# GAS PERMEATION PROPERTIES AND CHARACTERIZATION OF MATRIMID BASED CARBON TUBULAR MEMBRANE

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# ABSTRACT

Carbon membranes offer high potential in gas separation industry due to its highly selective. Therefore, this study aims to investigate the effect of carbonization parameter such as polymer composition, carbonization temperature, and carbonization environment on the gas separation properties. Polyimide (Matrimid 5218) was used as a precursor for carbon tubular membrane to produce high quality of carbon membrane via carbonization process. The polymer solution containing 5wt%, 10wt%, 13wt%, 15wt%, and 18wt% of Matrimid are prepared based carbon tubular membrane. The polymer solution was coated 3 times on the surface of tubular ceramic tubes by using dip-coating method. Dip-coating technique offer high potential in fabricating defect free carbon membrane. The polymer tubular membrane was then carbonized under nitrogen or argon atmosphere at temperature of 600, 750, and 850 $^{o}$C with heating rate of 2 $^{o}$C/min. Matrimid-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), thermal gravimetric analysis (TGA), and pure gas permeation system, respectively. From the results, it is found that the best polymer composition was 15wt% while the best carbonization temperature for the preparation of carbon membrane-based Matrimid 5218 was at 850 $^{o}$C. The highest $CO_2/CH_4$ and $CO_2/N_2$ selectivity of 83.30 and 75.73, was obtained for carbon membrane prepared under nitrogen environment. Meanwhile, for carbon membrane prepared under argon environment, the highest $CO_2/CH_4$ and $CO_2/N_2$ selectivity of 87.30 and 79.69, respectively, was achieved. The result indicated that the performance of the carbon tubular membrane can be controlled by varying the carbonization environment.

# ABSTRAK

Membran karbon menawarkan potensi yang tinggi dalam industri pemisahan gas kerana sifatnya mempunyai kepemilihan yang tinggi. Oleh itu, objektif kajian ini ialah untuk mengkaji kesan parameter pengkarbonan seperti komposisi polimer, suhu pengkarbonan dan persekitaran pengkarbonan terhadap sifat pemisahan gas. Polimida (Matrimid 5218) telah digunakan sebagai bahan utama bagi tiub membran karbon untuk menghasilkan membran karbon yang berkualiti tinggi melalui proses pengkarbonan. Larutan polimer yang mengandungi 5wt%, 10wt%, 13wt%, 15wt%, dan 18wt% Matrimid disediakan berdasarkan tiub membran karbon. Larutan polimer telah disalut 3 kali pada permukaan tiub seramik dengan menggunakan kaedah penyalutan celup. Kaedah penyalutan celup menawarkan potensi yang tinggi dalam menyediakan membran karbon yang sempurna. Polimer membran karbon kemudiannya dikarbonkan di bawah persekitaran gas nitrogen atau gas argon pada suhu 600, 750, dan 850 ºC dengan kadar pemanasan 2 ºC / min. Tiub membran karbon berasaskan Matrimid kemudian dicirikan dari segi struktur morfologi, struktur kimia, kestabilan terma, dan sifat-sifat penelapan gas dengan menggunakan mikroskopi imbasan elektron (SEM), spektroskopi inframerah (FTIR), analisis gravimetri terma (TGA), dan sistem penelapan gas tulen. Daripada keputusan kajian, didapati bahawa komposisi polimer yang terbaik adalah 15wt% manakala suhu pengkarbonan yang terbaik untuk penyediaan karbon membran berasaskan Matrimid 5218 adalah pada 850 ºC. Nilai tertinggi kememilihan untuk $CO_2/CH_4$ dan $CO_2/N_2$ ialah 83.30 dan 75.73, yang telah diperolehi daripada membran karbon yang disediakan di dalam persekitaran gas nitrogen. Sementara itu, bagi membran karbon yang disediakan di dalam persekitaran gas argon, nilai tertinggi kepemilihan yang untuk $CO_2/CH_4$ dan $CO_2/N_2$ ialah 87.30 dan 79.69. Keputusan yang diperolehi menunjukkan bahawa prestasi tiub membran karbon boleh dikawal dengan mengubah persekitaran pengkarbonan.

