Effect of Polymer Concentration on Matrimid 5218 based-Carbon Membrane for H$_2$ Separation

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ABSTRACT

Hydrogen (H$_2$)-based economy development is expected to create extensive need for efficient collecting strategies of fairly high purity H$_2$. The aim of a H$_2$-selective membrane is to manipulate H$_2$'s high diffusivity characteristics as well as to restrict the outcome of lower solubility. Carbon membranes offer high potential in gas separation industry due to its highly permeable and selective. Therefore, this study aims to investigate the effect of carbonization parameter, i.e., polymer concentration on the gas separation properties. Matrimid 5218 was used as a precursor for carbon tubular membrane preparation to produce high quality of carbon membrane via carbonization process. The polymer solution was coated on the surface of tubular ceramic tubes using dip-coating method. Matrimid 5218-based carbon tubular membranes were fabricated and characterized in terms of its structural morphology, chemical structure, thermal stability, and gas permeation properties by using scanning electron microscopy (SEM), Fourier transform infrared (FTIR), and pure gas permeation system, respectively. The polymer solution containing 15 wt% Matrimid 5218 shows the best formulation for the preparation of Matrimid 5218-based carbon tubular membrane. The highest H$_2$/N$_2$ selectivity of 401.08±2.56 was obtained for carbon membrane carbonized at 800°C with heating rate of 2°C/min.

Keywords: Hydrogen separation, carbon membrane, Matrimid 5218 type polyimide, and polymer concentration

1.0 INTRODUCTION

Even though the consideration of membrane usage was made earlier, utilization of small-diameter hollow-fiber membranes was only done during the late seventies before DuPont pioneered the usage. Nevertheless, the first-generation hollow fibers yields were very minor in order to accommodate the economical gas separations requirement. Monsanto Co. solved the issue by developing multicomponent polysulfone hollow-fiber membranes for hydrogen recovery. Restriction of discerning and dense areas of the fibers to a very small space, significantly increased fibers transportation. Adaptation of these asymmetric membranes in industrial-scale recovery of hydrogen from ammonia purge gases were fruitful. Then, Separex Corp. developed the Separex® spiral which is a membrane of wound cellulose acetate that targets similar separation

types as the earlier technology, purification as well as natural gas dehydration [1]. Membranes of cellulose acetate show good performance primarily due to its high resistance on hydrocarbon impurities. Near the mid-1980s, membrane application was usually found fir the purpose of advancing other implementations for example hydrogen recovery from refinery gas recycling. Polyimide membrane with the best solvent and heat resistance characteristics was first introduced by Ube in Japan. Application of this membrane was first done Seibu Oil's Onoba City refinery.

Lately, H_2 economy's popularity is the primary reason of hydrogen recovery increased attention as the main alternative in of energy sources for the energy intensive industrialized nations. One fossil fuel combustion appealing candidate for the purpose of power generation is the proton-exchange membrane (PEM) fuel cell [2]. PEM uses hydrogen as the source in transforming chemical energy to electrical energy. There are a few noted advantages of these fuel cells for example high efficiency of fuel than internal-combustion engines, produce nearly zero carbon monoxide, NOx or HC as well as producing low level of carbon dioxide [3]. Nevertheless, good hydrogen supply distribution is required for broad implementation of these fuel cells. Implementation potential of gas separation membranes in this process is crucial. Mechanism of solution-diffusion is incapable to wholly eliminate the trace contaminants which limits the economic competence of polymeric substance for products having especially high purity. The needs for further improvement in hydrogen gas separation membranes for application is understandable.

The process of membrane-based separations plays a crucial role in numerous industrial processes for example in the process of gas separation. Remarkable hard work was offered in order to construct new materials for membrane having good selectivity and permeability. Nowadays, carbon membranes are recognized as potential candidates for application in gas separations primarily due to their famous features of separation properties. In reality, various reports have provided proves of carbon membrane as the perfect contender for gas separation due to its outstanding selectivity and permeability [4]. Furthermore, carbon membrane also offers excellent performance with no increment in energy as well as processing cost due to the elimination of the cooling step [5]. Orientation dislocation of aromatic micro in glasslike matrix causes the rise in ultra-micro porosity and free volume. Microspores are normally nearly slit-shaped with pore mouth dimensions as large as the diameter of small molecules [6].

