Journal of Engineering and Applied Sciences 11 (9): 1958-1961, 2016
ISSN: 1816-949X

Effect of Progressive Heating on CO_2/CH_4 Separation Using Assymetric Hollow Fiber Polysulfone Membrane

[1]Muhamad Azwar Azhari, [1]O. Noooririnah and [2]Ahmad Fauzi bin Ismail
[1]Faculty of Engineering Technology, Universiti Teknikal Malaysia Melaka,
Durian Tunggal, Malaysia
[2]Advance Membrane Technology Research Centre, Universiti Teknologi Malaysia,
Johar Bahru, Malaysia

Abstract: This study reports the effect of progressive heating on carbon dioxide/methane separation characteristics in asymmetric hollow fiber polysulfone membranes. Glassy polymers are easily plasticized with the presence of plasticizing agents such as carbon dioxide. Progressive heating were applied to the membranes to suppress CO_2 induced plasticization. Membranes treated with progressive temperature heating exhibits lower pressure-normalize flux for both carbon dioxide and methane compared to untreated membranes. This was due to densification of membrane skin layer during progressive heating process. Denser skin layer increases the resistance in the membrane which resulted in decreased of pressure-normalize flux for both CO_2 and CH_4. CO_2/CH_4 separation decreases with the increase of feed pressure for untreated membranes due to plasticization caused by CO_2. However, CO_2/CH_4 separation increases and remains high for membranes treated with progressive heating technique showing that CO_2 induced plasticization has been successfully suppressed. From the results provided in this study, it can be concluded that plasticization of polysulfone hollow fiber membrane is successfully suppressed by progressive heating heat treatment process.
study

Key words: Study asymmetric polysulfone, CO_2/CH_4 separation, progressive heating, layer, polymers

INTRODUCTION

Glassy polymers are in the limelight of most important membrane separation processes for industrial or scientific interest. This is due to the superior gas separation factor as well as the high thermal and mechanical properties (Bernardo *et al*., 2009). The purity of product gas from membrane separation process depends highly on the ability of the membrane to select the desired and undesired gas.

While membrane systems for gas separation are proven attractive, it has a major disadvantage when dealing with plasticizing gases such as carbon dioxide. Carbon dioxide has an effect of plasticizing glassy polymers where polysulfone asymmetric hollow fiber membrane is also affected (Scholes *et al*., 2010). In case of carbon dioxide/methane separation, carbon dioxide acts as a plasticizer where it reduces the interaction between adjacent segments in the polysulfone polymer chains (Bos *et al*., 1999). This particular phenomenon is known as plasticization in glassy polymer (Kapantaidakis *et al*., 2003).

Carbon dioxide induced plasticization depends so much on the amount of sorbed CO_2 (Horn and Paul, 2011). At relatively low pentrant concentrations, permeation usually follows the dual sorption mode (Baker, 2002). At this time, the effects of penetrant sorption are mostly reversible over reasonable time periods. However, at high penetrated concentrations, plasticization occurs and the effect is commonly irreversible owing to increased free volume that facilitates molecular motions. In other words, the existence of carbon dioxide swells the polysulfone membrane during separation process (Bos *et al*., 1999). This will finally result in increase of the permeability of all gas species (Horn and Paul, 2011).

Plasticization in glassy polymers is a phenomenon where there is a reduction in the interaction between adjacent segments of the polymer chains. This can be seen as a swelling of the polymers and this swell is due to an exposure to certain substance. This swell will cause the penetrants to diffuse in an accelerated rate hence causing the permeance to be high (Kapantaidakis *et al*., 2003). It can be simply deduced that plasticization in glassy polymer is the weakening effect of the polymer membranes causing it to swell and lose its selectivity (Dong and Chen, 2011). As such this study reports the suppression of plasticization upon polysulfone membranes to increase the selectivity of CO_2/CH_4 separation through progressive heating techniques.

Corresponding Author: Muhamad Azwar Azhari, Faculty of Engineering Technology, Universiti Teknikal Malaysia Melaka, Durian Tunggal, Malaysia

MATERIALS AND METHODS

Asymmetric polysulfone hollow fiber membrane preparation: Dry/wet spinning technique was employed in fabricating asymmetric polysulfone hollow fiber membrane for this study. The dope solution contains polysulfone, N,N dimethylacetamide, tetrahydrofuran and ethanol. The solution is placed in a dope reservoir and kept at a temperature of 20°C during spinning. The spinneret used for spinning has a dimension of 0.6 mm for outer diameter and 0.3 mm for inner diameter. A solution mixture of 20% potassium acetate and 80% water was used as bore fluid. Upon extrusion from the spinneret, the nascent membrane is air dried using nitrogen gas in a small passage of 9 cm forced convection chamber. After dry spinning, the nascent membrane was then immersed in a coagulation bath of nonsolvent. Water at 16 °C was used as the external coagulation bath. The hollow fibers were spun at a dope extrusion rate of 2.5 $cm^3 min^{-1}$. The ratio dope extrusion rate and bore fluid kept constant at 3.

