

Bulk CO₂/CH₄ Separation for Offshore Operating Conditions using Membrane Process

(Pemisahan Pukal CO₂/CH₄ untuk Keadaan Operasi Luar Pesisir menggunakan Proses Membran)

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ABSTRACT

The increasing demands of natural gas pushes energy industries to explore the reservoirs contain high CO₂ concentration and impurities including heavy hydrocarbons. High efficiency of using membrane technology in CO₂-natural gas separation has extended its potential application to offshore environment. Due to the limited studies related with the separation of CO₂ under offshore conditions, the present work has investigated the separation performance of a commercial membrane in removing bulk CO₂ from methane at elevated pressure condition. A wide range of offshore operating conditions including pressure from 10 to 50 bar, CO₂ concentration from 25 to 70% and temperature of 30°C, 40°C and 50°C were studied. High relative CO₂ permeance and relative CO₂/CH₄ selectivity were observed when the pressure and the CO₂ concentration increased. This work, therefore substantial is to bridge the gap and facilitates the application of membrane technology for offshore operating conditions.

Keywords: Bulk CO₂; membrane process; natural gas separation

ABSTRAK

Peningkatan permintaan terhadap gas asli telah mendorong industri tenaga untuk meneroka takungan yang mengandungi kepekatan CO₂ dan bendasing yang tinggi termasuk hidrokarbon berat. Kecekapan tinggi dalam penggunaan teknologi membran dalam pemisahan CO₂-gas asli telah meningkatkan potensi aplikasi kepada persekitaran luar pesisir. Disebabkan kajian yang berkaitan dengan pemisahan CO₂ di luar pesisir yang terhad, kajian terkini telah mengkaji prestasi pemisahan membran komersial dalam mengeluarkan CO₂ pukal daripada metana pada keadaan tekanan yang tinggi. Pelbagai keadaan operasi luar pesisir termasuk tekanan dari 10 kepada 50 bar, kepekatan CO₂ dari 25% ke 70% dan suhu 30°C, 40°C dan 50°C telah dikaji. Ketelapan relatif CO₂ dan kepemilihan CO₂/CH₄ relatif yang tinggi telah diperhatikan apabila tekanan dan kepekatan CO₂ meningkat. Oleh itu, penyelidikan ini penting untuk merapatkan jurang dan memudahkan penggunaan teknologi membran bagi keadaan operasi luar pesisir.

Kata kunci: CO₂ pukal; pemisahan gas asli; proses membran

INTRODUCTION

Natural gas is a fuel that burns cleaner than the other traditional fossil fuels as it emits lower quantities of greenhouse gases during combustion. The raw natural gas usually contains undesirable impurities including CO₂, water and heavy hydrocarbons (Baker & Lokhandwala 2008). Since the demand of natural gas increases, a sophisticated process for CO₂ capture is necessary in order to reduce CO₂ emission to the environment during natural gas exploration and production activities. Besides, purification of natural gas is mandatory in order to meet the typical pipeline specifications of 2-5% of CO₂ (Mohammed Hosein 2009).

Natural gas contains different concentration of CO₂ ranging from 4-50% relying on the location of gas reservoirs (Ahmad et al. 2012). In Southeast Asia, the gas reservoirs that contain high CO₂ have been discovered in Natuna Field, Indonesia which contains CO₂ up to 76% (Hanif et al. 2002). However, the installation of current technologies such as adsorption and absorption

systems at offshore platforms requires a larger footprint and weight. Meanwhile, cryogenic technology needs high energy consumption for the refrigerant system. Therefore, the above technologies are not suitable to be implemented in offshore condition for bulk CO₂ removal processes. Consequently, this phenomenon has attracted the application of membrane technology in the removal of bulk CO₂ from natural gas under the offshore operating conditions. Membrane technology offers advantages in term of modular installation, smaller footprint, lower weight, easier maintenance, minimum utility requirement and low labour intensity (Schell & Houston 1983).

Previous works in the literature related with CO₂/CH₄ separations were mainly focused on low operating pressure (<10 bar) and low CO₂ content (<30%) (Hasan et al. 2009; Khulbe et al. 1997; Lee et al. 1994; Wirytmojo et al. 2009). However, the offshore operating pressure is typically ranging from 10-50 bar with the CO₂ content ranging from 10-70% of CO₂ (Zhai et al. 2012). Therefore, in the present work, the study on the separation of CO₂

from methane using membrane process under offshore operating condition such as elevated pressure and high CO₂ concentration is conducted.

