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Ionic Liquid Embedded in Polymeric Membrane for High Pressure CO_2 Separation

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In recent years, the societies are looking forward for green energy consumption thus making natural gas usage increased tremendously from the last few decades. The increasing natural gas demand has led to increasing number of environmental friendly research in natural gas purification techniques. Membrane separation technology is one of the green methods that experience breakthrough, substantial growth and advances for the carbon dioxide separation from natural gas. The advantages of membrane separation technology covered the simplicity in process, low energy consumption, low carbon and water footprint as well as more environmental compatibility. In particular, the current commercialized membranes are polymeric types such as polyimides as well as cellulose acetate. However, the applications of the commercialized membranes are still limited to remove low CO_2 content in the gas stream. Hence, the membrane improvement idea came across to develop membranes that can be applied for high CO_2 content separation. This paper intended to present our advanced polymeric membrane fabricated with the addition of ionic liquid. The separation performance was tested at various pressure ranging from 10 to 30 bar and the ideal separation reached up to 70. The fabricated membrane was also having dense morphology as analysed by FESEM which is preferable for gas separation. These results are believed to be an extended and novel future direction for membrane gas separation.

1. Introduction

As the world is promoting green technology to preserve the environment, natural gas is the best idea for the fuel consumption as it produces less carbon dioxide (CO_2) upon combustion. In addition, natural gas itself is also known as a green energy source since it releases less amount of toxic emissions like sulphur dioxide (SO_2) and nitrogen oxide (NO). In addition, the combustion of coal and fuel oil will also release tiny dust particles into the environment and some substances that do not burn but instead are suspended in the atmosphere and eventually contribute to air pollution like haze (Laboratory, 2010). Hence, the natural gas demand has been increasing since the last few decades and is expected to increase more in upcoming years (Blakey, 2010).
However, the natural gas cannot be used as it is taken from the wellhead, but instead, it needs to be purified. The unwanted substances like other higher hydrocarbons like ethane, propane and butane and water shall be removed before commercialize (Mohshim et al., 2013). Other than that, toxic gases like CO_2 and hydrogen sulphide (H_2S) must be removed as well since these gases will lower the calorific value of natural gas making it less useful (Nasir et al., 2013). Membrane gas separation is a one of the most attracting methods in natural gas separation due to its wide range of advantages. Membrane is a good selection for natural gas purification since membrane offers a very low carbon footprint process as compared to other separation methods (Shimekit and Mukhtar, 2012). There are few types of polymeric membranes are already commercialized in the market for the gas separation purpose (Mannan et al., 2013). The membranes include cellulose acetate, polyimide and also polysulfone. However, these membranes is yet to remove high CO_2 content of raw natural gas since their performance is for the pre-treated natural gas that contain a low CO_2 content (Passalacqua et al., 2014). Membranes with high separation performance to remove high CO_2 content is really required now since the government needs to

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monetise the high CO_2 content natural gas well in order to meet the world energy demand. Hence, an advance polymeric membrane was proposed to meet this requirement. This paper intended to explore the benefit of ionic liquid embedded into the polymeric membrane for the CO_2 separation purpose.

2. Experimental

Membrane with the third component in it is also known as fixed transport membrane (FTM). In FTM, the selection of polymer is a very crucial step since there are only few polymers are compatible for the third component; i.e. ionic liquid. The selected materials must be compatible to each other in order to get a good separation performance.

2.1 Raw Material Selection

Polyethersulfone (PES) has been chosen as the base of polymer matrix since PES is known to give goo CO_2 separation as well as having wide temperature limit, thermally and mechanically strong, chemically stable and it is known as a good membrane fabrication based (Cheryan, 1998). Other than that, ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, ([emim][Tf_2N]) was selected to be embedded into the polymer matrix as this IL has been widely used as CO_2 adsorbent due to its high CO_2 affinity (Maginn, 2012). N-Methyl-2-pyrrolidone (NMP) has been chosen as this solvent can dissolve the PES and form a homogenous blend upon mixed with both [emim][Tf_2N] and PES. Since we study the effects of ionic liquid in the PES membrane, the ionic liquid, [emim][Tf_2N] while The PES composition was fixed at 20 wt/wt%.

