

# **Supporting Information for Techno-Economic Analysis of Electrocatalytic CO<sub>2</sub> Reduction into Methanol: A Comparative Study between Alkaline Flow Cell and Neutral Membrane Electrode Assembly**

**Ke Wang <sup>1</sup>, Tongxin Qu <sup>2</sup>, Qiang Li <sup>2</sup>, Shuting Tan <sup>2</sup> and Xiaoxiang Chen <sup>1,\*</sup>**

<sup>1</sup> College of Environmental Engineering, Wuhan Textile University, 1 Sunshine Avenue,  
Wuhan 430200, China; kewang0430@163.com

<sup>2</sup> State Key Laboratory of Coal Combustion, School of Energy and Power Engineering,  
Huazhong University of Science and Technology, Wuhan 430074, China; qutongx@163.com  
(T.Q.);

hustliqiang@hust.edu.cn (Q.L.); hust71324@163.com (S.T.)

\* Correspondence: xxchen@wtu.edu.cn

Through reading and querying a large number of the relevant literature,<sup>[1-4]</sup> we simulated and found a suitable TEA model and showed methanol production costs by calculating the costs of each part, including CO<sub>2</sub> and H<sub>2</sub>O input costs, electrolytic cell costs, catalyst and membrane costs, electricity costs, other operating costs, anode separation costs, distillation costs, PSA separation costs, and calcium-alkali recovery-cycle cathode costs. The cost of anode separation only exists in MEA electrolytic cells; the cost of the thermal calcium-alkali recovery cycle is also unique to alkaline flow electrolyzer. We use the data in Table S1 below<sup>[5-8]</sup>:

**Table S1.** Invariable inputs data for neutral MEA cell and alkaline flow cell.

Lists of parameters	
Parameters	Value
Production rate (tonne CH <sub>3</sub> OH/day)	100
CO <sub>2</sub> cost (USD/tonne)	30
Electricity cost (USD/kWh)	0.02
Electrolyzer unit- price (USD/kW)	450
Balance of plant (%)	50
Catalyst/membrane lifetime (year)	5
Discount rate (%)	7
Electrolyte	0.1 mol/L KHCO <sub>3</sub>
Electrolyte cost (USD/tonne)	750
Electrolyte lifetime (years)	1
H <sub>2</sub> O price (USD/tonne)	0.6
Lang factor	1
Methanol density (kg/m <sup>3</sup> )	791

First, the amount of input CO<sub>2</sub> required to produce 100 tonnes of methanol is calculated, assuming no losses. This is purchased at the beginning of each operational day of the plant, and any CO<sub>2</sub> that is lost along the way (due to reaction with carbonate or simply unreacted) is separated and recycled back to the cathode input to be reduced

again.

The annual production is expressed in P tonnes/year, and the daily production is expressed in P1 tonnes/year. Assuming 350 days of work per year (two weeks for equipment maintenance),  $P1 = 100$  tonnes/day.

Capital recovery factor:  $CRF = i(1 + i)^{lifetime}/(1 + i)^{lifetime} - 1$ . All calculated discount rates are taken as  $i=7\%$ . Assuming the service life of the electrolytic cell system is 20 years,  $CRF1 = \frac{0.07(1+0.07)^{20}}{(1+0.07)^{20}-1} = 0.094393$ . Assuming the service life of the electrolyte is 1 year,  $CRF2 = 1.070000$ . Assuming a catalyst and membrane service life of 5 years,  $CRF3 = 0.243891$ .

## 1. Input of CO<sub>2</sub> and H<sub>2</sub>O

### 1.1 H<sub>2</sub>O amount carried by cathode CO<sub>2</sub>

In the MEA electrolytic cell, CO<sub>2</sub> carrying H<sub>2</sub>O is introduced. Assuming a room temperature of 25 °C, the CO<sub>2</sub>/H<sub>2</sub>O ratio is 30.96 vol./vol. CO<sub>2</sub> enters the cathode and is divided into three parts: (1) reduced CO<sub>2</sub>; (2) unreacted CO<sub>2</sub>; and (3) CO<sub>2</sub> transferred to the anode through an ion-exchange membrane.

(1) The calculation equation for the reduced CO<sub>2</sub> ( $n_1$ ) is as follows:

$$n_1 = \frac{CO_2 \text{ daily consumption(g/day)}}{CO_2 \text{ molecular weight(g/mol)}} \quad (1a)$$

where  $n_1 = 3125000$  (mol).