EXPERIMENTAL DETAILS

MATERIALS AND GAS PERMEATION MEASUREMENT

The polyamide composite membrane used in this work was supplied by industrial membrane manufacturer from the United States. All gases (natural gas, CO₂) used in this study were obtained from Gas Walker Sdn Bhd. The testing pressure for CO₂ was below 60 bars due to the critical pressure and temperature of CO₂ as well as a safety consideration.

Both pure and mixed gas measurements were determined using a permeation apparatus as shown in Figure 1. This system allowed the measurement of gas permeability and selectivity at various operating conditions. The experiments were conducted at pressure ranging from 10-50 bar, temperature from 30-50°C and CO₂ concentration from 25-70%.

A 14.86 cm² circular membrane area was mounted into the membrane test cell. The system was kept under vacuum before conducting an experiment in order to eliminate gases and vapors that may contain in the system. The leak tests were performed to ensure that the equipment is safe prior to experimental runs. A known amount of gas from the inlet feed was controlled and measured using a mass flow controller and the composition of the inlet feed gas was altered based on the desired operating condition. The feed gas was introduced into the membrane test cell (Milipore pressure filter holder (XX45 047 00)) and then both permeate and retentate streams from the membrane test cell were routed to the Fuji Infrared gas analyzer (type: ZRJ -5) for gas composition analysis. Stage cut of 1% was maintained in order to avoid concentration polarization in the upstream (Ahmad & Lau 2007; O'Brien et al.1986). The overall permeation system is installed in an insulated oven compartments where the main function of the oven is to regulate and control the temperature of the system.

The performance of membrane is evaluated based on its permeance and selectivity. The permeance and selectivity of the membrane were determined using the permeate flowrate obtained from the soap-film bubble flowmeter and the gas compositions recorded by the IR gas analyzer. The permeance of the pure gas was calculated using (1) as follows (Mohammadi et al. 2008):

$$\left(\frac{P'}{t}\right) = \frac{V_p}{A_m(f_h - f_l)}, \quad (1)$$

where (P'/t) is the permeance of the membrane; V_p is the permeate flow rate; A_m is the membrane area; and f_h and f_l are the fugacity in feed side and permeate side, respectively. For gas mixture measurements, the permeance of

component A (CO₂ or CH₄) in gas mixture is given in (2) and (3) as follows:

$$\left(\frac{P'_A}{t}\right) = \frac{V_p y_p}{A_m(f_h \bar{x}_0 - f_l y_p)}, \quad (2)$$

where

$$\bar{x}_0 = \left(\frac{x_f + x_r}{2}\right), \quad (3)$$

where y_p is the fraction of component A in permeate stream; x_f and x_r are the fraction of component A in feed side and retentate side, respectively. The gas permeance is reported in the unit of GPU (1 GPU=1×10⁻⁶cm³(STP)/s.cm².cmHg).

The ideal selectivity of gas pair is obtained by dividing the permeance of component A over component B as shown in (4) as follows (Geankoplis 1978):

$$\alpha_{ideal} = \left(\frac{P'_A}{t}\right) / \left(\frac{P'_B}{t}\right), \quad (4)$$

The real selectivity or separation factor of mixed gas measurement under nonzero downstream pressure can be achieved by using mole fraction of component A and B in permeate and feed streams.

$$\alpha_{A/B} = \left(\frac{y_A / y_B}{x_A / x_B}\right), \quad (5)$$

where y is the fraction of component in the permeate side; and x is the fraction of component in the feed stream. Non-ideal condition was taken into account as the study deals with high pressure condition and high concentration of CO₂. The fugacity of each component in the mixture at high pressure was calculated using Virial equation while the fugacity at permeate side was assumed as atmospheric condition (Ambrose et al. 2011; Vaughan & Carrington 1998; Weiss 1974).

