

Effect of evaporation time on cellulose acetate membrane for gas separation

W N R Jami'an^{1,2}, H Hasbullah^{1,2}, F Mohamed^{1,2}, N Yusof^{1,2}, N Ibrahim¹, R R Ali³

¹ Faculty of Petroleum and Renewable Energy Engineering, *Universiti Teknologi Malaysia*, 81310, Johor Bahru, Johor, Malaysia

² Advanced Membrane Technology Research Centre (AMTEC), *Universiti Teknologi Malaysia*, 81310, Johor Bahru, Johor, Malaysia

³ Faculty of Chemical Engineering, *Universiti Teknologi Malaysia*, 81310 Johor Bahru, Johor, Malaysia

E-mail: ¹hasrinah@petroleum.utm.my

Abstract. Throughout this decades, membrane technology has been the desirable option among the others gas separation technologies. However, few issues have been raised regarding the membrane gas separation application including the trade-off between its permeability and selectivity and also its effects towards environment. Therefore, for this research, a biopolymer membrane for gas separation application will be developed with reasonably high on both permeability and selectivity. The main objective of this research is to study the effect of solvent evaporation time on the flat sheet asymmetric membrane morphology and gas separation performance. The membranes were produced by a simple dry/wet phase inversion technique using a pneumatically controlled casting system. The dope solution for the membrane casting was prepared by dissolving the cellulose acetate (CA) polymer in N-Methyl-2-pyrrolidone (NMP) and the solvent evaporation time was varied. Permeability and selectivity of the membrane was performed by using pure gases of carbon dioxide, CO₂ and methane, CH₄. The increase in solvent evaporation time had improved the membrane morphologies as the porosity of the membrane surface decrease and formation of a more mature skin layer. The gas permeation tests determined that increasing in solvent evaporation time had increased the selectivity of CO₂/CH₄ but reduce the permeability of both gases

1. Introduction

The ability of polymeric membranes to separate common gases including O₂/N₂; CO₂/CH₄; H₂/N₂; He/air; H₂O/air and H₂/CH₄ has been known for more than a century [1-2]. As the energy cost increases, membrane technology get a consideration to replace the conventional process in reducing cost of industrial process. Membrane separation offers a number of significant advantages in term of low energy and capital investment. The membrane device are compact and modular that can be operated with a simple equipment and mild condition and membrane system are energy efficient owing to large reduction in power electricity and fuel consumption [3]. In addition, membrane can also be used in the combination with traditional gas separation method to take advantages both



technologies for certain occasions in which neither process can be achieve a proper result individually [4].

The goal of the membrane manufacturing is high selectivity and gas permeation flux with defect-free ultrathin dense layer of membrane structure, where most of membrane experts try to achieve it. According to Shilton *et al.*, rheological condition during manufacturing can affect the membrane performance as well as membrane material, dope preparation and fabrication technology [3]. Manipulation of solvent evaporation time prior to immersion in coagulation step strongly influences the surface skin-layer thickness. Dry-phase separation occurs at the initial stage of evaporation where the volatile solvent removed from casting solution. As a result, unstable top skin layer region of the nascent membrane will be formed due to the selective loss of the volatile solvent. It can be observed by the almost instantaneous onset turbidity in this top skin layer. Wet-phase separation occurs when the nascent membrane immersed in the nonsolvent coagulant. In this quench step, the bulk of the membrane structure is formed and the remaining solvent and nonsolvent are extracted [5-6].

There are three main types of membranes commercially available for CO₂ removal; cellulose acetate, polyimides and perfluoro-polymers and among of this three types, cellulose acetate (CA) had received the most attention for CO₂ separation from CH₄ [7]. CA is a biopolymer because its raw material which is cellulose, is made from a renewable resource and is readily degradable by a variety of mechanism such as biological degradation. Moreover, commercial availability, ease of processing, and favourable selectivity-permeability characteristics with acceptable mechanical and thermal properties make CA had received the most attention. In addition, CA consist higher thermal stability T_g of 198°C [8] compare to polysulfone (PSF) (T_g = 190°C).

Thus, the general aim for this research is to develop a biopolymer membrane using cellulose acetate polymer as membrane material for gas separation application. To achieve the aim of the research, the main objective is to study the effect of solvent evaporation time on the flat sheet asymmetric biopolymer membrane morphology and gas separation performance.

2. Experimental

2.1. Material

The base material used for the membrane material was cellulose acetate (CA) with 39.8% acetyl content produced by Aldrich Chemical Co. Inc. The solvent that was used for CA polymer is N-Methyl-2-pyrrolidone (NMP) supplied by Merck, Darmstadt, Germany. Tap water were used as a coagulation medium during wet phase inversion process and methanol and n-hexane was used in solvent exchange steps in order to produce membrane with the best permeation properties.

