Energy penalty of a single stage gas permeation process for CO₂ capture in post-combustion: a rigorous parametric analysis of temperature, humidity and membrane performances

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Abstract

Over the last decade, membrane separation processes have attracted considerable research attention. This is due to their potential for lowering the costs of post-combustion CO₂ capture compared with the more established technologies, which are based on the use of chemical solvents. It is well known that the performance of membrane-based CO₂ capture is related to several factors, including flue gas composition, membrane material and system design. Membrane working temperature is one of the operating parameters that have several implications on the CO₂ separation process. However, surprisingly, this key operating variable has not been investigated in detail. It not only influences the intrinsic membrane properties and the feed composition, but also indirectly affects the energy behavior of the whole capture system. Hence, the resulting outcome cannot be intuitively deduced.

This work aims to study the effect of membrane operating temperature on a CO₂ capture process, which is operated by means of a single stage unit with feed compression and permeate vacuum pumping. The flue gas from a coal-fired power plant is considered, and the variation in separation performances and energy expenses is evaluated with respect to two types of polymeric membranes, which have different gas separation properties (permeability, selectivity).

This study reveals that an increase in the membrane operating temperature negatively affects CO₂ permeate purity and power consumption to drive the separation process. In addition, the influence on area requirement is strictly related to the type of membrane material.

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Keywords: carbon capture; membrane separation; operating temperature; humidity.
1. Introduction

Despite the rapid growth of renewable energy, fossil fuels are still projected to play a central role in the power generation sector in the 21st century. In this context, carbon capture and storage technologies are regarded as a short-term solution to alleviate global warming effects, caused by the release of CO\textsubscript{2} from industrial and power generation facilities.

It is well known that the performance of post-combustion capture using membrane separation is closely related not only to the intrinsic properties of polymeric materials (permeability and selectivity), but also to the inlet conditions of flue gas that is to be treated and the design of the separation system. Aside from the configuration layout, a key role is played by the system operating conditions, which include the pressure ratio across the feed and permeate sides of the membrane and the module working temperature [1].

As well known, the increase of exhaust flue gas temperature, in the allowable range for membrane operation, produces a concurrent increase of moisture content in the saturated gas mixture. From a physical point of view, the increased water vapor content promotes an internal sweep, which in turn reduces the CO\textsubscript{2} partial pressure on the permeate side and enhances the driving force for its separation through the membrane [2]. On the other side, an increase of temperature also influences membrane separation properties, thus causing a variation of permeability and selectivity related to the intrinsic properties of membrane material [3,4]. Exhaust flue gas temperature and humidity have also a not negligible impact on membrane system energy requirement, due to the variation in power consumption of system utilities (compressors and vacuum pumps) and power production through energy recovery.

The interplay between flue gas temperature, inlet water content and water removal through flue gas compression has not been widely investigated in literature. These items, on occasion, have been effectively studied separately. However, to our knowledge, no study has systematically addressed the impact of these different variables using simulations performed on a multi-component mixture.

This paper is aimed at studying the combined role of temperature and humidity on membrane system operation, to assess the variations in gas separation performances, as well as its implications at a component level (e.g., compressors, pumps, and turboexpander) and on the membrane system as a whole. The study analyzes the CO\textsubscript{2} capture from a coal-fired boiler flue gas, operated by a single stage membrane unit. In the configuration proposed, pressure difference across the membrane is created through a combination of feed compression and permeate vacuum pumping, while an energy recovery system is used to produce power from retentate expansion. To broaden the scope of this investigation, two types of polymeric membranes are compared: the first is the Polyactive\textsuperscript{TM}1500 [5], a commercial multi-block copolymer that exhibits a high CO\textsubscript{2} over N\textsubscript{2} selectivity ($\alpha_{CO2/N2}= 53.2$) and a relatively low CO\textsubscript{2} permeability ($p_{CO2} = 181$ Barrer); the second is a polymer with intrinsic microporosity (PIM-1) [6], representing a new generation of membrane materials with improved gas permeability compared with conventional polymers ($p_{CO2}=3700$ Barrer).

### Nomenclature

#### Symbols

- $p$: permeability, Barrer
- $P$: power, MW
- $T$: temperature, °C

#### Greek symbols

- $\alpha$: selectivity

#### Subscripts

- COMPR: compressor
- MEMBR: membrane
- TURB: turboexpander
- VP: vacuum pump

#### Acronyms

- CR: capture ratio
- PIM: PIM-1
- POL: Polyactive\textsuperscript{TM}1500
2. Description of the study case and layout of CO₂ capture membrane system

