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Analysing the Effect of CO2 Concentration in Flue Gas on CO2 Capture Characteristics of Hollow Fibre Gas Membrane System

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Membrane technology has been established as an efficient technology for capturing CO2 from multicomponent flue gas mixtures. The primary focus of this study is to examine the potential influence of CO2 concentrations in the feed flue gas stream on the CO2 capture characteristics of hollow fibre membrane module systems, whose fibre materials are made of polyetherimide-polyimide. The experiments were conducted on pure gases (CO2, N2) and multicomponent gas mixtures (N₂ + CO₂ + O₂), containing fixed amount of O2 (4.3 %vol) and variable %vol of CO₂ and N2 respectively, at a fixed volumetric flow rate of 130 Nlh-1, at a temperature of 30 °C and a constant pressure difference of 8.57 bar. The objective was to determine and predict how flux, permeance, CO2/N2 selectivity/separation factor, stage cut through the membrane, retention coefficient as well recovery to the permeate stream vary with different CO2 feed compositions. The results demonstrated that CO₂ flux, permeance and percentage recovery kept increasing as the proportion of CO₂ in the feed gas stream increases. CO₂ permeance 6.29 GPU and recovery 96 % peaked at a feed concentration of 55 %vol CO₂, with a minimum retention coefficient of 4 %. In contrast, the highest CO₂ separation factor 3.3 occurred at a feed concentration of 25 %vol CO₂.

* 1. Introduction

Rapid industrialization since the mid-20th century has driven global warming due to increased CO₂ emissions. According to Nedoma and Netušil (2021), the last few decades have witnessed a surge in topics related to CO2 capture technologies in Europe and across the globe due to the high dependence on energy from fossil fuels. However, not only has CO2 emission been on a steep rise but also a massive advancement in carbon capture and utilization technologies. Varieties of CO2 capture technologies developed over the years are distinct, each with its pros and cons, however, energy utilization and consumption is a stand-out factor considered across all engineering fields (Habib et al., 2020). Membrane technology stands out among these methods due to its high energy efficiency, compact design, and scalability (Hu et al., 2022) and relatively lower cost (Adhikari et al., 2023). Zuberi et al. (2024) also suggested that CO2 capture and utilization technologies will be substantial in achieving Vision 2050 of zero CO2 emission. Yang et al. (2024) highlight that utilizing CO2 ​in pyrolysis and gasification improves product quality, boosts energy recovery, and reduces CO2 emissions and pollutants, promoting environmental sustainability. A membrane can be configured in different shapes, such as flat sheet, spiral, tubular and hollow fiber membrane modules. Hollow fibre membranes, made from various polymer materials, are widely used for CO₂ capture due to their high packing density and effective separation capabilities (Boram, 2021).

Jasim et al. (2023) modeled the optimal operating conditions for the separation of CO2 from CH4/CO2 mixture, at 2 to 10 mol% CO2 feed concentrations, and observed that the mass transfer coefficient, flux and gas diffusivity through the membrane surface increase with increase in the CO2 feed gas concentration. Xu et al. (2022) revealed that the purification of biogas improves with an increase in CO₂ concentration. Higher CO₂ feed concentrations enhance the efficiency of CO₂ capture by creating a larger concentration gradient. Similarly, Yan et al. (2022) found that during the upgrading of biogas, certain solvents perform better when the concentration of CO₂ in the biogas mixture is high. According to Michailos and Gibbins (2022), the efficiency of carbon capture from flue gases largely depends on the concentration of CO₂ in the flue gas feed. Wang and Song (2020) also noted that a higher percentage of CO₂ by volume in the feed flue gas positively impacts the efficiency of carbon capture technology being used. Aydani et al. (2020) explained that the effectiveness of capturing CO₂ from binary mixtures (such as CO₂/CH₄ and CO₂/N₂) increases with a higher concentration of CO₂ in the feed gas, as the increased CO₂ permeance implies the depletion of other gas components in the mixture. Fernández-Barquín et al. (2017) studied CO₂/N₂ separation using a two-stage membrane process with feed CO₂ concentrations of 5% to 65%. Their findings showed that membrane performance improves with higher concentrations of the target gas. Higher CO₂ concentrations in the feed gas enhance the efficiency of carbon capture technologies, reducing energy demands and solvent use in absorption processes. However, proper operational measures are essential to tackle challenges such as corrosion and system degradation (Xu et al., 2022). The physical, mechanical and thermal stability of membranes must be considered because their performance decline over time due to factors such as fouling and pore blockage (Jong Hak Kim, 2022). A review of the literature highlights a lack of studies on the impact of CO₂ concentrations variations on carbon capture technologies, particularly in membrane systems. Most research has concentrated on binary gas separations, such as CH₄/CO₂ or CO₂/N₂, using absorption or adsorption methods. This study aims to address this gap by experimentally analyzing how different CO₂ concentrations impact the efficiency and mass transfer characteristics of a hollow fiber membrane system, under fixed temperature and pressure conditions, with a particular emphasis on flue gas systems.

