DISK SUPPORTED CARBON MEMBRANE DERIVED FROM BASED POLYMER POLYIMIDE FOR CARBON DIOXIDE RELATED SEPARATION

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I am dedicating this work to myself, both of my dearest parents:
Mr. Ismail bin Kasa and Mrs. Fatimah binti Sharif
my siblings, in-laws, nephews and nieces
who nurtured me with their endless love, trust, constant encouragement and prayers
throughout the succession of my study

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ABSTRACT

Carbon membrane is known as a promising alternative for gas separation and has commonly been used for carbon dioxide (CO_2) separation. However, the challenge for the carbon membrane to be practically used is the difficulty of getting a good mechanical strength and defect-free membrane. In this study, a 4,4’-benzophenone tetracarboxylic dianhydride and 80% methyl phenylene- diamine plus 20% methylene diamine known as P84 were selected as the polymeric precursors and porous alumina disk as the supporting material. P84 has a superior gas separation performance, while the supporting material enhanced the mechanical strength of the carbon membrane. The preparation of the carbon membranes involved two main steps, which were polymeric membrane preparation and carbonization process. The polymeric membrane was prepared by a spray coating technique to obtain thin and defect-free carbon membrane layer. The carbon membrane was prepared at 600 to 900 °C under nitrogen (N_2) gas flow of 200 mL/min and heating rate of 3 °C/min. The alumina powder was utilized as an intermediate layer to decrease the penetration of the polymer solution within the porous alumina supporting material. The optimum composition of polymer precursor was studied to determine the best polymer formulation for disk-supported carbon membrane. During the carbonization process, the effect of carbonization temperature was investigated. The properties of the fabricated carbon membrane were characterized and analyzed in terms of their morphological structure and thermal properties. Pure gas permeation tests using pure gases (CO_2, N_2 and methane (CH_4)) were conducted at a room temperature and 4 bars. The CO_2/N_2 and CO_2/CH_4 selectivity of 24.54 and 65.43, respectively, were obtained for carbon membrane prepared with 12 wt% of the P84 by utilizing alumina powder as intermediate layer and after it was carbonized at 800 °C. As a conclusion, the disk supported carbon membrane was successfully fabricated and able to facilitate the development of gas purification technology.

ABSTRAK

Membran karbon dikenali sebagai salah satu alternatif yang berpotensi bagi pemisahan gas dan lazimnya digunakan untuk pemisahan karbon dioksida (CO_2). Walau bagaimanapun, cabaran utama untuk membran karbon digunakan ialah kesukaran untuk mendapatkan membran karbon yang mempunyai kekuatan mekanikal yang baik dan membran tanpa kecacatan. Dalam kajian ini, 4, 4 '-benzofenon tetrakarboksilik dianhidrida dan 80% metil fenilena-diamina ditambah 20% metilena diamina yang dikenali sebagai P84 telah dipilih sebagai pelopor polimer dan cakera alumina berliang sebagai bahan sokongan. P84 mempunyai prestasi pemisahan gas yang unggul, sementara bahan sokongan dapat meningkatkan kekuatan mekanikal membran karbon. Penyediaan membran karbon melibatkan dua langkah utama iaitu penyediaan membran polimer dan proses pengkarbonan. Membran polimer telah disediakan menggunakan teknik salutan semburan bagi mendapatkan membran karbon yang nipis dan lapisan tanpa kecacatan. Membran karbon ini disediakan pada suhu 600 hingga 900 °C di bawah aliran gas nitrogen (N_2) pada 200 mL/min dan kadar pemanasan pada 3 °C/min. Serbuk alumina telah digunakan sebagai lapisan perantaraan untuk mengurangkan larutan polimer daripada menembusi bahan sokongan alumina yang berliang. Komposisi optimum pelopor polimer telah dikaji untuk menentukan formulasi terbaik membran karbon dengan sokongan cakera. Semasa proses pengkarbonan, kesan suhu pengkarbonan telah disiasat. Sifat-sifat membran karbon telah dicirikan dan dianalisa dari segi struktur morfologi dan sifat haba. Ujian penelapan gas tulen (CO_2, N_2 dan metana (CH_4)) telah dijalankan pada suhu bilik dan pada tekanan 4 bar. Kememilihan CO_2/N_2 dan CO_2/CH_4 yang diperoleh masing-masing adalah 24.54 dan 65.43 untuk membran karbon yang disediakan dengan 12% berat P84 dengan menggunakan serbuk alumina sebagai lapisan pertengahan dan selepas dikarbonkan pada suhu 800 °C. Kesimpulannya, membran karbon dengan sokongan cakera telah berjaya dihasilkan dan dapat membantu dalam pembangunan teknologi penulenan gas.

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LIST OF ABBREVIATIONS

A	-	Area
Al_2O_3	-	Aluminium Oxide
ATR	-	Attenuated Total Reflectance
BET	-	Brunauer–Emmett–Teller
CA	-	Cellulose Acetate
CH_4	-	Methane Gas
C_2H_4	-	Ethylene
C_3H_6	-	Propene
CM	-	Carbon Membrane
CMS	-	Carbon Molecular Sieve
CO	-	Carbon Monoxide
CO_2	-	Carbon Dioxide
C-N	-	Nitrile
FTIR	-	Fourier Transform Infrared
h	-	Hours
H	-	Hydrogen atom
H_2	-	Hydrogen Gas
HBPI	-	Hyper Branched Polyimides
HCN	-	Hydrogen Cyanide
He	-	Helium Gas
KBr	-	Potassium Bromide
SEM	-	Scanning Electron Microscopy
MEA	-	Monoethanolamine
MFI	-	Modernite Frame-work Inverted (zeolite)
MMM	-	Mixed Matrix Membrane
N_2	-	Nitrogen
NH_3	-	Ammonia

Ni - Nickel
NMP - N-Methyl-2-pyrrolidone
O_2 - Oxygen Gas
O-H - Hydroxyl Group
O=C-N - Cyanate
OMC - Ordered Mesoporous Carbon
ΔP - Differential Pressure
P84 - Co-polyimide BTDA-TDI/MDI
PAN - Polyacrylonitrile
PBI - Polybenzimidazole
PDMS - Polydimethylsiloxane
PEG - Polyethylene Glycol
PEI - Poly (ethylenimine
PFA - Poly(furfuryl alcohol)
PFR - Phenol Formaldehyde Resin
PI - Polyimide
PPESK - Poly(phthalazinone ether sulfone ketone)
PPO - Poly(p-phenylene oxide)
PPSU - Polyphenylsulfone
PVDC - Poly(vinylidene chloride)
PVP - Polyvinylpyrrolidone
Q - Volumetric Flow Rate
STP - Standard Temperature and Pressure
RTIL - Room Temperature Ionic Liquid
SPPO - Sulfonated Poly(phenylene oxide)
s - Seconds
SiC - Silicon Carbide
TGA - Thermal Gravimetric Analysis
T_g - Glass Transition Temperature
T_d - Thermal Decomposition Temperature
TiO_2 - Titanium Dioxide
XRD - X-ray Diffraction

LIST OF SYMBOLS

Å - Angstrom
γ - Gamma
π - Pi
ω - Omega
λ - Lambda
θ - Theta
α - Alpha
μ - Mu
° - Degree
°C - Celsius
% - Percentage
wt% - