ can be expressed as a function of the faradaic efficiency (cf. Eq. 3). The Faradaic constant $F$ expresses the electric charge per mole of electrons. The product molecular weight $M_p$ and the required number of electrons $z_p$ are product-specific constants.

\[
w_{el} = w_{cell} + w_{SU} \tag{Eq. 1}
\]

\[
w_{cell} = \frac{P_{chem}}{\dot{m}_p} = \frac{U_{cell} \cdot I_{cell}}{\eta_{FE}} = \frac{U_{cell} \cdot z_p \cdot F}{\eta_{FE} \cdot M_p} \tag{Eq. 2}
\]

\[
I_{cell} = \frac{z_p \cdot F \cdot \dot{m}_p}{\eta_{FE} \cdot M_p} \tag{Eq. 3}
\]

---

**Figure 2**: Schematic Illustration of the eCO$_2$R model that allows calculating the electricity demand $P_{el}$, the required CO$_2$, and the required water per kg product (i.e., carbon monoxide (CO), methanol, or ethylene) depending on the variable parameters cell voltage, faradaic efficiency, and single-pass CO$_2$ conversion.
We assume all eCO$_2$R products to be gaseous under industrial operation temperature of 70-80 °C. Possible electrolyte and liquid product fractions are assumed to be recycled without further treatment or separation. This assumption defines a best-case since enrichment of liquid by-product fractions and pH drift can interfere with the eCO$_2$R process in alkaline electrolyzers.

The mass-specific separation duty $w_{SU}$ is estimated using the minimal thermodynamic demand based on mixing entropy and ideal gas law. The entropy of the mixed vapor outlet $\dot{S}_{vap}$ is higher than the entropy $\dot{S}_{sep}$ of the three separated streams: product stream (carbon monoxide, methanol, or ethylene), CO$_2$-recycle, and off-gases. Equation 4 determines the minimal amount of exergy required to overcome the second law of thermodynamics. $R$ defines the universal gas constant. $T$ refers to the ambient temperature of 25 °C.

$$w_{SU} = \frac{P_{SU}}{m_p} = \frac{1}{m_p} \cdot T \left( \dot{S}_{vap} - \dot{S}_{sep} \right)$$

$$w_{SU} = \frac{1}{m_p} \cdot RT \cdot \left[ -\sum_c \dot{n}_c^{vap} \ln(x_c^{vap}) + \sum_c \dot{n}_c^{sep} \ln(x_c^{sep}) \right] \quad \text{(Eq. 4)}$$

The vapor outlet flows $\dot{n}_c^{vap}$ and its composition $x_c^{vap}$ are a function of faradaic efficiency, CO$_2$ conversion, electric current, and the by-product distribution factor $d_{by}$. We do not consider gaseous water or electrolyte fractions in the outlet vapor. The product flow $\dot{n}_p^{vap}$ is determined by the faradaic efficiency and the electric current (cf. Eq. 5). The remaining electric current evolves in by-product formation $\dot{n}_p^{by}$ that is modeled by the distribution factor $d_{by}$ (cf. Eq. 6). We assume a commonly reported by-product distribution with 40 % of the remaining electric current contributing to H$_2$, 30 % to CO, 10 % to formate, 10 % to methane, and 10 % to ethylene.$^{12}$ If the main product is part of the by-product distribution, the by-product distribution is rescaled such that the by-products do not contain the main product. All by-products are regarded as waste and are released into the environment at fully oxidized state (off-gases). We do not consider heat integration from the oxidation of by-products. The
amount of unreacted CO$_2$ in the vapor outlet $\dot{n}^\text{vap}_{\text{CO}_2}$ can be calculated based on the required CO$_2$ flow $\dot{n}^\text{required}_{\text{CO}_2}$ and the CO$_2$ conversion $C_{\text{conv}}$ (cf. Eq. 7 & 8).

\[
\dot{n}^\text{vap}_{\text{p}} = \frac{\eta_{\text{FE}_P} \cdot I}{z_p \cdot F} \quad \text{(Eq. 5)}
\]

\[
\dot{n}^\text{vap}_{\text{by}} = \frac{d_{\text{by}} \cdot (1 - \eta_{\text{FE}_P}) \cdot I}{z_{\text{by}} \cdot F} \quad \text{(Eq. 6)}
\]

\[
\dot{n}_{\text{CO}_2\text{inlet}} = \dot{n}^\text{required}_{\text{CO}_2} + \dot{n}^\text{recycle}_{\text{CO}_2} = \dot{n}^\text{required}_{\text{CO}_2} + \dot{n}^\text{vap}_{\text{CO}_2} \quad \text{(Eq. 7)}
\]

\[
\dot{n}^\text{vap}_{\text{CO}_2} = \dot{n}_{\text{CO}_2\text{inlet}} (1 - C_{\text{conv}}) = \frac{\dot{n}^\text{required}_{\text{CO}_2} (1 - C_{\text{conv}})}{C_{\text{conv}}} \quad \text{(Eq. 8)}
\]

The required input flows carbon dioxide $\dot{n}^\text{required}_{\text{CO}_2}$ and water $\dot{n}^\text{required}_{\text{H}_2\text{O}}$ are calculated based on stoichiometry (cf. Eq. 9 & 10).

\[
\dot{n}^\text{required}_{\text{CO}_2} = \sum_c \frac{v_{\text{CO}_2}}{v_c} \dot{n}_c \quad \text{(Eq. 9)}
\]

\[
\dot{n}^\text{required}_{\text{H}_2\text{O}} = \sum_c \frac{v_{\text{H}_2\text{O}}}{v_c} \dot{n}_c \quad \text{(Eq. 10)}
\]

