Optimization of High-Performance Membrane Processes for Post-Combustion Carbon Capture

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Abstract

Membrane processes are emerging as an attractive alternative to absorption for carbon capture, thanks to the high energy efficiency and modularity. To assess the real potential of membrane technology at a large scale, operating conditions need to be optimized in combination with the selected material. In this work, for the first time, we report the results of the techno-economic optimization of a double-stage membrane process for post-combustion carbon capture in the presence of a wide range of membranes, corresponding to several combinations of CO2 permeance and CO2/N2 selectivity.

The optimization maps identify impact of various performance parameters on the cost. Also, the optimization results are used to chart out targets for permeance and selectivity, beyond which a further improvement does not result in cost reduction.

Overall, this work gives important insights into the impact of membrane performances on the techno-economic feasibility of the optimized capture process and into the performance targets to make the technology more competitive.

**Keywords**: membrane process, post-combustion carbon capture, cost minimization, techno-economic analysis, process design

# Introduction

Membrane technology has shown to be highly promising for post-combustion carbon capture, since it can reduce energy consumption with respect to state-of-art absorption from 3-4 MJ/kg to below 1 MJ/kg. This allows an important cost reduction for capture from coal power plant flue gas from 50 $/t to 20-30 $/t (Merkel et al., 2010).

Literature has reported several techno-economic studies on capture processes based on different membranes. (Merkel et al., 2010) showed the attractiveness of membrane processes by designing a double-stage process based on polymeric membranes by MTR PolarisTM. Recent studies focused also on composite membranes (Xu et al., 2019), facilitated transport membranes (Han & Ho, 2020), graphene membranes (Micari et al., 2021) and mixed matrix membranes (Fujita et al., 2022).

Depending on the membrane performance, several operating conditions and process configurations should be considered to optimize process performances. In this context, various contributions concerned the optimization of multi-stage processes and the minimization of total capture cost (Zamarripa et al., 2018). These include different approaches, from superstructure-based (Arias et al., 2016) to surrogate-based optimization (Graciano et al., 2018).

Generally, the optimized process configurations are reported for a selected membrane with a given performance. Therefore, it becomes challenging to compare membranes with varying performances (combination of CO2 permeance and CO2/N2 selectivity) because of the different techno-economic assumptions used in the literature.

In this work, for the first time, we report and compare the minimized capture costs and the relevant energy and membrane area requirements for a wide range of membrane performances. These results will allow to assess the impact of the membrane parameters on the optimal operating conditions and on the techno-economic feasibility of the optimized process. Finally, the findings will serve as guidelines for membrane developers and manufacturers to identify improvement targets for membrane performance parameters.

# Mathematical model

We developed a techno-economic model to simulate and design multi-stage membrane processes for gas separation and to assess their economic feasibility.

* + 1. Technical model

First, we built a modular technical model where multi-stage processes are represented as combinations of single membrane stages (Micari et al., 2021). Each single stage has a cross-flow arrangement (Figure 1, left) and is modelled under the following assumptions: (i) fixed temperature, (ii) permeance independent of concentration, (iii) negligible pressure drops and concentration polarization, (iv) no mixing in the permeate channel.

To model the single stage, we estimate the transmembrane flux of each component (*i*) along the z axis by applying the solution diffusion model, as in Eq. (1). The flux *J* is proportional to the partial pressure difference between feed and permeate channel, where the partial pressure is given by the product of the total pressure in the channel (*P*) and the molar fraction (*Xi*). The calculated fluxes are then used in mass balances, to assess the variation of flow rates and concentrations of each component along the length of the stage. More details on the model are reported in our previous work (Micari et al., 2021).

|  |  |
| --- | --- |
|  | (1) |

The process performances are defined in terms of purity and recovery. The purity corresponds to the concentration of the main component (CO2) in the outlet permeate stream. The recovery is given by the ratio between the flow rate of the main component in the permeate and that in the feed. To achieve high recovery and purity, a single stage process is often not enough and multi-stage processes need to be designed. This work presents the results for a double-stage process where the permeate produced by the first stage is fed to the second stage and the retentate produced by the second stage is recycled and mixed with the feed of the first stage, to increase driving force (Figure 1, right).