Gas transport mechanisms depend on both membrane and permeate properties. Gas separation process can be divided into a few separation mechanisms which are solution and Knudsen diffusions as well as the molecular sieve effect. Mentioned mechanisms are identified to be suitable for material systems and limited gases number. Mechanism of solution diffusion works according to the principle of mixture component having high rate of diffusion and high solubility permeates favourably across the membrane which is not dependent on the size of the component. Furthermore, solution-diffusion membranes are consist of free volume sites that cannot be filled with polymer chains due to limited motion as well as packing density of the polymer chains [7].

Transportation of the components across the membrane was done via uninterrupted movement of the transient free volume gaps near the feed side with those near the permeate side caused by the thermal motion of polymer chains segments. Past works reported that elaboration of numerous mechanisms can be done via gases transportation across the porous membrane. This offers a graphic diagram for gases permeation mechanisms via porous as well as dense membranes [8]. As enhancement in technology, separation necessities as well as its implementations grow, requirement of new membrane materials are essential in meeting the promised productivity as well as separation efficiency. Final membrane morphology acquired is exceptionally diverse, with variations primarily in materials properties as well as process conditions implemented.

The pore size of carbon membranes need to be in pore diameter range of larger than 30 Å to attain selectivity that is very high [9]. Carbon membranes have restriction in its carbon matrix that reaches absorbing species molecular dimensions [10]. Molecules having the size of three-dimensionally lesser than the size of planar shape with small cross-sections or slit width are selectively permeated via the molecular sieve [11]. Therefore, carbon membranes will effectively separate gas molecules of similar sizes. Figure 1 illustrates the usual mechanism of molecular sieving transport. In this mechanism, separation occurs via passage of gas mixture smaller molecules across the pores while blocking the larger molecules at the same time. It shows high gas mixture permeability and selectivity components [12].
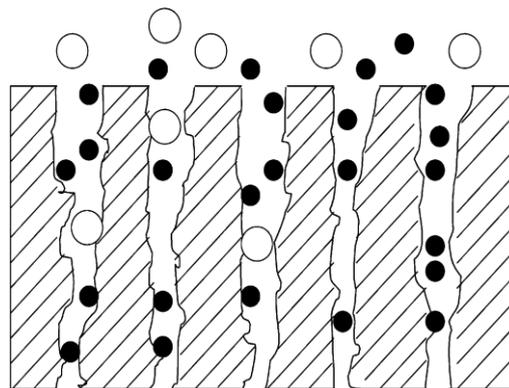

Figure 1 Typical molecular sieving transport mechanism [12]

The membrane concept for gas separation was identified during the early 1970 through polysulfone and cellulose esters formation [13]. Pyrolyzed carbon, metals or ceramics are normally used in designing inorganic membranes. Reported works can be found on the compression of micro porous carbon particles into stainless steel plugs as well as the measurement of diffusion coefficients intended for numerous gases such as hydrogen (H_2), helium (He), argon (Ar), krypton (Kr) plus nitrogen (N_2) [14]. Nevertheless, exceptional interest growth in the development of carbon membranes began in the 1980 through successful preparation of crack-free carbon molecular sieve membrane from cellulose hollow fiber membrane carbonization by previous researcher [15]. Ever since, the amount of research conducted as well as publications produced on carbon membranes increases [16]. Meanwhile, carbon membranes provide higher selectivity and permeability compared to polymeric membranes, however carbon membranes are expensive with complex utilization in large-scale manufacture [17]. Thus, it is highly needed in providing alternatives for cheaper with good selectivity and permeability trade-off membrane. Existence of carbon membranes can be found in numerous industrial

operations related to gas separation. In gas separation, permeability as well as selectivity of a membrane material indicates the competency of gas separation process.

There are two categories of membrane in accordance of its selectivity and density namely nonporous and porous membranes. Porous membrane is rigid with exceptional voided structure that can assists in inter-connected pores delivery. Materials separation via porous membrane is normally a function of membrane properties as well as permeate character namely distribution of pore-size, pore-size and the membrane polymer's molecular size. Essentially, molecules with great difference in size can be separated well by membranes of micro porous structures. A porous membrane is appropriately precise in its function and configuration to the normal filter. In gas separation, porous membranes have high density levels with only low value of selectivity. Characterization of micro porous membranes can be listed according to porosity of the membrane, pore average diameter, as well as membrane asymmetry. They exhibit distinctive properties of permeability for carbon dioxide with great selectivity to nitrogen and methane. Carbon membranes are consisting of amorphous porous structure fashioned by the advancement of volatile gases during polymeric precursor's carbonization. Porous structure in carbon membrane comprises of apertures or pores approaching molecular dimension similar to the diffusing gas molecules [18]. Usually, carbon membrane pore system is non-homogeneous due to the existence of broad opening amidst the uncommon conditions.