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# LIST OF SYMBOLS AND ABBREVIATIONS

$CO_2$ - Carbon dioxide
$H_2$ - Hidrogen
$O_2$ - Oxygen
$N_2$ - Nitrogen
$CH_4$ - Methane
SEM - Scanning electron microscopy
FTIR - Fourier transform infrared spectroscopy
TGA - Thermogravimetric analysis
TADS - Thermal analysis data station
$H_2S$ - Hydrogen sulfide
$H_2O$ - Water
KBr - Potassium bromide
PI - Polyimide
PPO - Polyphenylene oxide
PEI - Polyetherimide
PAN - Polyacrylonitrile
PFA - Polyfurfuryl alcohol
PVDC-AC - Polyvinylidene chloride-acrylate terpolymer
NMP - N-methyl-2-pyrrolidone
GPU - Gas permeation units
BTDA - 3, 3, 4, 4-benzophenone tetracarboxylic dianhydride

| | | |
|---|---|---|
| DAPI | - | 5(6)-amino-1-(4’-aminophenyl)-1,3-trimethylindane |
| $P$ | - | Permeability |
| $dp_P/dt$ | - | Pressure increase rate of permeate |
| $J_i$ | - | Permeate flux |
| $D$ | - | Diffusion coefficient |
| $dCi/dx$ | - | Concentration gradient |
| $T_g$ | - | Glass Transition Temperature |
| A | - | Membrane surface area |
| $(P/l)$ | - | Pressure normalized flux |
| Q | - | Volumetric flow rate |
| $i$ | - | Component i |
| $j$ | - | Component j |
| α | - | Selectivity |
| γ | - | Gamma |
| $\Delta p$ | - | Pressure difference |
| (SPPO) | - | Sulfonated poly(phenylene oxide) |
| 6FDA:BPDA-DAM | - | 6FDA dianhydride and DAM diamine monomers |
| Å | - | Kinetic Diameter |
| $AgNO_3$ | - | Silver nitrate |
| Ar | - | Argon |
| ASCM | - | Adsorption-selective carbon membrane |
| ATR | - | Attenuated total reflectance |
| C=C | - | Alkene |
| C=O | - | Carbonyl group |
| $C_5H_9NO$ | - | *N*-Methyl-2-pyrrolidone, *N*-Methyl-4-pyrrolidone, 4-Piperidinone, 2-Piperidinone |
| C-H | - | Alkane |

| | | |
|---|---|---|
| CM | - | Carbon Membrane |
| CMSM | - | Carbon molecular sieve membrane |
| C-N | - | Carbon–nitrogen bond |
| C-N-C | - | Alkane |
| CO | - | Carbon monoxide |
| ID | - | Internal Diameter |
| KBr | - | Potassium bromide |
| Kr | - | Krypton |
| N-H | - | Hydrogend Bond |
| OD | - | Outer Diameter |
| PBI | - | Poly(benzimidazole |
| PEG | - | polyethylene glycol |
| PES | - | Polyethersulfone |
| PMDA | - | Pyromellitic dianhydride |
| SPAEK | - | sulfonated poly(aryl ether ketone) |
| $TiO_2$ | - | Titanium Dioxide |
| $ZrO_2$ | - | Zirconium Dioxide |

# LIST OF APPENDICES

# CHAPTER 1

# INTRODUCTION

## 1.1 Background of the study

There are lots of membrane definitions proposed in the literature [1]. A selective barrier between two phases is a general definition of membrane and can be classified into biological and synthetic membranes[2-3]. The synthetic membranes can be classified into organic (polymer or liquid) and inorganic membranes while biological membranes is a separating membrane that acts as a selectively permeable barrier within living things. Membrane process is a process that uses membrane to achieve particular separation[4]. Membrane processes can also be categorized according to the driving force as shown in Table 1.1. As among those processes; membrane for gas separation process has the highest growth percentages from past decades. The continuity in development of membrane for gas separation process has been research by Baker, R.W.[5].

