Effect of coagulant bath on the gas permeation properties of cellulose acetate asymmetric membrane

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Abstract. Membrane based gas separation process technology has been recognized as one of the most efficient and advanced unit operation for gas separation. One of the problems in membrane gas separation is membrane performance. This paper explores the application of cellulose acetate (CA) membrane for natural gas purification and separation by improving its permeability and selectivity. The main interest in this research is to study the effect of quench medium on the gas separation performance towards its physical characteristics and gas separation performance of CA membrane. Cellulose acetate polymer was dissolved in n-methyl-2-pyrrolidone solvent and casted onto a glass plate using a pneumatically controlled casting system with fixed shear rate and solvent evaporation times. The parameter varied was the non-solvent used as quench medium during membrane post treatment that were methanol and n-hexane. The different quench media as post treatment affected the \( \text{O}_2 \) and \( \text{N}_2 \) gas permeation and \( \text{O}_2/\text{N}_2 \) selectivity as well as the tensile strength of the flat sheet asymmetric membrane. Combination of methanol and n-hexane as quench media gave the best result than the other steps. This solvent exchange step influenced the morphology by producing thin skin layer and thus gives better gas separation performance than other steps.

1. Introduction
Gas permeation system is the major breakthrough in the membrane technology’s research and development. Approximately, more than 5000 membrane units has been installed for nitrogen-air separation, 500 membrane refinery units for hydrogen separation and 200 membrane units for carbon dioxide-natural gas separation [1]. Membrane becomes an industrial favourite option because the permeation rate of a chemical species through the membrane can be controlled as desired as well as offering many advantages such as low energy use, easy to operate and compact equipment compared to other technologies. Membrane gas separation is based on semi-selective barrier allowing one gases passing through while preventing the other under the influence of a driving force [2]. Performance of membrane-based gas separation process strongly depends on permeability and selectivity of membrane. Membrane with higher permeability gives higher productivity and lower capital costs.
whereas membrane with higher selectivity gives more efficient separations, higher recovery and lower power costs; indeed, membranes that simultaneously possess high values of selectivity and permeability would lead to the most economical gas separation processes. Solvent exchange is one of the important step in membrane fabrication that resulted in membrane of different average pore size and pore size distribution. Generally, solvent exchange can be done in two step: 1) using alcohol to replace water, 2) using non-polar volatile liquid to replace alcohol and then the volatile liquid is evaporated leaving the dry membrane.

Cellulose acetate is the acetate ester of cellulose produced by the acetylation of purified cellulose from wood pulp, which is a renewable resource. The commercial cellulose acetate membrane available in the industry consist of the combination of cellulose acetate, cellulose diacetate and/or cellulose triacetate [3]. The first developer of high flux cellulose acetate asymmetric membrane is Loeb and Sourirajan for reverse osmosis of water desalination [4]. Cellulose acetate membrane is still preferable due to its low cost, ease of handling, unproblematic availability and good strength [5]. The permeability of cellulose acetate depends on the function of the degree of acetylation cause by the replacement of polar hydroxyl group with bulky acetate groups , which affecting the polymer density and membrane free volume [6].

The main objective of this research is to study the effect different quench medium for solvent exchange step on morphology and gas separation performance of cellulose acetate membrane.

2. Experimental

2.1. Materials
Cellulose acetate (CA) with 39.8% acetyl content was used as the membrane material and obtained from Aldrich Chemical Co. Inc. N-methyl-2-pyrrolidone (NMP,>99%) supplied by Merck, Darmstadt, Germany. Tap water was used as a coagulation medium during wet phase inversion process. Methanol and n-hexane was used as quench medium in solvent exchange step.

2.2. Dope solution preparation
The dope solution of 23wt% concentration was prepared by dissolving the CA polymers with NMP solvent. The essential amount of CA was slowly added to avoid agglomeration. The solution was mixed in a capped bottle and stirred by mechanical motor until complete polymer dissolution. When the polymers were completely dissolved, as indicated by observing a clear solution, the solution was degassed for 1 hour and then stored 1 day in room condition in order for complete removal of air bubble inside the solution.

