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The Role of Solvent Mixture, Acetic Acid and Water in the Formation of CA Membrane for CO2/N2 Separation

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Abstract

The improvement of Carbon dioxide (CO_2) separation efficiency from flue gases to reduce the total energy cost of sequestration technologies in coal-fired power plants has been identified as a high-priority research area. In the past three decades, membranes have attracted the attention of chemists and engineers due to their unique separation principles (i.e., selective transport and efficient separation compared to other unit operations). In this study, the formation of cellulose acetate (CA) membrane for CO_2/nitrogen (N_2) separation was investigated by wet phase inversion. In order to modify the CA membrane structure, different concentration ratio of solvent mixture (acetic acid:water), acetic acid and water were studied. The CA membranes were analyzed by Fourier transform infrared spectroscopy (FTIR). The separation results supported by the characterization, where the best formulate membrane with solvent mixture ratio of 70:30 (acetic acid:water), acetic acid concentration of 63 wt% and water concentration of 27 wt% had high CO_2 permeance of 400.92 GPU and slightly better CO_2/N_2 separation performance at 32.92 as compared to others literature.

Keywords: acetic acid concentration; gas separation; solvent mixture ratio; water concentration

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1. Introduction

The membrane gas separation is an energy saving, space efficient technology which is easily to be scaled up [1]. Also, membrane based gas separation has the advantage of being more compact and green technology [2]. Hence, the CO_2 separation using membrane technology has led to a promising future [1]. Gas separations using polymeric membranes have achieved important commercial success in some industrial processes since the first commercial-scale membrane gas separation system was produced in the late 1970s [3]. Polymeric membranes were categorized based on rubbery or glassy polymers. In recent years, the glassy polymer has received a great deal of attention due to its advantages in mechanical properties and relative economical processing capability [4].

In this study, the CA polymer was chosen due to high solubility of CO_2 within CA [5] and the high sorption capacity of CO_2 into CA chains [6]. Generally, CA is a thermoplastic polymer, which has both acetyl and hydroxyl groups that allows different types and degree of intra and intermolecular interactions [6]. CA membranes have been used commercially for many gas separation applications [7], due to its properties of being inexpensive [8]. The asymmetric CA membrane is typically fabricated using a phase inversion technique, which involves the immersion of the casted polymer film into a coagulation bath for film solidification. The solvent in the casting solution film will then be exchanged with the non-solvent in the coagulation bath, and phase separation occurs. This process produces an asymmetric membrane with a top skin layer [9] that is controlled by several variables, such as the composition of casting solutions [10], and the concentration of the interval non-solvent [11].

In general, the membrane synthesis method should be simple and environmental-friendly. Thus, the waste water discharge containing toxic solvents like DMF (dimethylformamide), N-methylpyrrolidone (NMP), and DMAC (dimethylacetamide) should be prevented [12,13]. Zhang *et al.* [12] proposed a new approach to fabricate asymmetric CA membranes using a greener process. In this process, acetic acid was chosen as the solvent and water as non-solvent. All the materials i.e., CA, acetic acid and water are cheap, easily available, and environmental-friendly. In fact, this one-step preparation method not only reduced the overall membrane production cost, but also produced non-toxic waste discharge during the fabrication process [12]. Hence, this preparation formulations i.e. the concentration of solvent mixture (acetic acid:water), acetic acid and water were investigated in the current study.

2. Experimental Section

2.1. Materials

CA (acetyl content: (54.6-56) %) was acquired from Sinopharm Chemical Reagent Co. Ltd., China. Acetic acid (CH_3COOH), ACS reagent $\geq$ 99.7%, was supplied by Sigma Aldrich (Malaysia). N-hexane and ethanol were supplied by Merck (Malaysia).

2.2. Membrane Preparation

Membranes were prepared by wet-phase inversion according to previously published studies [12, 14-16].

2.2.1. Effect of Solvent Mixture Ratio

The membrane was fabricated at acetic acid:water of 60:40 (M1), 70:30 (M2), and 80:20 (M3) from the solvent mixture (83 wt%) with polymer concentration of 17 wt% and casting thickness of 250 µm.

2.2.2. Effect of Acetic Acid Concentration

The membrane was fabricated at acetic acid concentration of 63 wt% (M4), 58 wt% (M5), and 56 wt% (M6) with polymer concentration of 10 wt%, 15 wt%, and 17 wt%, respectively and water concentration of 27 wt%. The membranes were casted at 250 µm.

2.2.3. Effect of Acetic Acid Concentration

The membrane was fabricated at water concentration of 27 wt% (M4), 22 wt% (M5), and 20 wt% (M6) with polymer concentration of 10 wt%, 15 wt%, and 17 wt%, respectively and acetic acid concentration of 63 wt%. The membranes were casted at 250 µm.