Membrane might be restricted into two categories depending to its structure or morphologies (symmetric and asymmetric). The determinations of the total membrane are from the thickness performance of the symmetric membranes. The thicknesses of symmetric membranes are around 10 up to 200 µm. The membrane thicknesses need to be decrease in order to increase the permeation ratio. In contrast, an asymmetric membrane involve of very solid top layer or skin with a thickness of 0.1 to 0.5 µm supported by a porous sub layer with a thickness about 50 up to 150 µm[6].

Table 1.1: Type of membrane process

| **Driving Force** | **Type of Membrane process** |
|---|---|
| **Pressure** | Gas separation, Reverse Osmosis, Ultrafiltration, Nanofiltration and Microfiltration. |
| **Concentration** | Dialysis, Controlled release, Donan dialysis |
| **Partial pressure** | Vapor Separation, Pervaporation |
| **Electrical Potential** | Membrane Electrolysis, Electrodialysis, Energy conversion |

Membrane technologies are used in a number of industrial processes such as the purification of $H_2$; the production of $O_2$ enriched air, separation of $CO_2$ and $H_2O$ from natural gas, and recovery of vapors from vent gases. Among these separation processes, separation of $CO_2$ from natural gas is the most emerging application because its emission is strongly associated with the industrial development and with the energy production from fossil sources which, and up to now, it cannot be substituted by any other sources except by nuclear energy[7]. Due to the economic risks involved in treating larger streams, initial acceptance was slow and limited to smaller streams. This is because of the general downturn in the oil and gas industry in the 1980s[8]. Membrane separation compromises an encouraging alternate towards conservative separation technologies for example the separation of $CO_2$ by amine absorption from light gases [8-9].

The separation of natural gas by thin barriers termed as membranes is a productive and promptly expanding, and it has been verified to be economically and technically excellent to additional appearing tools[2]. Recently, the membrane gas separation technology has prominently progressive and nowadays can be marked as a competing industrial gas separation technique[10]. The two furthermost significant parameters which can be determined by permeation measurement are the permeance and selectivity. Permeance is a measure of the amount of permeates that permits throughout a certain membrane area in a specified time and pressure difference, while the selectivity is a measure of the membrane quality. In this study, single gas permeation measurement was used in order to estimate the gas permeation properties of the carbon tubular membranes.

Nowadays, membranes processes are very important in the industry, for example in medical applications or separation of petrochemicals and waste water treatment. Conventional separation methods used for purification of chemical products, extraction, crystallization, and notably distillation are energy and cost intensive. The advantages contributed by membrane gas separation are its simplicity in operation that can be fitted easily onto the power plant without requiring complicated integration and no need to add chemical or to regenerate an absorbent or adsorbent[11]. To date, extensive schemes on polymeric membrane remain broadly applied in dissimilar separation methods besides require conquered the membrane market in the worldwide[12]. Polymide membrane can gives better separation plus satisfactory permeation flux. Yet, in the harsh environment, polymeric membranes are not right to be used for instance those prone towards erosion are high temperatures operation. As a result, inorganic membranes have rapidly received global attention in being considered as one of the potential candidates to replace available polymeric membranes.

Polymeric membranes as Matrimid 5218 are widely used in the membrane separation process due to their process ability, flexibility and of course low cost[13]. Superior membrane stability and durability, high permeation flux and selectivity and low production cost are always the most important criteria when developing a membrane for a specific separation[14]. In membrane processes, the permeability and selectivity are the most basic properties of a membrane that need to be considered. An important concern in membrane gas separations is to produce a membrane that is economically feasible while maintaining a high permeability and selectivity with good mechanical and thermal stability[15]. However, some limitations of thermal and mechanical stability need to be considered of the existing commercial polymers. It has been reported that the permeability's obtained with carbon membranes are much higher than those typically found with polymeric membranes, and these selectivity's are achieved without sacrificing productivity. Furthermore, carbon membranes show higher thermal and chemical stability. These features make the development of this type of membrane attractive for industrial gas separation systems[16].

Previous researcher stated that when the driving force (pressure ratio) was lower, the selectivity results was higher and the separation process said to be more appropriated; in fact, the operating costs for the separation system also lower[4]. When the permeability was higher, the cost of the system was lowered and the membrane needed was also small. In order to surpass Robeson's upper bound,  various researchers have been conducted. Previous membrane researchers mention that membranes which have the potential to exceed such upper bound were inorganic membranes. Therefore, ultramicroporous (0.3–0.5 nm) membranes such as carbon membranes have shown their promising performance[17]. Carbon membranes also lack of being damaged in thermal cycles and easily handle at high temperatures when work with supported ceramic membrane. High permeation flux and high selectivity are essential requirements for a successful membrane[18].

