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Experimental Study on CO_2 Membrane Separation from Flue Gas

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The paper scoped to evaluate the process characteristics of polyetherimide-polyimide hollow fibre membrane module to separate CO_2 of the model flue gas. The model gas was composed of 15.2 vol % CO_2 + 4.5 vol % O_2 + 80.3 vol % N_2, as referenced to the typical composition of flue gas emitted by an LPG-fired power plant. The effect of process variables on process characteristics was researched for various differential pressures between permeate 0.2 - 0.5 MPa (a) and retentate 0.5 - 1.0 MPa (a), feed flowrates 100 g h^{-1} and 200 g h^{-1}, all under the gas temperature of 30 °C. It was found out that the value of the separation factor (CO_2/N_2) was 6.9. The decrease of the separation factor (CO_2/N_2) by 4.1 compared to the ideal selectivity (CO_2/N_2). The separation factor (CO_2/O_2) was shallow; its maximum value of 1.8 was reached.

1. Introduction

CO_2 separation from flue gas by membrane process is nowadays viewed as a young and promising method with a very high commercial potential in Carbon Capture and Utilization technologies. As highlighted by Song et al. (2019), it is given by its simplicity in technical set-up, compactness, modularity, its simplicity in operation, control and maintenance, in its energy efficiency and scale-up flexibility. Gas membrane separation also evinces safety and environmental friendless because there is no requirement to use hazardous chemicals, e.g. as demanded by conventional CO_2 separation by absorption (Boulmal et al., 2017).
Generally known, gas membrane separation is a pressure-driven process that uses different diffusivities of individual gas components in a membrane cartridge to separate them. One or multi-stage configurations of laboratory or pilot gas membrane separation systems under TRL 3-6 are typically used to remove a given gas component from a feed. The configuration itself is primarily affected by flue gas composition, membrane characteristics (selectivity, permeability), and demanded permeate purity. Nevertheless, flue gas membrane separation has several limitations: low-temperature resistance up to 100°C, sensitivity to acid gases (SOX, NOX and H2S), varying long-term performance, and low selectivity and resilience (Song et al., 2019). Moreover, Xu et al. (2018) discussed that it is impossible to reach CO_2 purity higher than 95 % with low energy demand and capture cost.
Gas membrane separation is still under intensive development in laboratory or pilot plant scales aiming to find suitable membrane material, ambient operating conditions and low energy demand under favourable capture cost. Scientific activities historically dominantly scoped to test the efficiency of CO_2 removal from binary flue gas mixtures. Liu et al. (2020) modelled flue gas as binary mixture $CO_2 + N_2$ and used CHA-type membranes to remove CO_2 from the model gas at ambient temperatures. Torstensen et al. (2019) studied CO_2 removal from model flue gas as a mixture of 10 vol % CO_2 and 90 vol % N_2 in feed using PVA/nanocellulose nanocomposite membrane. Lee et al. (2015) tested a commercial hollow fibre module's separation efficiency to remove greenhouse gas impurities from industrial flue gas composed of 86.4 vol % N_2 + 13.4 vol % O_2 + 951 ppm SF_6 + 72.2 ppm CF_4 + 1198 ppm of CO_2. Choi et al. (2013) modelled LNG-fired flue gas as 10.8 vol % CO_2 + 89.2 vol % N_2 to experimentally develop multi-stage membrane process using PES hollow fibre membrane module. Ayadani et al. (2021) reported the potential of CO_2 separation from binary mixtures of CH_4, N_2 and H_2

using an SZZ-13 zeolite membrane. Nevertheless, there is also an effort to test the efficiency of CO_2 removal multicomponent gas mixtures. E.g. Liang et al. (2017) tested separation characteristics of PDMS/PAN composite membranes for the synthetic ternary gas mixture composed of 15 vol % CO_2 + 5 vol % O_2 + 80 vol % N_2. Bruntetti et al. (2020) investigated the use of poly-decyl methylsiloxane composite membrane to separate CO_2 from the model flue gas with composition 15 vol % CO_2 + 5 vol % O_2 + 80 vol % N_2.
This information follows that gas membrane separation processes nowadays primarily identify process characteristics of gas membrane separation for a given component from binary gas mixtures. There is little information about gas membrane separation from multicomponent gas mixtures like industrial flue gases. Thus, the paper deals to analyze and model separation fundamental process characteristics of membrane CO_2 removal from the model flue gas for a brand new developed membrane module in dependence on process parameters of the gas membrane separation process.

