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Removal of Bulk CO_2 from Methane with the Presenceof Heavy Hydrocarbon using Polyimide Membrane

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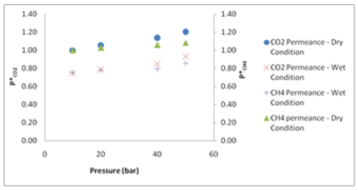
Graphical abstract



Abstract

The membrane process has advanced rapidly and continued to progress due to its advantages. Polyimide membrane has been widely applied for gas separation due to their promising permeability and selectivity. In this paper, the effect of heavy hydrocarbon (pentane) in removing bulk CO_2 from methane using polyimide membrane was studied. Higher operating pressure and temperature demonstrated the increment of CO_2 and CH_4 permeance while CO_2/CH_4 selectivity decreased for both dry and wet conditions. As CO_2 concentration increased, CO_2 and CH_4 permeance as well as CO_2/CH_4 selectivity enhanced. The presence of pentane in membrane separation contributed to the loss of CO_2/CH_4 selectivity.

Keywords: Polyimide; pentane; bulk CO_2; methane

■1.0 INTRODUCTION

Natural gas is a fuel that burns cleaner and more environmentally attractive than other traditional fossil fuels as it emits lower quantities of greenhouse gases during combustion. Raw natural gas contains typically 75% to 90% of methane from the total composition and significant amounts of ethane, propane, butane and 1% to 3% of other higher hydrocarbons [1]. In addition, the raw natural gas contains undesirable impurities, such as water, carbon dioxide (CO_2), nitrogen and hydrogen sulfide.

The composition of CO_2 found in the natural gas streams can reach as high as 80% from the total composition. CO_2, a type of acid gases, is highly corrosive when mixed with water and it will rapidly destroy pipelines and equipment's. In addition, CO_2 reduces the heating value of natural gas and freezes at relatively high temperature, forming blocks of dry ice that can clog equipment lines and damage pumps [2]. Therefore, it is very important to control the composition of the raw gas.

There are many types of separation technologies that are available for natural gas sweetening in the market; absorption, adsorption and cryogenic processes [3] However, these available commercial technologies have the limitations with respect to weight and space requirements, energy consumption and environmental concerns.

Hence, membrane separation process is chosen as it is suitable to separate bulk CO_2 from natural gas stream. Membrane gas separation is a pressure driven process that consists of thin barriers that allow selective permeation of certain gases. Membrane gas separation does not require phase change and presents significant advantages for remote application such as an offshore gas processing platform [4]. Besides, this technology is easy to operate, requires minimum utility and maintenance as well as easy for membrane replacement [5]. Therefore, setback as dominated by other commercial technologies is catered by application of membrane process.

Generally, polymeric membranes cannot withstand high temperatures and aggressive chemical environments. The presence of heavy hydrocarbon in the feed gas streams can bring significant negative effects to membrane, particularly in polyimide flat sheet membrane, when applied in petrochemical plants, refineries, offshore gas processing platform and natural gas treatment plant. As a result, it is important to evaluate separation performance of membrane material under adverse conditions. The present research works only demonstrated limited studies on this potential problem of the polyimide membrane material. Due to the complexity of heavy hydrocarbon and other impurities in natural gas, the impacts of these components on the membrane system have remained poorly understood until today [6]. Also, previous research works showed that was difficult to characterize the effects of heavy hydrocarbon and impurities experimentally. For that reason, it is important to evaluate separation performance of polyimide membrane material in natural gas sweetening under adverse conditions for membrane development in the future. Pentane was chosen as a model contaminant as it is the beginner of the heavy hydrocarbon series, where the amount of pentane is abundant in natural gas compared to other heavy hydrocarbons.