(2) The calculation equation for the unreacted CO<sub>2</sub> ( $n_2$ ) is as follows:

$$\text{single-pass conversion} = \frac{\text{Reduced } CO_2}{\text{Unreacted } CO_2 + \text{Reduced } CO_2} \quad (1b)$$

As a result, the unreacted CO<sub>2</sub> can be denoted as follows:

$$\begin{aligned}
\text{Unreacted CO}_2 &= \frac{\text{Reduced CO}_2}{\text{single-pass conversion}} - \text{Reduced CO}_2 \\
&= \frac{137.5 \text{ tonne/day}}{\text{single-pass conversion}} - 137.5 \text{ (tonne/day)} \\
n_2 &= 22727.27 \left( \frac{137.5}{\text{single-pass conversion}} - 137.5 \right) (\text{mol})
\end{aligned}$$

(3) CO<sub>2</sub> crossover from cathode to anode (n<sub>3</sub>) is calculated as follows:

$$\text{Crossover Ratio} = \frac{\text{CO}_2 \text{ crossover from cathode to anode}}{\text{Reduced CO}_2} \quad (1c)$$

n<sub>3</sub> = Reduced CO<sub>2</sub> × Crossover Ratio (C) = 137.5C tonnes/day, where

$$n_3 = \frac{137.5 \text{C tonne/day}}{44 \text{g/mol}} \times \frac{10^6 \text{g}}{1 \text{tonne}} = 3125000C (\text{mol/day}).$$

In particular, total CO<sub>2</sub> at the cathode inlet can be defined as:

$$n_{\text{总}} = n_1 + n_2 + n_3 = 3125000(1+C) + 22727.27 \left( \frac{137.5}{\text{single-pass conversion}} - 137.5 \right) (\text{mol})$$

because  $\frac{\text{CO}_2 \text{ pressure}}{\text{H}_2\text{O pressure}} = 30.96$ . Then, the amount of H<sub>2</sub>O carried by the cathode inlet

every year can be understood as follows:  $100936.69C + \frac{100936.69}{\text{single-pass conversion}} (\text{mol})$ .

Additionally, the cathode outlet water-flow rate can be calculated as follows:

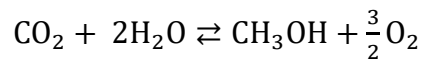
$1.2617C + \frac{1.2617}{\text{single-pass conversion}} (\text{L/min})$ ; the cathode outlet methanol flow rate is equal to

87.79L/min; and the cathode outlet methanol-solution flow rate should be defined as

follows:  $1.2617C + \frac{1.2617}{\text{single-pass conversion}} + 87.79 (\text{L/min})$ .

## 1.2 Input of CO<sub>2</sub>

The total reaction formula can be regulated as follows:



Subsequently, the daily CO<sub>2</sub> consumption (ton/day) should be arranged as follows:

$$\begin{aligned}
& \text{Consumption of CO}_2 \\
&= \frac{M(\text{CO}_2) \left( \frac{\text{g}}{\text{mol}} \right)}{M(\text{CH}_3\text{OH}) \left( \frac{\text{g}}{\text{mol}} \right)} \times \text{Daily methanol productin} \left( \frac{\text{tonne}}{\text{day}} \right) \\
&= \frac{137.5 \text{ tonne}}{\text{day}}
\end{aligned} \tag{2a}$$

The daily H<sub>2</sub>O consumption (tonne/day) should be the sum of the theoretical daily consumption of H<sub>2</sub>O- and CO<sub>2</sub>-carrying capacity.

As a result, the theoretical daily consumption of H<sub>2</sub>O can be arranged as follows:

$$\begin{aligned}
& \text{Consumption of H}_2\text{O} \\
&= \frac{\text{H}_2\text{O molecular} \frac{\text{g}}{\text{mol}}}{\text{CH}_3\text{OH molecular} \frac{\text{g}}{\text{mol}}} \times \text{Daily methanol production} \times 2 \\
&= 225 \frac{\text{tonne}}{\text{day}}
\end{aligned} \tag{2b}$$