RESULTS AND DISCUSSION

PURE AND MIXED GAS PERMEATION

In the present work, normalized permeance and selectivity are used to compare the performance of the membrane at different operation conditions. The normalized permeance and selectivity are expressed in (6) and (7) as follows:

$$P^* = \frac{P}{P_{ref}}, \quad (6)$$

$$\alpha^* = \frac{\alpha}{\alpha_{ref}}, \quad (7)$$

where P^* and α^* are normalized or relative permeance and selectivity, respectively. P is permeance at each condition while P_{ref} and α_{ref} are permeance and selectivity

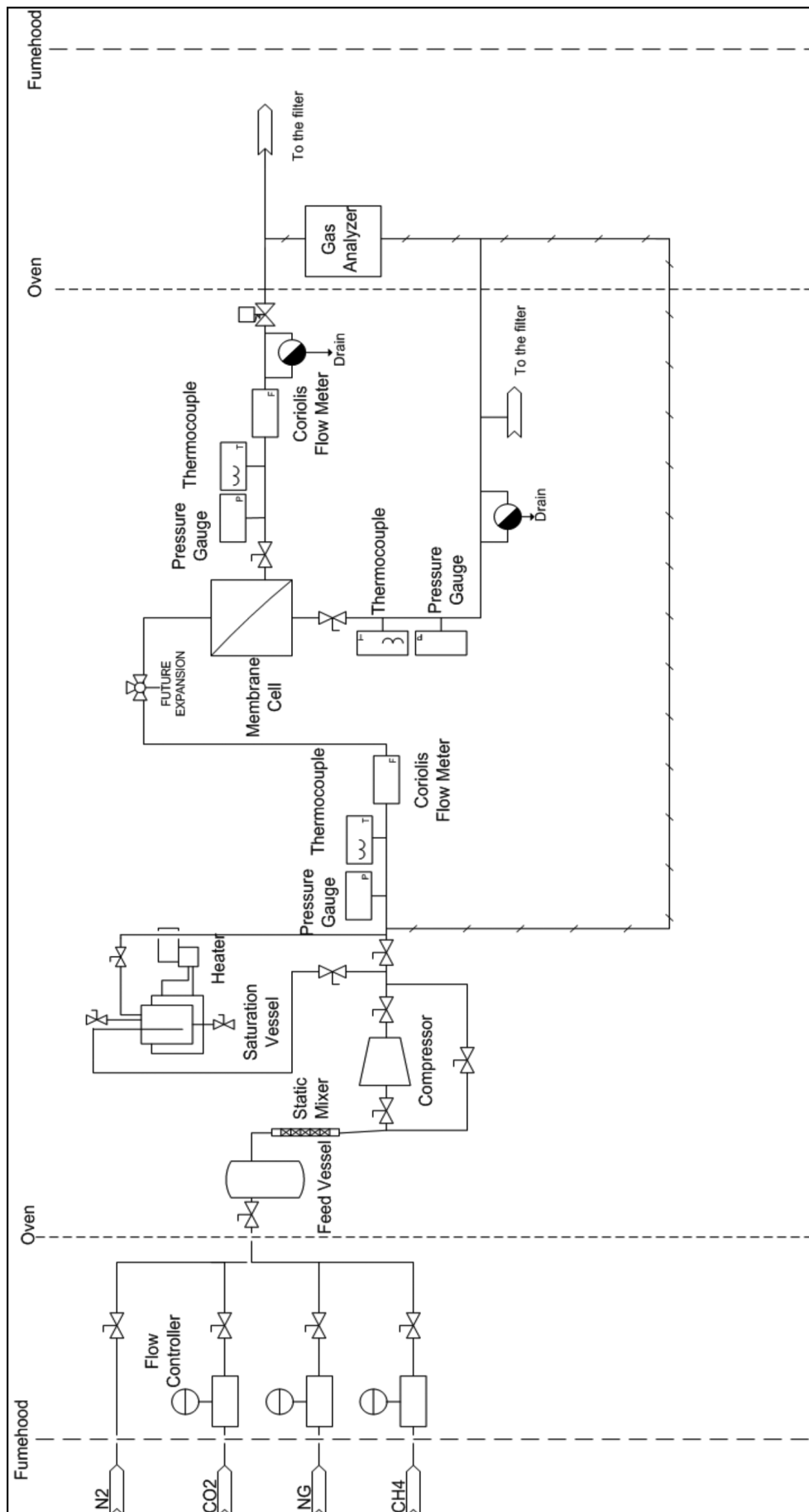


FIGURE 1. Schematic diagram of permeation apparatus

determined at reference operating condition, which was 10 bar, 30°C and 25% of CO₂ in the feed stream. At this condition, the permeance for CO₂ and CH₄ is 15 and 1.1 GPU, respectively. The normalized permeance of CO₂ and CH₄ and normalized selectivity of CO₂/CH₄ at different operating parameters are plotted and shown in Figures 2-9.