2.2 Membrane Preparation

Membranes were fabricated through solvent evaporation method. PES was bought from BASF in flakes form and was dried before used while both [emim][Tf_2N] and NMP were purchased from Sigma with 99 % purity and were used without any further purification. Emim[Tf_2N] was first mixed with the solvent and the weighted and dried polymer was dissolved in the mixture part by part. After all polymer dissolved, the solution were stirred for 24 h to ensure its homogeneity. The solution was casted on a glass plate using the solution casting machine. The membranes were dried in oven at 90 ^oC for 8 h then continue with 24 h at 160 ^oC to ensure all solvent was removed. The membrane was left to cool at room temperature and peeled of itself. Table 1 shows the fabricated membranes details in this project.

Table 1: Details of Fabricated Membrane Composition

Membrane	Polymer (PES) (wt/wt%)	Ionic Liquid (emim [Tf_2N]) wt/wt%
Pure PES	20	0
ILMPM_5	20	5
ILMPM_10	20	10
ILMPM_20	20	20

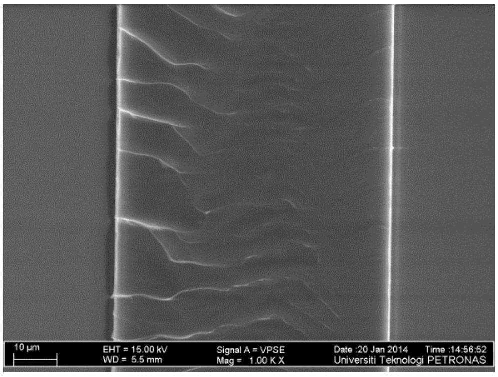
2.3 Membrane Characterization and Separation Performance

Different membrane must be characterized in terms of structure and mass transport properties to consequently cover the application. Different characterization techniques are available for different membrane to be used. The membranes were characterized in term of its morphology through field emission scanning electron microscopy (FESEM) and thermal analysis through thermal gravimetric analysed (TGA). The membranes gas separation performance of ILMPM was conducted using the gas separation performance apparatus at high pressure (30 bar) and the results were compared with the pure PES polymeric membrane.

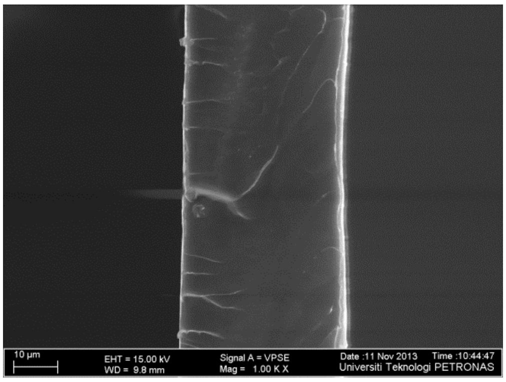
3. Results and Discussions

3.1 Membrane Morphology

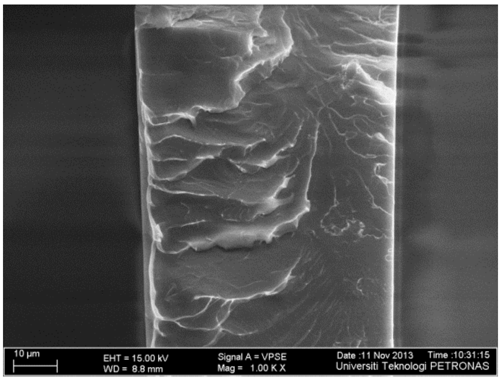
In this project, FESEM (ZEIS SUPRA TM 55VP) was used to determine the qualitative structural assessment of both surface and cross-section for the membranes. Figure 1 shows the cross-sectional images of pure PES polymeric membrane and membranes with different concentration of [emim][Tf_2N]. The addition of ionic liquid has no effects on the membrane morphology where the membranes are found to be dense for both types of ionic liquids and having no significant difference with membrane without the ionic liquid addition which also found in recent publication (Mohshim et al., 2014). The membrane thickness measured from FESEM analysis for the fabricated membranes was ranging from 50 to 70 μm.



