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Superstructure Modelling of Membrane Systems for the Optimization and Flexible Design of Post-combustion Carbon Capture Processes

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ABSTRACT

Membranes provide an efficient method for treating flue gases to capture CO_2 from various point sources, achieving high recovery and purity rates. However, the lack of systematic process-level design tools has limited the translation of advanced membrane materials into large-scale technical and economic metrics. Thus, in this study, we present a superstructure model for the design of membrane-based carbon capture, both from highly energy-intensive industries and from power plants. The superstructure model enables the flexible design and global optimization of multi-stage membrane systems. Multiple membranes are compared under technical performance indicators (specific energy and specific area), while the already commercialized polymeric membranes Polaris and PolyActive are taken into consideration for estimating their economic performance. The presented framework establishes a robust link between material innovation and optimal process design, providing a key tool for the large-scale deployment of membrane-based carbon capture.

Keywords: carbon capture, membrane systems, superstructure, optimization

INTRODUCTION

As 2050 approaches, the efforts to achieve the net-zero transition should be intensified. Under these terms, Carbon Capture, Utilization, and Storage (CCUS) technologies should be strengthened across technical, economic, and environmental dimensions and implemented at an industrial scale. Post-combustion carbon capture can assist energy-intensive industries and existing fossil-fuel power plants in their decarbonization. Various technologies have been proposed and evaluated for this purpose, with membrane process systems constituting a promising option [1].

More specifically, membrane systems are characterized by high energy efficiency, compact and modular design, operational simplicity, and significant environmental benefits relative to other state-of-the-art technologies, without the use of heating utilities, which can be both costly and environmentally impactful. Most recent advances focus on material development, while significant gaps remain in optimizing membrane systems that utilize these materials at process level, and measure their performance under industrial scales [2].

In particular, a comprehensive framework that finally links advanced material properties and large-scale process design is still missing. This work addresses this critical gap by introducing a superstructure modelling framework that systematically optimizes membrane systems for post-combustion carbon capture.

METHODOLOGY

Single-stage membrane model

Any membrane network is based on the combination of multiple single stages. To model such a single-stage system, the following assumptions have been made:

- Isothermal conditions along the length of the membrane.
- Negligible pressure drops or concentration polarization phenomena occur on the feed side of the membrane module.

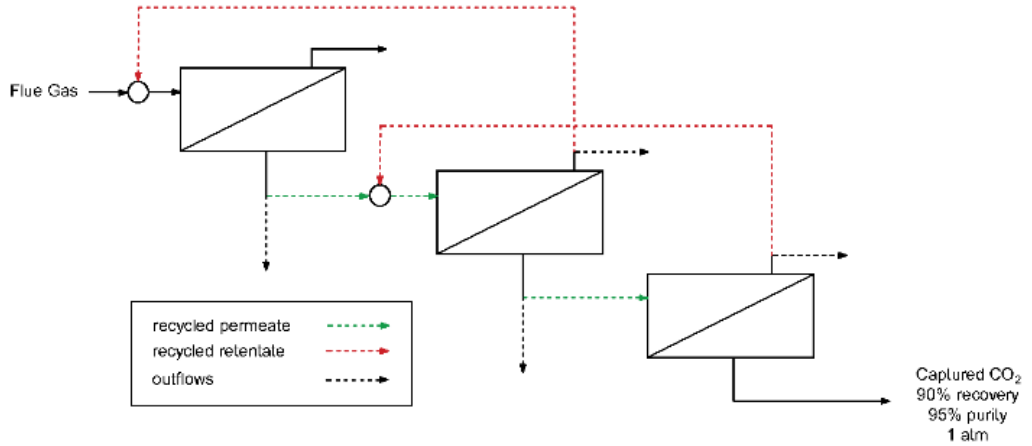

Figure 1. Developed membrane module network.

- A cross-current flow pattern is implemented.

In a single-stage membrane process, the membrane sheet is discretized along its length (z-axis) into a specific number of elements of length dz and area dA. In each one of them, the transmembrane flux of a component in a flue gas can be estimated using the solution-diffusion model.

$$J_i(z) = P_i(P_{feed}x_{feed,i}(z) - P_{perm}x_{perm,i}(z)) \quad (1)$$

where P_i the permeance of the component i, and is a characteristic of the membrane material used, P_{feed} and P_{perm} the pressure applied in the feed and the permeate channel, respectively, $x_{feed,i}$ and $x_{perm,i}$ the molar fractions of the component i in the feed stream and right after crossing the membrane. A multicomponent mixture is considered, so i corresponds to CO_2, N_2, O_2, and H_2O.