EFFECT OF PRESSURE

Figures 2, 3 and 4 illustrate the influence of pressure on the normalized CO₂ permeance, CH₄ permeance and CO₂/CH₄ selectivity for pure and mixed gas (25% CO₂ and 75% CH₄). The permeation properties were determined in a pressure range between 10 and 50 bars. The temperature of the system was maintained at 30°C throughout the experiment.

Referring to Figure 2, increment of 44% and 52% were observed for CO₂ permeance in pure gas and mixed gas, respectively, when the pressure increases from 10-50 bar. The increment of CO₂ permeance is due to the plasticization phenomena as the pressure increases. Plasticization phenomenon contributes towards the enhancement of local segmental motion of the membrane that increases the diffusion and permeation of the gases molecule (Al-Juaied & Koros 2006; Dhingra 1997). This behaviour can also be explained by the increment of hypothetical gaps and free volume available in the membrane matrix as well as due to loosen of the free chain in the polymer matrix that provided more spaces for the penetrant to permeate through the membrane (Madden 2005; Wu et al. 2006).

Based on Figure 2, the reduction of 20% of CO₂ permeance was observed in mixed gas compared to pure gas. This was mainly due to the competitive effect between CO₂ and CH₄ when they permeate through the membrane matrix (Hillock et al. 2008). The presence of CH₄ in a gas mixture has occupied the unrelaxed volume and therefore resulted in the reduction of the solubility coefficient of CO₂. Consequently, the CO₂ permeance decreases (Al-Juaied & Koros 2006; Chen 2012). Besides that, the presence of plasticization effect in the membrane

also causes the decrement of CO₂ permeance in mixed gas measurement.

From Figure 3, it can be seen that the CH₄ permeance declined for both pure and mixed gas permeation, as pressure increases. It was found that CH₄ permeance has reduced 23% in pure gas measurement. On the other hand, 36% of reduction for CH₄ permeance in mixed gas was observed, when the pressure increased from 10-50 bar. This observation can be explained by solution diffusion mechanism, where the permeance of gas is depending on the solubility and diffusivity of the gas in the membrane. As pressure increases, the solubility effect of the penetrant is dominant compared to the diffusion effect which leads to the increment of permeance for more soluble penetrant (Wu et al. 2006). Therefore, CH₄ permeance decreases when pressure rises, due to its lower condensability (*T_c* of -82.15°C) and greater kinetic diameter (3.8 Å) compared to CO₂ (*T_c* of 30.95°C and kinetic diameter of 3.3 Å) (Simons 2010).

A maximum enhancement of 70% of CH₄ permeance was also observed in Figure 3 for mixed gas compared to pure gas. This increment was due to the plasticization effect of CO₂ in a gas mixture that swells the membrane matrix and therefore, introduce additional free volume in the membrane matrix which contributes to the increment of diffusion and permeation of CH₄ through the membrane (Mohammadi et al. 2008). Thus, the CH₄ permeation in gas mixture increases compared to pure gas CH₄ permeation. This behavior is in accordance to previous publications (Koros et al. 1981; Liu et al. 2003).

