Optimisation of Polymeric Membrane Systems at Sub-Ambient Temperatures for Innovative Carbon Capture Processes.

Introduction

Amongst the variety of technologies available for Carbon Capture Utilisation and Storage (CCUS), the use of polymeric membranes is becoming increasingly attractive due to their relatively low capital cost and high energy efficiency. Membrane systems also tend to be considerably more compact than other technologies such as absorption or calcium looping, making them particularly appealing for retrofitting existing plants or for on-board carbon capture where space is limited. Despite these clear advantages, gas separation membranes suffer from one major drawback restraining their application in industry, being their performance limitation (i.e., upper bound) [Robeson, 1991]. Typically, a high-permeance polymeric material permitting a large CO_2 throughput and capture rate will do so at the expense of component selectivity, limiting the achieved product purity, and vice-versa. The last twenty years of membrane research pushed the boundary of that trade-off, notably through the development of polymers of intrinsic microporosity (PIMs) [McKeown et al., 2005]. This class of glassy polymers offers state-of-the-art performances in laboratory with both very high permeance (i.e., productivity) and selectivity, but lacks maturity and is yet to be used at large scales.

The operation of polymeric membranes at low temperature can present significant benefits on their permselective properties, and thus on their potential for industrial application. Glassy polymers offering high solubility selectivity towards CO_2 see that affinity amplified when operating temperature decreases. This was observed with a commercial polymer, Matrimid® [Liu et al., 2014], as well as a high-performance material, PIM-1 [Dieudonné et al., 2024]. At sub-ambient conditions, their CO_2 permeance moderately decreased due to reduced diffusivity, while their selectivity substantially rose, surpassing the upper-bound present at ambient temperature. This may bring considerable advantages in CCS processes, where product purity requirements usually hold-back the use of membrane-only configurations, prioritising hybrid systems adding a final purification step [Merkel et al., 2010].

The aim of this work is to put these opportunities into context and to present performant CCS processes taking advantage of the enhanced gas separation properties of PIMs at sub-ambient temperature. In order to weight the improved process performance against the additional cost resulting from the use of cryogenic cooling, a global approach of process simulation and costing was developed. This study assessed the industrial potential of several high-performance materials spanning several development levels in multiple process configurations for the treatment of a cement plant flue gas. For the first time, the membranes operating temperatures were treated as key decision parameters in a CCS process optimisation, with their potential value ranging between -40 °C and +70 °C.

Methodology for Process Simulation and Optimisation

The case study considered in this work was the capture of CO_2 from the cement plant flue gas presented in the CEMCAP project [Voldsund et al., 2019]. This reference was selected for the rigorous methodology for process evaluation and costing, and to enable direct comparison with the technologies investigated in its reports. Based on commonly used guidelines for CO_2 transport via pipeline, a minimum 95% CO_2 purity was enforced with under 50 ppm of water content in the final stream. Whenever possible, the CO_2 capture rate (i.e., recovery) was encouraged to be 90%, to match the typical targets found in literature. Contaminants such as SO_2 and H_2S were considered to be removed in the base plant which was costed accordingly.

A framework for process simulation and optimisation was developed combining a model of a hollow fibre membrane module built in Python with a full CCS process simulated in the industrial software *UniSim Design*®. The optimisation of the proposed processes, summarised in Figure 1, was implemented in Python, using the SciPy's Differential Evolution (DE) algorithm, which is particularly adapted to the process simulation framework. DE parameters were tuned to promote the exploration of the objective landscape and assure to consistently find the optimised process regardless of initialised given a number of decision variables. Candidate processes were evaluated based on a performance metric E (c.f., Eq,1), which was defined as the sum of their Total Annualised Cost TAC (in M€/yr) and the carbon tax cost C_{tax} associated with their equivalent emissions. Penalties were introduced to account for processes not satisfying pipeline transport constraints or other process targets.