In Eq. (2b), CO<sub>2</sub>-carrying capacity can be defined as:  $\left( \frac{137.5}{\text{single-pass conversion}} + 137.5C \right)$  tonne/day. Daily H<sub>2</sub>O consumption (tonne/day) can be defined as:  $225 \text{ tonne/day} + \left( \frac{137.5}{\text{single-pass conversion}} + 137.5C \right)$  tonne/day. We assume the CO<sub>2</sub> price is 30 USD/tonne and H<sub>2</sub>O price is 0.6 USD/tonne. Then, the cost of input CO<sub>2</sub> is equal to  $\text{CO}_2 \text{ price} \times 137.5 \text{ tonne/day} \times \frac{1}{100 \text{ tonne CH}_3\text{OH/day}} = 41.25 \left( \frac{\$}{\text{tonne methanol}} \right)$ . In addition, the input H<sub>2</sub>O is equal to:

$$\begin{aligned}
& \text{H}_2\text{O price} \times \left( 225 + \left( \frac{137.5}{\text{single-pass conversion}} + 137.5C \right) \right) \text{ tonne/day} \times \frac{1}{100 \text{ tonne CH}_3\text{OH/day}} = 0.35 \\
& + \left( \frac{0.825}{\text{single-pass conversion}} + 0.825C \right) \left( \frac{\$}{\text{tonne methanol}} \right).
\end{aligned}$$

**2. Capital Cost of Electrolyzer** (The price of the electrolyzer body used is 450USD /kW,<sup>[9]</sup> with a reference current density of 400 mA/cm<sup>2</sup>)

The one-time capital cost of the electrolytic cell in USD can be defined as follows:

$$\frac{\text{Electrolytic cell cost } \frac{\$}{\text{kW}} \times \text{Electrolytic cell power (kW)} \times \text{Reference current density } \left( \frac{\text{mA}}{\text{cm}^2} \right)}{\text{Electrolytic cell current density } \left( \frac{\text{mA}}{\text{cm}^2} \right)} \quad (3a)$$

Furthermore, the electrolyzer power (kw)=

$$\text{Electrolyzer current (A)} \times \text{Electrolyzer voltage (V)} \quad (3b)$$

$$\text{Electrolyzer current (A)} =$$

$$\frac{\text{Methanol yield } \left( \frac{\text{mol}}{\text{s}} \right) \times \text{electrons transferred} \times \text{Farada's constant } \left( \frac{\text{sA}}{\text{mol}} \right)}{\text{FE}} \quad (3c)$$

The capital cost per unit mass methanol electrolyzer  $\left( \frac{\$}{\text{tonne methanol}} \right)$  can be arranged as follows:

$$\frac{\text{CRF1} \times \text{One time investment cost of electrolyzer (\$)}}{\text{Annual methanol production } P \left[ \frac{\text{tonne}}{\text{year}} \right]} \quad (3d)$$

Taking into account the known amount of CRF1=0.094393, annual methanol production P = 35000 tonnes/year, Faraday constant F = 96485

sA/mol, and methanol yield is 36.17 mol/s.

The capital cost of the electrolyzer ( $\frac{\$}{\text{tonne methanol}}$ ) can be regulated as follows:

$$= \frac{0.094393}{35000 \text{ tonne/year}} \times \frac{450 \frac{\$}{\text{kW}} \times \frac{36.17 \frac{\text{mol}}{\text{s}} \times 6 \times 96485 \frac{\text{sA}}{\text{mol}} \times U[V]}{\text{FE} \times 1000 \frac{\text{J}}{\text{cm}^2}} \times 400 \frac{\text{mA}}{\text{cm}^2}}{10164.92 \frac{U}{\text{FE} \times J} \left( \frac{\$}{\text{tonne methanol}} \right)}$$

3. **Catalyst and membrane** (assuming 5% of the one-time capital cost of the electrolyzer)

The mass methanol catalyst and membrane cost ( $\frac{\$}{\text{tonne methanol}}$ ) is defined as follows:

$$\frac{\text{One time capital cost of electrolyzer}(\$) \times 5\% \times \text{CRF3}}{P} = 1313.20 \frac{U}{\text{FE} \times J} \left( \frac{\$}{\text{tonne methanol}} \right) \quad (4a)$$

#### 4. Electricity Cost

The unit mass methanol electricity cost ( $\frac{\$}{\text{tonne methanol}}$ ) can be calculated using Eq. (5a).