Permeates with correlated sizes are able to be separated if their solubility in the membrane differ which encouragingly assumed to be a necessity in the property of nonporous or dense membrane. Carbon membrane has the potential to be recognized globally with exceptional selectivity, permeability as well as good mechanical and chemical properties. Sazali. *et al.* (2017) reported that, the most wanted structure of membrane for industrial implementations is the asymmetric membranes primarily influenced by its high gas permeance [19]. In most circumstances, asymmetric membrane is usually applied in various gas separation membranes in order to enhance the permeability of the constructed membrane. The process of membrane fabrication requires the preparation of membranes of asymmetric structures through phase inversion methods which refer to the wet spinning as well as the dry-wet spinning [20].

Carbon matrix is considered to be impermeable, thus the pore system highly influence permeation through carbon membranes. Partial burn off or activation method is utilized to widen the pore system in carbon as well as hardening at elevated temperatures in inert atmosphere causing the pore to close which were recently implemented in order to prove gases permeability via molecular dimensions' pore system of carbon membranes. The pore system is comprises of reasonably broad openings with tight constructions [21]. The major parts of the pore volume is consists of the openings which are accountable for the capacity of adsorption, whereas the constrictions are accountable for the pore penetration stereo selectivity by host molecules as well as for penetration kinetics [22]. Therefore, gases diffusivity in carbon membrane alters sharply according to the shape and size of molecules due to the ultra-micropores contained in the carbon

membrane having pore size as well as critical pore mouth dimensions nearly the same as the gas molecules dimension. Pore size in the carbon molecular sieve is in accordance with the balance between the O_2 containing groups elimination on the surface near the pore mouth (pore enlargement) as well as crystallite rearrangement enhancing sintering (pore shrinkage).

This paper describes the research on carbon membrane using precursor of Matrimid. Matrimid is a thermoplastic polyimide based on a proprietary diamine, 5(6)-amino-1-(4'aminophenyl)-1,3, trimethylindane. This substance exhibits predominant gas selectivity, which is one of the most vigorous ever testified for polymeric films. Aside being used as carbon precursors, Matrimid can also produces high yield of carbon yields with simple graphitization and carbonization procedures. In addition, Matrimid offer solutions with high viscosity at low ratios of solvent or polymer. Polyimides that imidized fully under elevated glass transition temperatures (Tg) for example Matrimid, are appropriate polymer precursors due to its regular structure alteration during carbonization which is a vital feature in attaining Carbon Molecular Sieve Membranes (CMSM) that is free of defect. Matrimid is suitable as the primary polymeric precursor due to its readily soluble characteristics as well as exhibiting exceptional permeability and selectivity combination for various pairs of gasses that is grander than other commercial polymers. Matrimid is suitable as polymer for gas-separation membranes due to its attractiveness which offers great solubility in common organic solvents which allows bulk chemical alterations to be conducted as long as the reagents used do not cause chain degradation or reactions of cross linking with the

carbonyl structure present in imide and benzophenone that is highly sensitive. Treating Matrimid membrane with heat up to 800 ℃ leads to the formation of carbon membrane with both larger micropores as well as ultra-micropores.

2.0 STEPS INVOLVED IN CARBON MEMBRANE PREPARATION

Aromatic polymers carbonization is normally used in preparing carbon membranes [23]. Carbonization is the most crucial procedure in carbon membrane fabrication and is also assumed as the heart of carbon membrane manufacturing. Enhancement of carbon membrane performance is consisting of a few vital steps namely selection of precursor, preparation of membrane and conditions of carbonization. Further advancement in separation and technology requirements as well as implementations results in more challenges for example the requirement of new membrane to fulfil efficiency and productivity of separation. Fabrication of carbon membranes are conducted to eliminate the polymeric membranes shortcomings. Figure 2 illustrates carbon membrane preparation schematic diagram.

Choosing modified precursors might result in different carbon membranes. Hence, selecting polymeric precursor is the most vital factor. Selection of polymeric precursor materials involves chemical and thermal stability, good selectivity and permeability combination as well as decent mechanical properties in order to fabricate the most sought-after carbon membrane. In this study, Matrimid has been chosen as precursor due to its advantages which has been

discussed previously. Carbon membrane of polyimide based illustrates promising maximum performances. Membrane build from carbon with defect free characteristics is obtained from polyimide membrane with the ability to withstand elevated temperature without treatment softens and breaks down unexpectedly and rapidly. Utilization of these materials helps in producing carbon membrane having high yield of carbon as well as having the ability to maintain its structure even after being heated under elevated temperature due to abnormally sturdy as well as unexpected resistant to chemical and heat [24].