2.3. CA asymmetric membrane preparation
Asymmetric flat sheet membranes were prepared according to the dry/wet phase separation process. The polymer solution was casted on a clean glass plate using a pneumatically controlled membrane casting system as in figure 1. The casting time and solvent evaporation time was fixed at 15s and 15s respectively. After that, the membranes were immersed in water bath for 30 minutes for wet phase inversion process. Finally, the membrane was immersed the in quench medium as in table 1. Then, the membrane was dried for 24 h at atmospheric condition.
2.4. Membrane characterization

2.4.1. Scanning electron microscopy SEM. Membrane morphology was examined using scanning electron microscopy (SEM). The dried film samples were mounted on a metal stub with double-sided adhesive tape. The cross-section structure of the membrane sample was prepared by a liquid nitrogen freeze fracturing followed by gold sputtering before scanning on a scanning electron microscopy (SEM).

2.5. Membrane testing

2.5.1. Gas permeation test. Gas permeation tests were performed with a permeation membrane by using pure gases such as oxygen (O$_2$) and nitrogen (N$_2$). Circular membrane discs with an effective permeation area of 13.5 cm$^2$ were used. Feed pressure will be controlled with 10 bar as maximum pressure. Permeate side was opened to atmosphere. Experiments are carried out at ambient temperature (25°C). Gas permeation rates are measured by a soap bubble flow meter.

3. Results and discussions

3.1. Membrane morphology structure

Selection of the solvent and the non-solvent plays a vital role in controlling the membrane morphologies and properties. Figure 2 and figure 3 shows the SEM images of surface layer and cross-sections of asymmetric CA membrane respectively. It is found that asymmetric CA membranes could be produced using NMP and different non-solvents used. All these fabricated membranes consist of a skin layer supported above a closed-cell substructure. However, various non-solvents used in the study produced different membrane morphologies in terms macrovoid substructure and the skin layer.

It is observed that all four samples have similar membrane surface layer since it have similar solvent evaporation time which is 15 s as in figure 2. Solvent evaporation time plays important role for membrane surface condition because the longer time for solvent evaporation will affect the arrangement of membrane molecular orientation and causing the membrane surface to become closely pack. The closely pack membrane surface preventing the penetration of non-solvent thus decreasing the pore size on the membrane surface and reducing defects.

![Figure 1](image)

**Figure 1** Pneumatically-controlled flat sheet membrane casting system. (a) Nitrogen gas tank; (b) solution dope reservoir; (c) air compressor; (d) pneumatic system; (e) trolley and glass plate; (f) gear pump; (g) casting knife; (h) evaporation chamber; (i) coagulant bath

| Sample | Methanol | n-Hexane |
|--------|----------|----------|
| 1      | -        | -        |
| 2      | 20       | -        |
| 3      | -        | 20       |
| 4      | 20       | 20       |

Table 1. Quench medium condition.
Micrograph of asymmetric membrane surface prepared by dry/wet phase casting method with different quench medium (a) no quench medium (b) quenched methanol (c) quenched n-hexane (d) quenched methanol followed by quenched n-hexane.

Figure 3(a-d) shows a distinct dense skin layer on top of porous substructure of CA membrane. The formation of membrane dense skin layer is due to the evaporation of solvent on membrane surface causing the membrane molecular chain rearrangement forming closely pack membrane skin layer. The penetration of water during wet phase inversion process gives rise to the sponge-like microvoids due to the fast solvent exchange and quick precipitation of polymer [8].