The equation system is illustrated in Figure 3. The key operating parameters are colored in green, while the orange-colored parameters refer to the eCO2R exchange flows with the chemical background system.
Figure 3: Schematic illustration of the equation system of the eCO₂R model. \( U_{\text{cell}} \): cell voltage, \( \eta_{FE_P} \): faradaic efficiency toward the main product, \( C_{\text{conv}} \): CO₂ single-pass conversion, \( w_{\text{cell}} \): product-specific electricity demand of the electrochemical cell, \( w_{SU} \): product-specific electricity demand of separation unit, \( n_{\text{CO}_2}^{\text{required}} \): required carbon dioxide input flow, \( n_{H_2O}^{\text{required}} \): required water input flow, \( d_{by} \): distribution factor of by-products, \( \dot{n}_p^{\text{vap}} \): molar product flow in the vapor outlet, \( \dot{n}_p^{\text{by}} \): molar by-product flows in the vapor outlet, \( \dot{n}_{\text{CO}_2}^{\text{vap}} \): molar flow of unreacted carbon dioxide in the vapor outlet, \( x_p^{\text{vap}} \): molar composition of the vapor outlet, \( x_p^{\text{sep}} \): molar composition of the separated flows, \( S_v^{\text{vap}} \): entropy of the vapor outlet, \( S_s^{\text{sep}} \): entropy of the separated flows).
4. Development requirements for non-ideal separation

Figure 4 shows the effect of non-ideal separation on the development requirements. Figure 4A represents the minimum development requirements when using an ideal separation unit. Figure 4B illustrates the development requirements for a separation unit that requires 10 times the energy of an ideal separation unit. The development requirements are 6% more ambitious for the faradaic efficiency (from 57.9% to 61.3%) and 2% more ambitious for the cell voltage (from 2.53 V to 2.49 V). Figure 4C shows the development requirements if the separation unit requires 100 times the ideal energy for separation. This results in 44% more ambitious development requirements for the faradaic efficiency (from 57.9% to 83.4%) and 16% for the cell voltage (from 2.53 V to 2.12 V). The sensitivity analysis shows that inefficient separation processes increase the development requirements for eCO$_2$R toward low cell voltages and high faradaic efficiencies. Since a study on CO$_2$ sources$^{13}$ reports that the separation units require between 1.5 and 9 times the ideal separation duty, Figure 4B shows reasonable development requirements for eCO$_2$R to ethylene.
5. Economic Feasibility

Next to climate benefits, the eCO$_2$R pathways could yield economic gains over the H$_2$-based pathways. The one-step conversion of the direct eCO$_2$R to MeOH pathway and the direct eCO$_2$R to ethylene pathway offer reduced plant complexity and geographical independence from chemical production sites for pre- and post-processing. Furthermore, the omission of PEM electrolysis provides potential capital investment savings by using less expensive catalysts for eCO$_2$R than the noble metals for PEM electrolysis. However, given the different catalysts used for eCO$_2$R and divers cell construction types, a detailed techno-economic assessment remains uncertain and is out of the scope of this study.
In our study, we calculate operating expenditures (OPEX) to illustrate a preliminary techno-economic assessment. Table 3 shows the OPEX per kilogram chemical using wind power with 0.04 USD/kWh. Both the H$_2$-based pathways and the eCO$_2$R pathways refer to similar costs and depend highly on electricity costs. The comparison to the fossil-based state-of-the-art technologies shows that power-to-chemicals are almost always more expensive. Currently available H$_2$-based pathways increase the OPEX by 60-73 %, while best-case H$_2$-based pathways, operating at equilibrium voltage and 100 % faradaic efficiency, increase the OPEX by only 13-23 %. The best-case eCO$_2$R pathways range from a -4 % cost reduction to a 54 % cost increase. A detailed techno-economic assessment will further clarify the prospect of eCO$_2$R and can be the object of future work when higher technology readiness levels are achieved. A detailed assessment should also consider environmental policies, e.g., CO$_2$ taxes or emission trading schemes, which can render power-to-chemical pathways more competitive over the CO$_2$-intensive fossil routes.

Table 3: Comparison of OPEX per kilogram chemical of the fossil-based state-of-the-art technologies, the H$_2$-based pathways, and the eCO$_2$R pathways (in US Dollar/ton). Best-case implicates operation at equilibrium potential and 100 % faradaic efficiency. The relative reduction potentials refer to the fossil-based state-of-the-art.

<table>
<thead>
<tr>
<th>OPEX</th>
<th>Fossil state of the art$^1$</th>
<th>Wind-powered power-to-chemicals</th>
<th>H$_2$-based (Ref)</th>
<th>H$_2$-based (best-case)</th>
<th>best-case eCO$_2$R to CO (a)</th>
<th>best-case eCO$_2$R to methanol (b)</th>
<th>best-case eCO$_2$R to ethylene (c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>methanol (1)</td>
<td>350 USD/t</td>
<td>560 USD/t (+60 %)</td>
<td>395 USD/t (+13 %)</td>
<td>494 USD/t (+41 %)</td>
<td>346 USD/t (-1 %)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ethylene (2)</td>
<td>800 USD/t</td>
<td>1,386 USD/t (+73 %)</td>
<td>986 USD/t (+23 %)</td>
<td>1,228 USD/t (+54 %)</td>
<td>863 USD/t (+7 %)</td>
<td>772 USD/t (-4 %)</td>
<td></td>
</tr>
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</table>
References


