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Modelling and Analysis of CO_2 Electrolyzers Integrated with Downstream Separation Processes via Heat Pumps

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ABSTRACT

The electrification of chemical processes and carbon capture and utilisation represent two promising approaches to improve efficiency and decrease carbon emissions of the process industry. The development of electrolyzers has gathered momentum in the last decades, allowing for the possible introduction of renewable electrons into carbon dioxide-based chemicals manufacture. While the performance of the electrolyzers is subject to improvements driven by the experimental community, the generation of waste heat is unavoidable due to the electrical resistances and process inefficiencies within the electrochemical cells. The possibility of re-using this waste heat has not been investigated within the realm of carbon dioxide electrolyzers. Here we show the potential of upgrading this waste heat by means of a heat pump, for its utilisation in the downstream processing of formic acid obtained from carbon dioxide electroreduction. We found that the waste heat represents roughly 62% of the power input to the electrochemical cells and it can be upgraded from 35 °C to 112 °C to drive the extractive distillation of formic acid and water. For a system producing 25 kt/y of formic acid, this results in the electrification of 60% of the separation energy duty, yielding a decrease in carbon dioxide emissions of 39-58% for the downstream processing, while the addition of a heat pump has a payback period of ~4.4 years in the base case.

Keywords: Process Design, Carbon Dioxide, Electrification, Process Integration, Heat Pump

INTRODUCTION

Several strategies can be deployed to reduce the environmental burden of manufacturing processes, specifically for chemicals. Among these strategies, of prime importance is the substitution of fossil inputs with renewable ones, whether it be electricity, biomass, or carbon dioxide. To enable this, productions based on electrolysis have significant potential, as they exploit renewable electricity to drive the reactions and allow for the conversion of carbon dioxide. Both experimental efforts and techno-economic assessments are directing the concerted development of the field of carbon dioxide electrolysis [1-2].

However, electrolyzers generate waste heat due to ohmic and kinetic losses, which are overcome through the application of an overpotential. Notably, heat management for electrolyzers remains under-explored, particularly when referring to the realm of low temperature carbon dioxide electrolysis. Conversely, the field of water electrolysis has seen some research in this [3], but, as hydrogen production lacks significant downstream processing, the possibilities of waste heat utilisation in the plant are limited.

This is not true for carbon dioxide electrolysis, especially when yielding liquid products relying on thermal separations. As the waste heat is at low temperature, it cannot be directly exploited to drive the separations. To tackle this obstacle, heat pumps can be employed to upgrade the waste heat to useful temperature levels, thus enabling heat integration and further diminishing the need for fossil fuels in the separation section of the plant. An additional challenge is represented by the typical room temperature operation of carbon dioxide electrolyzer currently developed at the lab scale. This would imply a very high temperature lift for the heat pump, thus diminishing its performance. However, recent literature shows that optimal operation would lie between 60 and 70 °C [4], which can be more readily exploited by a heat pump.

PROBLEM STATEMENT

This study aims at assessing the potential of upgrading the waste heat from the electrolyzer via heat pump to drive the product recovery and purification processes. To showcase this, we have selected the production of formic acid, since it can be obtained with good performance through carbon dioxide electrolysis [5]. By designing the different parts of the process – electrolyzer stacks, separation processes, and heat pump – and combining them together, we have obtained a complete flowsheet for the integrated plant. This has allowed for the quantification of the reduction in the external load for the thermal separation and, consequently, of the carbon dioxide emissions of the process.

This work constitutes a proof of concept for the potential upgrade of waste heat from the electrolyzers, reporting preliminary results. The inclusion of a heat pump in the process is evaluated based on economics and environmental (carbon dioxide emissions) performance. However, the complete techno-economic assessment of the process, together with further heat integration and overall process optimization, are out of scope for this study.

METHODOLOGY

A process to produce formic acid (HCOOH) from carbon dioxide and water comprises three main parts, as shown in the block flow diagram of Figure 1: the electrolyzer stacks, the formic acid-water separation and the heat pump. To support the design, we simulated this process at steady state using Aspen Plus®. Considering the formic acid market [6], the plant is sized to produce 25 kt/y of FA at 85 wt.%, with 100% utilisation based on 8000 h/y of operation.