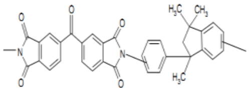
In addition, the conventional membrane separation research works for natural gas sweetening are mainly focused on low feed CO_2 composition and low feed pressure [7,8,9]. There are scarce works on the performance of membrane materials in high concentration of CO_2 and high pressure operating conditions. Therefore, it is imperative to conduct researches on adverse conditions, particularly on high CO_2 composition in feed stream and high feed pressure and consequently study the polymeric membrane performance.

■2.0 EXPERIMENTAL

2.1 Materials

The polyimide membrane used in this experimental work was Matrimid 5218, a commercially available polyimide made from the monomers 3,3'4,4'-benzophenone tetracarboxylic dianhydride and diaminophenly indane [10]. The chemical structure and physical properties of the Matrimid 5218 membrane was shown in Table 1. Matrimid 5218 membrane possesses high glass transition temperature, Tg = 302°C and density 1.24 g/cm3. The Matrimid 5218 membrane used in this study was purchased from Alpha Membrane Hi-Tech Pte. Ltd., Singapore.

Table 1 Chemical structure and physical properties of Matrimid 5218

Polymer	Chemical structure	Density (g/cm^3)	Tg (ºC)
Matrimid 5218		1.24	302

2.2 Chemical and Gases

Carbon dioxide and natural gas used in parametric study were gained from Sujin Resources Sdn Bhd. CO_2 cannot be operated at higher than 60 bars because of the critical pressure and temperature of CO_2 as well as a safety concerns. Natural gas was used as a working gas throughout the experimental work as the content of CH_4 in natural gas is higher than 90% [11]. Pentane was purchased from Avantis Laboratory Supply at 99% of purity and used as it is. The composition of the gases and chemicals used and typical concentration of impurities presence are given in Table 2.

Table 2 Gases used in experimental set up

Gas	Purity (%)	Composition
Natural Gas	93.07	$CH_4 \geq 93.07$ %, $C_2H_6 < 3.70\%$, $C_3H_8 < 0.90\%$, $C_4H_{10} < 0.42\%$, THC < 0.14%, $CO_2 < 1.10\%$, $N_2 < 0.68\%$
CO2	99.9995	$CO_2 \geq 99.995$ %, O_2 <10ppm, H_2O < 7ppm, N_2 < 25ppm, THC < 5ppm, CO < 2ppm
Pentane	99	

2.3 Gas Separation Equipment and Measurement

The experimental works were conducted using gas separation equipment as illustrated in Figure 1 to evaluate the performance of membrane in separating CO_2 from CH_4 with and without the presence of heavy hydrocarbon. Gas permeation equipment was developed to conduct the experiments at high concentration of CO_2 with the presence of heavy hydrocarbon under elevated pressure condition. This equipment is capable to measure pure and mixed gas condition.

Before performing the experiment, the membrane and overall permeation system were kept under vacuum to remove residual gases and impurities. The flowrate of feed gases were controlled and measured by the mass flow controllers. The feed gases then were admitted to a feed vessel and a static mixer to ensure gas homogenization before entering a gas compressor and a saturation vessel. The compressor compressed the mixed gas until desired pressure for experimental requirements was achieved.

Introduction of heavy hydrocarbon in the system offers a challenge to the current experimental equipment. The saturation vessel was developed to contact feed gas mixture with hydrocarbon liquid in the vessel.

For the main part of separation process (test section), polyimide membrane was placed in a membrane test cell, Milipore pressure filter holder (XX45 047 00) to study CO_2/CH_4 separation performance. This separation equipment is a one stage flow scheme where the feed gas was separated into a permeate stream rich in CO_2 and a retentate stream rich in methane.