The CO₂/CH₄ selectivity for pure and mixed gas with respect to the pressure is shown in Figure 4. It is observed that the ideal CO₂/CH₄ selectivity increases more than 100% whereas CO₂/CH₄ mixed gas selectivity shows increment of 80% when the pressure increases. These results are due to the higher ability of CO₂ to permeate through the membrane matrix compared to CH₄. The CO₂/CH₄ mixed gas selectivity reduced about three-fold compared with ideal CO₂/CH₄ selectivity. This was mainly

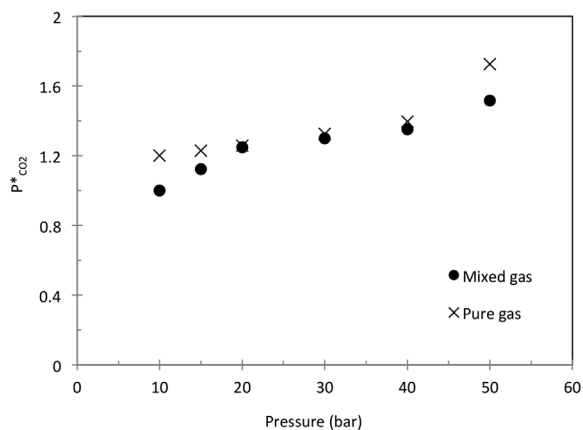


FIGURE 2. Effect of pressure on the normalized CO₂ permeance for pure gas and mixed gas (25% CO₂-75% CH₄) at 30°C

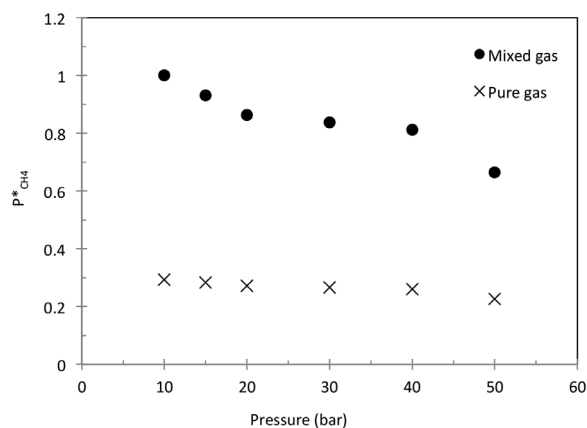


FIGURE 3. Effect of pressure on the normalized CH₄ permeance for pure gas and mixed gas (25% CO₂-75% CH₄) at 30°C

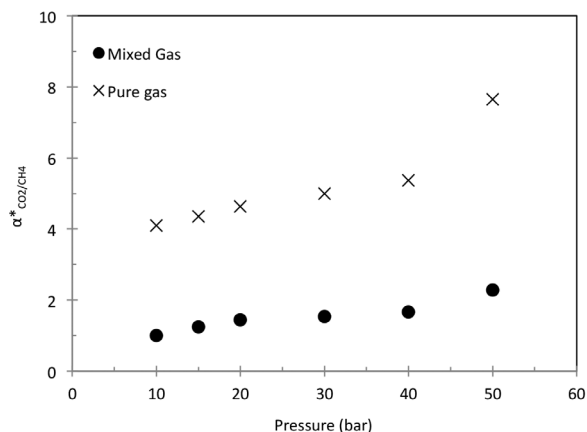


FIGURE 4. Effect of pressure on the normalized selectivity for pure gas and mixed gas (25% CO₂-75% CH₄) at 30°C

attributed to the presence of the plasticization phenomenon that encourages the bulkier molecule, CH₄ to permeate through the membrane and compete with CO₂ through the membrane matrix (Hillock et al. 2008).

EFFECT OF TEMPERATURE

The effect of temperature on the normalized CO₂ permeance, CH₄ permeance and CO₂/CH₄ selectivity for pure and mixed gas are shown in Figures 5, 6 and 7, respectively. The permeation properties of CO₂ and CH₄ were determined in a temperature range of 30-50°C. The pressure was maintained at 20 bars throughout the experiment.

Referring to Figures 5 and 6, a maximum reduction of 35 and 39% were obtained for CO₂ permeance in pure and mixed gas, respectively, when the temperature increases from 30-50°C. On the other hand, 5 and 30% reduction was found for pure CH₄ permeance and mixed gas CH₄ permeance in the same temperature range. The effect of temperature in gas permeation can also be described by the solution diffusion mechanism, where it depends on the solubility and diffusivity of the gases on the membrane (Mohammadi et al. 2008). In this case, the effect of temperature on the gas permeance was determined at high pressure of 20 bar. Therefore, the polymer chains are flexible and the sorption uptake of permeant is high (Liu 2008). Thus, the increment of temperature is anticipated to encourage more significant reduction in the solubility rather than the increment in the diffusivity as illustrated by Van't Hoff relationship as shown in (8) and (9) as follows (Baker et al. 1998; Khan et al. 2011). Therefore, the permeances of CO₂ and CH₄ reduce as temperature increases.

