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PI/NCC Carbon Membrane: Effect of Additives loading Towards Hydrogen Separation

N Sazali[1,2]*, R Mamat[2], J P Siregar[1,2], T Gunawan[3], W N W Salleh[4], and N A H M Nordin[5].

[1]Centre of Excellence for Advanced Research in Fluid Flow (CARIFF), Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang, Malaysia.
[2]Faculty of Mechanical Engineering, Universiti Malaysia Pahang, 26600 Pekan, Pahang, Malaysia.
[3] Department of Chemistry, Faculty of Science, Institut Teknologi Sepuluh Nopember, Surabaya 60111, Indonesia.
[4]Advanced Membrane Technology Resea+rch Centre (AMTEC), School of Chemical and Energy, Faculty of Engineering, Universiti Teknologi Malaysia, 81310 Skudai, Johor Darul Takzim, Malaysia.
[5]Department of Chemical Engineering, Universiti Teknologi PETRONAS (UTP), 32610 Seri Iskandar, Perak Darul Ridzuan, Malaysia

Abstract. Incorporating thermally labile polymer-based additives is a facile and practical approach in developing superior carbon membranes. In this study, three different thermally labile polymers, microcrystalline cellulose (MCC), nanocrystalline cellulose (NCC), and polyvinylpyrrolidone (PVP), were introduced separately to P84-copolyimide (PI) solution as additive and their impact on membrane performance were investigated. Firstly, NCC was added as the membrane pore former for hydrogen gas (H_2) separation. The addition of NCC significantly increased pore channels in the membrane, hence contributed to high gas permeance and selectivity. The tests involving pure H_2 and N_2 permeation were carried out at room temperature. Carbon membranes carbonized at a final temperature of 800^oC with the heating rate of 3^oC/min under Ar flow achieved the greatest H_2/N_2 selectivity of 434.68 ± 1.39, hence proving the potential of NCC as a good additive.

1.Introduction

One of the most emerging renewable resources for energy is hydrogen where it can be produced through renewable resources such as biomass [10]. The chemoheterotrophic ("dark") fermentation receives certain benefits due to several advantages such as low energy demands, high bacterial growth rate, minimal pollution generation, low capital costs, higher hydrogen production rate as well as no oxygen limitation problems for at least small-scale production [11]. The H_2 production provides greater prospect for H_2 generation compared to the steam methane reforming, however the process is usually accompanied with by-products of CO_2, volatile organic compounds (VOC), H_2S and NH_3 producing hydrogen in the range of 35~65 (vol.)% [12]. H_2 purification technology available are cryogenics distillation, pressure swing adsorption (PSA), and palladium (Pd) membranes [13, 14]. However, for small-scale H_2 productions via fermentation processes, the cryogenics and conventional PSA will cost a lot of money. Similar problem also applies to the palladium membranes. The commercialized Pd membrane such as H_2 Pure™ and HYSEP have high production cost and short lifetime due to the embrittlement of H_2 leading to a high capital expenditure (CAPEX).

Membrane technology for gas separation has been explored over the past three decades [1, 2]. Membranes for gas separation is very promising due to its low energy consumption, simple operation, low operating cost with no chemical requirement [3-5]. Although polymeric membrane is proven technology in large scale, its low to moderate separation factor is the major drawback of the process. On contrary, inorganic membranes are known for their robustness against harsh operation conditions with excellent gas separation properties compared to polymeric membrane. Among them, carbon membranes is on of excellent inorganic membrane with permeability and selectivity far above Robeson Upperbound, the limiting performance of polymeric membrane [7-9]. In addition, carbon membranes can be easily

prepared using polymeric materials. They are far more superior than polymeric membranes in terms of chemical and thermal resistance, thus preventing physical aging and plasticization. The polymeric precursor and other important parameters must be in perfect condition in order to avoid problems during carbon membrane fabrication as well as to produce excellent carbon membranes.