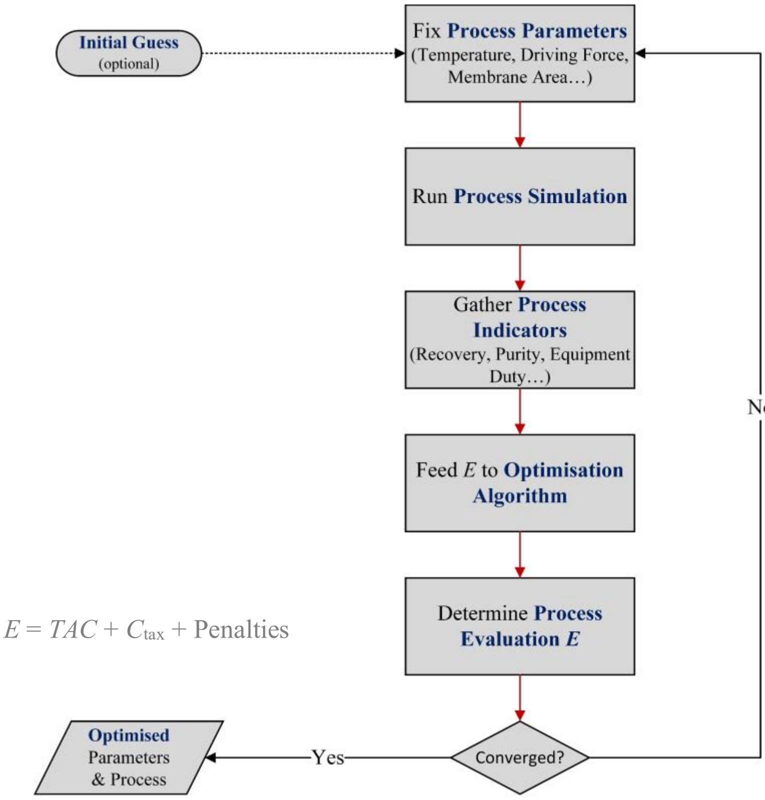

***Figure 1** Logic cycle for process optimisation framework.*

Low Operating Temperature for High-Recovery Membrane Systems

Counter-intuitively, low-temperature operation can help membrane processes reach higher recovery. This is because for high-permeance low-selectivity materials, recovery is limited by the purity constraints at high stage cuts. A first comparison was made using a basic dual membrane (**DM**) system presented in Figure 2.

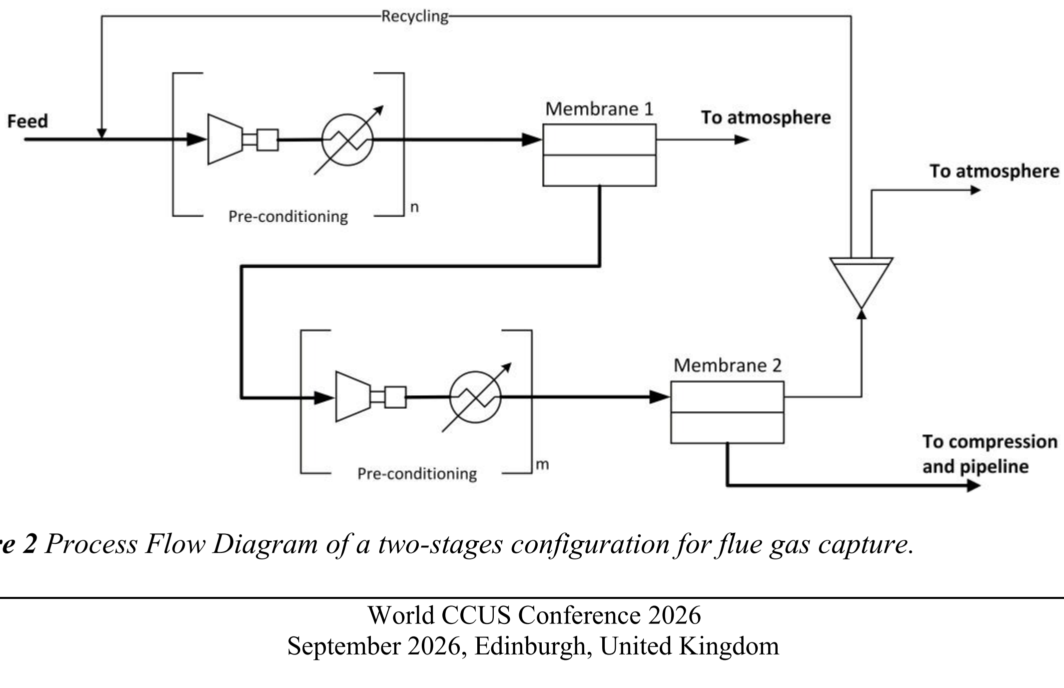

***Figure 2** Process Flow Diagram of a two-stages configuration for flue gas capture.*

The optimisation of the DM configuration using a PIM-1 membrane was conducted twice with no constraints on recovery, once without and once with temperature as a decision parameter (**DM-A** and **DM-B** respectively). The aim of these optimisations was to reach the highest economical capture rate under a carbon tax of 100 €/tn_{CO2}. Practically, this represents the CO_2 recovery value for which capturing one extra ton of CO_2 would cost more than 100 €. Table 1 presents their optimised performances.

***Table 1** Summary of optimisation results for DM-A/B.*

	DM-A	**DM-B**
Temperature as a parameter?	*No*	*Yes*
Recovery (-)	**79.8%**	**86.5%**
Total Annual Cost (M€)	**38.3**	**37.5**
of which cryogenic cooling (M€)	0.0	4.0
Total Power Consumption (MWh/yr)	**306**	**254**
Cost of Capture (€/tn_{CO2})	**59.0**	**53.2**

Operating the two separation stages at sub-ambient temperature (−11 °C and −33 °C, respectively) enabled DM-B to achieve substantially higher CO_2 recovery than DM-A, which fixed both membranes at ambient conditions. With the increase of material selectivity at low temperature, both membrane stage cuts can be raised while maintaining high permeate purity which transcribes into a higher achievable capture rate. The purer permeate stream of the cold membranes is also less bulky, reducing downstream equipment size and duty and therefore both capital and operating costs. The added 4 M€/yr cost of cryogenic cooling was thus largely offset by these reductions, resulting in a lower *TAC*. These observations were also seen in a three-stages Counter-current Recycle Membrane Cascades (CRMC) system. Due to the addition of a rectifying stage in CRMC comparing to DM, 90% recovery could easily be reached with or with tuning the membranes temperatures. However, using temperature as a process parameter resulted in a 10% decrease in cost of capture at equivalent recovery rate, although only the final stripping stages required cryogenic operation (-38 °C). Despite this, the DM configuration still yielded better performances for that extent of separation, with a third optimisation (**DM-C**) reaching 90% recovery at a cost of capture of 54.3 €/tn_{CO2}, versus 57.7 €/tn_{CO2} for the fully optimised CRMC.