* 1. Methods

**2.1. Experimental set-up**

The experiments were conducted to evaluate the impact of varying CO₂ concentrations in flue gas streams on the capture of CO₂. This was achieved using a laboratory membrane unit, the Ralex GSU-LAB 200, manufactured by MemBrain. The full characteristics of the membrane system are detailed in Table 1, while Figure 1 provides a schematic representation of the process. Initially, tests were performed using pure gases (100 %vol CO₂ and N₂) at the same volumetric flow rate of 130 Nlh⁻¹, with variable feed-side pressure ranges and a constant permeate pressure of 1.43 bar. Following this, six different model flue gas mixtures with varying compositions, as outlined in Table 2, were passed through the membrane gas analyzer/separator under steady-state conditions. The complete experimental configuration and analysis were carried out at a constant volumetric flow rate of 130 Nlh⁻¹, at an average process temperature of 30 °C, with feed and permeate pressures maintained at 10 bar and 1.43 bar, respectively.

*Table 1:* *Hollow fibre membrane module (P2-1.2) system* properties

|  |  |
| --- | --- |
| Fibre material | Polyetherimide |
| Quantity of fibre | 2900 pieces |
| external fibre diameter | 0.3 mm |
| Active length of fibre | 0.3 m |
| Fibre wall thickness | 0.00006 m |
| Mass transfer surface area | 0.82 m2  |

Table 2: The compositions of the model feed gas mixtures used in this study

|  |  |  |  |
| --- | --- | --- | --- |
| Model gas mixture %composition (N2 + CO2 + O2) | N2 (%) | CO2 (%) | O2 (%) |
| 90.7-5-4.3 | 90.7 | 5.0 | 4.3 |
| 80.7-15-4.3 | 80.7 | 15.0 | 4.3 |
| 70.7-25-4.3 | 70.7 | 25.0 | 4.3 |
| 60.7-35-4.3 | 60.7 | 35.0 | 4.3 |
| 50.7-45-4.3 | 50.7 | 45.0 | 4.3 |
| 40.7-55-4.3 | 40.7 | 55.0 | 4.3 |

membrane

permeate

retentate

N2

N2+O2

CO2

Gas

mixer

heater

GAS ANALYSIS

PIR

TIRC

PIRC

TIR

FIR

PIRC

TIR

FIRC

FIRC

FIRC

 *Figure 1: Block diagram illustrating CO2 membrane separation process from the flue gas stream*

**2.2. Data analysis**

Experimental data were analyzed to calculate key gas flow properties, including permeate flux (molm-2s-1), Permeability $P\_{i}$ (barrer), Permeance *(*$\frac{P\_{i}}{l})$ (GPU), Selectivity$ α\_{i}$, Stage cut ϴ using standard equations from literature (Kratky et al., 2020). The calculations assumed ideal gas behavior, incompressible, laminar, Newtonian flow under steady-state conditions. Parameters such as separation factors (Sf\*), CO2 recovery in the permeate stream R and CO2 retention coefficient $Rc $are also determined using the equations below, to ascertain their interactions with different CO2 feed concentrations in the multicomponent gas mixtures.

$R=\frac{n\_{i}^{p}}{n\_{i}^{f}}$ $∙$100% (1)

Rc = $\frac{n\_{i}^{f}-n\_{i}^{p}}{n\_{i}^{f}}$ (2)

Sf\* $={\frac{c\_{i}^{p}}{c\_{j}^{p}}}/{\frac{c\_{i}^{f}}{c\_{j}^{f}}}  $= ${\frac{n\_{i}^{p}}{n\_{j}^{p}}}/{\frac{n\_{i}^{f}}{n\_{j}^{f}}}  $ (3)

where *n* (mols-1) represents gas concentrations, superscripts p and f refer to permeate and feed sides respectively while the subscripts i and j represents CO2 and any other gas respectively.