Figure 1. Schematic representation of the single-stage process (left) and of the double-stage process with recycle of the retentate from the second stage (right).

We design double-stage processes with given sets of pressures in the feed and permeate channel by identifying the membrane areas in the two stages that minimize the difference between calculated and target values of recovery and purity (design objective function).

* + 1. Economic model

The economic model calculates the capital and operating costs of the membrane process based on the outputs of the technical model, i.e., membrane area and energy consumption. The model is reported in detail in (Micari et al., 2023). The capital costs are given by the direct costs for purchase and installation of all pieces of equipment (membrane modules with specific membrane cost of 100 $/m2, compressors, vacuum pumps, and blowers), the indirect costs (14% of the direct costs) and the contingency and fee costs (35% of the sum of direct and indirect costs). These costs are then annualized by assuming a capital charge factor (equal to 0.125) to obtain the CAPEX [$/y].

The operating costs include the cost for energy, for maintenance and labor, and for membrane replacement. The specific cost of energy is taken equal to 0.05 $/kWh and the membranes are replaced every 5 years. The total operating cost is defined as OPEX [$/y].

The capture penalty is given by the sum of CAPEX and OPEX divided by the total amount of CO2 produced per year [t/y].

* + 1. Process optimization

For each set of CO2 permeance and CO2/N2 selectivity, we found the set of operating pressures (Pfeed,1, Pperm,1 and Pperm,2 as in Figure 1 (right), while Pfeed,2 is equal to 1 bar) that minimizes the capture penalty (techno-economic objective function).

For the optimization, we used the shooting method, where a coarse grid search is followed by optimization via Sequential Least Square Programming (SLSQP from *scipy* library in Python). Figure 2 shows an example for the case of permeance of 500 GPU and selectivity of 20, where the grid search allowed to identify narrow ranges of the optimization variables within which we performed local optimization (minimum value of 72 $/t, represented with a circular marker in the map of Figure 2).

# Description of the system and the operating conditions

The membrane process presents two stages as in the scheme of Figure 1 (right), where the membrane areas are designed to achieve the targets of 90% CO2 recovery and 95% CO2 purity. The flue gas fed to the membrane process is produced by a coal power plant, the flow rate is 4385 mol/s (corresponding to 0.6 million tonCO2/y captured) and the composition is: 13.5% CO2, 15% H2O, 3% O2 and 68.5% N2 (Micari et al., 2021). The simulations take into account the multicomponent feed and assume a fixed CO2/H2O and CO2/O2 selectivity of 1 and 12.6, respectively (Micari et al., 2021). We vary CO2 permeance and CO2/N2 selectivity from 500 to 10000 GPU (Gas Permeation Unit, 1 GPU = 3.35 × 10-10 mol/ (m2 s Pa)) and from 20 to 100, respectively.

# Results and discussion

The optimization maps of membrane area, energy consumption, and capture penalty are reported in Figure 3. From the map of membrane area (Figure 3A), we observe that in general membrane area is controlled by permeance. This is particularly evident when the permeance is low (< 1000 GPU) or when the permeance is high (> 7000 GPU). In the intermediate region, the selectivity plays a role, and an increase of selectivity causes an increase in membrane area. This can be explained by considering that: (i) at higher selectivity, the optimal feed pressure is lower and the optimal permeate pressure is higher, since lower driving force is preferred to reduce energy; (ii) for a given CO2 permeance, when CO2/N2 selectivity increases, the N2 permeance decreases; (iii) the higher CO2 concentration in the permeate given by the higher selectivity reduces driving force along the length of the stage.



Figure 2. Example of optimization process for permeance of 500 GPU and selectivity of 20.

In the map of specific energy (Figure 3B) we can identify a region (selectivity < 40) where the energy is almost only controlled by the selectivity. Conversely, at higher selectivity values, the permeance starts to play a role and, in particular, the energy increases when permeance decreases below 3000 GPU. As evident from the curve at 1.0 MJ/kg, the selectivity needs to increase when permeance reduces to keep the same value of specific energy, because of the higher feed compression requirement at lower permeance.