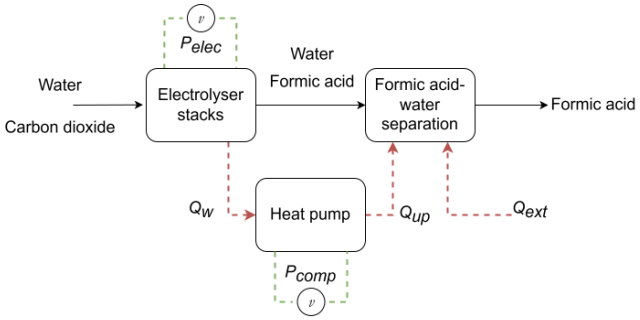

Figure 1. Block flow diagram for the process, highlighting the three sections in which the system can be broken down. The main material and energy flows are also displayed.

A three compartment electrolyzer, based on the set up of Yang et al. [7], is chosen, as it reduces the complexity of the process by yielding directly formic acid instead of the formate salt, obtained from the combination of the product and the cation of the electrolyte. To design the electrolyzer, we considered several trade-offs between major decision variables, namely the cell voltage, the current density, the faradaic efficiency and the product concentration in the outlet stream [8]. The current density determines, for a given production capacity, the electrolyzer size required, and its dependence on the cell voltage can be obtained by fitting experimental data [7]. The availability of experimental data up to 4 V for the polarization curve provides an upper limit to the investigated cell voltage ranges.

The waste heat Q_W developed by the electrolyzers is calculated using in Eq. 1, where i_k is the partial current for product k ($i_k = FE_k\ i$, with FE_k Faradaic efficiency for product k, and i total current), E_{cell} is the total cell voltage, and $E_{tn,k}$ is the thermoneutral voltage for product k (i.e. the voltage such that the cell would have isothermal operation) [3]. The waste heat, together with the total power input to the cell P_{cell}, determines also the cell efficiency ϵ, as expressed in Eq. 2.

$$Q_W = \sum_k i_k (E_{cell} - E_{tn,k}) \quad (1)$$

$$\epsilon = \frac{P_{cell} - Q_W}{P_{cell}} \quad (2)$$

The separation of formic acid from water is based on the work of Ramdin et al. [9], where it is carried out through extractive distillation with 2-methyltetrahydrofuran. Notably, this separation technology keeps the main reboiler temperature at 106 °C, which is key to enable a more efficient performance for the heat pump. Since the goal of this work is to demonstrate the potential of upgrading the waste heat, systematic improvements to the downstream processing are out of scope.

The selection of the heat pump technology is limited to the mechanically-driven ones in order to maximise the electrification of the process via the compressor power input. The investigation space is thus reduced to vapor compression and compression resorption heat pumps [10]. Due to the scope constraints of this work, the implementation of compression resorption heat pumps, which might result in higher efficiency, is deferred to future studies. We have analyzed the performance of different working fluids, with the goal of maximising the coefficient of performance (COP) of the system, as defined in Eq. 3, where Q_{up} is the upgraded heat flow and P_{comp} is the power input to the compressor.

$$COP = \frac{Q_{up}}{P_{comp}} \quad (3)$$

Simplified economics, based on the Total Annualised Costs (TAC, see Eq. 4) have been exploited for the design of the electrolyzer.