The representative study case is the flue gas from a coal-fired power plant with a design rated capacity of 550 MW and specific CO₂ emissions of approximately 856 kg/MWh [7]. Based on a flue gas flow rate of 635.5 kg/s, the CO₂ and water vapor molar fractions, at a temperature of 57°C, are 13.5% and 15.2% respectively. Figure 1 shows the layout of a single stage membrane system, which is based on feed side compression and vacuum pumping on the permeate side. In this system, the exhaust flue gas is compressed into a two-stage compressor with intercooling, thereby allowing for the removal of condensed water via flash separation. The compressed flue gas, at 6 bar, is then sent to a single stage membrane unit for CO₂ capture. The retentate stream is expanded in a two-stage turboexpander, which reduces the net power consumption of the membrane system. Specifically, thermal integration between the energy recovery and the feed compression systems has been performed, to enhance the power production from the retentate expansion by increasing the temperature at the turboexpander inlet. On the other side, the CO₂ enriched permeate stream is kept at a base pressure of 0.2 bar using a two-stage vacuum pump. Hence, combining feed compression and vacuum pumping, the pressure ratio across the membrane states at 30. Membrane gas separation has been simulated using the proprietary software tool M3PRO [8], properly integrated into Aspen Plus environment [9], to carry out the energy analysis of the whole system.

Fig.1. CO₂ capture system: four mains blocks can be identified, i.e., the feed compression and cooling system, the energy recovery system, the membrane separation unit and the permeate vacuum pumping system

3. Assessing the effect of operating temperature on membrane system performance parameters

In this study, the performance parameters of the capture system have been compared by varying the membrane operating temperature (T₉₀) from 30°C to 70°C. Assuming T₀ =30°C, the molar content of water vapor at the membrane inlet is less than 1%, thus reducing compared to the value at the exit of desulfurization unit, due to the concurrent pressure increase and flue gas cooling. On the other hand, increasing T₀ results in an increase in the flue gas water vapor content, due to the higher intercooling temperature of the two-stage compressor unit.

Moreover, T₀ has a non-negligible impact on gas separation properties. Assuming the same temperature variation, CO₂ permeability more than doubles in the case of Polyactive™1500 to approximately 378 Barrer. In contrast, α_{CO₂/N₂} reduces from 53 to 20.4 (-60%). In the case of PIM-1, CO₂ permeability decreases slightly to 3005 Barrer (≈ -20%), while α_{CO₂/N₂} reduces from 24 to 12. It is also notable that the influence of T₀ on water vapor separation properties has been neglected because its permeability is much higher than the other gas species for both Polyactive™1500 (p_{H₂O}=85500 Barrer) and PIM-1 (p_{H₂O}=80000 Barrer) membranes [10].
3.1. The effect on permeate purity and membrane area requirement

Figure 2a highlights that as $T_{\text{oper}}$ increases from 30°C to 70°C, the separation performances worsen. The decrease in membrane selectivity more than offsets the sweep effect promoted by the greater water vapor molar fraction. The decrease in permeate purity is fairly independent of the capture ratio, stating at approximately 16% pts and 12% pts for the Polyactive$^{\text{TM}}$1500 and PIM-1, respectively. As shown in Figure 2b, the very high CO$_2$ permeability of PIM-1, due to its large free fractional volume, allows to drastically reduce membrane area requirement compared to Polyactive$^{\text{TM}}$1500. In the latter case, assuming a thickness of active layer of 1.5 µm, the area steadily increases with the capture ratio (CR) and reaches a maximum value of 2.5 Mm$^2$ (CR=90%, $T_{\text{oper}}$=30°C). Considering the same operating conditions with a PIM-1 membrane, the area requirement reduces to 102×10$^3$ m$^2$.

The increase of $T_{\text{oper}}$ positively affects the area requirement of Polyactive$^{\text{TM}}$1500 to such an extent that it is more pronounced with the increase in CO$_2$ recovery. As a result, with a CR=90%, the membrane area decreases of approximately 60%, stating at 964×10$^3$ m$^2$. The effect of temperature on PIM-1 is much less apparent, where the reduced CO$_2$ permeability allows for a slight increase (+5%) of area requirement, that reaches a maximum value of 107×10$^3$ m$^2$ (CR=90%, $T_{\text{oper}}$=70°C).

3.2. The effect on membrane system power consumption

As shown in Figure 3c, the net membrane power consumption ($P_{\text{NET MEMBR}}$) logically increases with the capture ratio. At $T_{\text{oper}}$=30°C, $P_{\text{NET MEMBR}}$ rises from 35 MW (CR=20%) up to approximately 70-80 MW (CR=90%), which corresponds to 12-14% of power plant design capacity. This can be explained with the simultaneous decrease of power production of turboexpander ($P_{\text{TURB}}$) and the increase of power consumption of vacuum pumping system ($P_{\text{VP}}$), which arises from the corresponding variation of retentate and permeate stream flows. Conversely, the specific energy requirement ($E_{\text{MEMBR}}$), referred to CO$_2$ permeated, has a decreasing asymptotic trend with the CR value, stating at 161.3 kWh/tonne CO$_2$$_p$ (Polyactive$^{\text{TM}}$1500) and 186.1 kWh/tonne CO$_2$$_p$ (PIM-1) (Fig. 3d).