The overall effect of membrane permeance and selectivity is shown in the map of capture penalty (Figure 3C). Here, we can isolate three regions: (i) selectivity < 40; (ii) selectivity > 40 and permeance < 3000 GPU; (iii) selectivity > 40 and permeance > 3000 GPU.

In the first region, as shown in the curves at 40 and 50 $/t, the capture penalty is controlled by selectivity as it is driven by the operating cost (specific energy, Figure 3B). In the second region, as shown by the same curves in the range of higher selectivity values, the capture penalty is controlled by the permeance because of the larger investment cost for membrane area which changes sharply with permeance (Figure 3A). Finally, in the last region, as shown in the curve at 30 $/t, both membrane parameters play a role in determining the capture penalty and, within this range, the higher the parameters, the lower the minimized capture penalty.

It is also important to mention that minimized capture penalties below 40 $/t are found for a wide range of membrane parameters. We can define a feasibility space of parameters with permeance > 2000 GPU and selectivity > 40, where membranes are highly competitive with absorption process.

Figure 4 shows the Pareto curves in the specific energy vs. specific area charts for given couples of permeance and selectivity. The Pareto curves are obtained from all the points representing double-stage processes with variable pressures in the first and second stage, that fulfill the recovery and purity targets. When permeance is varied from 500 to 10000 GPU, the membrane area also varies by one order of magnitude. The specific area in the Pareto curves ranges from 10 to 50 × 103 m2/(kg/s) for permeance of 500 GPU and from around 1 to 2.5 × 103 m2/(kg/s) with 10000 GPU. Importantly, for a fixed permeance, the Pareto curves at variable selectivity shift vertically along the specific energy axis and show a much bigger drop when selectivity increases from 20 to 40 than when it increases from 40 to 100. This is due to the fact that the system performance is controlled by selectivity when this is below 40, as observed also in the maps of Figure 3. Thus, a further increase in selectivity has a lower impact on the overall capture cost.



Figure 3. Maps of specific area (A) and energy (B) corresponding to the minimum capture penalty (C) at variable permeance and selectivity. Targets: 90% CO2 recovery and 95% CO2 purity.

On the other hand, in the lower charts, the Pareto curves at different permeances are located in the region of 2 MJ/kg of specific energy when selectivity is 20 and of 1 MJ/kg when selectivity is 100.

Notably, when permeance increases, the curves shift to left along the specific area axis, showing how permeance mostly impacts membrane area rather than energy consumption.

The gap between the curves at 500 and 3000 GPU is larger than that between the curves at higher permeances. Analogously to selectivity, this comparison shows that the effect of permeance variations is stronger when permeance is lower than 3000 GPU and a further increase has limited impact on global system performances.

# Conclusions

This work presents a comprehensive assessment of the impact of membrane performance parameters, namely CO2 permeance and CO2/N2 selectivity, on the techno-economic figures of the optimized double-stage membrane processes for post-combustion capture from coal power plants flue gas. The maps of minimized capture penalty and of the corresponding specific membrane area and energy consumption are powerful tools to identify regions with different roles of the two parameters. In particular, we can identify three regions: (i) selectivity-controlled, when selectivity is below 40 at any permeance, (ii) permeance-controlled, when permeance is below 3000 GPU and selectivity is above 40, (iii) both permeance- and selectivity-controlled, when permeance is higher than 3000 GPU and selectivity higher than 40. Also, the Pareto curves reported at variable selectivity or permeance values are important to understand to what extent the parameters impact the technical and economic figures and when their further increase starts to have a negligible role in terms of cost reduction. These results are very important as they provide useful guidelines to the membranes manufacturers concerning the parameters to improve and the impact of parameters variations depending on the region to which the specific membranes belong. Finally, a wide feasibility space of parameters reports optimized capture penalties below 40 $/t, thus showing the high competitiveness of membrane technology for post-combustion capture from the coal-fired power plants.



Figure 4. Pareto curves of specific energy vs. specific area at fixed CO2 permeance and variable CO2/N2 selectivity (upper charts) and at fixed selectivity and variable permeance (lower charts). The points represent the systems at 90% recovery and 95% purity with variable pressures.

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