2. Methods

2.1 Experimental set-up

The laboratory membrane unit RALEX GSU-LAB-200 was used to carry out all the experiments. Its experimental set-up is plotted in Figure 1. The tertiary gas mixture, the modelling flue gas produced by the LPG-fired power plant, was tested. The feed composition was set-up as 15.2 vol % CO_2 + 4.5 vol % O_2 + 80.3 vol % N_2. Two flow rates of the gas mixture being 100 g h^{-1} and 200 g h^{-1} were used in experiments under one mean process gas temperature of 30 °C. The mixture was fed into the membrane module with polyetherimide-polyimide hollow fibres (Membrain Ltd, CZ). The internal diameter of fibre was 0.188 mm, the wall thickness of fibre was 0.06 mm, and the active mass transfer surface 0.8 m^2. The effect of process variables on process characteristics was researched for various differential pressures between retentate and permeate set according to working pressure ranges for permeate 0.2-0.5 MPa(a) and retentate 0.5-1.0 MPa(a). The mass gas flow rate was measured in feed and retentate streams. The volumetric concentrations of individual gas components in feed, permeate, and retentate streams were continuously analyzed by gas analyzers Emerson at steady-state conditions of the gas membrane separation process.

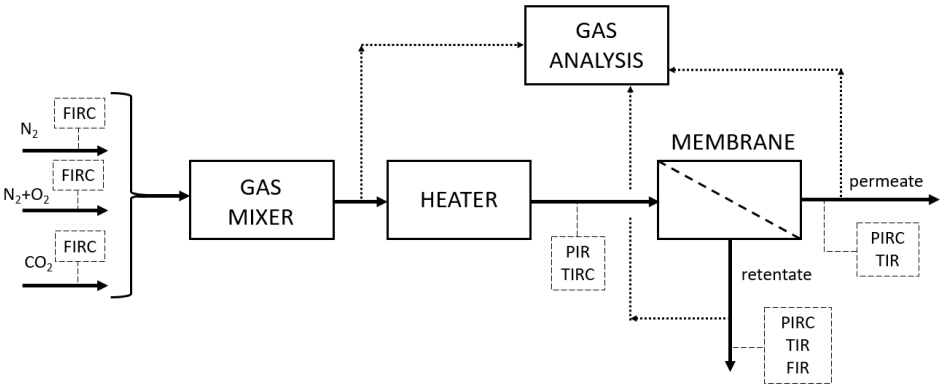

Figure 1: Technological scheme of the membrane unit.

2.2 Data analysis

The data analysis and evaluation supposed the ideal gas behaviour. The data evaluation was based on the application of the law of mass conservation, general definitions of the amount of substance, molar mass for individual components and gas mixtures. Based on this data, CO_2 stage cut θ_{CO2} (-), permeate flux J_{CO2} (mol m^{-2} s^{-1}), CO_2 permeability P_{CO2} (barrer), CO_2 permeance P_{CO2}/l (GPU) and separation factor S_F (-) were calculated as:

$$\theta_{CO2} = \frac{m_{CO2}^P}{m_{CO2}^F} \quad (1)$$

$$J_{CO2}^P = \frac{n_{CO2}^P}{A} \quad (2)$$

$$\frac{P_{CO2}}{l} = \frac{J_{CO2}^{P}}{p_{CO2}^{P} \cdot 3.35 \cdot 10^{-10}} \tag{3}$$

$$S_F\ (CO_2/i) = \frac{\frac{c_{CO2}^{nP}}{c_i^{nP}}}{\frac{c_{CO2}^{nF}}{c_i^{nF}}} \tag{4}$$

where *A* (m^2) represents the active mass transfer surface of the membrane module, *l* (mm) is the wall thickness of membrane fibre, p_{CO2}^{P}(Pa) defines partial pressure of CO_2 in permeate stream, and i (-) means a gas component, CO_2 excluded.