Among strategies to improve membrane performance is using of polymer blend materials, whereby one polymer precursor is blended with other polymer or inorganic materials with different thermal degradation properties [15]. This technique helps to control the pore formation of the resulted membrane, thus potentially tailored to specific separation. In gas separation, the effect of polymer blending is described by analyzing the performance of the resultant membranes. Carbon membrane using polymer blend precursor has receive great attention [27-29]. Yong and co-workers fabricated PIM-1/Matrimid carbon membranes in hollow fibre configuration with remarkable separation performance [23]. Well-structured hollow fibre membrane with excellent gas pair selectivity (90% of the intrinsic value) was prepared from dope solution containing 5 wt% PIM-1 using optimized spinning conditions. In the case of membranes containing 10 and 15 wt% PIM-1, post-annealing and additional silicone rubber coating are necessary. These membranes show great potential for applications such as CO_2 capture, hydrogen purification, and air separation.

Modification of polymer precursor blend through the introduction of additives such as microcrystalline cellulose (MCC), nanocrystalline cellulose (NCC), and polyvinylpyrrolidone (PVP) is important in order to enhance gas separation performance. These additives will decompose straightaway during the carbonization process as they would not melt or soften indicating them to be suitable for usage. MCC, for example, has been used to manufacture composite due to its excellent reinforcing capability and environmental benefits. The addition of MCC as carbon membrane pore former would increase the micropores structure, hence improving the pathways for gas diffusive transport. Comparatively, NCC was prepared with the well-tailored structure to be used as membrane additive [18, 20, 21]. NCC was utilized as an additive and pore former due to its low degradation temperature, low cost, effective processing and commercial availability for mass production. Besides, it is well-known for its capability to withstand extreme chemical and thermal conditions and has highly porous structure. NCC was synthesized from cellulose extraction mostly via chemical modification. [22]. The common thermal labile polymer is PVP. The addition of PVP improved the gas permeability of carbon membranes, whereby the permeation performances were affected by carbonization temperature and PVP molecular weight [16-18]. Besides, the use of higher molecular weight PVP increased the gas permeance of the carbon membranes due to the increased diffusion pathways.

Hence, this work focuses on blending of the PI-based carbon membrane with NCC, MCC, and PVP which is identified as thermally labile additives for H_2 separation. The focus of this work is on the development of novel carbon membranes using various thermally labile additives to improve H_2 separation performance. Comparative performance analysis for different additives in polymeric and carbon membrane counterpart are evaluated thoroughly.

2. Experimental section

2.1 Materials

MCC and PVP were supplied by Sigma Aldrich while N-methyl-2-pyrrolidone (NMP) was obtained from Merck Millipore (Germany). NCC was synthesized similarly as reported in the previous study [10]. Porous TiO_2 tubular support (length = 8 cm, thickness = 3 mm, pore size = 0.2μm, porosity = 40-50%) was purchased from Shanghai Gongtao Ceramics Co., Ltd.

2.2 Preparation of tubular carbon membrane

The dope solution was prepared by constant stirring of 15 wt% PI into 85 wt% of NMP for 24 hours at 80°C. Different additives (**Table 1**) were pre-added into the dope solution. Subsequently, the solution was continuously stirred until the homogeneous solution was obtained. If there are any trapped bubbles, the solution was sonicated for 12 hours. After the solution was readied, the tubular support was dip-coated immediately in it for 45 minutes. The produced membranes were soaked into methanol for 2 hours, before being dried in an oven at the temperature of 100°C for 24 hours.