The total flux can be estimated by the summation of the fluxes of the individual components (Equation (2)). By implementing the total and partial mass balances among the elements, the rest of the flows and compositions can be determined, through Equations (3-6):

$$J_{tot}(z) = \sum_{i=1}^{components} J_i(z) \quad (2)$$

$$Q_{ret}(z) = Q_{feed}(z) - J_{tot}(z)\,dA \quad (3)$$

$$x_{i,ret}(z)\,Q_{ret}(z) = x_{i,feed}(z)\,Q_{feed}(z) - J_i(z)\,dA \quad (4)$$

$$Q_{perm} = \sum_{z=0}^{L} J_{tot}(z)dA \quad (5)$$

$$X_{i,perm} = \frac{\sum_{z=0}^{L} J_i(z)dA}{Q_{perm}} \quad (6)$$

where Q_{feed} and x_{ifeed}, Q_{ret} and $x_{i,ret}$ and Q_{perm} and $x_{i,perm}$ the flow rates and the molar fractions comprising the feed the retentate and the permeated side streams [3, 4].

Membrane module network

The implemented superstructure model is comprised of 3 membrane stages. To model this network, Equations (1)-(6) are developed once for each stage, and additional mass balances are introduced to specify the connections between them. The retentate stream of each stage can either exit the system or be recycled to the feed of the previous stage. The retentate from the 1st-stage has the lowest CO_2 content, thus it is assumed to exit the system directly. For the permeate streams concentrated in CO_2, the option of feeding them to the next stage or bypassing this route is available for all 3 stages. This feature enables the determination of the presence or the absence of a membrane stage without introducing integer variables, despite the discrete nature of the decision [3, 5].

In Figure 1, a schematic of the developed network is shown, with all allowable connections depicted. Dashed lines correspond to plausible flows, whose presence or absence gives the final configuration of the system, and is a subject of the optimization performed.

To increase the driving force at each stage, compressors and vacuum pumps are installed on the feed and permeate sides, respectively. To determine their energy consumption (kW), Equation (7) is applied to either the compressors (c) or the vacuum pumps (vp), using the corresponding efficiency and flow rate.

$$W_{c/vp} = \frac{10^{-3}}{\eta_{c/vp}} \cdot \frac{\gamma}{\gamma - 1} \cdot RTQ \cdot \left[\left(\frac{P_{high}}{P_{low}} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right] \quad (7)$$

Turbines are also included in the network at the side

of the retentate streams that either exit the system or being recycled, to recover part of the electricity used for compression. The recovered energy (kW) is calculated through Equation 8.

$$W_{turb} = \frac{\eta_{turb}}{10^3} \cdot \frac{\gamma}{\gamma - 1} \cdot RTQ \cdot \left[1 - \left(\frac{P_{low}}{P_{high}}\right)^{\frac{\gamma-1}{\gamma}}\right] \quad (8)$$

The heat capacity ratio γ (-) is determined based on the composition of each gaseous stream, while the efficiency for the compressors, the vacuum pumps and the turbines are equal to 0.85, 0.7 and 0.9 [6].

Key performance indicators

In this analysis, the developed superstructure membrane module network is used to estimate both the technical and economic performance of different membrane materials. Thus, appropriate key performance indicators are defined. Based on them, the evaluation of the designed systems is determined.

The primary key process performance metrics are specific energy (MJ/kg$_{CO_2}$) and specific area (m^2/(kg$_{CO_2}$/s)). These two metrics are strongly influenced by the properties of the membrane material and the composition of the flue gas being treated, and they exhibit a trade-off.

$$sE = \frac{W_{total}}{X_{CO_2,perm}\, Q_{perm} MW_{CO_2}} \quad (9)$$

$$sA = \frac{A_{total} 10^3}{X_{CO_2,perm}\, Q_{perm}\, MW_{CO_2}} \quad (10)$$

Moreover, during the design of a carbon capture system regardless of the technology implemented, specific purity and recovery rates should be achieved. For this reason, the corresponding metrics can be calculated through Equations (11-12), respectively. These two metrics are introduced as constraints during the design of the membrane systems studied here.

$$Pu_{CO2} = \frac{X_{CO_2,perm}}{1 - X_{H_2O,perm}} \quad (11)$$

$$Rec_{CO2} = \frac{X_{CO_2,perm} \cdot Q_{perm}}{X_{CO_2,feed} \cdot Q_{feed}} \quad (12)$$

From literature, the purity of the final stream of captured CO_2 should be at least 95% to enable storage or utilization as raw material, while recovery should reach values of 90%.