After the precursor was chosen, the polymer solution mixtures of five different concentrations were prepared by combining NMP and Matrimid powder. The mixtures were stirred for 24 hours and the temperature is fixed to be below the NMP boiling point. The solution then located in sonication bath for 24 hours for bubbles removal. NMP is appropriate to be utilized as a solvent in the preparation of Matrimid solution. Then, the solution is transferred to a flat glass plate before being cast into thin film membranes. Next, to eliminate the residual solvents, the membranes are submerged in methanol for 2 hours. Then, the membranes were dried inside the fume hood until it fully curing. The polymeric membrane was formed after those processes were done. Then, to convert the polymeric membrane into carbon membrane, the carbon membrane produced will be treated under heat. This heat treatment process is the primary technique that must be conducted in order to transform polymeric precursor membranes into carbon membranes.

Carbonization process is the most important step among the whole steps required in preparing carbon

membrane and is also deemed as the heart of the carbon membrane manufacturing process. Pore structure for the carbon membrane is fashioned in this phase which outlines the ability of carbon membrane to detect gases [32]. Heat treatment process was conducted by putting the precursor membrane at the center of Carbolite (Model CTF 12/65/550) wire wound tube furnace. After this process was completed, carbon membrane was produced.
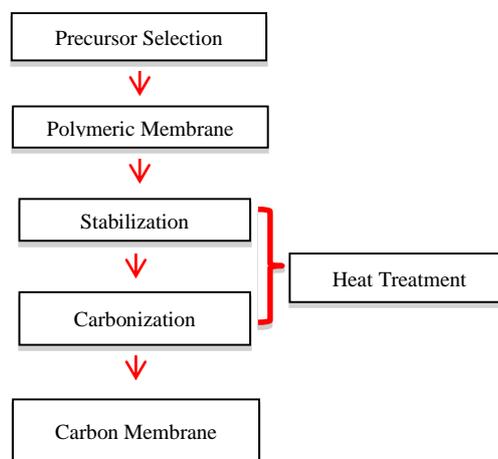

Figure 2 Schematic diagram of the carbon membrane preparation

3.0 EFFECT OF POLYMER CONCENTRATION

The morphology of the membrane will be adjusted during the carbonization process due to changes in some components. Factors that affect the membrane during the carbonization process are the concentration of precursor, temperature, and atmosphere during the carbonization process. The concentration of polymer is the most significant factor compared to other factors since it plays an important role in determining the separation performance of the membrane. The morphology of the carbon membrane can be adjusted by precursor concentration with different rates of solvent evaporation. Generally, low polymer concentration has a larger

pore size compared to high polymer concentration which leads to the production of non-selective carbon membrane [25]. This is due to its fast solvent evaporation. In the case of high polymer concentration, slower phase inversion takes place resulting in gas permeation restriction and slow solvent evaporation which will produce a membrane with a thicker dense layer or smaller pore size. The detail explanation of the membrane solvent evaporation is discussed in the development of polymeric membrane. The carbon membrane should possess particular pore size that is small enough to allow the desired gas to pass through the membrane also separate it from larger penetrant. Researches on the performance of carbon membrane with different polymer concentrations should be carried out to investigate their behaviour during the preparation of the polymeric precursor [26-28]. This section focusing on the carbonization of five different concentrations of Matrimid ® 5218 which are 5 wt.%, 10 wt.%, 13 wt.%, 15 wt.% and 18 wt.% at a temperature of 800°C with N_2 condition. The lower concentration than 5 wt.% of Matrimid has been used, however, the solution becomes too dilute causing the solution does not stick to the ceramic support. Higher concentration than 18wt.% also has been used, but the solution becomes too thick and a lot of time was required to dilute it to make it suitable to produce a membrane. These concentrations were chosen to be suitable for tubular membrane production, however, for characterization, only flat sheet configuration can be used due to apparatus limitation. Therefore, the chosen polymer concentrations were considered as the most appropriate concentrations to produce membranes. The characterization of membranes produced were performed by FTIR and SEM. The separation capability of the

membrane with different polymer precursor concentrations was studied via gas permeation test employing N_2, and H_2.