Electricity cost

$$= \frac{\text{Electrolytic cell power(kw)} \times \frac{24 \text{ hours}}{\text{day}} \times \text{electricity price}}{P1} = 5025.40 \frac{U \times \text{electricity price}}{\text{FE}} \left( \frac{\$}{\text{tonne methanol}} \right) \quad (5a)$$

**5. Other operating costs** (considering additional costs, such as repairing and a 10% increase in labor costs for electricity)

Other operating costs per unit of methanol can be written as follows:

$$\begin{aligned} & \text{Electricity cost} \times 10\% \\ & = 502.54 \frac{U \times \text{electricity price} \left( \frac{\$}{\text{tonne methanol}} \right)}{FE} \end{aligned} \quad (5b)$$

**6. Anode separation** (only for MEA cell, cross ratio expressed in C)

The unit methanol anode separation cost can be written as follows:

$$\begin{aligned} & \frac{\text{CO}_2 \text{ molecular weight} \left( \frac{\text{g}}{\text{mol}} \right)}{\text{CH}_3\text{OH molecular weight} \left( \frac{\text{g}}{\text{mol}} \right)} \times \text{molar ratio} \times \text{crossover ratio} \times \text{CO}_2 \text{ cost} \\ & = 41.25C \left( \frac{\$}{\text{tonne methanol}} \right) \end{aligned} \quad (7a)$$

**7. Electrolyte cost** (for neutral MEA). Assuming the anolyte is 0.1mol/L KHCO<sub>3</sub>, its price is 750 USD/tonne, and the water price is the same as above at 0.6 USD/tonne. For alkaline flow cells, assuming a catholyte of 7mol/L KOH, the price cost is 1000USD /tonne.

$$\text{Anolyte cost per tonne of methanol} = \frac{\text{Cost of anolyte} \times \text{CRF}_2}{P} \quad (8a)$$

where anolyte cost = KHCO<sub>3</sub> cost + H<sub>2</sub>O cost; KHCO<sub>3</sub> cost = KHCO<sub>3</sub> amount × 750 USD/tonne; H<sub>2</sub>O cost = H<sub>2</sub>O amount × H<sub>2</sub>O price, KHCO<sub>3</sub> amount = total volume of electrolyte × 0.1 mol/L × KHCO<sub>3</sub> molar mass; and H<sub>2</sub>O mass = total volume of electrolyte × H<sub>2</sub>O density.

The electrolytic cell area (S) is written as follows:



$$S = \frac{\text{Electrolytic cell current [mA]}}{\left(\frac{100\text{cm}}{1\text{m}}\right)^2 \times J \text{ (mA/cm}^2\text{)}} \quad (8b)$$

$$= \frac{2093917.47}{FE \times J} \text{ (m}^2\text{)}$$

By using a fixed volume ratio of 100 liters of electrolyte per square meter of electrolytic cell, the total volume of electrolyte = Electrolytic cell area (m<sup>2</sup>) × 100 L/m<sup>2</sup>

$$= \frac{209391747}{FE \times J} \text{ (L)}$$

$$\text{The total mass of KHCO}_3\text{(g)} = 0.1 \frac{\text{mol}}{\text{L}} \times 100 \frac{\text{g}}{\text{mol}} \times \frac{209391747}{FE \times J} \text{ L} = \frac{2093917470}{FE \times J} \text{ (g)}$$

$$\text{KHCO}_3 \text{ cost (USD)} = \text{KHCO}_3 \text{ quality (g)} \times \frac{1 \text{ tonne}}{10^6 \text{ g}} \times 750 \frac{\$}{\text{tonne}} = \frac{1570438.10}{FE \times J} \text{ (\$)}$$

$$\text{Total mass of H}_2\text{O (g)} = \text{Total volume of electrolyte (L)} \times 1 \text{ kg/L}$$

$$= \frac{209391747}{FE \times J} \text{ (kg)}$$

The H<sub>2</sub>O cost is equal to

$$\text{H}_2\text{O quality (kg)} \times \text{H}_2\text{O cost (\$)}$$

$$= \frac{125635.05}{FE \times J} \text{ \$}$$

The electrolyte cost per tonne of methanol equals

$$\text{cost of electrolyte} = \frac{\text{Cost of anode solution} \times \text{CRF2}}{P}$$

$$= \frac{51.85}{FE \times J} \left( \frac{\$}{\text{tonne methanol}} \right)$$

Similar to the anolyte, the catholyte cost per tonne of methanol is as follows:

$$\frac{\text{Cost of catholyte} \times \text{CRF2}}{P}$$

$$= \frac{2513.19}{FE \times J} \left( \frac{\$}{\text{tonne methanol}} \right)$$

## 8. Cathode separation

**8.1 Distillation tower separation** (separating methanol from methanol solution).

The separation processes were modeled using the RadFrac block in Aspen Plus, and capital and utility costs were estimated using the Aspen

Plus Economic Analyzer<sup>[10]</sup>. Distillation separation was modeled as a single-column system, and the concentration of CH<sub>3</sub>OH in the products was 95 wt.% after distillation. Assuming the reference capital cost in Aspen is USD 4162240, the electrolyte flow rate is 1000L/min, and the operating cost is 9895 USD/day.