$$TAC = \mathrm{OPEX} + \frac{CAPEX}{lifetime} \quad (4)$$

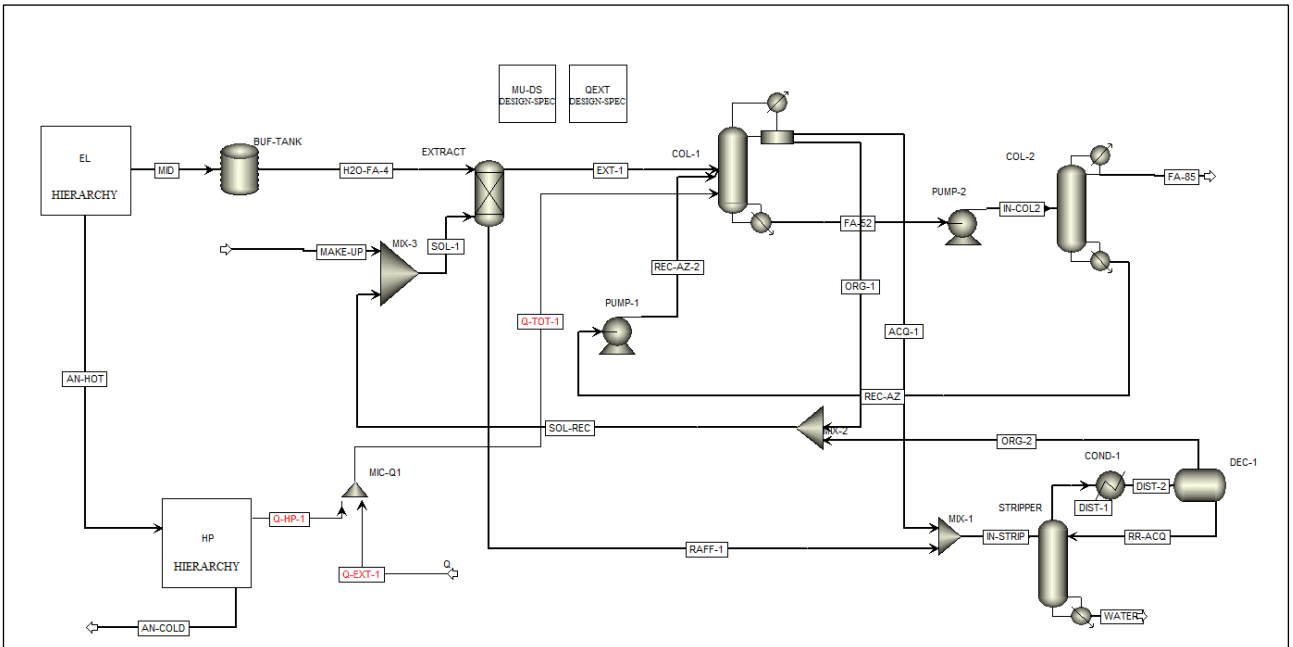

Figure 2. Aspen Plus® flowsheet for the process, showing the separation system and the two hierarchical blocks containing the electrolyzers and the heat pump models.

Moreover, the payback period for the heat pump has been calculated to evaluate the investment from an economic perspective (compressor and heat exchangers capital costs estimated according to [11]). Carbon dioxide emissions per unit product, based on the energy demand and its origin, provide support and context for the decisions on design and the benefits of upgrading the waste heat by means of the heat pump.

The Aspen Plus® implementation of the model rests on the choice of different thermodynamic packages for different parts of the flowsheet, namely: ELECNRTL for the electrolyzer stacks and balance of plant; UNIQUAC-HOC for the formic acid-water separation; and REFPROP for the heat pump, tailoring each of these models to the specific application. The REFPROP library contains several, fluid-specific models based on fundamental equations of state, as discussed in [12].

RESULTS AND DISCUSSION

The flowsheet for the whole process, as developed in Aspen Plus®, is reported in Figure 2, which displays the downstream separation, while the electrolyzers and the heat pump are included in hierarchy blocks. The electrolyzer is modelled in Excel, which is embedded as a calculator block in the Aspen Plus® simulation, while the heat pump is modelled as a closed loop vapor compression system (evaporator, compressor, condenser, and expansion valve). The following sections present first the results for the electrolyzer design, followed by the heat pump selection and the heat integration in the process. Finally, simplified metrics to evaluate the carbon dioxide emissions and the economic performance of the design are described and discussed.

Electrolyzer design

The design of the electrolyzer has been defined through an optimisation of the different trade-offs discussed in the previous section. The sensitivity of the cell voltage which allows to minimise the TAC, based on the electricity price and the electrolyzer cost, is shown in Figure 3.