2.2. Method

2.2.1. Dope Solution Preparation. The method that was used in preparing 23 wt% the dope solution is by dissolving the cellulose acetate in the solvent used, which is N-Methyl-2-pyrrolidone. The solution was mixed in the round bottom reaction vessel, sealed with paraffin film and was stirred using a mechanical stirrer with temperature 56 °C, until a homogenous solution is produced. After that, the homogeneous solution was placed in the ultrasonic water bath to remove the gas bubbles that may exist in the solution prior to membrane casting process.

2.2.2. Flat Sheet Membrane Preparation. Dry/wet phase inversion technique was used to prepare the asymmetric flat sheet membranes. The polymer solution was casted on a clean glass plate using a pneumatically controlled membrane casting system [10]. The casting speed was fixed at 64s⁻¹ at varied solvent evaporation time from 10s to 30s. After the evaporation step, the membranes were immersed in the water bath for about 30 minutes (wet phase inversion). Finally, the washed membrane was solvent exchanged with ethanol and n-hexane for about 20 minutes respectively (solvent exchange steps) and dry at atmospheric condition for another 24 h.

2.3. Structural Characterization.

Scanning electron microscopy (SEM) was used to examine the membrane dense skin layer, porous substructure and cross section. The dry membrane samples was mounted on a metal stub with double-sided carbon adhesive tape. The cross-section structure of the membrane sample was prepared by a liquid nitrogen freeze fracturing follow by gold sputtering before scanning on a SEM.

2.4. Membrane Testing

Gas permeation test was applied in this study to obtain the pressure-normalized flux of the membrane. Pure CO₂ and CH₄ was used as test gases, using upstream pressure of 1 to 5 bar and at ambient temperature. Volumetric gas permeation rates were determined with a local design soap-bubble flow meter.

3. Result and Discussion

3.1. Morphological and structural analysis of CA flat sheet asymmetric membrane

The solvent evaporation step was considered essential for the formation of the asymmetric membrane and was critically importance in determining the membrane structures. Different solvent evaporation time had revealed different membrane morphologies. Figure 1 and 2 shows the SEM image of top surface layer and cross-sections of asymmetric CA membrane prepared at various solvent evaporation time prior to immersion in the coagulation bath in the dry/wet phase inversion step. The membrane developed in this study achieved the asymmetric structure which consists of thin dense skin layer at the top and thick, porous substructure at the bottom that provides the mechanical strength for the membrane. However, different solvent evaporation time produced different membrane morphologies in terms of porosity, macro void substructure and the skin layer.

As shown in Figure 1, the increment of solvent evaporation time decreases the porosity of the

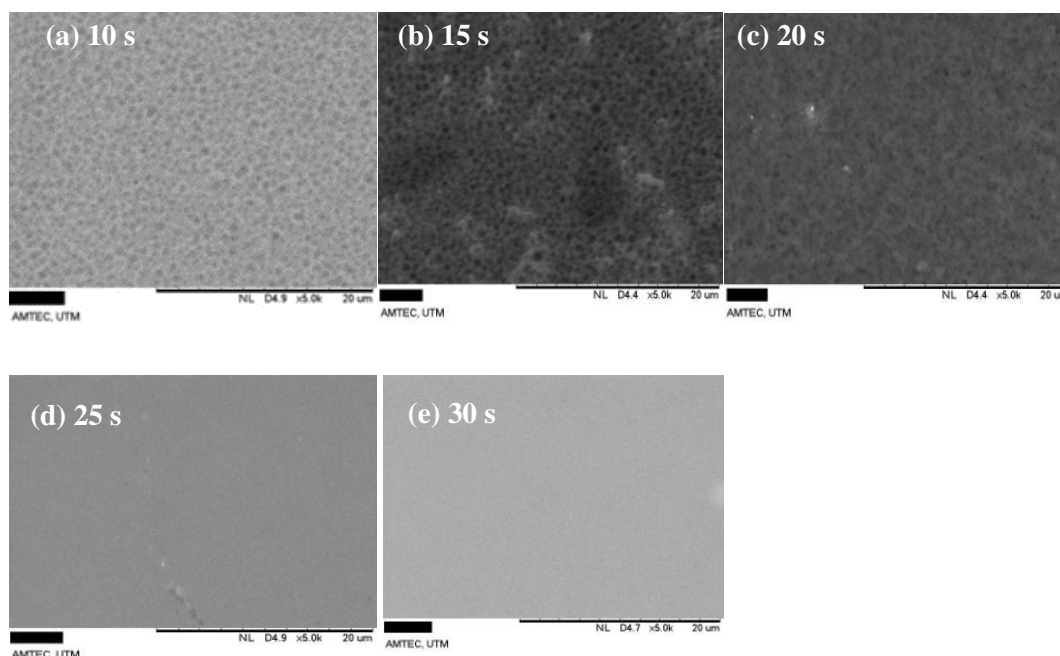


Figure 1. SEM pictures of 23 wt% cellulose acetate asymmetric membrane surface layer at different solvent evaporation time