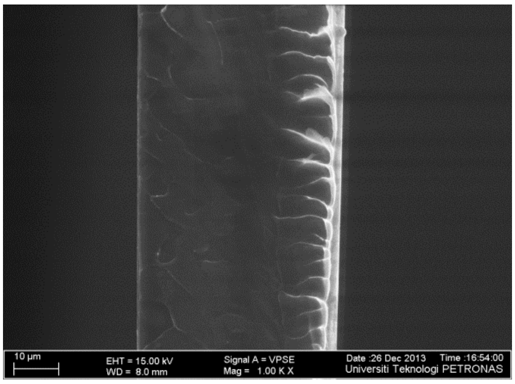
(a) Pure PES Membrane



(b) ILMPM_5



(c) ILMPM_10



(d) ILMPM_20

Figure 1: Cross-Sectional Morphology Analysis through FESEM

3.2 Thermal Analysis

All fabricated membranes were subjected to the same TGA experimental procedure. Figure 2 shows the weight loss of PES polymeric membrane with emim[Tf_2N]. It was observed that all fabricated ionic liquid membranes were seemed to be free from moisture as there is no weight loss up to 100 °C. However, the membranes with ionic liquid addition decomposition temperature have started earlier as compared to the pure PES polymeric membrane. Membranes with emim[Tf_2N] started to decompose at 410 °C. This quantified that the addition of ionic liquid has decreased the thermal stability of the PES polymer which has been also discussed in (Cakal et al., 2012) treating gas composition and in (Mohshim et al., 2014) focusing on ionic liquids.

3.3 Gas Separation Performance

The gas permeation analysis of single gases was performed at room temperature by using a constant volume technique and the permeate side was maintained essentially at atmospheric pressure. In order to observe the effects of ionic liquid addition into the pure PES membrane, the experiment was conducted at fix feed pressure of 20 bar and the ionic liquid composition was varied at 5, 10 and 20 wt/wt%. Figure 3a and 3b show the CO_2 gas permeation and ideal CO_2/CH_4 selectivity of fabricated membranes.
From Figure 3a, it was noticed that the ionic liquid presence was strongly affected the gas separation performance. In this figure, the CO_2 permeation increased significantly as the emim[Tf_2N] concentration was increased. This trending was expected since emim[Tf_2N] was known to have CO_2 affinity (Cadena et al., 2004). By the increasing of emim[Tf_2N] content, the CO_2/CH_4 selectivity was also increased expressively as shown in Figure 3b since the emim[Tf_2N] have positive effects on CO_2 permeance compared to CH_4 permeance. Good affinity of CO_2 in emim[Tf_2N] has resulted in high solubility of this gas in the membrane (Mirarab et al., 2014).

