

## Supporting information

# Economically viable CO<sub>2</sub> electroreduction embedded within ethylene oxide manufacturing

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## Contents

CO2R Unit Calculations.....	3
Inlet flow rate calculations .....	3
CO2R Products flow rate calculations: .....	3
Required electrode area .....	4
Current required for operation (based on main product flow) .....	4
Power needed .....	4
Process streams calculations.....	4
Electrolyzer inlet (gas) .....	4
Electrolyzer outlet (gas) .....	4
Ethylene-rich stream recycled back to EO reactor .....	5
Capital cost calculations .....	5
Electrolyzer capital cost & balance of the plant.....	5
Operational costs calculation.....	6
Utilities cost indicators.....	6
Heat balance of the electrolyzer .....	6
Maintenance costs .....	6
Overall operating costs.....	6
CO <sub>2</sub> emissions balance .....	7
List of symbols .....	8
Latin symbols .....	8
Greek symbols.....	8
Supplemental references.....	9

## CO2R Unit Calculations

### Inlet flow rate calculations

The electrolyser is designed to converted between 50% and 100% of CO<sub>2</sub> stream emitted by a typical medium-size EO plant<sup>1</sup>.

- Plant capacity: ca. 330 kta for EO production
- CO<sub>2</sub> waste stream generated: 103 mol/s (this amount of CO<sub>2</sub> is generated as reaction by-product)

In case of low conversion (50%): The complete stream of separated CO<sub>2</sub> is sent to the electroreduction unit. Unconverted CO<sub>2</sub> is recycled back to the reactor with ethylene and other gases. As small part of CO<sub>2</sub> is recycled, the stream of CO<sub>2</sub> separated in the absorption column is readjusted to ensure that overall mass balances are met:

$$CO_2 \text{ to be separated} = \frac{CO_2 \text{ from side reaction}}{1 - CO_2R \text{ conversion efficiency} \cdot \text{membrane separation efficiency}} \quad (1)$$

$$CO_2 \text{ to be separated} = 103 \frac{\text{mol}}{\text{s}} / (1 - 0.5 \cdot 0.5) = 137 \frac{\text{mol}}{\text{s}} \quad (2)$$

From EO manufacturing perspective it is most profitable to convert CO<sub>2</sub> into an ethylene-rich stream. Hence, a highly ethylene-selective system was chosen<sup>2</sup>.

- Electrode: Cu
- Current density: 300 mA/cm<sup>2</sup>
- Faradaic efficiencies: values reported<sup>2</sup> were normalized to Faradaic efficiency =100% to account for possible experimental errors and extract the worst-case scenario from the experimental data.

### CO2R Products flow rate calculations:

$$\text{product flow} \left( \frac{\text{mol}}{\text{s} \cdot \text{cm}^2} \right) = \frac{\text{current} \left( \frac{\text{A}}{\text{cm}^2} \right) \cdot \text{Faradaic efficiency}}{\text{nb of electrones transferred} \cdot \text{Faraday constant} \left( \frac{\text{C}}{\text{mol}} \right)} \quad (3)$$

### Required electrode area

Moles of CO<sub>2</sub> converted during reaction are calculated stoichiometrically. In order to achieve certain conversion of available CO<sub>2</sub>, following electrode area is needed:

$$\text{electrode area (m}^2\text{)} = \frac{\text{available CO}_2\left(\frac{\text{mol}}{\text{s}}\right) \cdot \text{CO}_2 \text{ conversion}}{\text{CO}_2 \text{ converted during reaction}\left(\frac{\text{mol}}{\text{s} \cdot \text{cm}^2}\right) \cdot 10000\left(\frac{\text{cm}^2}{\text{m}^2}\right)} \quad (4)$$

Based on electrode area, flow of each product is calculated. (See Article Table 4).

### Current required for operation (based on main product flow)

$$\text{current (A)} = \frac{\text{product flow}\left(\frac{\text{mol}}{\text{s}}\right) \cdot \text{nb of electrones needed} \cdot \text{Faraday constant}\left(\frac{\text{C}}{\text{mol}}\right)}{\text{Faradaic efficiency}} \quad (5)$$

### Power needed

$$\text{power} = \text{cell voltage (V)} \cdot \text{total current (A)} \quad (6)$$

## Process streams calculations

### Electrolyzer inlet (gas)

Composition of this stream is the same as waste CO<sub>2</sub> stream reported for the base-case design EO process<sup>1</sup>. The size of the stream is readjusted in order to ensure enough CO<sub>2</sub> removal from process gases (see point 1). Minor impurities accounting for ca. 0.3% of inlet stream are not modelled.

### Electrolyzer outlet (gas)

This stream includes reaction products, minor quantities of compounds introduced with the feed (like e.g. ethylene) and unconverted CO<sub>2</sub>.

## Ethylene-rich stream recycled back to EO reactor

The cathode output of the CO<sub>2</sub> electroreduction unit will consist also of a minor quantity of carbon oxide and hydrogen, which are usually not used in EO reactors. We simulated what would be the concentration of these compounds when diluted with the fresh ethylene feed to the EO reactor (Table 1). According to the simulation results, carbon oxide and hydrogen would be present in ppm levels which have a potential to be acceptable for the reactor operation. To avoid the compounds build-up, carbon oxide and hydrogen can be removed from recycled gas stream by the existing purge unit, used for removal of other impurities such as e.g. ethane.