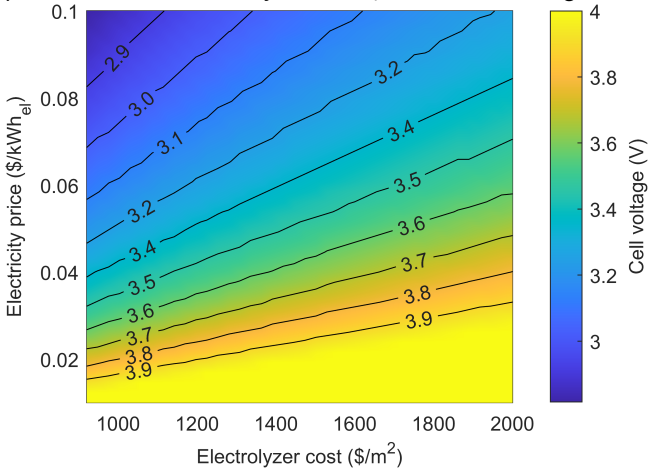

Figure 3. Cell voltage that minimises total annualised costs as a function of electrolyzer and electricity cost.

Cheap electricity (below 0.03 $/kWh$_{el}$) would favor operation at maximum voltages, regardless of the electrolyzer cost, because the current density, a function of the cell voltage, is pushed to higher values, resulting in smaller, and thus cheaper, reactors. This effect can also be observed at constant electricity price, with an increasing trend in the optimal voltage with higher electrolyzer prices, thanks to the inverse proportionality between cell voltage and electrolyzer area required. The capital costs

of the electrolyzer do not become dominant in the range considered (based on [13]), therefore the optimal operation is not found at lower voltages.

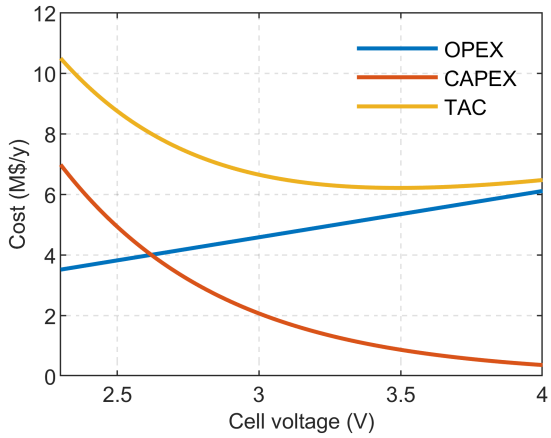

Figure 4. Trade-off between OPEX and CAPEX for the electrolyzer as a function of the cell voltage (electricty price: 0.05 $/kWh$_{el}$; electrolyzer cost: 1500 $/m^2).

For the base case values of 0.05 $/kWh$_{el}$ and 1500 $/m^2 for electricity price and electrolyzer cost, respectively, the trade-off between OPEX and CAPEX is displayed in Figure 4. The OPEX are linearly dependent on the cell voltage, for a given production capacity, while the CAPEX decrease with E_{cell}, since the current density rises, leading to smaller units. An optimum value of the cell voltage can be identified, as ~3.5 V, which corresponds to a current density of ~130 mA/cm^2. Table 1 summarizes the design variables chosen, as well as some relevant design parameters and process inputs.

Table 1: Main process design variables chosen, together with the carbon intensity of relevant energy sources. FE is Faradaic efficiency. The subscript *th* and *el* distinguish between thermal and electrical energy.