3.1 SEM Analysis

Scanning electron microscopy (SEM) determines the morphology structures of Matrimid-based membranes which highly affects its gas separation performance. The results show that the Matrimid concentration produced has a dense structure. Low polymer concentration usually causes the rapid solvent evaporation which resulting in non-selective carbon membrane while slower phase inversion occurs at high polymer concentration leads to the production of thicker dense layer causes by slow solvent evaporation and restricted gas permeation [29]. These occurrences can be explained by the entanglement of the polymer chain caused by reorientation of the polymer chain at various polymer concentration. The cross-sections of the carbon membrane fabricated from several polymer concentrations captured via SEM is shown in Figure 3.
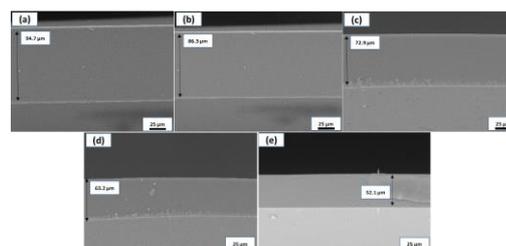

Figure 3 SEM images of cross-sections of the carbon membrane prepared from (a) 5 wt% concentration, (b) 10 wt% concentration, (c) 13 wt% concentration, (d) 15 wt% concentration and (e) 18 wt% concentration

SEM characterization analysis employs dense carbon membrane fabricated without tubular support since the process in fabricating supported

carbon membrane is complicated. These circumstances take place during the stabilization phase. Densification will occur if the membrane is further heated. For 5 wt.% Matrimid, the thickness of the membrane obtained is about 94.7 μm. As the polymer concentration increases, the thickness of the membrane decreases. The thicknesses of the membrane are 86.3 μm, 72.9 μm and 63.2 μm for 10 wt.%, 13 wt.% and 15 wt.% respectively. However, at 18 wt.% Matrimid, the thickness of the membrane decreased to 52.1 μm. The slower phase inversion causes a decrease in the thickness of the membrane until a particular polymer concentration. This is because there is sufficient time provided for the reorientation of the polymer chain to occur which results in a thinner dense layer membrane [30]. A thicker membrane is produced if the polymer concentration is beyond the ideal concentration due to the drastic entanglement of the polymer chain. Similar polymer solution concentrations are utilized in fabricating tubular carbon membrane and its structure is produced in the process of dip-coating. There are no significant changes showed on the structure of the membrane at various polymer concentrations other than changes in the thickness of the membrane. Different carbon membrane structure and gas permeation characteristics were obtained after the carbonization process depending on the polymer concentration accumulated on the ceramic support. From the images obtained from the SEM analysis, a significant difference in membrane thickness is observed in which affecting the solvent evaporation. For supported membranes, the membrane structure obtained at the end of the process depends on the degree of solvent elimination also the polymer concentration.

3.2 FTIR Results

Fourier Transform Infrared spectroscopy (FTIR) functions to measure the molecular orientation of the Matrimid-based membrane. The result from FTIR analysis of polymer membrane fabricated at various polymer concentrations is shown in Figure 4. FTIR capable to detect the changes in the chemical structure during the transformation of polymer into carbon.
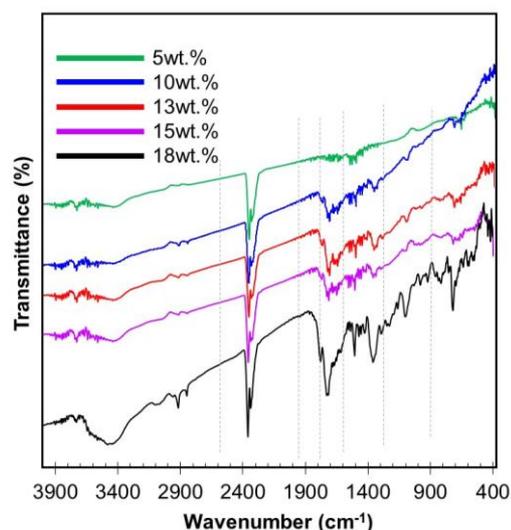

Figure 4 FTIR analysis of polymeric precursor membrane prepared at different polymer concentration