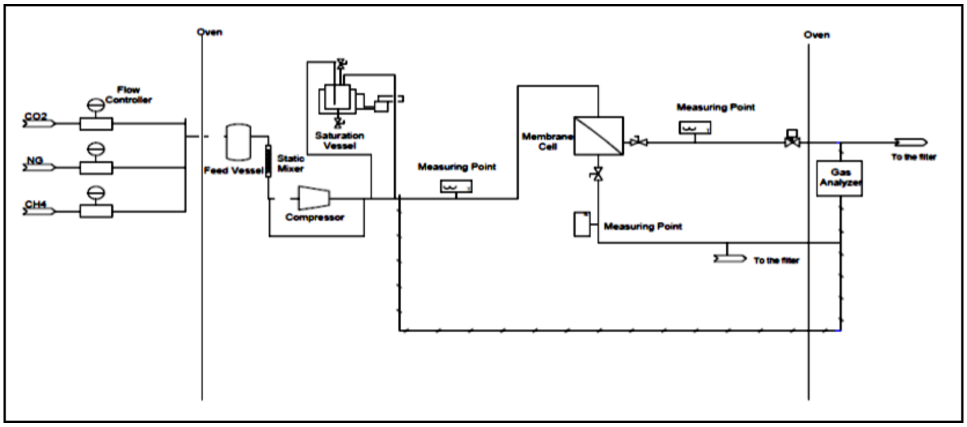


Figure 1 Illustration of gas separation equipment

The permeate and retentate release then routed to the IR gas analyzer for composition analysis. The pressure, temperature and flowrate at measuring points (namely feed, permeate and retentate stream) were logged onto a computer using a data acquisition system. This separation equipment was supplied with high pressure rated > 1000 psi of fittings and valves.

The overall system was insulated in two compartments including oven and fume hood. The oven was functioned to control process temperature, while the fume hood was used as a post treatment system before released gases to the environment.

The performance of membrane was evaluated based on its permeance and selectivity. The permeance of component A (CO_2) in the gas mixture was determined as below [12]:

$$\left(\frac{P'_A}{t}\right)=\frac{V_p y_p}{A_m\left(f_h\breve{x}_0-f_l y_p\right)} \tag{1}$$

Where

$$\breve{x}_0=\left(\frac{x_f+x_r}{2}\right) \tag{2}$$

Where (P_A/t) is the permeance of membrane for component *A*, V_p is the permeate flow rate, y_p is the fraction of component *A* in permeate stream, A_m is the membrane area , f_h and f_l are the fugacity in feed side and permeate side respectively, x_f is the fraction of component *A* in feed side and x_r is the fraction of component *A* in retentate side. The permeance of component *B* (CH_4) can be calculated using an equation similar to the equation for component *A*.

$$\left(\frac{P'_B}{t}\right)=\frac{V_p\left(1-y_p\right)}{A_m\left[f_h\left(1-\breve{x}_0\right)-f_l\left(1-y_p\right)\right]} \tag{3}$$

Where (P_B/t) is the permeance of component *B*. The permeance of the membrane was stated in the unit of GPU (1 GPU=1×10-6 cm3(STP)/s.cm2.cmHg).

The selectivity for mixed gas measurement was measured by using mole fraction of component *A* and *B* in permeate and feed streams.

$$\alpha_{A/B}=\left(\frac{y_A/y_B}{x_A/x_B}\right) \tag{4}$$

Where, *x* and *y* is the fraction of component in feed and permeates side respectively. The real selectivity was expected to give a same value as ideal selectivity if the permeate pressure is zero and when the interaction between penetrant and polymer is weak.

Non ideal condition was considered as the study involved with bulk CO_2 and high pressure condition. For non-ideal gases case, the driving force described in Equation 1 and 3 was replaced with the fugacity terms. Non ideal Equation of State (EOS) was used to calculate the fugacity at high pressure side [13]. The non-ideality of gases at permeate side was neglected as the permeate pressure in atmospheric pressure.

■3.0 RESULTS AND DISCUSSION

3.1 Permeation of Mixed Gas (With and Without the Presence of Heavy Hydrocarbon)

The membrane sample was tested for its permeation properties in terms of permeance and selectivity using a permeation system as discussed in Section 2.3. The manipulated variables of the experiments were pressure, temperature and CO_2 concentration in feed gas mixture. The permeation experiments were completed by evaluating the membrane performance for two different conditions; CO_2-CH_4 mixture (dry condition) and CO_2-CH_4-pentane (wet condition).