membrane surface. This is because those membranes had enough time for the rearrangement of membrane molecular chains and causing the membrane surface to become closely pack thus

decreasing the pore size on the membrane surface and reducing defects. Figure 2 shows the membrane cross-section. A distinct and dense skin layer was more visible on the longer evaporation time. Phase separation occurs initially at the surface of the casting membrane leading to a high concentration gradient of the polymer. A longer evaporation time would form a more concentrated polymer region at the open top of the casting membrane due to the loss of highly volatile solvents. The formation of the skin layer would affect the formation mechanism of asymmetric CA membrane substructure. A skin layer acts as a barrier for solvent–coagulant exchange during the immersion precipitation period. A longer evaporation step generally leads to a thicker skin layer [12]. A thicker skin slows down the solvent–coagulant exchange and thus reducing the membrane porosity. In short, by increasing the solvent evaporation time, the membrane substructure layer change from more porous to a less porous structure.

3.2. Effect of solvent evaporation time on gas separation performance

Table 1 and Figure 3 shows the gas permeability coefficients and selectivity of the CA asymmetric membrane respectively. Experimental result of this show that the optimum permeability of the CO₂ and CH₄ gases was at evaporation time of 15s with CO₂ permeance of 45.58 GPU and CH₄ permeance of 14.62, while the selectivity of CO₂/CH₄ at 15s was 3.12.

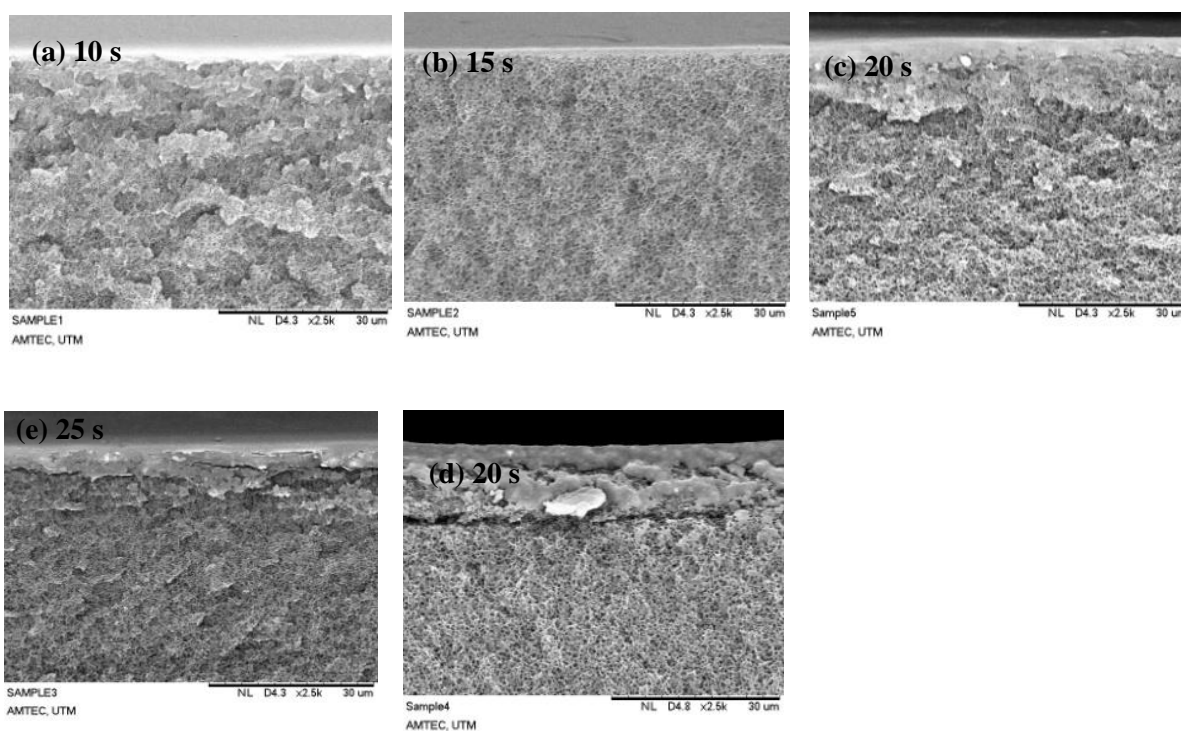


Figure 2. SEM pictures of 23 wt% cellulose acetate asymmetric membrane cross-section at different solvent evaporation time.

