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Effect of stabilization temperature during pyrolysis process of P84 co-polyimide-based tubular carbon membrane for H₂/N₂ and He/N₂ separations

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Abstract. In this study, the effect of stabilization temperature on the performance of tubular carbon membrane was being investigated. P84 co-polyimide-based tubular carbon membrane will be fabricated through the dip-coating technique. The tubular carbon membrane performance can be controlled by manipulating the pyrolysis conditions which was conducted at different stabilization temperatures of 250, 300, 350, 400, and 450°C under N₂ environment (200 ml/min). The prepared membranes were characterized by using scanning electron microscopy (SEM), x-ray diffraction (XRD), and pure gas permeation system. The pure gas of H₂, He, and N₂ were used to determine the permeation properties of the carbon membrane. The P84 co-polyimide-based tubular carbon membrane stabilized at 300°C demonstrated an excellent permeation property with H₂, He, and N₂ gas permeance of 1134.5±2.87, 1287.22±2.86 and 2.98±1.28GPU, respectively. The highest H₂/N₂ and He/N₂ selectivity of 380.71±2.34 and 431.95±2.61 was obtained when the stabilization temperature of 450°C was applied. It is concluded that the stabilization temperatures have a protractive effect on the carbon membrane properties specifically their pore structure, and eventually their gas separation properties.

1. Introduction

Nowadays, hydrogen invention from biomass is the greatest favourable development because of the waste decreasing matter and the concerns for the sustainable growth. A common technology used in producing hydrogen (H₂) from natural gas is by steam reforming [1]. However, H₂ production (as an alternative of consuming fossil fuel-like steam methane reforming) offers a boundless chance for H₂ generation, but the process typically produces a humidified gas consist of H₂ and CO₂ where hydrogen content usually ranges between 35 and 65 (vol.) %, else may also contain volatile organic compounds (VOC), H₂S and NH₃ [2]. The purification process of H₂ from the main product stream is compulsory prior usage. The current technologies for H₂ purification are pressure swing adsorption (PSA), cryogenics, palladium (Pd) membranes [3]. Conventional PSA or cryogenics will not be appropriate for minor scale H₂ productions from fermentation processes due to the predictable high costs. Although the palladium membranes have even now been commercialized for H₂ purification such as H₂ Pure™ and HYSEP, the membrane invention cost is still high, and the period of usage is quite short due to the H₂ embrittlement, which leads to a high investment spending (CAPEX). Some literature has already reviewed the status of different polymeric membranes for hydrogen purification [4]. The problems and tasks with gas separation membranes to be practical for the composition of fermentatively produced H₂ gas has been reviewed recently by Bakonyi et. al., [4]. They stated that the highest H₂/CO₂ gas selectivity (1.62) could be achieved at feed pressure, separation temperature and recovery value of ~2.2 bar, 55 °C and 0.6, respectively, using a 65 vol% hydrogen/35 vol% carbon-dioxide binary mixture. Li et al. equated the H₂-selective and CO₂-selective membrane materials and processes, and find out the
forthcoming path on the advance of energy-efficient membranes [5]. With respect to the non-porous polymeric and mixed matrix membranes, it is relatively challenging to accomplish a high H₂ purity (>99%) obligation with low selectivity (<10) [6,7]. Additionally, the composition of the biohydrogen gas mixture, its contamination (e.g., H₂S) content was initiate to significantly affect the polymeric PDMS membrane performance reported by Bakonyi et al. [8]. They also mention that polymeric membranes were frequently tried under ideal laboratory conditions in the literature; yet, the hydrogen generated by fermentation process is a part of a complex biogas stream, leading to the possible transformations in the elements behaviour. A hybrid polymeric membrane/absorber system might be a solution to achieve the separation requirement for biohydrogen purification reported by Bakonyi et al. [9], the process complexity and economic feasibility should be further investigated. The above defined tasks to the development of an alternative membrane material with high H₂/N₂ selectivity and good chemical stability showing to the impurities (e.g., H₂S). This contaminant which are frequently occurred in the raw biohydrogen gas mixture, and can carry down the H₂ purification cost, and possibly increase the H₂ production. Furthermore, carbon membranes are also predictable to tolerate the impurities (e.g., H₂S) when visible to a fermentation gas stream. This statement is based on experience accomplished with a carbon membrane pilot tested at a biogas plant in Southern Norway [10]. In this study, our goal is to fabricate polyimide based tubular carbon membrane for both H₂ purification and flue gas treatment.