Based on figure 3, the order of decreasing of membrane substructure porosity is (d) > (b) > (c) > (a). No quench medium membrane has less macrovoids in the substructure as in figure 3(a) compared to other membranes due to the collapsed of membrane substructure cause by high surface tension water leaving the membrane consist of strong capillary forces within the finely porous substructure during the drying process [9]. Figure 3(c) shows that n-hexane quench membrane has more porous substructure than no quench medium membrane due to the n-hexane that helps water leaving the membrane better and preventing the membrane structure from collapsing during drying process [9]. The methanol quench membrane as in figure 3(b) has more porous substructure due to the swelling of polymer matrix that enhance the membrane free volume as well as complete removal of residual solvent [10]. The quench methanol followed by quenched n-hexane membrane shown in figure 3(d) has the greatest membrane structure porosity compared to the other membrane. The immersions of membrane in methanol quench medium causing the membrane polymer matrix to swell and replacing the water. The further immersions in n-hexane quench medium cause the substructure of swell membrane polymer matrix become stronger and prevented from being collapsed during membrane drying process.

Figure 3. Micrograph of asymmetric membrane cross section prepared by dry/wet phase casting method with different quench medium (a) no quench medium (b) quenched methanol (c) quenched n-hexane (d) quenched methanol followed by quenched n-hexane.

3.2. Gas permeation measurement

The gas separation characteristic is determined by plotting the permeance of O₂, N₂ and O₂/N₂ ideal selectivity of each membrane against the membrane with different type of quench medium. The permeate side was maintained at essentially atmospheric pressure. The permeance of O₂ and N₂ of membrane with various quench medium are presented in table 2.
It is clearly shown that combination quench medium methanol and n-hexane gives the best permeability of O$_2$ and N$_2$ gas. This means that this type of solvent exchange steps produces high permeability with good pore size of membrane. The significant differences of gas permeance among membranes prepared from various solvent–non-solvent pairs could be explained by referring to their morphologies as shown by SEM images (figure 3). Since high value of permeability can be achieved in asymmetric membrane with very thin skin layer [11], it can be concluded that the rest of membranes have less porous substructure that did not allow gas to permeate well.

Table 2. Gas O$_2$, N$_2$ permeance with different quench medium

| Permeability       | O$_2$  | N$_2$  |
|--------------------|--------|--------|
| No quench medium   | 0.1354 | 0.1059 |
| Methanol           | 0.3811 | 0.3626 |
| N-Hexane           | 0.1502 | 0.1338 |
| Methanol and N-Hexane | 4.4187 | 1.6856 |

Figure 4 shows selectivity of O$_2$/N$_2$ gas towards CA membrane that prepared with different quench medium. Membrane with water, methanol and n-hexane as quench medium gives the best selectivity of gas O$_2$/N$_2$ than other membrane that prepared with different quench medium. It indicated that membrane prepared with water, methanol and n-hexane as quench medium was able to do the gas separation very well. While the other membranes have low selectivity of membrane which indicate that the membrane did not be able to do gas separation very well and it may be because of CA membranes prepared have less pore size that allowed O$_2$ and N$_2$ passes through the membrane. As discuss earlier, since combination methanol and n-hexane as quench medium succeed to prepared a membrane with thin skin layer it will gives better selectivity than other membranes that have less porous substructure.

**Figure 4.** Graph of selectivity of O$_2$/N$_2$ against CA membrane with different quench medium

4. Conclusion
The effects of solvent–non-solvent pairs on the morphology of asymmetric CA membrane and its relation to the O$_2$/N$_2$ separation performance have been investigated. The prepared membranes that formed via dry/wet phase inversion process possessed an asymmetric structure with thin skin layer at the top and porous substructure at the bottom. The porosity of the membrane surface is almost the same for all the membranes prepared but differ in the compactness of substructure. This difference occurred because of different quench medium that affect the solvent exchange process. Quench medium using methanol and followed by n-hexane possessed the best CA membrane since it shows double performance of gas permeability and selectivity compared to other type of quench medium thus
indicates that the membrane have very thin skin layer that allowed gas to pass through the membrane very well.

5. References
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