3. Results and Discussion

The experimental analysis of process characteristics for the tested module was done both for single gases and the model flue gas.

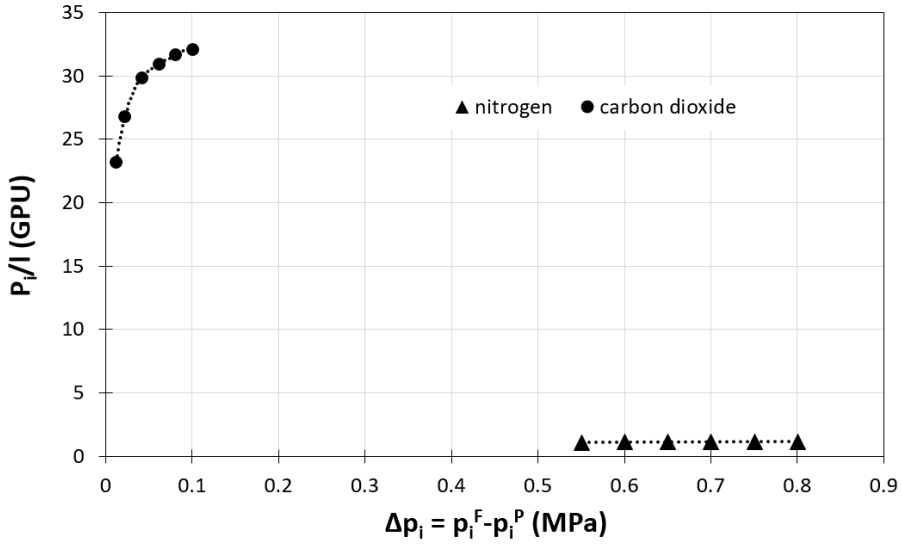

Figure 2: CO_2 and N_2 permeances in dependence on the partial pressure difference between feed and permeate (the lines represent only the trend).

The use of single gases, i.e. nitrogen and carbon dioxide, was applied to characterize the permeability of the membrane cartridge for the individual gases in dependence on partial pressure difference of given component between feed and permeate stream. The results are plotted in Figure 2. The CO_2 flowrate from feed to permeate stream was firmly linearly proportional to the given component's partial pressure difference between feed and permeate stream. Similar trends were reported by Choi et al. (2013). It was determined that the maximum CO_2 permeance of 32.09 GPU was an order of magnitude higher than the maximum N_2 permeance being 1.15 GPU. Based on these values, the ideal selectivity of the given module was calculated as:

$$\alpha_{CO_2/N_2} = \frac{\frac{P_{CO_2}}{l}}{\frac{P_{N_2}}{l}} = \frac{32.09}{1.15} = 28 \tag{5}$$

The ideal selectivity α_{CO_2/N_2} is equal to 43 GPU for polyimide and to 20 GPU for polyetherimide (Šípek, 2014). From this follows that the ideal selectivity α_{CO_2/N_2} of the tested module being 28 GPU is realistic regarding the given selectivities of its material composition and its process behaviour are closer to the polyetherimide

matrix. Finally, the comparison of its parameters with other membrane modules is plotted in Figure 3, being at the upper bound as defined by Robeson (2008).

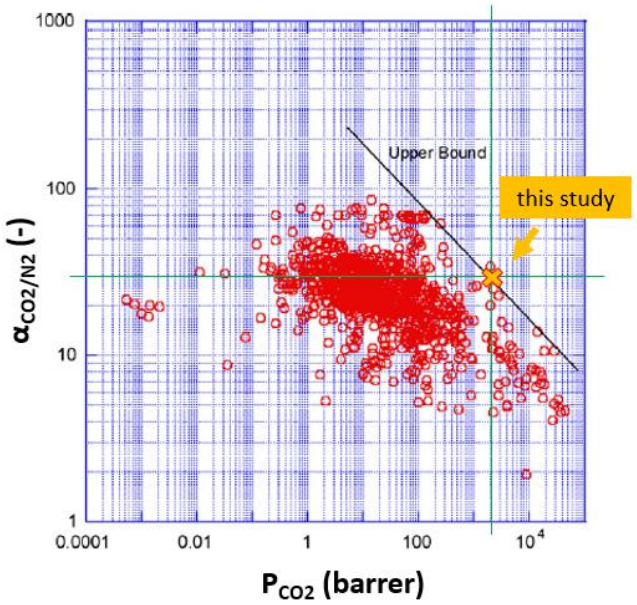

Figure 3: The implementation of the experimental results to the Robeson diagram (Robeson, 2008).