To the best of our expertise, there are only a few number of publications that approach tubular carbon membranes for H₂/N₂ separation. Helium is a valuable gas with limited properties, applications and still the prominent industrial cause of helium is natural gas. At the present time, the demand of Helium (He) for aerospace and cryogenic technology applications are obviously increased. Regrettably He is quite occasional, and this shortage hinders the enhancement in both research and industry [11]. It is of massive consequence to accumulate a competent method to separate He as this would generate a chance for recovering He from characteristic gas with lower grouping of He in an economically practical process.

Alternations in the membrane configurations as well as hybridization of membranes with cryogenic and pressure swing adsorption processes are among the valuable options for optimizing techno-economic viability of helium separation and purification. However, there is some experimental information on He purification using pressure swing adsorption utilizing adsorbents, for instance activated carbon, are reachable [12,13]. According to previous study, there are difficulties to examined He/N₂ separation these membranes are bounded by the exchange between the membrane permeability and selectivity whereby high He selectivity was achieved by sacrificing permeability or vice-versa [13,14]. In overall, inorganic membranes such as carbon membrane have shown good performance in helium separation, but production of such membranes has not yet become viable on the commercial scale. Consecutively, inorganic and mixed matrix membranes (MMMs) are recommended as feasible candidates to overwhelm these difficulties [15]. Hence, this study can provide convenient understandings on fabrication of tubular carbon membrane for H₂/N₂ and He/N₂ separations.

Carbon membrane is one of the capable materials in enhancing gas separation performance [16]. Carbon membrane is one of the potential methods that provide better selectivity, and their higher thermal and chemical stability; comparing to their polymeric counterpart [17]. Different precursors would require different stabilization conditions due to the chemical structure and thermal behaviour of those precursor materials. Based from previous study, carbon membranes are more suitable to be applied at high temperature (500-900°C) [18]. Cipriani et al. have completed pyrolysis on a thin film polyacrylonitrile (PAN) at a stabilization temperature below 400°C where the final structure of the samples resembled graphitisé structures [19]. Chemical reaction is started during the isothermal step when stabilization process take place, indicating that most of nitriles take part in the cyclization and trimerization reactions below 400°C [19]. Barbosa-Coutinho et al. revealed that a severe degradation of the polyetherimide-based carbon membrane was detected when stabilization temperature above 500°C was applied. They have proved that membrane exposure under maximum temperature of stabilization were decisive in the final membrane morphologic characteristics and properties. In addition, when the stabilization temperature was above 500°C, an intensive degradation of the fiber was observed. This is because the level of membrane acquaintance below maximum temperature of stabilization was significant with the final membrane morphologic characteristics and properties [20].
Besides, Hameed et al. had studied the effect of oxidative stabilization and pyrolysis processes on the structure, mass and mechanical properties of polyacrylonitrile (PAN) precursor fibres. The results indicated that after stabilization at a maximum temperature of 255°C and pyrolysis at a maximum temperature of 800°C, the tensile strength and modulus of the fibres had increased [21].

Table 1 summarized the pyrolysis conditions and types of gas separation used by previous researchers in carbon membranes preparation. Despite their impact on carbon membrane properties, researches specifically on the stabilization conditions are very limited in the current literature since most researches focusing on pyrolysis conditions. Based on the author’s knowledge, the effects of stabilization temperatures on P84 co-polyimide-based tubular carbon membranes have not been reported in the current literature. Therefore, in this study, the effects of stabilization temperature on the gas permeation properties of the P84 co-polyimide-based tubular carbon membranes were explored. It is expected that the findings from this study would help bridge the literature gap in the understanding of the influence of stabilization temperature for the improvement of gas separation properties of the carbon membrane.

Table 1. Carbon membrane reported by previous researchers.

| Material                                      | Configuration   | Stabilization Temp (°C) | Pyrolysis Temp (°C) | Applications              | Ref.  |
|-----------------------------------------------|-----------------|------------------------|---------------------|---------------------------|-------|
| Sulfonated poly (aryl ether ketone), SPAEK    | Flat sheet      | 250                    | 800                 | H₂ and CO₂ separation     | [22]  |
| Matrimid 5218                                 | Tubular support | 300                    | 850                 | CO₂ separation            | [23]  |
| Polyacrylonitrile/ Polyvinylpyrrolidone        | Flat sheet      | 200                    | 800                 | Super capacitor performance | [24] |
| Phenolic novolac resin                         | Tubular support | 150-300                | 600-900             | N₂ separation             | [25]  |
| Poly (amic acid)/ zeolite ZSM-5 Polyacrylonitrile (PAN) | Flat sheet      | 100-350                | 600                 | O₂/N₂ separation          | [26]  |

2. Experimental procedures

2.1 Materials

BTDA-TDI/MDI (P-84) co-polyimide are marketable bought from Sigma Aldrich (CAS#: 58698-66-1) was select as a precursor to produce carbon membranes. N-Methyl-2-Pyrrolidone (NMP) was used as a solvent and purchased from Merck (Germany). Tubular support membrane contains of TiO₂ (4.5-5.5mm), with a coating of ZrO₂ (2-3nm) on the inner surface was purchased from Shanghai Gongtiao Ceramics Co., Ltd. The dimensions of the tubular support were 8cm in length and 13mm in diameter. The porosity of the support was 40-50% with an average pore size of 0.2μm.

2.2 Carbon Membrane Preparation

The dope solution was prepared by stirred of 15wt% of P84 co-polyimide and 85wt% of NMP for 24 hours. Tubular carbon membrane was prepared through dip-coating technique; where tubular support were dip-coated with the dope solution for 15 min to form a uniform layer of polymeric precursor over the outside surface of the tubular support. The membrane was then dried at 80°C for 24 hours. Next, the
membranes were immersed in methanol for 2 hours, followed by drying for 24 hours. The dip-coating cycles were repeated three times to remove any pinhole occurrences on the surface of the prepared tubular membranes. The prepared tubular precursor membranes were then placed inside a Carbolite horizontal tubular furnace for stabilization and pyrolysis processes. In this study, two steps of the heat treatment were employed. In the first step, the membranes were heated at different stabilization temperatures (250, 300, 350, 400 and 450°C) with a heating rate of 3°C/min under N₂ atmosphere (200ml/min). In the second step, the membranes were pyrolyzed up to 800°C at the same heating rate and gas flow as mentioned in step 1. The nomenclature of the resultant carbon membranes was given in the form of (CM-stabilization temperature); CM-250/CM-300/CM-350/CM-400/CM-450. Carbon membranes without tubular support were also prepared through similar procedures for characterization purposes.

2.3 Membrane Characterization

The morphological structures of the P84 co-polyimide-based membranes were viewed via scanning electron microscopy (SEM), model JEOL JSM-5610LV. A small piece of the tested membranes was cut and conditioned in liquid nitrogen to leave an unreformed structure to be mounted on sample stubs. The microstructure properties of the prepared carbon membranes were examined on X’Pert PRO X-ray diffractometer (XRD) from PANalytical with the diffraction angle of 2θ, between 10° and 50°. Ni-filtered CuKα radiation with a wavelength of λ= 1.54 Å was applied in the experiments. The interplanar distance (d-spacing) of the carbon membranes were calculated by the Bragg equation [27,28,29].