The methanol solution flow rate at the cathode is equal to  $1.26C + \frac{1.26}{\text{single-pass conversion}} + 87.79$  (L/min)

The capital cost of distillation is calculated by converting the reference cost calculated in Aspen into the volumetric flow rate of the electrolyte. Thus, the capital cost of distillation tower is as follows:

$$4162240\$ \times \left( \frac{1.26C + \frac{1.26}{\text{single-pass conversion}} + 87.79 \left( \frac{\text{L}}{\text{min}} \right)}{\frac{1000 \text{ L}}{\text{min}}} \right)^{0.7} \quad (9a)$$

We assume that the service life of the distillation tower is the same as that of the electrolytic cell for 20 years, and the capital cost per tonne of methanol is as follows:

$$\frac{\text{CRF}_1 \times \text{Capital cost}(\text{精馏})}{P} \quad (9b)$$

The capital cost of distillation tower is written as:

$$\frac{0.094393 \times 4162240\$ \times \left( \frac{1.26C + \frac{1.26}{\text{single-pass conversion}} + 87.79 \text{ (L/min)}}{1000 \text{ L/min}} \right)^{0.7}}{35000 \text{ tonne}}$$

Then, the operating cost of distillation is calculated by scaling the reference cost to the flow rate, which can be defined as follows:

$$\begin{aligned}
&= \left( \frac{1.26C + \frac{1.26}{\text{single-pass conversion}} + 87.79 \left( \frac{\text{L}}{\text{min}} \right)}{1000 \text{L/min}} \right) \times 9895 \$/\text{day} \\
&= 9.9 \left( 1.26C + \frac{1.26}{\text{single-pass conversion}} + 87.79 \right) \$/\text{day}
\end{aligned}$$

The operating cost per tonne of methanol is equal to

$$0.12C + \frac{0.12}{\text{single-pass conversion}} + 8.69 \left( \frac{\$}{\text{tonne methanol}} \right)$$

.

## 8.2 PSA separation (separation of CO<sub>2</sub> and H<sub>2</sub>)

A model was used to calculate these costs, which describes the capital and operating costs of the PSA system used for biogas upgrading. The model adopts a flow capacity of 1000 m<sup>3</sup>/h, a proportional coefficient of 0.7, an energy consumption of 0.25 kW/m<sup>3</sup>, and a reference cost of USD 1989043.<sup>[11]</sup> Capital and operating costs can be written as:

$$\text{The PSA capital cost} = 1989043 \$ \times \left( \frac{\text{flow rate}}{1000} \right)^{0.7} \quad (9c)$$

The PSA operating cost equals to:

$$\text{energy consumption} \times \text{flow rate} \times \frac{24 \text{ hours}}{\text{day}} \times \text{electricity price} \quad (9d)$$

Then, the total flow rate at the cathode outlet = CO<sub>2</sub> flow rate + H<sub>2</sub> flow rate.

We then calculate the flow rate of carbon dioxide flowing out of the cathode through one-way conversion and assuming constant pressure:

$$\frac{\text{CH}_3\text{OH flow rate} \times \text{molar ratio}}{\text{single-pass conversion}} \times (100 - \text{single pass conversion}) \quad (9e)$$

Substituting known quantities:

$$\text{CO}_2 \text{ flow rate} = \frac{36.17 \text{ mol/s} \times 1}{\text{single-pass conversion}} \times (100\text{-single pass conversion})$$

$$= \frac{36.17 (100\text{-single pass conversion})}{\text{single pass conversion}} \text{ (mol/s)}$$

It can also be seen from the state equation of ideal gas that the volume of 1mol CO<sub>2</sub> in standard state is 22.4L, and the flow rate of CO<sub>2</sub> can be defined as follows:

$$\text{CO}_2 \text{ flow rate} = \frac{2916.76 (100\text{-single pass conversion})}{\text{single pass conversion}} \text{ (m}^3\text{/hour)}$$