For cost calculations, the methodology presented in previous works [4, 7] is followed. In the present work, we adopted fixed values for the electricity price and for the membrane material, equal to 0.1$/kWh and 50$/m^2 [4, 7].

Membrane materials and case studies

In Table 1, the material properties of CO_2 permeance (GPU) and the selectivity values for CO_2/N_2, CO_2/O_2, and CO_2/H_2O (-) required by the process model are reported for 5 materials. The selected membranes belong to different material classes, resulting in markedly different combinations of their properties. Two are polymeric and already at commercial scale (Polaris and PolyActive); two are facilitated-transport-based (FSC and FT-PVAm); and one is an inorganic, graphene-based membrane (NSLG, nanoporous single-layer graphene).

Table 1: Material properties of membranes tested during the analysis/optimization [4, 8].

Material	P_{CO_2} (GPU)	a_{CO_2/N_2}	a_{CO_2/O_2}	a_{CO_2/H_2O}
Polaris	2200	50	10	0.1
PolyActive	1450	46	17	0.1
FSC	838	95	21	0.1
FT-PVAm	1456	165	10	0.1
NSLG	10000	30	13	1.0

These materials and their performances are tested for the treatment of a number of flue gases, ranging from highly concentrated point-sources, with CO_2 content of 13-24% (coal power plant, cement plant, oil refinery) to more diluted ones with <8% CO_2 content (natural gas power plant, aluminium industry).

Optimization framework

The aforementioned membrane module network is formulated as a nonlinear programming (NLP) problem in the GAMS-Python environment, GamsPy. No integer variables are introduced into the system of equations, and discrete decisions, such as the presence or absence of a membrane module in the final system configuration, are determined entirely by the model's continuous variables. Despite the absence of integer variables, the final problem remains non-convex due to the nature of the equations that comprise the model of the developed superstructure. Such optimization problems can be difficult to solve and to guarantee global optimality. To prevent such issues, the global solver BARON [9] is used.

Two different optimization problems are solved for each material and case study:

- the bi-objective optimization of specific energy and specific area, by implementing the weighting method, and
- the single objective minimization of the capture cost.

In both cases, optimization is performed subject to two constraints: purity (95%) and recovery (90%), which are implemented as inequality constraints.