2.4 Gas Permeation Test

The pure gas permeation system used for gas permeation test can be found elsewhere [23,29]. The prepared membrane was placed in a stainless steel module prior the gas test. O-rings rubber was used so that leaks can be prohibited when the membranes were housed within the module. Pure gas H₂ (0.289 nm), N₂ (0.364 nm) and He (0.260nm), were fed individually at a trans membrane pressure of 8 bars into the module. The permeance, P/l (GPU) and selectivity, α of the membranes were calculated using equations below:

\[
\frac{P}{l} = \frac{Q_i}{A \Delta p} = \frac{Q}{\eta \pi D l \Delta p}
\]

Selectivity, α : 

\[
\alpha_{A/B} = \frac{P_A}{P_B} = \frac{(P/l)_A}{(P/l)_B}
\]

where P/l is the membrane permeance, Qi the gas i’s volumetric flow rate of at standard temperature and pressure (cm³ (STP)/s), p the difference in pressure between the feed the permeation side of the membrane (cmHg), A the area of membrane surface (cm²), n the fiber quantity in module, D the membrane’s outer diameter (cm), and l the membrane’s effective length (cm). The selectivity is defined as the permeation ratio of fast gas permeation to slow gas permeation.

3. Results and discussion

3.1 Morphological structure analysis

Figure 1 (a) presented the cross-section microphotographs of the precursor membrane, while Figure 1 (b) to (f) showed the cross-section microphotographs of carbon membranes prepared at various stabilization temperatures. Due to the difficulty in preparing SEM samples for the supported carbon
membrane, self-supported carbon membrane prepared without tubular support was used for SEM characterization. Referring to Figure 1 (a), precursor membranes have sponge-like structures. From Figure 1(b) to (f), all prepared carbon membranes with different stabilization temperatures are observed to have a pore structure with more open pores [30]. This phenomenon is likely due to the stabilization of thermoplastic polymers in air permits oxygen scaffolds to be made between aromatic molecules that repress the reworking and development of aromatic crystallites amidst the pyrolysis step. Principally, during the stabilization step, the precursor would experience various physical and substance changes because of a mixture of exothermic chemical reactions, including decay, cyclisation, dehydrogenation, oxidation, cross-linking and fracture [31]. Therefore, after pyrolysis at elevated temperature, the resulted carbon membrane became more porous as stabilization temperature increase. Work by Hosseini and Chung (2009) suggested that the porous structure allows high permeability while the molecular sieving network provides the efficient size and shape selection of molecules [32]. Furthermore, as the stabilization temperature increased, the level of decomposition and cross-linking in the membrane expanded, which brought about distinctive micropore structures of the carbon membranes that can be utilised to tune gas division [31].

![Figure 1. SEM images of P84 co-polyimide-based: (a) Precursor membrane (b) CM-250 (c) CM-300 (d) CM-350 (e) CM-400 (f) CM-450.](image)

3.2 Wide-angle X-ray diffraction pattern
The XRD pattern of the prepared membrane was shown in Figure 2. The XRD spectra were shifted accordingly in order to show a clear x-ray diffraction result without affecting the diffraction angle. The average d-spacing between the individual layers of carbon was calculated by adopting Bragg’s Law. These d-spacing values were determined at the maxima of broad peaks and only reflect the average space between the centres of the chain segments in the polymer matrix [32]. The reflection at $2\theta=23.02$ (d-spacing: 0.498nm) can be observed for polymeric precursor membrane (P84 co-polyimide), while the carbon membrane reflection for all stabilized temperature from CM-250 until CM-450 were at $2\theta=24.75$ (d-spacing: 0.402nm), $2\theta=24.81$ (d-spacing: 0.384nm), $2\theta=26.23$ (d-spacing: 0.369nm), $2\theta=26.75$ (d-spacing: 0.351nm), and $2\theta=27.03$ (d-spacing: 0.351nm), respectively. The pattern for all carbon membranes indicated that there was not much difference. Based on the data, the d-spacing value decreased as the stabilization temperature increased from 250 until 450°C. This was due to the formation of more compact structures with higher packing density, and the d-spacing increment may coincide to the evolution of a more ordered microstructure with efficiently packed graphite layers [31].