Energy-Efficient Carbon Capture Processes with Sub-Ambient Temperature Membranes

As the optimum configuration found for PIM-1, DM-C was compared to three technologies presented in the CEMCAP report: membrane-assisted liquefaction (**MAL**), amine-based CO_2 absorption (**MEA**), and **Oxyfuel** combustion, which was deemed the best available technology for the case study considered.

***Table 2** Summary of economic key performance indicator for DM-C and benchmarked technologies for a 90% capture rate of a cement plant flue gas.*

	DM-C	**MAL**	**MEA**	**Oxyfuel**
Total Annual Cost (M€)	**40**	**40**	**38**	**22**
Net Electric Energy Consumption (GJ/$tn_{clinker}$)	2.2	2.2	0.9	1.4
Natural Gas Energy Consumption (GJ/$tn_{clinker}$)	-	-	3.1	-
Equivalent CO_2 avoided (-)	82%	78%	64%	82%
Cost of Capture (€/tn_{CO2})	**54.3**	**54.4**	**51.9**	**30.2**
Cost of Avoidance (€/tn_{CO2})	**60.2**	**83.5**	**80.2**	**42.4**
Specific Primary Energy Consumption for CO_2 Avoided (MJ/kg_{CO2})	3.3	3.2	7.1	1.6

Comparing only the cost of capture, DM-C seems fairly unattractive for this process, as it stays as the same level than MAL, another membrane-based technology, and well over MEA and Oxyfuel. However, when taking into account the full picture of the carbon capture chain and considering the secondary emissions due to energy use, DM-C became much more competitive. Indeed, membrane processes are known to be particularly energy efficient, which is even more true for the fully optimised processes proposed in this study. This made DM-C preferable to processes using thermal-based energy such as MEA when comparing their cost of avoidance. Oxyfuel remained more suitable for this case as its integration to the base plant considerably reduced secondary emissions by limiting the additional amount of energy to be spent on the carbon capture process. It must be noted thought that while the DM-C option can be retrofit to any plant, the oxyfuel technology requires significant modification of the cement plant.

Finally, a parametric study was conducted, notably revealing the important of electricity price in the economic performance of a membrane-based CCS process. A decrease of 25% in the cost of electricity brought down the cost of capture of DM-C by about 10%. This highlighted the importance of plant location in the choice of technology applicable to carbon capture and utilisation processes.

Conclusions

This study presents an innovative approach to membrane-based process optimisation. Considering polymeric membranes operating temperatures as a variable parameter unveiled the true performance and potential of a range of polymeric materials that are often put aside because only tested at ambient temperature. The optimisation of several membrane configurations in the case of a cement plant flue gas capture revealed that these fully optimised membrane-based processes can be competitive to other technologies when considering a global approach to CCUS.

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References

Dieudonné, P., Rea, R., Lasseuguette, E., and Ferrari, M.-C. [2024]. Impact of Sub-Ambient Temperature on Aging Rate and Gas Separation Properties of Polymers of Intrinsic Microporosity. *Membranes*, ***14***(6), 132.

Liu, L., Sanders, E. S., Kulkarni, S. S., Hasse, D. J., and Koros, W. J. [2014]. Sub-ambient temperature flue gas carbon dioxide capture via Matrimid® hollow fiber membranes. *Journal of Membrane Science*, ***465***, 49–55.

McKeown, N. B., Budd, P. M., Msayib, K. J., Ghanem, B. S., Kingston, H. J., Tattershall, C. E., Makhseed, S., Reynolds, K. J., and Fritsch, D. [2005]. Polymers of Intrinsic Microporosity (PIMs): Bridging the Void between Microporous and Polymeric Materials. *Chemistry - A European Journal*, ***11***(9), 2610–2620.

Merkel, T. C., Lin, H., Wei, X., and Baker, R. [2010]. Power plant post-combustion carbon dioxide capture: An opportunity for membranes. *Journal of Membrane Science*, ***359***(1–2), 126–139.

Robeson, L. M. [1991]. Correlation of separation factor versus permeability for polymeric membranes. *Journal of Membrane Science*, ***62***(2), 165–185.

Voldsund, M., Gardarsdottir, S. O., De Lena, E., Pérez-Calvo, J. F., Jamali, A., Berstad, D., … Jordal, K. [2019]. Comparison of technologies for CO 2 capture from cement production—Part 1: Technical evaluation. *Energies*, ***12***(3).