Heat treatment: In this study progressive heating technique was applied. The membranes produced were placed in a hot air oven and the temperature was brought up from 35°C to the desired 70°C (later in the text known as progressive 70) and 90°C (progressive 90) at a rate of 1°C per minute. Upon reaching the desired temperature, heating continues for another 10 min before the membranes were removed from the oven and cooled down to room temperature naturally.

RESULTS AND DISCUSSION

The permeation of carbon dioxide through untreated and progressive heating treated membranes exhibited no dramatic increment or experience any fluctuation with increment of feed pressure as depicted in Fig. 1. The pressure-normalized fluxes for carbon dioxide for untreated membranes showed an increase with the increment of feed pressure. This is due to the swelling in the membranes caused by high concentration of carbon dioxide. The molecular chain of polysulfone can be changed with the introduction of small amount of sorbed carbon dioxide. This particular phenomenon is known as plasticization in glassy polymer. This will result in higher mobility of polymer segments which gives higher chances of diffusive jumps by penetrant molecules (Dong). As a result of plasticization in the membranes, permeation of carbon dioxide accelerated as the pressure increases.

However, it is evident that progressive heated membranes do not show a minimum value or any increasing trend. A more stabilized reading can conclude that carbon dioxide do not disrupt the molecular chain packing causing the membranes to swell and plasticized and permeate excessive gases at higher feed pressures (Ismail and Yaacob, 2006). This clearly shows that polymer densification has taken place, hence making the diffusion of gas molecules slower in the polymer matrix (Ettourney and Majeed, 1997). This can be concluded as plasticization for asymmetric hollow fiber polysulfone membranes has been suppressed through progressive heating at 70 and 90°C to a pressure up to 10 bars.

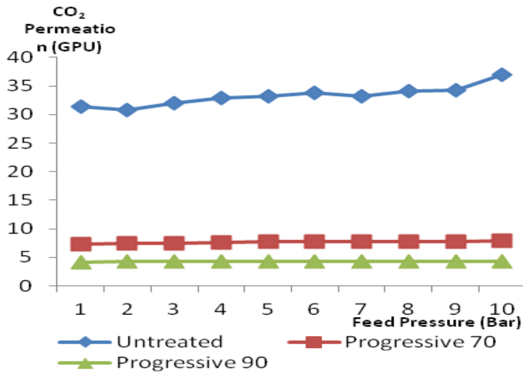

Fig. 1: CO_2 permeation for untreated members, progressive 90 membranes

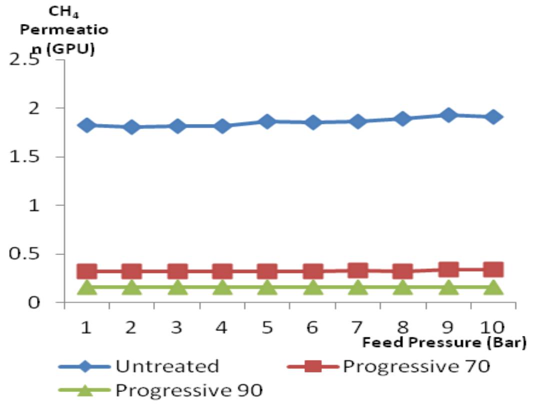

Fig. 2: CH_4 permeation for untreated members, progressive 90 membranes

Figure 2 describes the pressure-normalize flux for methane using untreated membranes and membranes heated with progressive heating. There is no apparent evident showing fluctuation of CH_4 with the increment of feed pressure. This is because CH_4 do not plasticize the polysulfone membranes. This constant value obtained was in agreement to the dual-sorption mode model studied by Krol *et al.* (2001). However, with the effect of progressive heating, the permeation of CH_4 decreases and it further decreases when the heating temperature increases from 70-90°C.