H<sub>2</sub> yield is equal to:

$$\frac{I(\text{H}_2) \times \frac{3600 \text{ s}}{\text{hour}}}{\text{electrons transferred}(\text{H}_2) \times F} \quad (9f)$$

$$I(\text{H}_2) = \text{Electrolytic cell current} \times \frac{100\text{-FE}}{100} = 209391.75 \frac{100\text{-FE}}{\text{FE}} \text{ A}$$

$$\text{H}_2 \text{ yield} = \frac{I(\text{H}_2) \times 3600 \text{ s/hour}}{\text{electrons transferred}(\text{H}_2) \times F} = 3906.36 \frac{100\text{-FE}}{\text{FE}} \text{ (mol/hour)}$$

$$\text{H}_2 \text{ flow rate} = 3906.36 \times \frac{100\text{-FE}}{\text{FE}} \text{ (mol/hour)} \times 22.4 \text{ L/mol} = 87502.46 \frac{100\text{-FE}}{\text{FE}} \text{ (m}^3\text{/hour)}$$

$$\text{Cathode outlet flow rate} = \text{CO}_2 \text{ flow rate} + \text{H}_2 \text{ flow rate}$$

$$= \frac{2916.76 (100\text{-single pass conversion})}{\text{single pass conversion}} + 87502.46 \times \frac{100\text{-FE}}{\text{FE}} \text{ (m}^3\text{/hour)}$$

PSA capital cost equation

$$= 1989043 \times \left( \frac{2.92 (100\text{-single pass conversion})}{\text{single pass conversion}} + 87.50 \times \frac{100\text{-FE}}{\text{FE}} \right)^{0.7} (\$)$$

The capital cost per tonne of methanol can be expressed by assuming that the PSA life is the same as that of the electrolytic cell life (20 years), then the PSA capital cost per tonne of methanol is equal to (PSA capital cost  $\times$  CRF)/Annual Methanol Production=

$$1989043 \times \left( \frac{2.92(100 - \text{single pass conversion})}{\text{single pass conversion}} + 87.50 \times \frac{100 - \text{FE}}{\text{FE}} \right)^{0.7} \times \text{CRF} / 35000 \text{ (tonne/year)}$$

Based on Eq. (9d), the PSA operating cost per tonne of methanol equals:

$$\left( \frac{175.00 \times (100 - \text{single pass conversion})}{\text{single pass conversion}} \right) + 5250.14 \times \frac{100 - \text{FE}}{\text{FE}} \times \text{electricity price} \left( \frac{\$}{\text{tonne methanol}} \right)$$

**9. Balance of Plant (BoP) and installation costs** (assuming BoP balance of 50% and Lang coefficient of 1)

This section scales all capital costs to estimate the price of the peripheral equipment around the electrolyzer and separation units. All capital costs were measured, including the sum of costs for electrolytic cells, membranes and catalysts, cathode separation, and anode separation. (Note: Because we do not know the breakdown of operating and capital costs for anode separation costs, we assume that half comes from operating costs and half comes from capital costs.)

Total Capital Costs

$$\begin{aligned} &= \left( 11478.12 \frac{U}{\text{FE} \times J} \left( \frac{\$}{\text{tonne methanol}} \right) \right. \\ &+ 11.23 \left( \frac{1.26C + \frac{1.26}{\text{single} - \text{pass conversion}} + 87.79 \text{ (L/min)}}{1000 \text{ L/min}} \right)^{0.7} \\ &+ 1989043 \left( \frac{2.92 (100 - \text{single} - \text{pass conversion})}{\text{single} - \text{pass conversion}} \right. \\ &\left. + 87.50 \frac{100 - \text{FE}}{\text{FE}} \right)^{0.7} + \frac{41.25C}{2} \left( \frac{\$}{\text{tonne methanol}} \right) \end{aligned}$$

The capital cost of balance of plant:

$$\begin{aligned} &\text{Capital cost of BoP} = \text{BoP Factor} \times \text{Total Capital Costs (10a)} : \\ &= 5739.06 \frac{U}{\text{FE} \times J} + 994521.5 \times \left( \frac{2.92(100 - \text{single pass conversion})}{1000 \text{ single pass conversion}} + 87.50 \frac{100 - \text{FE}}{\text{FE}} \right)^{0.7} \\ &+ 5.6 \left( \frac{1.26C + \frac{1.26}{\text{single pass conversion}} + 87.79 \left( \frac{\text{L}}{\text{min}} \right)}{1000 \text{ L/min}} \right)^{0.7} + 10.31C \left( \frac{\$}{\text{tonne methanol}} \right) \end{aligned}$$