2.3. Characterization

Membranes spectra were obtained by attenuated total reflectance-FTIR (ATR-FTIR) method with Diamond crystal over wavenumber range of 4000-525 cm^{-1} by a Thermo Scientific FTIR model NICOLET iS10 spectrometer system.

2.4. Gas Permeation Measurement

The gas separation measurements were performed according to previously published studies [14-16].

3. Results and Discussion

3.1. Effect of Solvent Mixture Ratio

M1 was excluded because the CA polymer unable to dissolve in the casting solution of the synthesize membrane. This might be due to the low solvent mixture of $CH_3COOH:H_2O$ (60:40), which significantly affected its physical and chemical properties.

ATR-FTIR was used to validate the interaction between solvent mixture ($CH_3COOH:H_2O$), as demonstrated in Fig 1. M2 consists of four main peaks, i.e. 3468.39 cm^{-1}, 1735.98 cm^{-1}, 1220.68 cm^{-1} and 1032.21 cm^{-1} for O-H, C=O, CH_3CO, and C-O-C, respectively (Fig 1a). As compared to M3 (Fig 1b), there is a shift downward for O-H, C=O, CH_3CO, and C-O-C to 3467.95 cm^{-1}, 1735.35 cm^{-1}, 1217 cm^{-1} and 1031.09 cm^{-1}, respectively (Fig 1b). This may be due to the increment in the acetic acid concentration that faster the exchange rate between the solvent (acetic acid) and the non-solvent (water) [17]. Thus, it weakens the stretching vibration of O-H, C=O, CH_3CO, and C-O-C, respectively, within the membrane structure of M3.
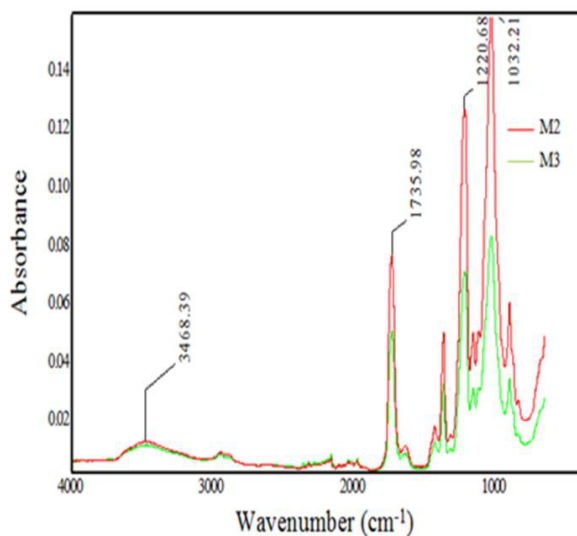

Fig 1. ATR-FTIR of membrane fabricated at solvent mixture of (a,b) 70:30 (M2), and (c,d) 80:20 (M3) with polymer concentration of 17 wt% and casting thickness of 250 µm.

3.2. Effect of Acetic Acid Concentration

When the concentration of acetic acid was decreased from 63 wt% (M4) to 58 wt% (M5) into CA matrix (Fig 2a-b), the peaks at 3468.01 cm^{-1}, 1739.14 cm^{-1}, 1227.78 cm^{-1}, and 1037.7 cm^{-1} that representing the stretching vibration of O-H, C=O, CH_3CO, and C-O-C, respectively were decreased slightly. Meanwhile, the stretching vibrations were remained closed when the acetic acid concentration was reduced from 58 wt% (M5) to 56 wt% (M6), as shown in Fig 2b-c. This might be due to the reduction in the $H3O^+$ ion also decreased by reducing the acetic acid in the casting solution. Thus, the acetic acid additive is believed to reduce the influx rate of the coagulant medium for acid-base equilibrium as the HCl additive does [18].
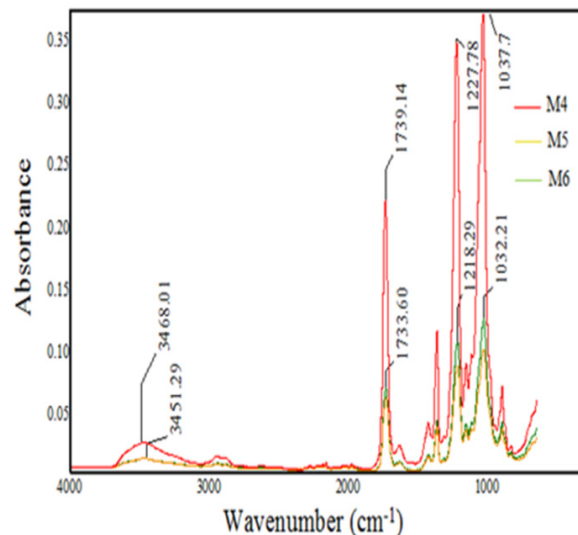