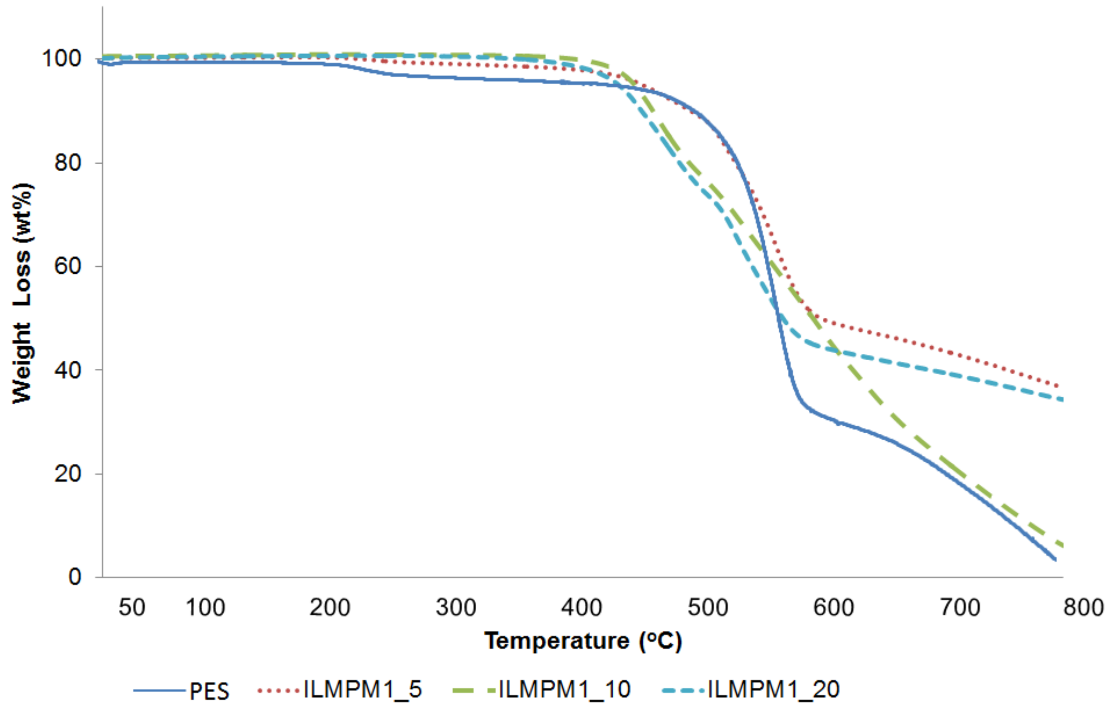
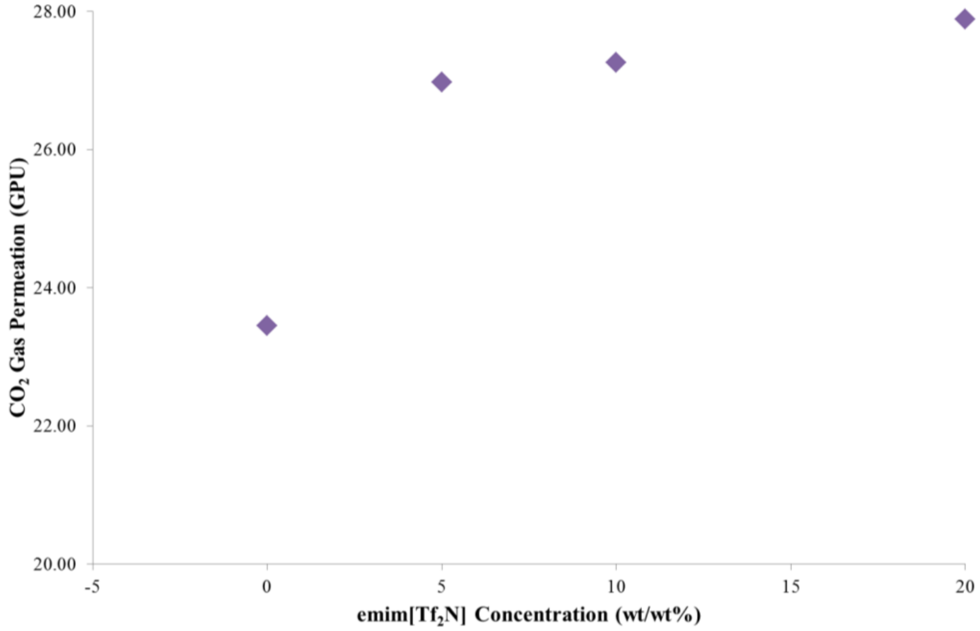