The increase in membrane operating temperature produces contrasting effects on the energy recovery system and power utilities (compressors/vacuum pumps). First, the higher intercooling water temperature allows for an increase in power consumption for feed compression ($P_{\text{COMPR}}$), due to the higher compressor inlet temperature and the lower water condensation, thereby allowing for an increase in the flue gas flow rate. Therefore, by increasing $T_{\text{oper}}$ from 30°C to 70°C, $P_{\text{COMPR}}$ increases by approximately +25% (138.6 MW). Another aspect to be considered is
represented by the increase of $P_{VP}$ (Fig. 3a), which is due to the greater permeate stream flow rate, as promoted by the reduced selectivity and water condensation. Assuming CR=90%, $P_{VP}$ increases by more than 50% for both membrane types, and reaches a maximum value of 38.7 MW (Polyactive\textsuperscript{TM} 1500) and 46.9 MW (PIM-1).

The last effect related to the increase of $T_{oper}$ corresponds to the rise of the turboexpander inlet temperature, promoting $P_{TURB}$ (Fig. 3b). Nevertheless, the increase in $P_{TURB}$ reduces more and more with the CO\textsubscript{2} separation degree, and becomes almost negligible at CR=90%. Indeed, due to the reduced membrane selectivity at higher temperatures, the retentate stream flow rate undergoes a more pronounced decrease with the same capture ratio, thereby compensating the beneficial effects of the higher turboexpander inlet temperature.

Considering the system as a whole, the increase in operating temperature negatively affects $P_{NET\_MEMBR}$. Hence, assuming CR=90%, $P_{NET\_MEMBR}$ increases by 58% (107.6 MW) and 54% (121.6 MW) for the Polyactive\textsuperscript{TM} 1500 and PIM-1 membranes, which represents approximately 20% of the design power plant capacity. Additionally, in the case of PIM-1, with the same increase of $P_{NET\_MEMBR}$, the specific energy requirement reaches a peak value of 287 kWh/tonne CO\textsubscript{2,p}. Assuming a mean energy conversion efficiency for electricity generation of 38% and CR=90%, the specific energy requirement, on a thermal basis, ranges from 1.5 GJ/tonne CO\textsubscript{2,p} (Polyactive\textsuperscript{TM} 1500, $T_{oper}$=30°C) to 2.7 GJ/tonne CO\textsubscript{2,p} (PIM-1, $T_{oper}$=70°C).

![Fig. 3. Effect of membrane operating temperature on $P_{VP}$ (a), $P_{TURB}$ (b), $P_{NET\_MEMBR}$ (c) and $E_{MEMBR}$ (d).](image)

4. Conclusions

This paper assessed the effects of membrane working temperature ($T_{oper}$) and feed humidity on the performance of a membrane separation system used to capture 90% of the inlet CO\textsubscript{2} with a single membrane stage, based on a pressure ratio of 30. The simulations have been made for a 550 MW coal-fired power plant taken as reference. Considering a configuration layout with feed side compression and vacuum pumping of permeate, the behavior of
two membrane types with opposite separation properties was evaluated.

Simulation results have highlighted the following: the CO\textsubscript{2} permeate purity drastically reduces with \( T_{\text{oper}} \), due to the prevailing effect exerted by the decrease of CO\textsubscript{2} over N\textsubscript{2} selectivity compared to the sweep effect promoted by the greater water vapor molar content. Assuming CR=90\%, CO\textsubscript{2} permeate purity reduces from 70.3\% to 53.8\% and from 56.2\% to 43.8\% for Polyactive\textsuperscript{TM} 1500 and PIM-1, respectively. Regarding the membrane area, it reduces of 60\% in the case of Polyactive\textsuperscript{TM} 1500 (964×10\textsuperscript{3} m\textsuperscript{2}), while a slight increase is observed for PIM-1 (107×10\textsuperscript{3} m\textsuperscript{2}), as a result of the reduced CO\textsubscript{2} permeability.

From the energy point of view, an increase in \( T_{\text{oper}} \) negatively affects the power consumption for compression because of the increase in the intercooling temperature and the reduced water condensation. The last aspect, together with the increase in the permeate stream flow rate as promoted by greater gas permeabilities, is responsible for an increase in the power consumption for vacuum pumping. As a result, the net membrane system achieves a maximum increase of approximately 60\% (CR=90\%), stating at 107.6 MW and 121.6 MW for the Polyactive\textsuperscript{TM} 1500 and PIM-1, respectively. Assuming the same operating conditions, the specific energy requirement on a thermal basis ranges from 2.4 GJ\textsubscript{th}/tonne CO\textsubscript{2,p} (Polyactive\textsuperscript{TM} 1500) to 2.7 GJ\textsubscript{th}/tonne CO\textsubscript{2,p} (PIM-1).

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References