According to the literature, carbon membranes have continuously earned world attention and considered as one of future nominee to replace any others membrane such as polymeric membranes. There are a lot of studies of carbon membranes such as membrane synthesis, characterization, membrane fabrication, and theoretical modeling have been done to get a superior membrane performance[19]. As a result, the interest in carbon membrane application in various separation developments has been increased.

## 1.2 Problem Statement

Polymeric membranes seem to have several disadvantages that limit their industrial applications, since the performance of polymeric membranes would deteriorate with time when they are used in harsh environment[20]. The inadequacies of polymeric membranes in separation process have encouraged the researchers to study carbon membrane. This is because of their mechanical strength, high thermal and chemical resistance and higher pore volume with high separation factors, as compared to polymeric membrane. In early 1980s, carbon membranes produced from the carbonization of polymeric materials have proved to be very effective for gas separation by Koresh and Soffer[21] as well as Kapoor and Yang[22]. The pore dimensions of the prepared carbon membrane can be fined by controlling the carbonization conditions. Carbon membrane has been identified as a solution for the challenges faced by the current membrane technology[23]. It offers a good combination of permeability-selectivity trade-off and the separation maintained in the environment that was prohibited by polymeric membranes previously.

Carbon membranes are very brittle and fragile. Without any support, it will not easily operate in the system. The most common substrate used by the previous researchers are $\alpha$-$Al_2O_3$[24], TiO2-ZrO2 macroporous tubes[25], and porous graphite[26]. When a supporting substrate is used for the development of carbon membrane, the substrate must be chemically and physically stable and possess a diffusion resistance, which is lower than that of the carbon membrane. Tubular substrates are mechanically stronger against a compressing pressure than flat substrates. In this study, a ceramic tube is used as a supporter to overcome the brittleness of the carbon membranes. It is due to high thermal resistance; which necessary to sustain high carbonization temperature and chemically stable against various solvent [27].

Different process condition will result in different structure of carbon membrane and gas permeation performance. There are many types of precursor that have used by previous researchers to develop carbon membrane with better selectivity and permeability. In fact, it is well known that the membrane performance appears to be a trade-off between a selectivity and permeability, for example, a highly selective membrane tends to have low permeability[28]. Therefore, in order to prepare a good performance of carbon membrane, several process parameters was manipulated in this study. It is involving the manipulation of polymer composition, carbonization temperature, and carbonization environment.

## 1.3 Objectives

Based on the research background and the problem statements above-mentioned, the objectives of this study are:

1. To fabricate and characterize Matrimid-based carbon tubular membrane in terms of its thermal stability and structural morphology properties.

2. To study the effect of process parameter (polymer composition, carbonization temperature and carbonization environment) on the gas separation performance ($CO_2/CH_4$ and $CO_2/N_2$ separation).

## 1.4 Scope of the Study

In turn to achieve the above mentioned objectives, the subsequent scopes of works have been drawn:

1. The polymer solution formulation (5wt%, 10wt%, 13wt%, 15wt%, and 18wt %) is fabricated for polymer tubular membrane.
2. The polymer tubular membrane is fabricated by using 3 times dip-coating process.
3. The thermal and structural properties of the polymer tubular membranes is characterize using thermal gravimetric analysis (TGA), scanning electron microscopy (SEM), and Fourier transform infrared (FTIR) .
4. The carbon tubular membrane is prepared by heat treatment process.
5. The thermal and structural properties of the carbon tubular membranes is characterized using thermal gravimetric analysis (TGA), scanning electron microscopy (SEM), and Fourier transform infrared (FTIR) .
6. The effect of polymer composition (5wt%, 10wt%, 13wt%, 15wt%, and 18wt %), carbonization temperature (600 °C, 750°C, and 850 °C) and carbonization environment (Nitrogen or Argon gas) is studied on the gas separation performance.

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