![Figure 2. XRD spectra of precursor and carbon membrane prepared at different stabilization temperatures.](image)

3.3 Gas permeation results
The gas permeation properties of the prepared tubular carbon membranes were measured using the gas permeation test apparatus at room temperature. The permeance of three pure gases with different molecular sizes, $H_2$ (0.289 nm), $N_2$ (0.364 nm) and He (0.260nm) over the resulted tubular carbon membranes prepared at different stabilization temperatures were shown in Table 2. As demonstrated in table below, the stabilization temperature during pyrolysis process is principally affect the performance of the consequent tubular carbon membrane. The results indicated that carbon membrane with stabilization temperature of 300°C showed superior selectivity compared to the others stabilized temperature. This was due to its pore system contains of wide-ranging openings with narrow constriction [28]. The partition is created by the passage of smaller gas atoms (He and $H_2$) over the pores while the bigger gas particles are stuck, because of the transport mechanism. Additionally, tubular carbon membranes offer an outstanding performance due to the prearrangement of pore structure by cross-
linking and volatilization of minor vaporous particles delivered by thermal degradation during stabilization process. Based on previous study, the maximum ideal selectivity values obtained for He/N₂ and H₂/N₂ gas couples were up to 350 and 600, respectively [12].

**Table 2.** Gas permeation properties of P84 co-polyimide-based tubular polymeric and carbon membranes.

| Membrane | Permeability | Selectivity |
|----------|--------------|-------------|
|          | N₂          | H₂          | He          | H₂/N₂      | He/N₂       |
| Polymeric| 0.67±2.81   | 32.67±2.94  | 38.30±4.22  | 48.76±2.76 | 57.17±1.19  |
| CM-250   | 2.65±2.43   | 975.81±1.28 | 1027.33±2.41| 368.23±2.28| 387.67±3.11 |
| CM-300   | 2.98±1.28   | 1134.51±2.87| 1287.22±2.86| 380.71±2.34| 431.95±2.61 |
| CM-350   | 2.31±1.54   | 772.81±4.32 | 802.44±5.11 | 334.55±2.39| 347.38±3.12 |
| CM-400   | 2.26±3.22   | 742.55±2.83 | 787.21±2.19 | 328.56±4.51| 348.32±2.19 |
| CM-450   | 2.11±3.29   | 682.87±1.98 | 726.77±4.31 | 323.64±1.65| 344.13±7.66 |

Furthermore, the degree of deterioration and cross-linking in the membrane was increased as the stabilization temperature was increased. Therefore, it will result in changed micropore structures of resultant carbon membranes; as noticeable via the SEM images. It is suggested that the gas permeation properties of the carbon membrane could be controlled by the stabilization conditions. Previous researchers have agreed that the microstructure of carbon membranes (pore size, pore volume and pore distribution) could be tailored by monitoring the heat treatment process.

4. Conclusion
The gas permeation properties of the P84 co-polyimide-based tubular carbon membranes were obviously improved in magnitude compared to the polymeric precursor membranes. This was due to the formation of pore structures by cross-linking and volatilization of small gaseous molecules produced by minor thermal degradation during stabilization process. Stabilization temperatures have protrusive effect on the membrane properties specifically their pore structure, and eventually their gas separation properties. Tubular carbon membrane that stabilized at 300°C possessed superior gas separation for H₂/N₂ and He/N₂ gas pairs of 380.71±2.34 and 431.95±2.61, respectively. The overall results demonstrated that the P84 co-polyimide-based carbon membrane is a promising material for H₂/N₂ and He/N₂ separation application.