$$S = S_o \exp\left[-\frac{\Delta H_s}{RT}\right], \quad (8)$$

where

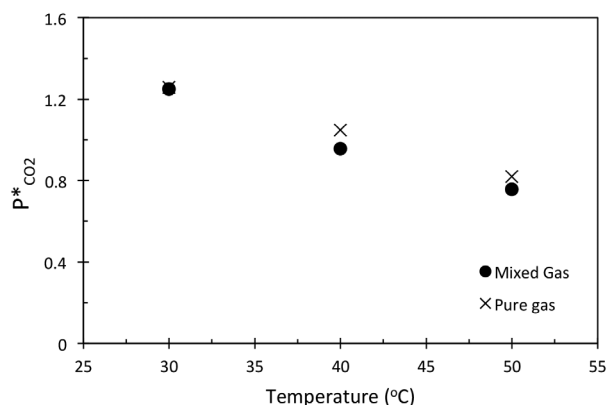


FIGURE 5. Effect of temperature on the normalized CO₂ permeance for pure gas and mixed gas (25% CO₂-75% CH₄) at 20 bar

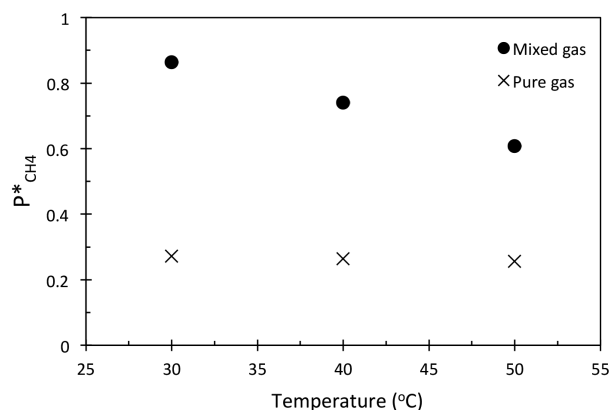


FIGURE 6. Effect of temperature on the normalized CH₄ permeance for pure gas and mixed gas (25% CO₂-75% CH₄) at 20 bar

$$\Delta H_s = \Delta H_{condensation} + \Delta H_{mixing} \quad (9)$$

where, S_o is a pre-exponential factor of solubility; ΔH_s is the partial molar enthalpy of sorption; R is the universal gas constant and T is the temperature.

Based on (8) and (9), the increment of temperature leads to the reduction in solubility in which further causes the permeances of CO₂ and CH₄ reduce as temperature increases. This behaviour contributed from the negative value of ΔH_s due to negative enthalpy change for both mixing and condensation (exothermic process) (Chatterjee et al. 1997; Khan et al. 2011). Hence, as a result, 31% reduction of ideal gas selectivity CO₂/CH₄ and 14% reduction of CO₂/CH₄ mixed gas selectivity were found when the temperature increases. This was mainly due to the decrement of both CO₂ and CH₄ permeances as shown in Figures 5 and 6.

In addition to that, it can be observed from Figures 5 and 7 that the reduction of 9.5% for CO₂ permeance and more than 100% reduction of CO₂/CH₄ selectivity were observed in mixed gas permeation compared to pure gas permeance. However, CH₄ permeance in mixed gas is 65% higher compared to pure gas as illustrated in Figure 6. As

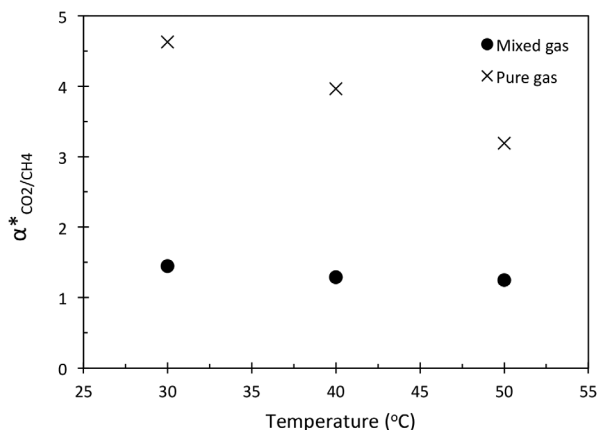


FIGURE 7. Effect of temperature on the normalized selectivity for pure gas and mixed gas (25% CO₂-75% CH₄) at 20 bar