CO_2 and CH_4 permeances as well as CO_2/CH_4 selectivity were plotted versus studied parameters (pressure, temperature and CO_2 concentration). Normalized permeance and selectivity were applied to observe the difference in terms of permeance and selectivity due to the presence of heavy hydrocarbon. The normalized permeance and selectivity were described as below:

$$P^*=\frac{P}{P_{ref}}\qquad \alpha^*=\frac{\alpha}{\alpha_{ref}} \tag{5}$$

Where P^* is the normalized or relative permeance and α^* is the normalized or relative selectivity. P and α are the permeance and selectivity at each condition, respectively and P_{ref} and α_{ref} are the permeance and selectivity at 10 bar, 30°C with 25% of CO_2 concentration correspondingly.

The membrane performances in CO2/CH4 separation with and without the presence of heavy hydrocarbon at different operating conditions were discussed in the following subsection.

3.1.1 Effect of Pressure

Figure 2 and 3 demonstrated CO_2 and CH_4 permeances as well as selectivities in both dry and wet conditions as a function of feed pressure, which was varied from 10 to 50 bar. The temperature at 30°C was maintained throughout the experiment.

Based on Figure 2, CO_2 permeance increased as pressure increased for both dry and wet conditions. These observations can be explained by the plasticization phenomena due to the preferentially sorbed CO_2 gas with the pressure increment. Plasticization behavior caused the polymer matrix swelled, introduced additional volume, increased segmental mobility as well as increased the softness and ductility of the material [14,15,16]. This behavior led to the increment of penetrant permeance.

According to Figure 2, CH_4 permeance for both dry and wet conditions increased when pressure rised. This enhancement can be interpreted by the effect of CO_2 plasticization that caused the flexibility of the polymer chains and more penetration of CH_4 [17].

Therefore, Figure 3 showed the decrement of CO_2/CH_4 selectivity for dry and wet conditions as the increment of CH_4 permeance due to the plasticization effect as explained earlier.

3.1.2 Effect of Temperature

Figure 4 and 5 showed the effect of temperature towards CO_2 and CH_4 permeances as well as CO_2/CH_4 selectivity in dry and wet conditions. The permeation of CO_2 and CH_4 were determined for a temperature range of 30 - 50°C.

From Figure 4, it was observed that CO_2 permeance increased when temperature increased for dry and wet conditions. This result can be explained by the increment of molecules diffusion and reduction in sorption of the gases in polymer matrix. Enhancement of temperature caused the chain mobility of the polymer increased and led to the increment of diffusion coefficients as temperature increased. As the permeance is a combination of sorption and diffusion, the increment in permeance showed that the effect of increment of diffusion coefficient was greater than the effect of sorption coefficient. However, CO_2 permeance only slightly increased with temperature because the enthalpy of sorption was more negative and therefore its solubility coefficient reduced as temperature increased [12,18]. As a result, the increment of permeance was moderate when temperature increased even though CO_2 has a smaller kinetic diameter compared to CH_4.

Based on Figure 4, CH_4 permeance also increased in both dry and wet conditions with the increase of temperature. The effect of temperature was more significant to CH_4 compared to CO_2 due to the increment in molecular motion at higher temperature. The larger molecular motion contributed by CH_4 created larger penetrant scale transient gaps for diffusion [19]. Therefore, the larger kinetic diameter of CH_4 gave a result to higher permeance compared to a small diameter molecule as CO_2.

Hence, Figure 5 showed CO2/CH_4 selectivity for dry and wet conditions reduced as temperature enhanced due to higher permeance of CH_4 as compared to CO_2 as explained above.