Fig 2. ATR-FTIR of membrane fabricated at acetic acid concentration of (a) 63 wt% (M4), (b) 58 wt% (M5), and (c) 56 wt% (M6) with casting thickness of 250 µm

3.3. Effect of Water Concentration

From Fig 3a-c, the higher absorption peaks were observed (M4 > M7 > M8) when lower concentration ratio of water were added during fabrication (concentration of H_2O for M8 < M7 < M4). This observation has further confirmed the effect of water during the fabrication. In fact, the addition of water causes the formation of new hydrogen bonds with acetic acid and to a much lesser extent CA, thereby intensifying the hydrogen bonds in solution [19]. When the concentration of water reduced, these bonds were reduced. It is expected to further affect the interactions with CO_2 as well as the solubility of penetrants within CA polymer matrix during gas separation processes. Thus, M4 was favorable in this study.

The separation performance of the present work is summarized and compared to other research work [5, 20] in Table 1. From Table 1, the optimal CA membrane (M4) in the present study was observed to have high permeance and slightly better CO_2/N_2 selectivity. The main reason that improved the gas separation performance was the best concentration of solvent mixture (70:30), acetic acid (63 wt%), and water (27 wt%) in the formation of CA membrane. Besides, a higher acetyl content for the CA polymer is used in this study (Table 1) compared to Puleo *et al.* [5] and Ulloa [20]. It enhances the CO_2 solubility [5] and the CO_2 sorption capacity into CA chains [6,15].
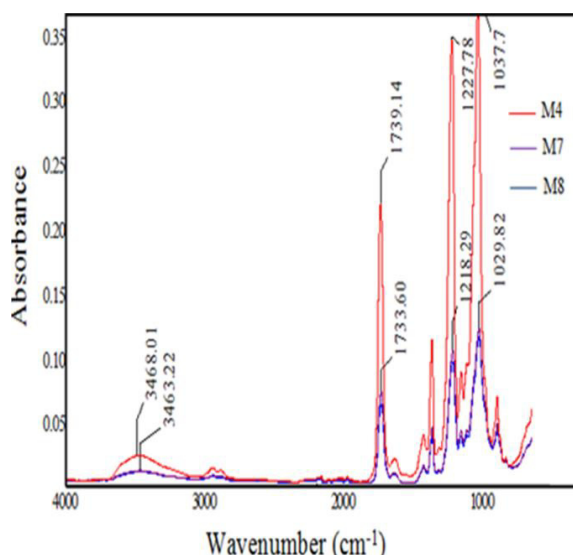
Fig 3. ATR-FTIR of membrane fabricated at water concentration of (a) 27 wt% (M4), (b) 22 wt% (M5), and (c) 20 wt% (M6) with casting thickness of 250 µm

Table 1. Summary of CO_2/N_2 permeation properties achieved by the present work compared to other research works [15]

Reference	P (CO_2)	P (N_2)	$\alpha_{CO2/N2}$ (-)	Conditions
Present work	400.93[*]	12.18[*]	32.92	27°C, DS**=1-3, (54.6-56%)
Puleo *et al.*, 1989				1 atm, 35°C
	1.84[#]	0.057[#]	32.30	DS=1.75, (32.0%), 2-methoxyethanol
	4.75[#]	0.15[#]	31.70	DS=2.45, (39.5%), acetone
	6.56[#]	0.23[#]	28.50	DS=2.85, (43.5%), methylene chloride
Ulloa C.J., 2012	48.30[*]	1.36[*]	35.60	27°C, DS=2.5, (39.8%), CA hollow fiber
	42.80[*]	1.58[*]	27.60	35°C, DS=2.5, (39.8%), CA hollow fiber

*GPU, # Barrer, ** Degree of substitution, ( ) acetyl content

4. Conclusion

CA membranes were developed from CA polymer, acetic acid water. Different concentrations ratio of solvent mixture (acetic acid:water), acetic acid and water were used to evaluate its effects on the membrane morphologies and gas permeation performance. CA membrane that synthesized from solvent mixture of acetic acid:water of 70:30 appeared to have less compact skin layer. In term of performance, it was proven that M4 with acetic acid concentration of 63 wt% and water concentration of 27 wt% have a high CO_2 permeance of 400.92 GPU and better CO_2/N_2 separation performance at 32.92 as compared to others literature.