Stream	Value	Units of measure
Cell voltage	3.5	V
FE (HCOOH)	90%	(-)
FE (CO)	2%	(-)
FE (H_2)	8%	(-)
Product concentration (middle compartment outlet)	10%	w/w
Electrolyzer lifetime	5	years
Electrolyzer temperature	50	°C
Carbon intensity MP steam	237	gCO2/kWh$_{th}$
Carbon intensity electricity (grid, EU-27)[15]	251	gCO2/kWh$_{el}$
Carbon intensity electricity (renewables)[16]	19	gCO2/kWh$_{el}$

The choice of the cell voltage determines also the amount of waste heat available for upgrading via the heat pump, according to Eq. 1. This effect is shown in Figure 5, which on the right y-axis reports both the total power input to the electrolyzers and the available waste heat as a function of the cell voltage, while the left y-axis shows the electrolysis cell energy efficiency (Eq. 2). This highlights how the design of the electrolyzer has cascade effects on the performance of the rest of the process, as the electrolyzer efficiency could be improved, but this would increase the demand for external energy inputs for the downstream separation in the integrated system. For the cell voltage chosen, ~8.3 MW of waste heat is obtained, while the cell operates at ~38% efficiency.

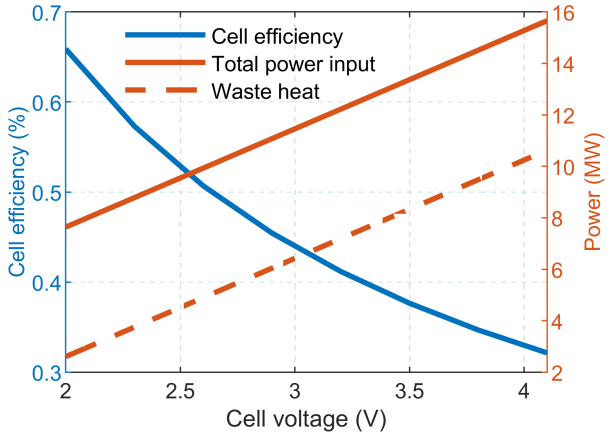

Figure 5. System trade-off showing the total power input to, and the waste heat developed by, the electrolyzers, as a function of the cell voltage. The cell efficiency vs. the voltage is also provided.

Heat pump selection and heat integration

The waste heat available can be upgraded by means of a heat pump. The performance of the heat pump, measured by the COP, is strongly dependent on the temperature lift required, defined as the difference between the temperature of the upgraded heat and that of the waste heat. In our case, based on the electrolyzer operating temperature of 50 °C, electrolyte return temperature of 40 °C, and reboiler temperature of 106 °C, the temperature lift is 77 °C (35 °C to 112 °C).

After screening different working fluids, we have identified a vapour compression heat pump using HFO-1233zd and one using ammonia as a suitable candidates, due to their performance, appropriate critical temperature, and low global warming potential and ozone depletion potential [14]. Based on the conditions, the heat pump can reach a COP of ~2.8-3.1, employing compressors requiring ~4-4.5 MW$_{el}$, and leading to upgraded heat of ~12-13 MW$_{th}$ at the desired temperature. The results presented below are based on the ammonia case, as they are substantially the same for HFO-1233zd.

Table 2: Impact of different heat pump technologies and working fluid on the upgraded heat and on carbon dioxide emissions for the downstream processing (DSP). Note that the emissions do not represent the full carbon footprint of the product.

Heat pump	Working fluid	COP	Electricity source	Carbon dioxide emissions DSP ($kgCO_2$/kg product)	Carbon dioxide reduction (%)
No	N/A	N/A	N/A	2.55	N/A
Yes	Ammonia	3.06	Offshore wind	1.07	-64%
Yes	Ammonia	3.06	Grid	1.56	-42%

The reboiler heat duties for the azeotropic distillation and the vacuum distillation (COL-1 and COL-2 in Figure 2) are 13.5 MW_{th} and 7 MW_{th}, respectively. Figure 6 summarizes the main energy flows among the three sections of the system: it is possible to observe that the upgraded heat covers the vast majority of the duty of the azeotropic distillation column (COL-1), leaving COL-2 to be supplied by external heat. The heat pump thus accomplishes the dual goal of providing cooling to the electrolyzer system, and delivering high temperature heat to the separation. Electricity constitutes ~70% of the energy inputs to the process, while the upgraded heat covers ~60% of the thermal duties.