3.1.3 Effect of Concentration

Figure 6 and 7 showed the separation performance of the mixed gas feeds as a function of CO_2 concentration for dry and wet conditions. The CO_2 composition in the feed varied from 25% to 70% at a fixed pressure of 20 bar and temperature of 30°C.

As shown in Figure 6, CO_2 permeance increased as CO_2 concentration increased for both dry and wet conditions. At a higher level of CO_2 concentration, CO_2 acted as a plasticizer and contributed towards the membrane swelling and dilation of polymer. Dilation is the phenomena where the additional free volume involves and changes in macroscopic volume occur during gas permeation in membrane matrix [20]. As a result, CO_2 permeance increased with the increase in CO_2 concentration.

From Figure 6, CH_4 permeance in dry and wet conditions increased as CO_2 concentration increased. This enhancement can be explained by the effect of membrane swelling of CO_2 that contributed to the increment of hypothetical gaps as well as free volume that caused more CH_4 to penetrate through membrane matrix. Nevertheless, the effect of CO_2 concentration on CH_4 permeance was less significant compared to CO_2 permeance because of the adsorption coverage for CH_4 reduced compared to CO_2 as CO_2 concentration increased from 25 -70%. This behavior was contributed by the favorable competition effect of CO_2 compared to CH_4 in membrane matrix [21]. Therefore, CH_4 permeance slightly increased as CO_2 concentration increased.

As a result, Figure 7 showed the enhancement of CO_2/CH_4 selectivity in dry and wet conditions as the increment of CO_2 permeance and slightly increment of CH_4 permeance as explained above.

3.1.4 Effect of Heavy Hydrocarbon Conditioning

Heavy hydrocarbon exposure caused the decrement in CO_2 and CH_4 permeances as well as CO_2/CH_4 selectivity. Based on Figure 2 and 3, the presence of pentane in wet condition caused a maximum reduction of 26% for CO_2 permeance and 25% for CH_4 permeance whereas 1.5% for CO_2/CH_4 selectivity compared to dry condition with respect to the pressure. From Figure 4 and 5, CO_2 permeance showed 24% decrement, 26% reduction of CH_4 permeance and 1.8% declination of CO_2/CH_4 selectivity in wet condition as a function of temperature. Based on Figure 6 and 7, 24% of maximum decrement in CO_2 permeance, 22% decrement in CH_4 permeance and 1.5% reduction in CO_2/CH_4 selectivity were observed when pentane presented in a gas mixture compared to dry condition.

The increment of CO_2 and CH_4 permeances when exposed to heavy hydrocarbon were expected due to the plasticization phenomena. Strong sorbing components of CO_2 and pentane were plasticizing agents that promote the flexibility of chain and free volume to increase the permeance of both CO_2 and CH_4. Even though CH_4 is a larger molecule, the diffusion of CH_4 increased as supported by the facilitation of segmental motion. Consequently, CO_2/CH_4 selectivity reduced due to the increment of CH_4 permeation in which contributed by the plasticization effect of CO_2 and pentane.

However, as comparison with dry condition, membrane performance showed a declination in terms of permeance and selectivity when exposed to heavy hydrocarbon. This behavior might be contributed by the competition effect between the penetrants to permeate through polymer matrix [22]. The presence of pentane restrained the transports of CO_2 to pass through the membrane matrix. Pentane represented as the greatest competitor during permeation process since it has the highest critical temperature (196.7°C) compared to CO_2 (31.1°C) and CH_4 (-82.7°C) components which led to the permeation reduction.14 Although pentane and CO_2 were known as a great plastizing agent and caused the increment of permeation and reduction and selectivity as explained earlier, but the plasticization effect offset with the competition effect between penetrants, thereby resulted in reduction of membrane performance compared to dry condition.

The possible explanation for the decrement of membrane performance can be related to the potential of pentane molecules that entered and blocked macrovoids and microvoids in polymer matrix efficiently and consequently inhibited the transportation of other penetrants such as CO_2. Therefore, we can conclude that the competition effect dominated the permeation instead of plasticization effect when pentane presented in gas mixture.