The installation cost=Lang Factor × Total Capital Costs

$$\begin{aligned}
 &= (10164.92 + 1313.20) \frac{U}{FE \times J} \left( \frac{\$}{\text{tonne methanol}} \right) \\
 &+ 11.23 \left( \frac{1.26C + \frac{1.26}{\text{single pass conversion}} + 87.79 \text{ (L/min)}}{1000 \text{ L/min}} \right)^{0.7} \\
 &+ 1989043 \times \left( \frac{2.92(100 - \text{single pass conversion})}{\text{single pass conversion}} + 87.50 \frac{100 - FE}{FE} \right)^{0.7} \\
 &\quad + \frac{41.25C}{2} \left( \frac{\$}{\text{tonne methanol}} \right) \times 1
 \end{aligned} \tag{10b}$$

#### 10. Carbonate regeneration (only for alkaline-flow-cell electrolyzer)

For the alkaline flow cell, CO<sub>2</sub> that is lost to carbonate does not bubble out of the electrolyte like the neutral MEA, but rather it remains in solution. In order to recover the CO<sub>2</sub> and electrolyte that is lost during this process, we use energy requirements from a model built in Aspen Plus for a calcium caustic loop.<sup>[12,13]</sup> The modelled loop consists of three steps: a pellet reactor, calciner, and slaker.

These steps consume 27 kWh/tonne CO<sub>2</sub>, 4.05 GJ/tonne CO<sub>2</sub>, and 77 kWh/tonne CO<sub>2</sub>, respectively, and all together this system uses 1229 kWh/tonne CO<sub>2</sub>. By assuming that 24 CO<sub>2</sub> molecules are lost to carbonate for every molecule of CO<sub>2</sub> that is reduced to ethylene, we can find the cost of regenerating CO<sub>2</sub> and electrolyte as follows:

$$\begin{aligned}
 &\text{Reduced CO}_2 \text{ (tonne)} \\
 &= \frac{P1 \times \text{mole ratio} \times \text{CO}_2 \text{ molecular weight}}{\text{CH}_3\text{OH molecular weight}} \\
 &= 137.5 \text{ tonne/day}
 \end{aligned} \tag{11a}$$

CO<sub>2</sub> lost to KOH = 137.5T tonne/day,

T represents the carbonate formation rate

We can find the required energy as follows:

$$\begin{aligned}\text{Energy required (kWh)} &= \text{CO}_2 \text{ lost to KOH(tonne)} \times 1229 \text{ kWh/tonne CO}_2 \\ &= 168987.5 \text{ T kWh/day}\end{aligned}$$

Multiplying by the electricity price and dividing by the daily methanol production rate:

$$\begin{aligned}\text{Operating cost} &= \frac{168987.5 \text{ T kWh/day} \times \text{electricity price}}{P1} \\ &= 1689.88 \text{ T} \times \text{electricity price} \left( \frac{\$}{\text{tonne methanol}} \right)\end{aligned}\quad (11b)$$

We use a similar plant-scaling model as above to find capital costs for this system. By summing all equipment costs (except for the air contractor), we obtain a total capital cost of USD 232900000 for a plant with a capacity of 0.98 megatons CO<sub>2</sub> per year. We scale this one-time cost using:

$$\begin{aligned}\text{Capital cost (USD)} &= \text{Reference cost}(\$) \times \left( \frac{\text{CO}_2 \text{ to regenerate} \left( \frac{\text{tonne CO}_2}{\text{year}} \right)}{\text{Ref Plant Capacity} \left( \frac{\text{tonne CO}_2}{\text{year}} \right)} \right)^{0.7}\end{aligned}\quad (11c)$$

It is useful to note that the scaling factor of 0.7 used here, as well as for our cathode separation unit, is a commonly accepted factor when information about plant scaling is unknown. To find the amount of CO<sub>2</sub> that must be recovered for our system:

$$\begin{aligned}\text{CO}_2 \text{ to regenerate} \left( \frac{\text{tonne CO}_2}{\text{year}} \right) &= \frac{\text{molecular weight CO}_2 (\text{g/mol})}{\text{molecular weight CH}_3\text{OH} (\text{g/mol})} \times \text{molar ratio} \times T \times 350 \text{ day/year} \times 100 \text{ tonne/day} \\ &= 48125 \text{ T} \left( \frac{\text{tonne CO}_2}{\text{year}} \right)\end{aligned}$$

Substitute (11c), now we can find our total capital costs:

$$\text{Capital cost (USD)} = 232900000 \times (0.05T)^{0.7}$$

We can turn this one-time cost into a cost per tonne of methanol,

$$\begin{aligned} & \text{Capital cost} \left( \frac{\$}{\text{tonne methanol}} \right) \\ &= \frac{\text{CRF1} \times \text{One-time capital cost}}{P} \\ &= 628.12(0.05T)^{0.7} \left( \frac{\$}{\text{tonne methanol}} \right) \end{aligned} \quad (11d)$$