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References
[1] Haider S 2018 *Sep. Purif. Technol.* **190** 177-189
[2] Levin D B, Pitt L and Love M 2004 *Int. J. of Hyd. Energy* **29** 173-18
[3] Guo Y, Jin Y, Wu H, Zhou L, Chen Q, Zhang X and Li X 2014 *Int. J. of Hyd. Energy* **39** 21044-21052
[4] Bakonyi P, Nemestôthy N and Bélafi-Bakó K 2013 *Int. J. of Hyd. Energy* **38** 9673-9687
[5] Li P, Wang Z, Qiao Z, Liu Y, Cao X, Li W, Wang J and Wang S 2015 *J. Membr. Sci.* **495** 130-168
[6] Mohamad I N, Rohani R Mastar@Masdar, M S Mohd Nor and M T Md Jahim 2016 *Int. J. of Hyd. Energy* **41** 4474-4488

[7] Zhuang G L, Tseng H-H and Wey M Y 2014 *Int. J. of Hyd. Energy* **39** 17178-17190

[8] Bakonyi P 2013 *Int. J. of Hyd. Energy* **38** 15092-15099

[9] Bakonyi P, Bogdán F, Kocsi V, Nemestóthy N, Bélafi-Bakó K and Buitrón G 2016 *Sep. Purif. Technol.* **157** 222-228

[10] J.A. Lie, X. He, I. Kumakiri, H. Kita and M.-B. Hägg 2017- Books 405-431

[11] Scholes C A and U Ghosh, 2016 *J. Membr. Sci.* **520** 221-230

[12] Scholes C A, G W Stevens and S E Kentish 2012 *Fuel* **96** 15-28

[13] Favvas E P 2015 *Sep. Purif. Technol.* **142** 176-181

[14] Favvas E P 2014 *Sep. Purif. Technol.* 2014 **122** 262-269

[15] Ye P 2016 *AIChE Journal* **62** 2833-2842

[16] He X and M-B Hägg 2012 *J. Membr. Sci.* **390-391** 23-31

[17] Lee H-J 2007 *J. Membr. Sci.*, **296** 139-146

[18] Fu Y-J 2011 *Micropor Mesopor Mat.*, **143** 78-86

[19] Cipriani E 2016 *Polym. Degrad. Stab.* **123** 178-188

[20] Barbosa-Coutinho E, V M M Salim and C Piacsek Borges 2003 *Carbon* **41** 1707-1714

[21] Hameed N 2016 *Polym. Degrad. Stab.* **128** 39-45

[22] Xiao Y 2010 *Carbon*, **48** 408-416

[23] Sazali N 2015 *Int. J. of Hyd. Energy* **3** 167-171

[24] Fan H 2014 *J Energy Chem.* **23** 684-693

[25] Lee P-S 2016 *Micropor Mesopor Mat* **224** 332-338

[26] Liu Q 2006 *Chem. Commun.* **11** 1230-1232

[27] Ismail N H, Salleh W N W, Sazali N and Ismail A F 2017 *Sep. Sci. Technol.* 1-13

[28] Ismail N H, Salleh W N W, Sazali N and Ismail A F 2017 *J. Ind. Eng. Chem.* **45** 145-149

[29] Sazali N, Salleh, W N W Ismail and A. F. 2017 *Int. J. of Hyd. Energy* **42** 9952-9957

[30] Zhang K, J D Way, 2011, *J. Membr. Sci.*, **369** 243-249

[31] Salleh W N W and A F Ismail 2013 *Sep. Sci. Technol.* **48** 1030-1039

[32] Hosseini S S and T S Chung 2009 *J. Membr. Sci.* **328** 174-185