Figure 2: Thermogravimetric Analysis (TGA) of Fabricated Membranes

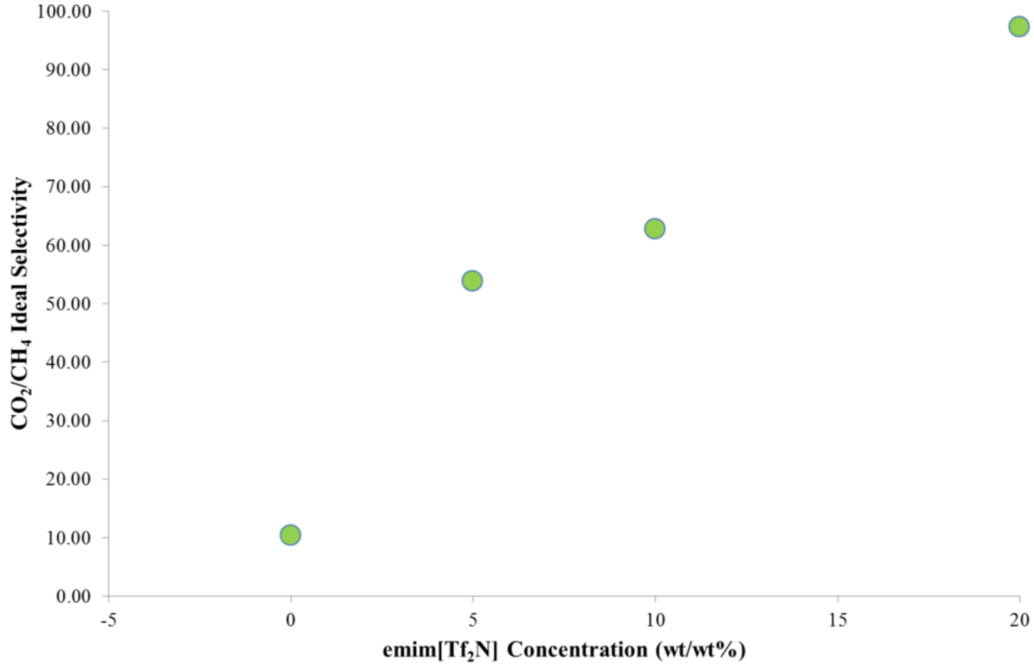
4. Conclusion

Three membranes with different ionic liquid concentrations were fabricated by incorporating ionic liquid into pure PES membranes. The membranes were characterized in terms of its physical and thermal propertied. The developed membranes were found to be dense in structure as they were prepared by dry phase inversion technique. Membranes containing ionic liquid were observed to have lower thermal stability where ILMPM decomposed at an earlier temperature as compared to pure PES polymeric membrane.

However, membrane with ionic liquid show great CO_2 separation improvement where the CO_2 permeation increased around 21 % while the ideal selectivity was also increased tremendously with 20 wt/wt% ionic liquid. This composition was not optimized and further experiment shall be conducted in the future in order to get the optimum ionic liquid composition in the membrane. Instead, this preliminary experiment was a good starter to fabricated membranes with ionic liquid embedded inside.



(a) CO_2 Permeance



(b) CO_2/CH_4 Ideal Selectivity

Figure 3: (a) CO_2 Permance and (b) CO_2/CH_4 Ideal Selectivity of Fabricated Membranes

Acknowledgement

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References

Blakey S., 2010, Natural gas Supply and Demand Outlook to 2030, ECT Gas Forum, Eurogas, St. Petersburg, Russia.

Cadena C., Anthony J.L., Shah J.K., Morrow T.I., Brennecke J.F. Maginn E.J., 2004, Why is CO_2 so soluble in imidazolium-based ionic liquids?, Journal of the American Chemical Society, 126, 5300-5308.

Cakal U., Yilmaz L., Kalipcilar H., 2012. Effect of feed gas composition on the separation of CO2/CH4 mixtures by PES-SAPO 34-HMA mixed matrix membranes, Journal of Membrane Science, 417–418, 45-51.

Cheryan M., 1998, Ultrafiltration and Microfiltration Handbook, Taylor & Francis, United States.

National Physical Laboratory, 2010, Traceable primary standards for natural gas analysis, National Physical Laboratory, Middlesex, United Kingdom.

Mannan H.A., Mukhtar H., Murugesan T., Nasir R., Mohshim D.F., Mushtaq A., 2013. Recent Applications of Polymer Blends in Gas Separation Membranes, Chemical Engineering & Technology, 36, 1838-1846.

Mirarab M., Sharifi M., Ghayyem M.A., Mirarab F., 2014, Prediction of solubility of CO_2 in ethanol–[EMIM][Tf2N] ionic liquid mixtures using artificial neural networks based on genetic algorithm, Fluid Phase Equilibria, 371, 6-14.

Mohshim D.F., Mukhtar H., Man Z., 2014, The Effect of Incorporating Ionic Liquid into Polyethersulfone-SAPO34 Mixed Based Matrix Membrane on CO_2 Gas Separation Performance, Separation and Purification Technology, 135, 252–258.

Mohshim D.F., Mukhtar H.B., Man Z., Nasir R., 2013, Latest Development on Membrane Fabrication for Natural Gas Purification: A Review. Journal of Engineering, 2013, 101746.

Nasir R., Mukhtar H., Man Z., Mohshim D.F., 2013, Material Advancements in Fabrication of Mixed-Matrix Membranes, Chemical Engineering & Technology, 36, 717-727.

Passalacqua R., Ampelli C., Perathoner S., Centi G., 2014, Self-Standing TiO_2 Nanotubular Membranes for Sustainable Production of Energy, Chemical Engineering, 41, 319-324.

Shimekit B., Mukhtar H., 2012, Natural Gas Purification Technologies - Major Advances for CO_2 Separation and Future Directions, Advances in Natural Gas Technology, InTech, Malaysia.