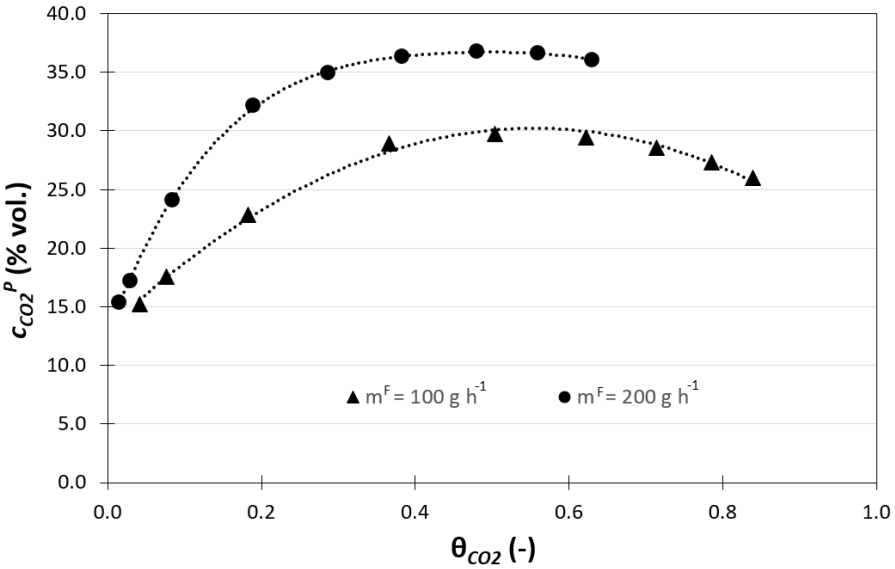

Figure 4: CO_2 concentration in permeate in dependence on stage cut θ_{CO2} and feed flowrate m^F (the lines represent only the trend) at constant permeate pressure of 2 bar(a).

The dependence of CO_2 concentration on stage cut is expressed in Figure 4. CO_2 concentration in permeate is increasing with the increase in stage cut and feed flowrate. Nevertheless, the maximum concentration of 38 % vol. of CO_2 was reached for the stage cut is higher than 0.4 at a feed flow rate of 200 g h^{-1}. This effect was caused by mass transfer limitations given by process parameters and available mass transfer surface. E.g. Liu et al. (2020) regarded the same trends due to the influence of concentration polarization. Figure 5 depicts the dependence of individual separation factors on the permeability of CO_2. It is evident that the separation factor decreases with an increase in CO_2 permeability and feed flowrate. The maximum separation factor $S_{F(CO2/N2)}$ of 6.9 was reached at CO_2 permeability of 478 barrer. Nevertheless, the separation factor $S_{F(CO2/O2)}$ evinces shallow values. Its maximum value of 1.8 was reached at CO_2 permeability of 478 barrer. The presented experimental

data are following the findings served by Brunetti et al. (2020). The team also reported moderate selectivities CO_2/N_2 = 8.7 at permeability close to 1000 barrer for CO_2 removal from model flue gas using poly-decyl methylsiloxane composite membrane. Regarding the presented experimental data, the authors finally stated that the tested module is efficient to separate CO_2 from N_2, but there is very low selectivity for CO_2 to O_2 mixture.