Table 1. Simulated composition of the EO reactor feed with possible post-electrolysis impurities.

Compound	Mass%	Molar %
H <sub>2</sub> O	0.7%	1.0%
C <sub>2</sub> H <sub>4</sub>	41.2%	38.8%
CO <sub>2</sub>	8.3%	5.0%
C <sub>2</sub> H <sub>4</sub> O	0 %	0.0%
O <sub>2</sub>	8.4%	6.9%
CH <sub>4</sub>	21.1%	34.8%
Ar	20.3%	13.4%
C <sub>2</sub> H <sub>6</sub>	441 ppm	0.0%
<i>Post-electrolysis impurities</i>		
CO	254 ppm	0.0%
H <sub>2</sub>	36 ppm	0.0%

## Capital cost calculations

### Electrolyzer capital cost & balance of the plant

Electrolyzer capital costs calculation is based on DOE H2A analysis<sup>3</sup>, used previously for cost estimation of big-scale CO<sub>2</sub> electroreduction unit by Jouny et al.<sup>4</sup>. The electrolyzer analyzed by DOE costs 250.25 \$/kW and operates at 0.175 A/cm<sup>2</sup>; 1.75 V. This cost was recalculated per surface area (with installation factor of 1.2) and multiplied by the area of the CO<sub>2</sub> electrolyzer.

$$\begin{aligned}
 &CO_2 \text{ electrolyzer cost} && (7) \\
 &= \text{reference cost} \left( \frac{\$}{kW} \right) \cdot \text{current density} \left( \frac{A}{cm^2} \right) \cdot \text{cell vol.}
 \end{aligned}$$

Balance of the plant is assumed to be 35% of the total cost and the stack is 65%.

## Operational costs calculation

### Utilities cost indicators

Cost of electricity, C<sub>2</sub>H<sub>4</sub> and CH<sub>4</sub> is taken from EO base-case design<sup>1</sup>. Cost of water for reaction 0.0054 \$/gal is taken as reported by Jouny et al.<sup>4</sup> and recalculated to \$/mol:

$$\text{water cost} = 0.0054 \frac{\$}{gal} \cdot \frac{1 \text{ gal}}{3.785 \text{ l}} \cdot \frac{l}{kg} \cdot 0.018 \frac{kg}{mol} = 0.00003 \frac{\$}{mol} \quad (8)$$

### Heat balance of the electrolyzer

The total enthalpy required for an electrochemical reaction is converted first to the voltage equivalent. The difference between the cell voltage (2V) and the enthalpy voltage equivalent represents total potential losses throughout the electrochemical activation, Ohmic heating effect and other minor sources. Those potential losses correspond to the maximum heat produced by CO<sub>2</sub>R reactor. The empirical gas-phase molar-enthalpy data is extracted from NIST databases<sup>5</sup>. Even though the operation in elevated temperatures might be favorable<sup>6,7</sup>, the total heat generated in the CO<sub>2</sub> reactor was assumed to be removed to follow the economically worst-case scenario.

### Maintenance costs

Maintenance costs of electrolyzer are roughly evaluated as 2.5% of capital costs per year:

$$\text{maintenance cost} = 2.5\% \cdot \text{capital cost} \quad (9)$$

### Overall operating costs

Overall operating costs are the sum of electricity consumption by the electrolyzer unit, compressors and maintenance costs.

## CO<sub>2</sub> emissions balance

To assess whether our process indeed minimizes CO<sub>2</sub> emissions, we calculated the CO<sub>2</sub> emissions balance for the new processing section (Section 5, Fig. 3), as the difference between the additional utilities consumption (electricity) and CO<sub>2</sub> emissions savings. CO<sub>2</sub> emission coefficients were extracted from the most detailed industrial reports available<sup>8,9</sup>

$$\begin{aligned} CO_2 \text{ emissions for Section 5} & \\ = - CO_2 \text{ flowrate} \left( \frac{kg_{CO_2}}{s} \right) & + \text{electricity consumption} \left( \frac{MJ}{s} \right) \cdot \frac{1 \text{ kWh}}{3.6 \text{ MJ}} \cdot CO_2 \text{ emission c} \\ & \left( \frac{kg_{CO_2}}{kWh} \right) \end{aligned} \quad (10)$$

We focus here on electricity consumption due to its prevailing effect on the environmental impact. Furthermore, other minor source of impact like for e.g. energy use for cooling have a great potential to be further minimized throughout heat integration.

## List of symbols

### Latin symbols

$F$	Faraday constant (C/mol)
$n$	Number of moles (mol)
$n_f$	Total feed flow rate (kmol/s)
$P$	Feed pressure (bar)
$Q$	Total flow of charge (C)
$R$	Gas constant (J/mol K)
$T_f$	Feed temperature (K)
$T_{out}$	Outlet temperature compressor (K)
$W_c$	Power required for compressor (MW)
$z$	Number of electrons (-)

### Greek symbols

$\xi_{Far}$	Faradaic efficiency (-)
$\gamma$	Adiabatic expansion coefficient (-)
$\eta_c$	Compressor efficiency (-)

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