Table 1. The dope solution composition studied in this work

Sample	Concentration (wt.%)	
	PI	Additive
PI/PVP	15	9
PI/NCC	15	7
PI/MCC	15	7

Carbon membranes were developed by carbonizing the polymeric membranes inside Carbolite horizontal tubular furnace under N_2 atmosphere (T = 800°C, flow rate = 200 ml/min), following the procedures used in our previous study [10].Heat treatment profiles are shown in **Figure 1**. In the meantime, carbon membranes (without substrate) in flat sheet configuration were fabricated as control samples.
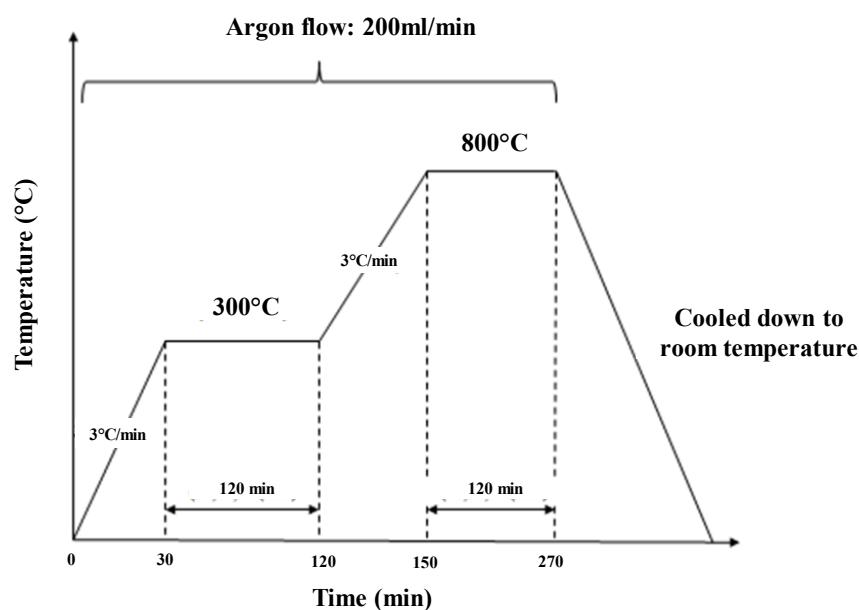
Figure 1: Heat treatment profile

2.3 Pure gas permeation measurements

The gas permeation system portrayed in this study to test the performance of carbon tubular membranes is similar to the system used in our previous study [8]. Initially, a tubular stainless-steel module with the length of 14cm was selected and the carbon tubular membrane was put inside it. Moreover, the O-ring rubber band was fitted to the module, in order to avoid any leakage. The pure gas measurement was conducted in room temperature and at a pressure of 8 bars. In the beginning, pure H_2 gas (0.289 nm) was fed separately into the module system, followed by N_2 gas (0.364 nm). The gas permeation apparatus is shown in **Figure 2**. The permeance and selectivity of the membrane were calculated using Equation (1) and (2) for *P/l* (GPU) and selectivity, *α*, respectively.

Permeance, *P:*

$$(P/l)_i = \frac{Q_i}{\Delta p.A} = \frac{Q}{\eta \pi D l \Delta P}$$

(1)

Selectivity, α :

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

(2)

where *P/l* represents gas permeance, *Qi* represents gas volumetric flow rate at STP (cm^3 (STP/s), *p* denotes pressure difference (cmHg), *A* is the effective surface area (cm^2), *n* signifies the number of fibers, *D* represents the membrane outer diameter (cm) and *l* is the fiber length (cm). The selectivity, on the other hand, can be defined as the permeation ratio of fast gas over slow gas permeation.

Figure 2: Gas permeation apparatus

3. Results and discussion
3.1 Gas Permeation Measurements
The gas separation performance of all polymeric precursor membranes is presented in **Table 2**. Compared to the pure PI membrane, membrane with the addition of NCC, MCC and PVP as additives has enhanced membrane gas permeation performance significantly. The blending of PI/NCC possessed the highest gas permeance for both H_2 and N_2 at 24.52±1.34 GPU, followed by PI/MCC and PI/PVP. In addition, PI/NCC polymeric membrane was shown to possess the highest H_2/N_2 selectivity of 26.09±2.49. The results showed that H_2 permeance are higher than N_2 permeance for all membrane. As the diameters of H_2 (2.89 Å) and N_2 (3.64 Å) are vastly different, the separation are considered unattractive (far below Robeson Upperbound limit). This is likely due to inefficient pore formed by inclusion of the additives; thus, molecular sieve mechanism does not govern the separation effectively.