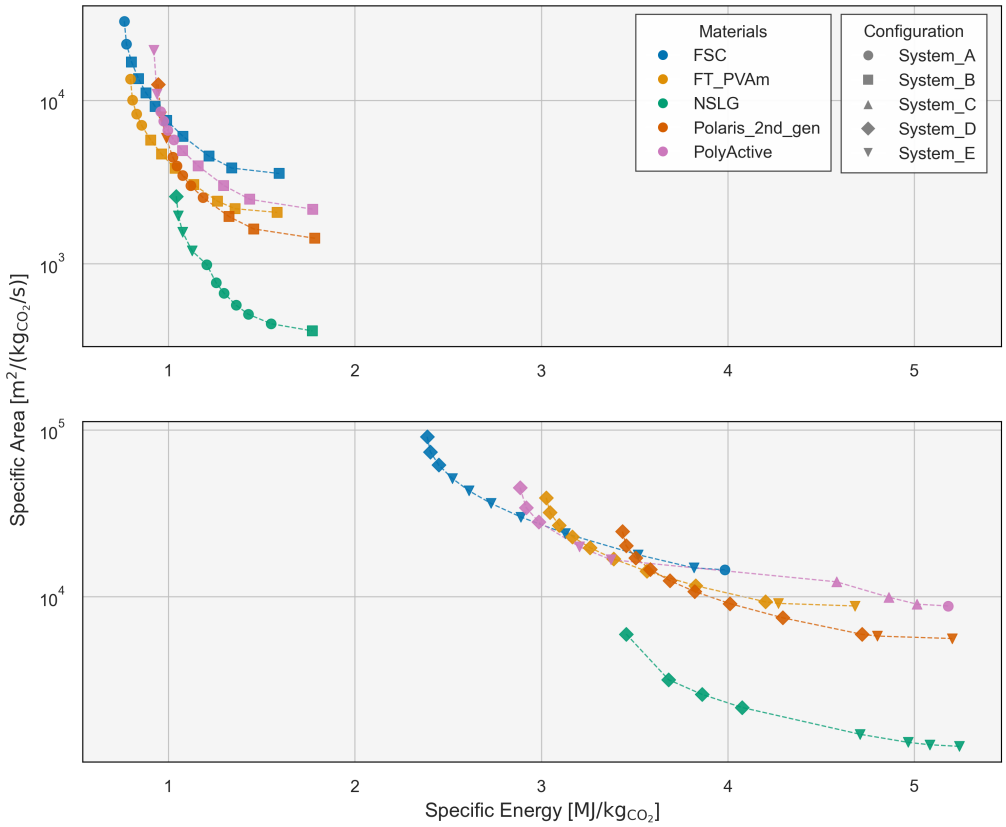

Figure 2: Technical Pareto fronts when treating a flue gas from a coal power plant with composition x_{CO_2}=13.7%, x_{N_2}=72.8%, x_{O_2}=3.6% (up) and from a natural gas power plant with composition x_{CO_2}=3.9%, x_{N_2}=75.2%, x_{O_2}=12.3% (below), under purity and recovery constraints of 905 and 90% respectively. Each curve is comprised of points with a variety of system configurations.

RESULTS AND DISCUSSION

Technical bi-objective optimization

In this series of optimization problems, the Pareto front curves for the specific energy and specific area of the studied membrane materials are generated for all membrane materials listed in Table 1. We report the results for two case studies with high and low CO_2 concentrations (Figure 2). The two objectives are closely correlated with the composition of the treated flue gas and the material properties. By using the superstructure model rather than a fixed-configuration model for membrane process, we produce Pareto fronts along which the points represent optimal configurations with different numbers of membrane stages and connections among them. The exact configurations suggested by the optimization are described in Table 2 and are shown in the Pareto fronts of Figure 2 with different symbols.

This approach finally allows a detailed comparison between materials, and the identification of limiting properties that determine each material's performance depending on the case study.

From this analysis, we observe that the CO_2/O_2 selectivity of the membrane material affects the allowable and feasible configurations on the Pareto front, particularly when the O_2 content is high. For example, in the Pareto fronts of specific energy-specific area of the FSC and FT-PVAm membranes, for the coal power plant case study, all the points correspond to systems with 2 stages thanks to the high selectivity. At the same time, the lower CO_2 permeance of these materials leads to higher specific area values.

For diluted flue gases with CO_2 concentrations < 8%, as in a natural gas power plant, the estimated specific energy and specific area values increase significantly. More specifically, the curves of most materials consist of points corresponding to systems with 3 stages, and only the curves for FSC and PolyActive (which have higher CO_2/O_2 selectivity) contain points corresponding to systems with 2 stages.

Moreover, we notice that some of the tested membranes achieve similar performances in terms of specific energy and area, by adopting different operating conditions or system configurations depending on the membrane properties. However, with diluted flue gases, the