## References

- [1] Sisler, J.; Khan, S.; Ip, A.H.; Schreiber, M.W.; Jaffer, S.A.; Bobicki, E.R.; Dinh, C.T.; Sargent, E.H. Ethylene electrosynthesis: A comparative techno-economic analysis of alkaline vs membrane electrode assembly vs CO<sub>2</sub>–CO–C<sub>2</sub>H<sub>4</sub> tandems. *ACS Energy Lett.* **2021**, *6*, 997.
- [2] De Luna, P.; Hahn, C.; Higgins, D.; Jaffer, S.A.; Jaramillo, T.F.; Sargent, E.H. What would it take for renewably powered electrosynthesis to displace petrochemical processes? *Science* **2019**, *364*, 3506.
- [3] Bushuyev, O.S.; De Luna, P.; Dinh, C.T.; Tao, C.; Saur, G.; van de Lagemaat, J.; Kelley, S.O.; Sargent, E.H. What should we make with CO<sub>2</sub> and how can we make it?. *Joule*, **2018**, *2*, 825–832. <https://doi.org/10.1016/j.joule.2017.09.003>
- [4] Spurgeon J.M., Kumar. B. A comparative technoeconomic analysis of pathways for commercial electrochemical CO<sub>2</sub> reduction to liquid products. *Energy Environ. Sci.* **2018**, *11*, 1536–1551. <https://doi.org/10.1039/C8EE00097B>.
- [5] Bagchi, D.; Raj, J.; Singh, A.K.; Cherevotan, A.; Roy, S.; Manoj, K.S.; Vinod, C.P.; Peter, S.C. Structure-tailored surface oxide on Cu-Ga intermetallics enhances CO<sub>2</sub> reduction selectivity to methanol at ultralow potential. *Adv. Mater.* **2022**, *34*, e2109426.
- [6] El-Shafie, O. A.; El-Maghraby, R. M.; Albo, J.; Fateen, S.-E.K.; Abdelghany. A. Modeling and numerical investigation of the performance of gas diffusion electrodes for the electrochemical reduction of carbon dioxide to methanol. *Ind. Eng. Chem.*, **2020**, *59*, 20929–20942. <https://doi.org/10.1021/acs.iecr.0c02358>.



- [7] Jones, J.P.; Prakash, G. K. S.; Olah, G. A. Electrochemical CO<sub>2</sub> reduction: recent advances and current trends. *Isr. J. Chem.* **2014**, *54*, 1451–1466. <https://doi.org/10.1002/ijch.201400081>.
- [8] Ma, W.; Xie, S.; Liu, T.; Fan, Q.; Ye, J.; Sun, F.; Jiang, Z.; Zhang, Q.; Cheng, J.; Wang, Y.; Electrocatalytic reduction of CO<sub>2</sub> to ethylene and ethanol through hydrogen-assisted C–C coupling over fluorine-modified copper. *Nat. Catal.* **2020**, *3*, 478–487. <https://doi.org/10.1038/s41929-020-0450-0>.
- [9] Ruth, M F.; Mayyas, A T.; Mann, M K. Manufacturing competitiveness analysis for PEM and alkaline water electrolysis systems. In Proceedings of the Manufacturing Competitiveness Analysis for PEM and Alkaline Water Electrolysis Systems, USA, Long Beach, CA, USA, 6–9 November 2017
- [10] Jouny, M.; Luc, W.W.; Jiao, F. General Techno-Economic Analysis of CO<sub>2</sub> Electrolysis Systems. *Ind. Eng. Chem. Res.* **2020**, *57*, 2165–2177. <https://doi.org/10.1021/acs.iecr.7b03514>.
- [11] Paturska, A.; Repele, M.; Bazbauers, G. Economic assessment of biomethane supply system based on natural gas infrastructure. *Energy Procedia*, **2015**, *72*, 71–78. <https://doi.org/10.1016/j.egypro.2015.06.011>.
- [12] Keith, D.W. Why capture CO<sub>2</sub> from the atmosphere?. *Science*, **2009**, *325*, 1654–1655. <https://doi.org/10.1126/science.1175680>.
- [13] Baumann C.; Lopatnikov A. Scaling laws: Uses and misuses in industrial plant and equipment replacement cost estimates. *The MTS Journal*, **2017**, *33*, 38–44.