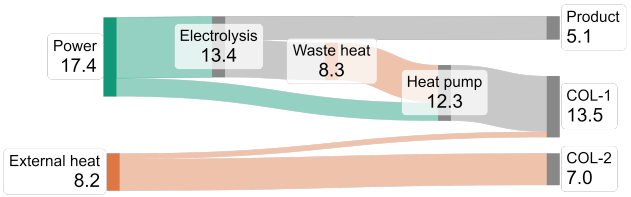

Figure 6. Sankey diagram displaying the energy flows (in MW) in the system. Electric energy is shown as green, while thermal energy is represented in orange.

Emissions and economic metrics

Table 2 provides a comparison between the case of implementation of a heat pump versus a system in which the separation duty is fully provided via an external source (steam boiler with natural gas). The results show that the heat pump allows for significant improvements in the carbon dioxide emissions of downstream process, with a reduction of -58% when using fully renewable electricity (based on median offshore wind emissions [16]) and -39% when connected to a national grid (assuming the current average grid emissions for the European Union-27 [15]). This reduction in emissions results from a decrease in the primary energy input through the energy multiplying effect of the heat pump.

While the heat pump brings benefits from the environmental perspective regardless of the source of the electricity, economic considerations should not be overlooked for its widespread adoption. Therefore, we have calculated the payback period for the addition of the heat pump to the system, as displayed in Figure 7 for different scenarios of electricity and fuel prices. The figure shows that the investment is paid back in less than ~4.5 years, except for when electricity is expensive (0.09 $\$/kWh_{el}$). In this case, the investment is not attractive, as the additional electricity input to the system for the heat pump compressor does not offset the reduced primary energy demand. Furthermore, it can be observed that the system is sensitive to increases in the fuel prices, given that the payback period for scenario 4 (electricity price of 0.05 $\$/kWh_{el}$ and fuel price of 0.045 $\$/kWh_{th}$) is about half of that for scenario 1 (same electricity price, 0.03 $\$/kWh_{th}$ for fuel).

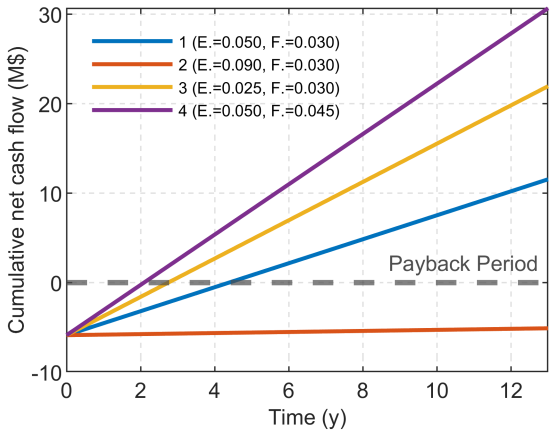

Figure 7. Cumulative net cash flow over a plant lifetime of 20 years for the investment in the heat pump, showing different scenarios based on the electricity (E.) and fuel (F.) price (reported in $\$/kWh_{el}$ and $\$/kWh_{th}$, respectively).

CONCLUSIONS AND FUTURE WORK

This work shows how the waste heat from the electrolyzer can be upgraded for heat integration, thus reducing the need for external energy inputs for the separation of products. This type of assessment can be extended to other processes operating with electrolyzers and similar conditions, including those downstream of water electrolysis for hydrogen generation.

Moreover, the application of a multi-pronged

electrification strategy, in which renewable electrons are used to both drive reactions and the energy integration of the system, is demonstrated. This is key in the perspective of the reduction of carbon dioxide emissions, as it offsets the use of conventional heating media in the downstream separations by ~60% and increases electricity inputs to 70% of the total energy demand. Additionally, the economic performance of the heat pump would justify the increased capital investment, given that the payback period is a few years, with the exception of higher electricity prices.

These results justify future work on a detailed techno-economic assessment of the whole process, including a system-wide optimisation to find the best design and operating conditions under different sets of inputs (electricity price, renewable electricity availability, heat pump technology). Moreover, the potential for waste heat upgrade in other electrolysis-based processes merits further investigation.

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