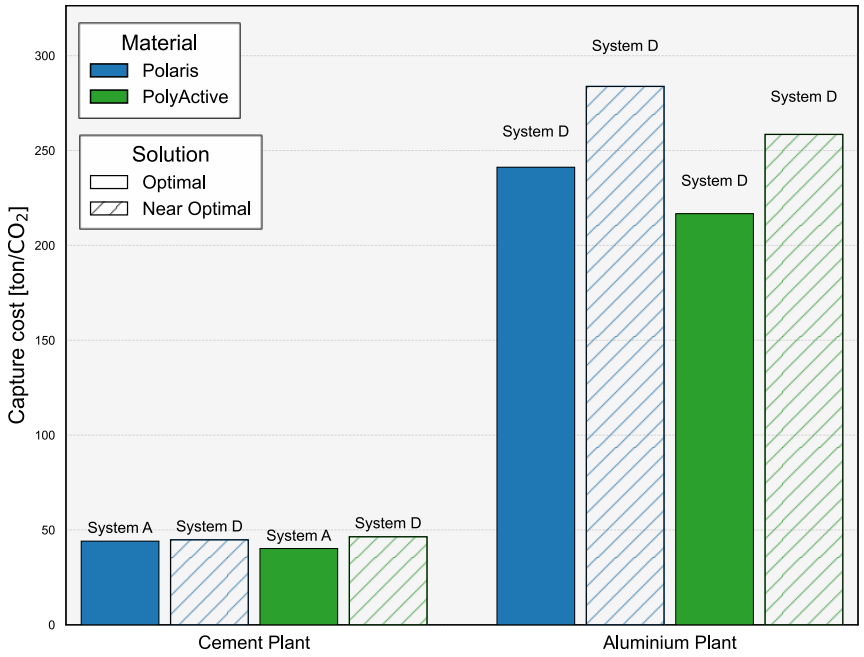

Figure 3. Best two minimum capture cost values for Polaris and PolyActive for capturing CO_2 from a cement plant, and an aluminium plant.

separation is more challenging, and all membranes require more complex configurations to meet the constraints of recovery and purity.

Table 2: Description of the membrane networks suggested after the technical and economic optimization.

Double Stage Systems	
System A	Recycle of the 2nd stage retentate to the 1st stage feed
System B	Recycle of the 2nd stage retentate to the 1st stage feed and bypass of the 1st permeate to the final outlet
System C	Recycle of the 2nd stage retentate to the 1st stage feed and recycle of the 2nd stage permeate to the 2nd stage feed
Triple Stage Systems	
System D	Recycle of the 2nd and 3rd stages retentates to the feed of the previous stage
System E	Recycle of the 2nd and 3rd stages retentates to the feed of the previous stage and bypass of the 2nd stage permeate to the final outlet

Cost minimization

The evaluation of economic performance is limited to the commercialised membrane materials, Polaris and PolyActive, for which price data are available. In this analysis, the capture cost is used as the objective function. In Figure 3, we report the results for two case studies: one with high CO_2 content (cement plant: x_{CO_2}=18%, x_{N_2}=63%, x_{O_2}=10%) and one with lower CO_2 content (aluminium plant: x_{CO_2}=4%, x_{N_2}=74.6%, x_{O_2}=20.5%). In particular, we show the minimum capture cost (optimal), along with the next-best optimal value (near-optimal).

In the case of the Cement plant, with high CO_2 content, the minimum capture cost can be secured with a double-stage system. However, for the membrane material Polaris, a slightly higher capture cost (~2%) can be achieved with a triple-stage system. The analysis of near-optimal solutions can be very helpful during decision-making. Indeed, a triple-stage system has typically lower specific energy consumption, thus it can be preferred in cases of an increase in the electricity price, which is always prone to a plethora of uncertainties, to enhance robustness in the economic performance of the system.

For the more dilute flue gas from aluminium plants, the next-best points for both materials have higher specific energy and specific area values, under the same system configuration. This means that, for challenging separations with low CO_2 and high O_2 concentrations, the points with minimum cost lie at the very end of the Pareto front, in the region of lower specific energy. In this case, achieving a similar capture cost with a different configuration would require adding a 4th stage, which would lower specific energy and increase specific area.

Robustness of the computational framework

The presented framework constitutes a key tool for

evaluating the performance of both established and emerging membrane materials at the process level. To improve the robustness and the computational efficiency of the model simultaneously, we have built the model as a non-linear program, avoiding discrete variables and defining a maximum number of possible recycle and bypass streams based on preliminary analysis. Also, we use the global solver BARON to ensure global optimality, given the non-convex behaviour of the superstructure that introduces many local minima in the solution domain.

Finally, the framework allows to perform both technical and economic optimization of different material properties under multiple case studies. By determining the optimal membrane network and operating conditions for each available material, we can determine the best option for each case study.

These results may also contribute to identify material properties that are desirable to improve the performance of the membrane process and to drive material enhancements in this direction. Finally, the ability to identify alternative designs with similar performance metrics provides the flexibility to consider both the operability of each design in real-life applications and its robustness under uncertainty.

CONCLUSION

We present an inclusive and detailed superstructure model capable of addressing multiple case studies across membrane materials and flue gas compositions. The framework enables us to identify optimal process configurations through fast and robust multi-objective technical and economic optimization. A range of membrane materials with varying material properties is tested, and the optimal configuration at both the structural and operational levels is determined. Through technical optimization, material performance targets are established to improve process feasibility. Such a framework constitutes an important advance in bridging the gap between small-scale material development and large-scale implementation of membrane process systems.

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