The formation of C-H aroma monosubstituted benzene can be known with the magnitude of bands lies in the range between 719.97 up to 882.24 cm^{-1} while the value of wavelengths between 2718.08 to about 3880.65 cm^{-1} represents imide groups with the symmetric and asymmetric C=O stretching vibrations. The imide groups that consist of aliphatic C-N stretch give the magnitude bands from 1363.12 to 1663.47 cm^{-1} for all concentrations. Furthermore, the bands for the aromatic C=C bending vibration and C-N-C transverse stretch polymeric membrane are from 1506.71 to 1808.35 cm^{-1} and from 993.57 to 1399.30 cm^{-1} respectively. Based on previous research,

the amide group with C=O stretch has bands at 3461 cm^{-1} while amide group with C-N stretch or/and N-H bend has bands approximately 1339 cm^{-1} (100) [25]. For 18wt.%, it is noticeable that the peaks intensify greatly at 600 cm^{-1} and 1650 cm^{-1} compared to other membrane concentrations due to its composition is too high which it takes almost 30 hours to be diluted.

The FTIR results show that there is no noticeable bond in the range between 400 to 3900 cm^{-1} compared to polymeric membranes. Other than that, it is reported that the chemical structure and bond deconcentrates and breaks at carbonization temperature. The characterization of other polymers structure that has been modified corresponding to the thermal history has been studied by Ismail [31]. The finding shows that for all carbon membranes, there is a drastic reduction of peaks in higher polymer concentration during the carbonization process. The transmission intensity decreases because the structure of the membrane becomes compact and closer to the ATR crystal interface [32]. To conclude, the carbonization process is not dependent on the type of polymer concentration used where the carbonization will occur in any polymer concentration.

3.3 Gas Permeation Characteristics

The gas permeation properties of carbon membrane fabricated at different polymer concentration is shown in Table 1. As the polymer concentrations increase between 5 wt.% to 15 wt.%, the permeation properties for all gases increase. Densification may occur because of the increasing polymer concentration that causes the reduction of permeance for all gases. However, it is observed that the selective layers are well-combined and there is no addition in the mass transport resistance as for the tested gases [5]. In contrast, for higher polymer concentration which is 18 wt.%, the permeance for all gases decreases. This is due to the occurrence of polymer chain entanglement and its compaction structure under the condition greater than ideal concentration [33].

Table 1 Gas Permeation Properties of the Matrimid–based Carbon Tubular Membrane prepared at different polymer concentration.

Carbon membrane	Permeance (GPU)		Selectivity
	H$_2$	N$_2$	H$_2$/N$_2$
CM-5 wt%	1156.44±1.34	3.45±1.88	335.20±3.42
CM-10 wt%	1170.35±1.23	3.40±2.51	344.22±2.63
CM-13 wt%	1189.78±2.41	3.37±1.53	353.05±3.37
CM-15 wt%	1247.37±1.52	3.11±3.59	401.08±2.56
CM-18 wt%	1209.44±1.86	3.35±3.59	361.03±3.12

The results show that the carbon membrane execute high performance compared to the polymeric membrane. It was observed that the prepared membrane become more selective as the polymer concentration increase, with exception of 18wt%. Since kinetic diameter of H$_2$ (2.89Å) are relatively smaller than N$_2$ (3.8Å), the increase in H$_2$ permeance are more prominent. As a result, H$_2$/N$_2$ selectivity increase as polymer concentration increase up to 15wt%. The selectivity of the prepared carbon membrane starts to decrease at polymer concentration of 18wt% due to subtraction collapse and form unselective voids. The results reveal that the most suitable and ideal polymer concentration for the preparation of carbon membrane was 15wt% of Matrimid in which it gives the best performance in term of both permeablity and selectivity. Similar results of the same concentration were reported by Favvas's group, which they used carbon hollow fibre

membranes based on Matrimid 5218 precursor. In addition, the results conclude that the H_2/N_2 have high selectivity characteristic due to the tighter structure provided by the linkages among the macromolecules as similar reported by Hosseini and co-workers [5]. Therefore, in order to investigates the effect of carbonization temperature, the polymer membrane prepared from 15wt% of Matrimid was used.

4.0 CONCLUSIONS

In completion, the carbon membrane was believed as the alternative for the separation process in near future. The use of carbon tubular membrane also shows that the characteristic and properties of carbon are the advantage for separation process compared to the other membrane material based on the research conducted using two gases such as H_2 and N_2. In this way, the future work for the carbon membrane should be working on in order for its commercialization. Carbon tubular membrane was successfully fabricated and characterized in terms of structural morphology properties. The result shows that all the carbon tubular membrane was dense structure. Polymer solution containing 15 wt% Matrimid shows the best formulation for the carbon tubular membranes preparation.

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