As we can see from the Table 1, the permeability for CO₂ and CH₄ decrease with increasing solvent evaporation time while the selectivity of CO₂/CH₄ increase with increasing of solvent evaporation time. The cause of this difference was due to the structural changes in the skin layer of asymmetric membrane or could be explained by referring to the morphologies of the membrane as shown by SEM images in Figure 1 and 2. Increasing the solvent evaporation time caused a decrease in pore size and surface porosity but an increase in skin thickness. This resulted in increasing selectivity but decreasing permeability of the membrane.

Table 1. CO₂ and CH₄ permeability coefficients at varied solvent evaporation time of CA flat sheet asymmetric membrane

Solvent Evaporation Time (s)	Permeability (GPU) CO ₂	Permeability (GPU) CH ₄
10	78.3378	69.5458
15	45.5758	14.6222
20	1.0083	0.1696
25	0.6444	0.0322
30	0.4490	0.0209

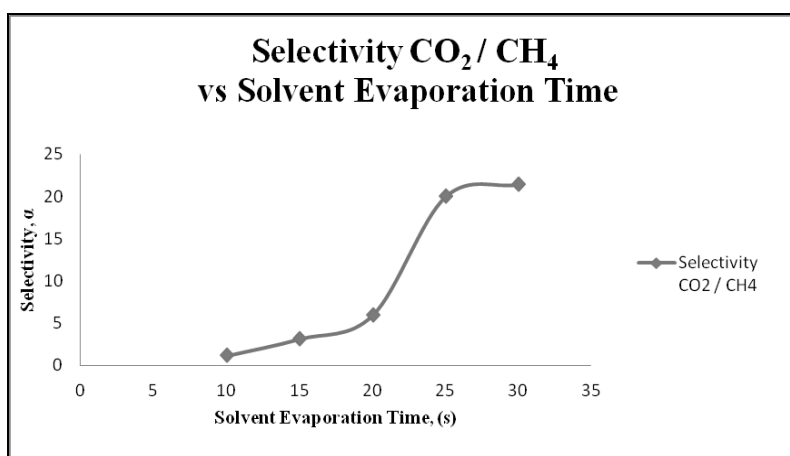


Figure 3. Selectivity of CO₂/CH₄ at varied solvent evaporation time of CA flat sheet asymmetric membrane

4. Conclusion

The cellulose acetate membrane was prepared by casting the dope solution at different solvent evaporation time. The polymer concentration at 23 wt% was used in the dope solution as a critical polymer concentration. The prepared membranes that formed via dry/wet phase inversion process possessed an asymmetric structure with thin skin layer at the top and porous structure at the bottom. The porosity of the membrane surface decreases with increasing evaporation time. As the evaporation time increase, the formation of bottom layer support structure become more compact. The gas permeation tests determined that the increasing in solvent evaporation time would increase the selectivity of CO₂/CH₄ gases but reduced the permeability of both gases through the CA asymmetric membrane. The membrane is recommended to be further modified by coating with silicone rubber coated material (PDMS) to enhance the performance of the membrane.

5. References

- [1] Robeson L M 1999 *Solid State Mater. Sci.* **4** 549
- [2] Robeson L, Burgoyne W, Langsam M, Savoca A C, and Tien C Fration 1994 *Polymer* **35** 4970
- [3] Kusworo T D, Ismail A F, Mustafa A, and Matsuura T 2008 *Sep. Purif. Technol.* **61** 249
- [4] Sadegi M, Mousavi S, Hashemi M, Pourafshari Chenar M and Roosta Azad R 2007 *J. Appl. Polym. Science* **105** 2683
- [5] Kawakami H, Mikawa M, and Nagaoka S 1997 *J. Memb. Sci.* **137** 241
- [6] Wan Jin L, Duek San K and Jin Hwan K 2000 *Korean J. Chem. Eng.* **17**, 143
- [7] Scholes C A, Stevens G W and. Kentish S E 2012 *Fuel* **96** 15–28
- [8] Puleo A and Paul D 1989 *J. Memb. Sci.* **47** 301

- [9] Ismail A F and Lai P Y 2003 *Sep. Purif. Technol.* **33** 127
- [10] Ismail A F, Ng B C and Abdul Rahman W A 2003 *Sep. Purif. Technol.* **33** 255
- [11] Chung T, Teoh S, Hu X, and Shung T 1997 *J. Memb. Sci.* **133** 161
- [12] Iqbal M, Man Z, Mukhtar H and Dutta B K 2008 *J. Memb. Sci.* **318** 167

Acknowledgement

We gratefully acknowledge the financial support from the Universiti Teknologi Malaysia and Ministry of Education Malaysia (Grant no: 4F652 and 4L116).