Furthermore, the reduction of CO_2/CH_4 selectivity as the presence of pentane was also due to the compaction effect. This phenomenon occurred when the membrane matrix swelled by the presence of pentane which was promoted by the plasticization then led to the decrement of modulus of the fiber substructure. The combination of the decrement of membrane modulus and elevated pressure employed in the system intensified the compaction of porous substructure [23]. This compaction phenomenon contributed to the additional resistance for mass transfer of gases, thereby caused loss in membrane performance even exposed at low mass fraction of contaminants [24].

■4.0 CONCLUSION

The objective to study the effect of heavy hydrocarbon on the polyimide membrane performance in CO_2/CH_4 separation was successfully achieved. Parametric analyses at different pressure, temperature and CO_2 concentration have been conducted. CO_2 and CH_4 permeances increased which resulted in the decrease of CO_2/CH_4 selectivity as pressure increased from 10 – 50 bar. The increment of temperature showed that CO_2 increased and CH_4 permeance slightly increased whereas CO_2/CH_4 selectivity decreased when temperature elevated. For the effect of CO_2

concentration, CO_2 and CH_4 permeances increased while CO_2/CH_4 selectivity experienced a decrement. The presence of pentane as heavy hydrocarbon in gas mixture contributed to the increment of CO_2 and CH_4 permeances and declination of CO_2/CH_4 selectivity of membrane. These results were due to the dominating effect of plasticization and compaction, which offset with the competitive effect between penetrants. Therefore, separation performance of polyimide membrane was affected with the presence of heavy hydrocarbon. Also, the report demonstrated polyimide membrane faced a trade-off limitation between permeability and selectivity as it was difficult to have high membrane permeability and selectivity at the same time.

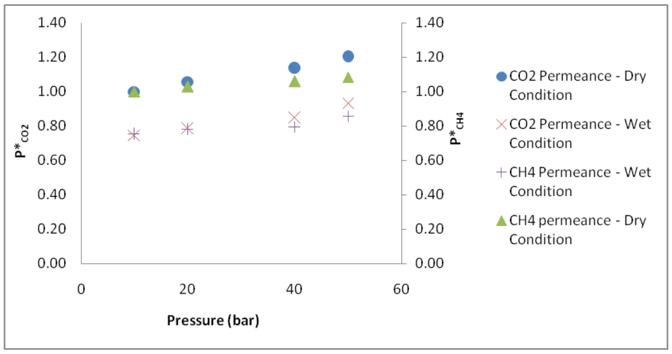


Figure 2 Pressure variation effect on CO_2 and CH_4 permeance of polyimide membrane under 25% CO_2 -75% CH_4 mixture with (wet condition) and without pentane (dry condition) at 30°C

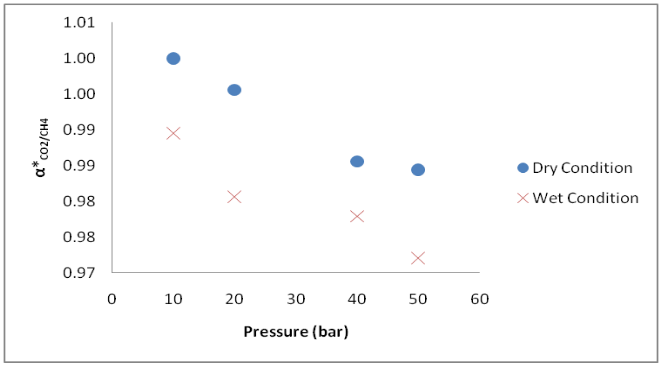


Figure 3 Pressure variation effect on selectivity of polyimide membrane under 25% CO_2 -75% CH_4 mixture with (wet condition) and without pentane (dry condition) at 30°C