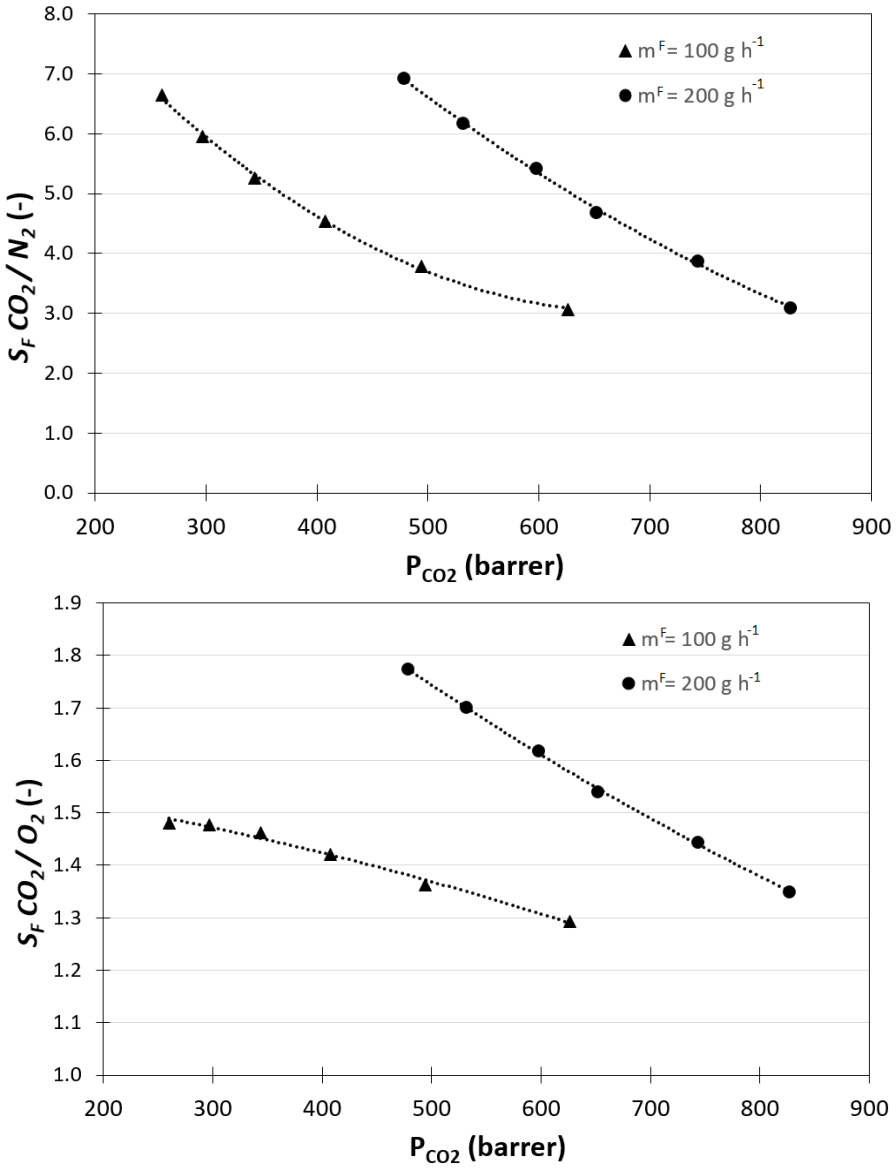

Figure 5: Separation factor S_F (CO_2/O_2) and S_F (CO_2/N_2) in dependence of CO_2 permeability and feed flowrate m^F(the lines represent only the trend).

The summarization of the most important experimental results is overviewed in Table 1. The separation of the gas mixture achieves significantly worse parameters than in testing, which would take place only on pure gases. Experimentally identified CO_2 permeance for model flue gas is more than two times lower than the permeance of single pure gas. The same behaviour is also evident for selectivity. The achieved separation factor is approximately four times smaller than the achieved ideal selectivity. It is evident that there is a mutual interaction among individual gas components resulting in lower permeances and separation factors in the gas mixture than single gases. E.g. Liang et al. (2017) reported the mutual effect of individual gas components on separation factor and presented separation factor CO_2/N_2 = 11.1. Choi et al. (2013) found that the gas component from the gas mixture was lower than the pure component's ideal selectivity. Thus, it is a practical example of the interaction of components as they pass through the membrane, as pointed out by Robeson (2008), Choi et al. (2013) or He and Wang (2018).