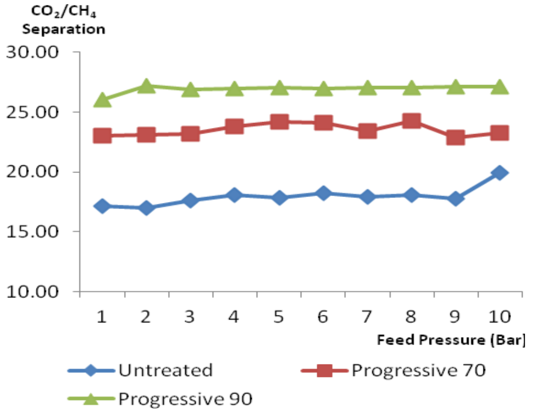

Fig. 3: CO_2/CH_4 separation for untreated membranes, progressive 70 and progressive 90 membranes

Progressive heated membranes illustrate a very lowpressure-normalize flux for methane and on the other hand staying high on carbon dioxide pressure-normalized flux as illustrated in Fig. 1 and 2. The lower pressure-normalized flux for methane is the main reason of getting a higher selectivity for membranes treated with progressive heating. The reason for higher selectivity has a lot to do with the modification of molecular structure of the membranes due to heating (Ismail and Lorna, 2002). The selectivity of progressive heated membranes is much higher compared to the untreated membranes as exhibited in Fig. 3. It is also evident from Fig. 3 that the selectivity increases with increase of temperature. The selectivity trend is also more stable especially for progressive 90°C where the selectivity value does not fluctuate when the feed pressure increases. Enhancement of molecular structures may somehow elevate the selectivity values to beyond their intrinsic selectivity value (Ismail *et al*., 1999). The same results could also be observed from previous researches by Bos *et al*., 1999, Ismail *et al*., 1999, Ismail and Yaacob (2006) and Kawakimi *et al*. (2003). This clearly showed that plasticization has been successfully suppressed through progressive heating at the 2 temperatures.

CONCLUSION

With application of progressive heating at 70° and 90°C upon the membranes, the pressure-normalized fluxes of methane and carbon dioxide reduces. As a result, the CO_2/CH_4 selectivity increases. The decrease of pressure-normalized flux is due to the densification of membranes following heat treatment process. From the experimental data, it is clear that at the same heating temperature, progressive heating gives a better permeation and selectivity data. It is also evident that employment of progressive heating at 90°C gives a better CO_2/CH_4 selectivity.

ACKNOWLEDGEMENTS

The researchers would like to acknowledge the Ministry of Science Technology and Innovation, Universiti Teknikal Malaysia Melaka and Universiti Teknologi Malaysiafor the support and funding throughout this study.

REFERENCES

Baker, R.W., 2002. Future directions of membrane gas separation technology. Ind. Eng. Chem. Res., 41: 1393-1411.

Bernardo, P., E. Drioli and G. Golemme, 2009. Membrane gas separation: A review/state of the art. Ind. Eng. Chem. Res., 48: 4638-4663.

Bos, A., I.G.M. Punt, M. Wessling and H. Strathmann, 1999. CO_2-induced plasticization phenomena in glassy polymers. J. Membr. Sci., 155: 67-78.

Dong, G., H. Li and V. Chen, 2011. Plasticization mechanisms and effects of thermal annealing of Matrimid hollow fiber membranes for CO_2 removal. J. Membr. Sci., 369: 206-220.

Ettouney, H. and U. Majeed, 1997. Permeability functions for pure and mixture gases in silicone rubber and polysulfone membranes: Dependence on pressure and composition. J. Membr. Sci., 135: 251-261.

Horn, N.R. and D.R. Paul, 2011. Carbon dioxide plasticization and conditioning effects in thick vs. thin glassy polymer films. Polym., 52: 1619-1627.

Ismail, A.F. and N. Yaacob, 2006. Performance of treated and untreated asymmetric polysulfone hollow fiber membrane in series and cascade module configurations for CO_2/CH_4 gas separation system. J. Membr. Sci., 275: 151-165.

Ismail, A.F. and W. Lorna, 2002. Penetrant-induced plasticization phenomenon in glassy polymers for gas separation membrane. Sep. Purif. Technol., 27: 173-194.

Ismail, A.F., I.R. Dunkin, S.L. Gallivan and S.J. Shilton, 1999. Production of super selective polysulfone hollow fiber membranes for gas separation. Polym., 40: 6499-6506.

Kapantaidakis, G.C., G.H. Koops, M. Wessling, S.P. Kaldis and G.P. Sakellaropoulos, 2003. CO_2 Plasticization of polyethersulfone/polyimide gas separation membranes. AIChE. J., 49: 1702-1711.

Kawakami, H., K. Nakajima, H. Shimizu and S. Nagaoka, 2003. Gas permeation stability of asymmetric polyimide membrane with thin skin layer: Effect of polyimide structure. J. Membr. Sci., 212: 195-203.

Krol, J.J., M. Boerrigter and G.H. Koops, 2001. Polyimide h ollow fiber gas separation membranes: Preparation and the suppression of plasticization in propane/propylene environments. J. Membr. Sci., 184: 275-286.

Scholes, C.A., G.Q. Chen, G.W. Stevens and S.E. Kentish, 2010. Plasticization of ultra-thin polysulfone membranes by carbon dioxide. J. Membr. Sci., 346: 208-214.