mentioned earlier, the reduction of CO₂ permeance and CO₂/CH₄ selectivity and the reduction of CH₄ permeance were mainly due to the occurrence of plasticization phenomenon which enhances the flexibility of polymer chain and consequently encourages the transport of higher kinetic diameter of CH₄ through the membrane.

EFFECT OF CONCENTRATION

Figures 8 and 9 illustrate the membrane separation performance as a function of CO₂ concentration in the mixed gas condition. The CO₂ concentration in the feed varied from 25% to 70% at pressure of 20 bars and temperature of 30°C.

As shown in Figure 8, CO₂ permeance increases when CO₂ concentration increased from 25-70%. This was mainly due to higher solubility of CO₂ and strong synergistic interaction between CO₂ and the membrane (Costello & Koros 1992; Khulbe et al. 1997). This behaviour leads to the swelling of membrane matrix which causes chain segments flexibility and thus increases the penetration of CO₂ through membrane. Furthermore,

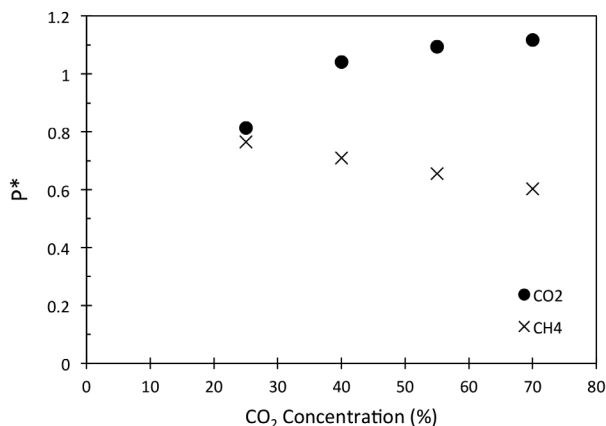


FIGURE 8. Effect of concentration on the normalized CO₂ and CH₄ permeance for mixed gas at 20 bar, 30°C

the conditioning effect of CO₂ molecules also causes the dilation phenomenon which resulted in a macroscopic changes in volume during the sorption of the CO₂ molecules in the polymer matrix (Weiss 1974). Referring to Figure 8, CH₄ permeance reduces about 15% when CO₂ concentration increases. This behaviour was due to the favourable competition effect of CO₂ compared to CH₄ in the membrane matrix that causes the adsorption coverage for CO₂ on the feed side increases as compared to CH₄ when the CO₂ concentration increases from 25 to 70%. Hence, CH₄ permeance reduces as the CO₂ concentration increases.

Figure 9 shows the CO₂/CH₄ selectivity with respect to the CO₂ concentration. Referring to Figure 9, 54% increment of CO₂/CH₄ selectivity was observed when CO₂ concentration increases. The increment of CO₂/CH₄ selectivity was due to the increment of CO₂ permeance and the reduction of CH₄ as shown in Figure 8.

COMPARISON WITH LITERATURE STUDIES ON THE GAS SEPARATION PERFORMANCE

The separation study on CO₂ and CH₄ reported from the literature are normally focused on low operating pressure (up to 10 bar) and low concentration of CO₂ (<30%). At low operating pressure, the gas permeance decreases when pressure increases. This observation can be explained by two sorption sites available in polymer matrix including Henry and Langmuir sorption site (Wirytmojo et al. 2009). The gas uptake in the membrane enhances when pressure increases, but the increment is lesser than the factor that contributes to the reduction of permeability (Lee et al. 2010). This has occurred due to filling and saturated of the Langmuir sorption sites, thus additional gas can only pass through the slower Henry sorption site (Tin 2005). Meanwhile, at high operating pressure, the permeability of the permeants increases with the increasing of pressure. This is mainly due to the domination of Henry's mode sorption which causes high degree of swelling and higher diffusivity of penetrant molecules. The swelling