Table 2. The polymeric membrane gas permeation performance

Sample	Polymeric membrane		
	Permeance (GPU)		Selectivity
	H_2	N_2	H_2/N_2
PI	12.87±2.81	0.70 ±5.23	18.39±1.33
PI/NCC	24.52±1.34	0.94±3.54	26.09±2.49
PI/MCC	19.57±1.65	0.81±2.44	24.16±2.65
PI/PVP	17.88±2.62	0.80±3.11	22.35±1.84

Interestingly, their carbon membranes counterpart performs far superior (**Table 3**). As carbonization take place, the degradation of functional groups in the polymer creates micropores that allows superior molecular sieving for H_2/N_2 separation. Among the prepared carbon membrane, PI/NCC displayed the highest H_2 permeance of 1399.66±5.22 GPU with H_2/N_2 selectivity of 434.68±1.39. This is due to more compact microporous structure of the membrane compared to using MCC and PVP as additives. The presence of pore forming agents further promotes pores formation when the additives decomposed at lower temperature compares to PI. Hence, the use of different additives resulting in the carbon membrane pore size, pore volume and diffusive pathway for gas transport, as observed by increased in H_2/N_2 separation performance. In addition, the addition of additives creates more diffusion pathway for gas molecules inside the thermally labile polymer. Among the three additives, PVP showed the lowest impact on the improvement of PI carbon membrane gas selectivity and permeance compared to MCC and NCC. This is due to the increased resistance for the smaller gas molecules to enter the minuscule channels created by PVP. These results proved that separation of gas occurred via molecular sieving mechanism.

Table 3. The carbon membranes gas permeation performance

Membrane	Permeance (GPU)		Selectivity
	H_2	N_2	H_2/N_2
PI	1226.61±4.12	3.08±3.65	398.25±2.31
PI/NCC	1399.66±5.22	3.22±3.21	434.68±1.39
PI/MCC	1341.20±1.67	3.18±4.16	421.76±4.33
PI/PVP	1274.01±2.85	3.11±3.98	409.65±2.18

As there was lack of previous effort conducted utilizing available MCC and synthesized NCC as carbon membrane additives, several studies provided an idea that the addition of MCC and NCC in polymer blends offer better membrane separation performances compared to using other available additives [7, 18, 20, 31, 32]. Cellulose is made up of repeating d-glucose units of monomer condensed via beta (1–4) glycosidic bonds, forming straight chains of polymer stabilized by plenty inter- and intramolecular hydrogen bonds between hydroxyl functionalities. Cellulose chains are packed closely to each other providing high crystallinity areas. Recently, the shifting of economic landscape has provided the opportunity to fully utilize this ubiquitous natural polymer therefore motivated the effort to prepare PI/NCC-based carbon membrane in this study.

Thus, the use of thermally labile polymer additives such as NCC with a proper control of carbonization conditions and polymer concentration may alter the membrane pore structure, which later can improve the gas separation performance. This work also coincide with the previously reported work, where cellulose incorporated carbon membranes displayed excellent separation performances of O_2/N_2, CO_2/CH_4 [33], H_2 and He [10, 20, 34]. In this work, it was found that carbon membrane prepared from pure PI has lower gas permeability than carbon membranes added with additives. It is known that during the carbonization process, the presence of additives causes the cracks formation in the membrane. In the case of NCC, its aromatic carbon structure signifies the molecules as starting to decompose and form micropores [35].

4. Conclusion

With regards to the findings, it was proven that tubular carbon membrane prepared by blending NCC with PI improved the H_2/N_2 separation. Besides, the impacts of adding different types of thermally labile additives on membrane performance were studied and discussed. Generally, incorporation of either additive (NCC, MCC and PVP) reduced the thermal resistance of the polymer blend. Among the three additives, NCC provides the membrane with optimized physicochemical properties due to its nanocrystalline structure. The results showed a substantial increase of membrane gas permeance after the addition of additives. It appears that PI/NCC carbon tubular membrane has the best H_2/N_2 selectivity of 434.68±1.39. In conclusion, the use of NCC as thermally labile additive resulted to positive impacts on the development of high-performance carbon membrane. These whole findings may provide a strong foundation for future endeavors using natural resources as polymeric additives.

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