3. Results and Discussion

**3.1 Pure gases**

Figure 2a: CO2 permeance against partial pressure difference

Figure 2b: N2 permeance against partial pressure difference

Figures 2a and 2b illustrate the relationship between the permeance of individual pure gases through the hollow fiber membrane and partial pressure differences at a constant temperature under steady-state conditions. The membrane exhibited high CO₂ permeance, emphasizing its potential for efficient and cost-effective CO₂ capture. CO₂ permeates easily through the membrane, while N₂ remains largely in the retentate stream, highlighting the module's selectivity for CO₂ over N₂.

The data also revealed that CO₂ permeance decreases as the partial pressure difference increases, while N₂ permeance shows a slight increase. This behavior differs from the typical trend of permeate flux, which generally rises with increasing partial pressure difference. The inverse relationship between CO₂ permeance and partial pressure difference arises because permeance depends directly on permeate flux but inversely on the pressure difference. The decrease in gas flux efficiency at high pressures can be attributed to plasticization, as condensable gases like CO₂ can induce this effect in polyimide membranes. Plasticization causes swelling in the polymer matrix, altering free volume and inter-chain spacing. This increases polymer segment mobility, reducing the size-sieving ability of polyimide membranes and ultimately decreasing selectivity (Zhang et al., 2019). Similar observations were made by Thundyil et al. (1999), who noted a decline in pure CO₂ permeability with rising pressure differentials, and by Jasim et al. (2023), who reported reduced CO₂ diffusivity (a property linked to permeability) as pressure differences increased.

**3.2 Effect of different CO2 concentrations on the CO2 capture from the model flue gas**

This section delves into the effect of increasing CO2 concentrations (% by volume) in the model gas on the mechanisms of mass transfer involving CO2 capture from flue gas stream.

*Figure 3a: Effect of different CO2 concentrations on CO2 permeate flux*

*Figure 3b: Effect of different CO2 concentrations on CO2 permeability*

Figures 3a and 3b illustrate the impact of increasing CO₂ concentrations on CO₂ flux and permeability in the hollow fiber membrane system. The data show a direct relationship between CO₂ concentration, permeate flux and CO₂ permeability. Permeate flux exhibits a sharp, continuous increase with rising CO₂ concentrations across all levels. However, CO₂ permeability shows the most significant increase between 5 %vol and 25 %vol CO₂ concentration, with the rate of increase slowing beyond this range. Figure 3b highlights the steepest rise in permeability between 5 %vol and 15 %vol, followed by a slower increase from 15 %vol to 25 %vol, and a more pronounced decline in the rate of increase above 25 %vol. This trend suggests that very high CO₂ concentrations may negatively affect CO₂ selectivity and separation factor from the gas mixture. Figure 3a illustrates that permeate flux increases directly with an increase in CO2 concentrations because higher CO2 concentrations result in higher concentration or partial pressure difference (driving force) across the two sides of the membrane (Jasim et al., 2023). Xu et al. (2022) and Jasim et al. (2023) reported a similar trend in the permeate flux with CO2 concentrations.

Figure 4a: Effect of CO2 feed concentrations on CO2 recovery (R$)$ and retention coefficient (Rc$)$

*Figure 4b: Effect of CO2 feed concentrations on Stage cut θ(CO2)and selectivity α(CO₂/N₂)*

Figures 4a and 4b illustrate the effects of feed CO₂ concentration on CO₂ recovery, retention coefficient, stage cut, and selectivity in a membrane system. CO₂ recovery refers to the proportion of CO₂ in the feed gas that reaches the permeate stream, while the retention coefficient measures the amount of CO₂ retained in the retentate stream. The data show that as feed CO₂ concentration increases, CO₂ recovery rises due to the membrane’s high CO₂ permeability, while the retention coefficient declines. This occurs because higher CO₂ concentrations drive more CO₂ into the permeate stream, leaving the retentate with reduced CO₂ content, indicating higher purity in the permeate stream. These findings align with Fernández-Barquín et al. (2017), who linked higher CO₂ recovery to the increased driving force at elevated feed CO₂ levels. Figure 4b highlights that stage cut (fraction of feed gas passing through the membrane) increases with rising feed CO₂ concentrations. However, CO₂ selectivity peaked at 15 %vol feed CO₂ concentration and then declined as feed concentration increased further, suggesting that excessively high CO₂ levels may negatively impact selectivity. This trend, consistent with Aydani et al. (2020), implies a trade-off between stage cut and selectivity, as selectivity decreases with increasing stage cut. This observation also aligns with Seghman et al. (2022).