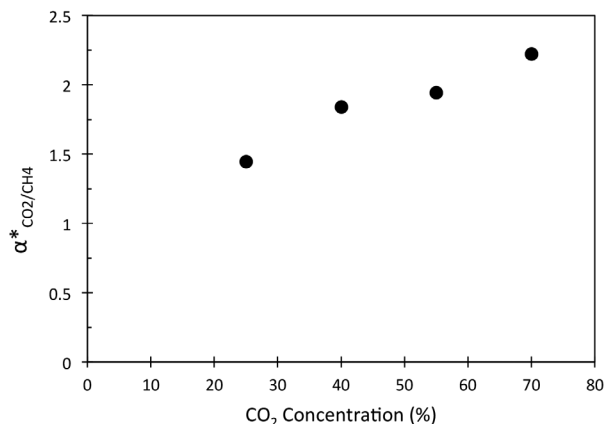


FIGURE 9. Effect of concentration on the normalized selectivity for mixed gas at 20 bar, 30°C

above plasticization pressure causes the facilitation of segmental motion which encourages the molecules to lose more densely packed entanglement and long chain rearrangement (Wessling et al. 1991).

On the other hand, the effect of temperature on the permeation behavior of the penetrants can be explained by the solubility and diffusivity. The impact of temperature on the solubility and diffusivity is controlled by the pressure where the sorption uptake of the penetrants in the membrane is affected. Basically the diffusivity increases while solubility decreases as temperature rises since the sorption process is exothermic (Husain & Koros 2007). Therefore, the increment of temperature increases the permeance of CO₂ and CH₄ at low feed pressure. This is due to the limitation on the sorption uptake which causes the increment of diffusivity occurred more significant than the decrement in the solubility when the temperature rises, which resulting in the enhancement of permeance (Mohammadi et al. 2008). Meanwhile, at high pressure, the polymer chain are flexible and sorption uptake is high and thus, the diffusivity is high and causes a significant reduction in solubility compared to diffusivity when temperature increases (Liu 2008). Therefore, decrement of permeance is observed.

The decrement of permeance was observed when CO₂ concentration increases at low CO₂ concentration (Yoshimune & Haraya 2013). This phenomenon can be explained by the favorable penetration of gas molecule that is allowed to pass through easily at low concentration until the microvoids is saturated with the penetrants. Based on Maeda and Paul (1987) findings, at low concentration of CO₂, the CO₂ molecules behaves as antiplasticizers in the membrane matrix where the increment of penetrant concentration is expected to hinder the segmental mobility of the membrane matrix. Hence, the permeability reduces at low CO₂ concentration. These effects can be related to the lower specific volume of the penetrant/polymer mixture in the glassy state and the specific volume of the pure polymer in the glassy state. Meanwhile, at high CO₂ concentration, permeability of the penetrants increases with the increment of CO₂ concentration. This observation is mainly attributed to the swelling effect by the condensable CO₂, which acts as a plasticizer in the membrane matrix and contributes to the disruption of polymer chain packing and segmental mobility within the polymer matrix (Duda et al. 1994).

CONCLUSION

Study of the separation of CO₂ from CH₄ under offshore operating conditions, i.e. high pressure and high CO₂ concentration were conducted in the present work. Based on the results obtained, CO₂ permeance and CO₂/CH₄ selectivity increased when the feed pressure increased from 10 to 50 bars, while CH₄ permeance decreases. The results on the influence of temperature toward separation performance showed that both CO₂ and CH₄ permeances as well as CO₂/CH₄ selectivity decreased

when temperature increased. Higher CO₂ concentration contributed to the increment of CO₂ permeance and CO₂/CH₄ selectivity while the CH₄ permeance decreased. Due to the competition effect between the penetrants through the membrane matrix, CO₂ permeance and CO₂/CH₄ selectivity obtained for the mixed gas condition decreased compared to those results obtained from pure gas conditions. The presence of bulk CO₂ under elevated pressure condition showed a better separation result with higher CO₂ permeance and higher CO₂/CH₄ selectivity when the pressure and the CO₂ concentration increased. Therefore, it can be concluded that the results obtained in the present work can be used as a benchmark for the future development in membrane separation process under a simulated offshore environment.

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