Table 1: The overview of characteristics for the given membrane module at process temperature 30 °C.

	flue gas m_F = 100 g h^{-1}	m_F = 200 g h^{-1}	single gas membrane module	pure polyetherimid*	pure polyimide*
permeance CO_2 (GPU)	13.1	13.8	32.1	52.5	735.0
permeance N_2 (GPU)	2.1	2.8	1.2	not defined	not defined
permeance O_2 (GPU)	5.3	5.9	not analyzed	not defined	not defined
ideal selectivity CO_2/N_2 (-)	not defined	not defined	28.0	20.0	43.0
separation factor CO_2/N_2 (-)	6.6	6.9	not defined	not defined	not defined
separation factor CO_2/O_2 (-)	1.5	1.8	not defined	not defined	not defined

* referenced by Šípek (2014)

4. Conclusions

The experimental identification of process characteristics was carried out for the given membrane module and model tertiary gas mixture that corresponded with its composition to the LPG-fired power plant. It was found that the separation factor may not reach the ideal selectivity. When separating the modelled flue gases, the value of the separation factor CO_2/N_2 was almost 7. The decrease of the separation factor CO_2/N_2 compared to the ideal selectivity (CO_2/N_2 is approximately four times. The separation factor CO_2/O_2 is deficient; its value is between 1 and 2. The CO_2 permeation of the module decreased two to three times in the case of the separation of the gas mixture compared to the separation of pure carbon dioxide.

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References

Ayadani A., Brunetti A., Maghsoudi H., Barbieri G., 2021, CO_2 separation from binary mixtures of CH_4, N_2 and H_2 by using SSZ-13 zeolite membrane, Separation and Purification Technology, 256, 117796-117804.

Boulmal N., Rivera-Tinoco R., Bouallou C., 2017, Lipophilic amine aqueous solutions for CO_2 capture: comparison of absorption rates for hexylamine (hxa), dimethylcyclohexylamine (dmca) and hxa-dmca mixtures, Chemical Engineering Transactions, 61, 1201-1207.

Brunetti A., Zito P.F., Borisov I., Grushevenko E., Volkov V., Volkov A., Barbieri G., 2020, CO_2 separation from humidified ternary gas mixtures using a polydeclymethylsiloxane composite membrane, Fuel Processing Technology, 210, 106550-106559.

Choi S.H., Kim J.H., Lee Y., 2013, Pilot-scale multi-stage membrane process for the separation of CO_2 from LNG-fired flue gas, Separation and Purification Technology, 110, 170-180.

He Z., Wang K., 2018, The ideal selectivity vs true selectivity for permeation of gas mixture in nanoporous membranes, IOP Conference Series: Materials Science and Engineering, 323, 1757-8981.

Lee S., Choi J.W., Lee S.H., 2015, separation of greenhouse gases (SF_6, CF_4 and CO_2) in an industrial flue gas using pilot scale membrane, Separation and Purification Technology, 148, 15-24.

Liang C.Z., Yong W.F., Chung T.S., 2017, High-performance composite hollow fibre membrane for flue gas and air separations, Journal of Membrane Science, 541, 367-377.

Liu B., Tang C., Li X., Wang B., Zhou R., 2020, High-performance SAPO-34 membranes for CO_2 separations from simulated flue gas, Microporous and Mesorporous Materials, 292, 109712-109722.

Robeson L.M., 2008, The upper bound revisited, Journal of Membrane Science, 320, 390-400.

Šípek M. (Ed), 2014, Membránové dělení plynů a par. University of Chemistry and Technology in Prague, CZ.

Song Ch., Liu Q., Deng S., Li H., Kitamura Y., 2019, Cryogenic based CO_2 capture technologies: State of the art developments and current challenges, Renewable and Sustainable Energy Reviews, 101, 265-278.

Torstensen J.Φ., Helberg R.M.L., Deng L., Gregersen Φ.W., 2019, PVA/nanocellulose nanocomposite membranes for CO_2 separation from flue gas, International Journal of Greenhouse Gas Control, 81, 93-102.

Xu J., Wu H., Wang Z., Qiao Z., Zhao S., Wang J., 2018, Recent advances on the membrane processes for CO_2 separation, Chinese Journal of Chemical Engineering, 26, 2280-2291.