*Figure 5a: Effect of different CO2 concentrations on separation factors*

*Figure 5b: Relationship between separation factor and permeability at different CO2 concentrations.*

Figures 5a and 5b delineate the correlation between CO₂ separation factors about the other two gases (N₂ and O₂) and CO₂ concentrations and permeability. The results indicated that the separation factor Sf\*(CO₂/N₂) is far greater than the separation factor Sf\*(CO₂/O₂) across all CO₂ concentrations, emphasizing the membrane's superior ability to separate CO₂ from N₂ due to the substantial difference in their diffusivities. This affirms the efficacy of the membrane module used in this study for the separation of CO2 and N2 Mixtures. A further perusal through Figure 5a also revealed maximum separation factor Sf\*(CO₂/N₂) of 3.3 was recorded at 25 %vol feed CO2 concentration; further increase in CO2 concentrations results in a decrease in the separation factors. Figure 5b easily portrayed that the increase in CO2 separation factors CO2 with permeability was short-lived as maximum separation factor Sf\*(CO₂/N₂) was obtained at CO2 permeability of 363 barrer, after which a downtrend sets in. This agrees with our earlier assumption that very high CO2 concentrations in the feed gas may be detrimental to CO2 selectivity and separation factor. This pattern aligns with the understanding that membranes with high permeability often exhibit reduced selectivity, a trend supported by Jong Hak Kim (2022). Kratky et al. (2021) observed that the separation factor decreases as CO2 permeability and feed flux increases.

Table 3: The overview of the mass transfer properties of CO₂ in the model gas mixtures used

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| cCO₂F | $P\_{CO₂}$ (GPU) | % R | % Rc | θ(CO₂) | α(CO₂/N₂) | Sf\*(CO₂/N₂) | Sf\*(CO₂/O₂) |
| 5% | 5.01 | 61% | 39% | 0.61 | 4.02 | 2.97 | 1.28 |
| 15% | 5.79 | 74% | 26% | 0.74 | 4.27 | 3.24 | 1.38 |
| 25% | 6.05 | 82% | 18% | 0.82 | 4.14 | 3.30 | 1.40 |
| 35% | 6.16 | 88% | 12% | 0.88 | 3.84 | 3.17 | 1.38 |
| 45% | 6.24 | 92% | 8% | 0.92 | 3.43 | 2.93 | 1.33 |
| 55% | 6.29 | 96% | 4% | 0.96 | 2.90 | 2.56 | 1.26 |
| 100% | 30.0 |  |  |  |  |  |  |

* 1. Conclusions

This study highlights the effectiveness of the selected hollow fiber membrane for separating CO₂/N₂ mixtures, with CO₂ predominantly diffusing to the permeate stream and N₂ remaining in the retentate. CO₂ concentrations in flue gases typically range from 8–15 %vol but can exceed 80 %vol in oxy-fuel combustion due to the absence of nitrogen. Higher CO₂ concentrations in the feed gas enhance the separation process by increasing the driving force, resulting in improved recovery rates and membrane permeability. This also lowers operational costs and energy requirements as nitrogen composition in the feed gas decreases. The study observed that CO₂ flux, stage cut, and recovery increased with higher CO₂ concentrations, while the retention coefficient declined due to elevated partial pressure differences. The peak of the separation factors Sf\*(CO₂/N₂) and Sf\*(CO₂/O₂) are 3.3 and 1.40 respectively at 25 %vol CO₂ feed concentration, indicating optimal selectivity at moderate concentrations. However, at very high CO₂ feed concentrations, plasticization effects could occur, thereby reducing the membrane's selectivity despite an overall increase in permeability. These findings demonstrate that the improved performance of the membrane at high CO₂ %vol feed concentrations is primarily due to enhanced permeability, though selectivity may be compromised at extreme levels of CO2 in the multicomponent feed gas.

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