Acknowledgment

References

[1] H. Yang, Z. Xu, M. Fan, R. Gupta, R.B. Slimane, A.E. Bland, I. Wright, Progress in carbon dioxide separation and capture: A review, J Environ Sci 20 (2008) 14-27.

[2] S.M. Sanip, A.F. Ismail, P.S. Goh, T. Soga, M. Tanemura, H. Yasuhiko, Gas separation properties of functionalized carbon nanotubes mixed matrix membranes, Sep. Purif. Technol. 78 (2011) 208-213.

[3] D. Wang, W.K. Teo, K. Li, Preparation and characterization of high-flux polysulfone hollow fibre gas separation membranes, J. Membr. Sci. 204 (2002) 247-256.

[4] A.F. Ismail, P.S. Goh, S.M. Sanip, M. Aziz, Transport and separation properties of carbon nanotube-mixed matrix membrane, Sep. Purif. Technol. 70 (2009) 12-26.

[5] A.C. Puleo, D.R. Paul, S.S. Kelley, The effect of degree of acetylation on gas sorption and transport behavior in cellulose acetate, J. Membr. Sci. 47 (1989) 301-332.

[6] D.M.P. Rodriguez, Aminosilane-functionalized cellulosic polymers for increased carbon dioxide sorption, in: Chemical Engineering, Georgia Institue of Technology, 2010, pp. 199.

[7] W.J. Schell, C.G. Wensley, M.S.K. Chen, K.G. Venugopal, B.D. Miller, J.A. Stuart, Recent advances in cellulosic membranes for gas separation and pervaporation, Gas Separation & Purification 3 (1989) 162-169.

[8] J. Li, S. Wang, K. Nagai, T. Nakagawa, A.W.H. Mau, Effect of polyethyleneglycol (peg) on gas permeabilities and permselectivities in its cellulose acetate (ca) blend membranes, J. Membr. Sci. 138 (1998) 143-152.

[9] A. Rahimpour, S.S. Madaeni, Polyethersulfone (pes)/cellulose acetate phthalate (cap) blend ultrafiltration membranes: Preparation, morphology, performance and antifouling properties, J. Membr. Sci. 305 (2007) 299-312.

[10] S. Basu, A. Cano-Odena, I.F.J. Vankelecom, Asymmetric membrane based on matrimid and polysulphone blends for enhanced permeance and stability in binary gas (co_2/ch_4) mixture separations, Sep. Purif. Technol. 75 (2010) 15-21.

[11] J.C. Jansen, M.G. Buonomenna, A. Figoli, E. Drioli, Asymmetric membranes of modified poly(ether ether ketone) with an ultra-thin skin for gas and vapour separations, J. Membr. Sci. 272 (2006) 188-197.

[12] X.R. Zhang, L.Z. Zhang, H.M. Liu, L.X. Pei, One-step fabrication and analysis of an asymmetric cellulose acetate membrane for heat and moisture recovery, J. Membr. Sci. 366 (2011) 158-165.

[13] T. Mohammadi, E. Saljoughi, Effect of production conditions on morphology and permeability of asymmetric cellulose acetate membranes, Desalination 243 (2009) 1-7.

[14] J. Wijmans, R. Baker, The solution-diffusion model: A review, J. Membr. Sci. 107 (1995) 1-21.

[15] Z. Jawad, A. Ahmad, S. Low, S. Zein, Incorporation of inorganic carbon nanotubes fillers into the ca polymeric matrix for improvement in co2/n2 separation, Curr. Nanosci. 11 (2015) 69-79.

[16] Z.A. Jawad, A.L. Ahmad, S.C. Low, T.L. Chew, S.H.S. Zein, Influence of solvent exchange time on mixed matrix membrane separation performance for co2/n2 and a kinetic sorption study, J. Membr. Sci. 476 (2015) 590-601.

[17] J.H. Choi, J. Jegal, W.N. Kim, Fabrication and characterization of multi-walled carbon nanotubes/polymer blend membranes, J. Membr. Sci. 284 (2006) 406-415.

[18] W.Y. Chuang, T.H. Young, W.Y. Chiu, The effect of acetic acid on the structure and filtration properties of poly(vinyl alcohol) membranes, J. Membr. Sci. 172 (2000) 241-251.

[19] C. Appaw, Rheology and microstructure of cellulose acetate in mixed solvent systems, in: Chemical and Biomolecular Engineering, North Carolina State University, 2004, pp. 209.

[20] C.J. Ulloa, Remediation of cellulose acetate gas separation membranes contaminated by heavy hydrocarbons, in: Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada, 2012, pp. 114.