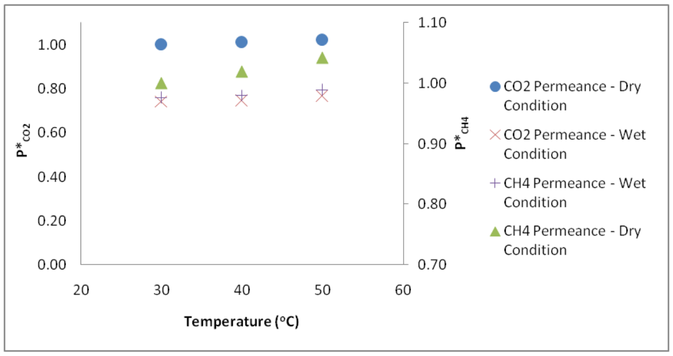


Figure 4 Temperature variation effect on CO_2 and CH_4 permeance of membrane sample under 25% CO2-75% CH_4 mixture with (wet condition) and without pentane (dry condition) at 20 bar

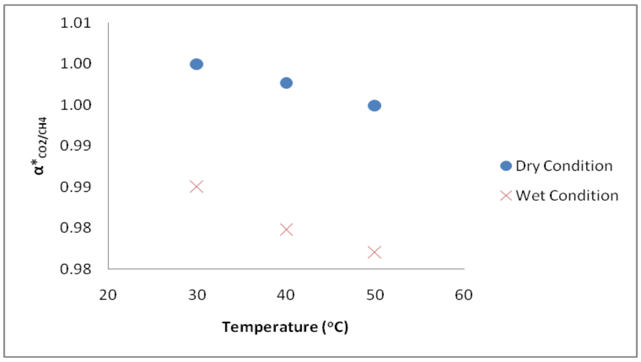


Figure 5 Temperature variation effect on selectivity of membrane sample under 25% CO2-75% CH_4 mixture with (wet condition) and without pentane (dry condition) at 20 bar

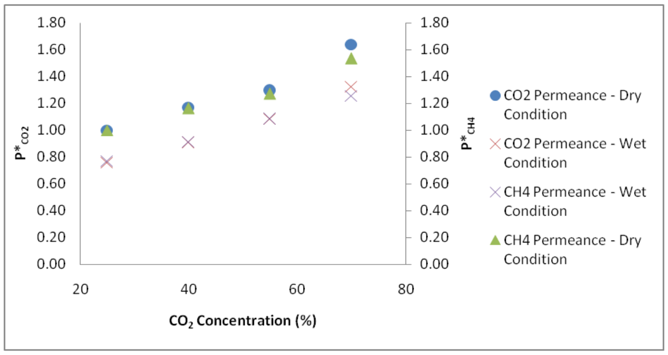


Figure 6 Concentration variation effect on CO_2 and CH_4 permeance of membrane sample with (wet condition) and without pentane (dry condition) at 20 bar, 30°C

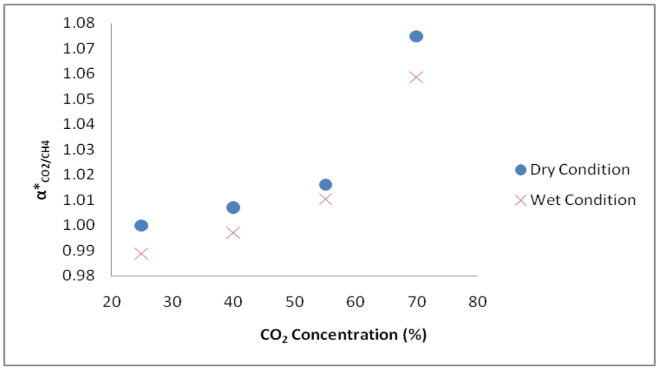


Figure 7 Concentration variation effect on selectivity of membrane sample with (wet condition) and without pentane (dry condition) at 20 bar, 30°C

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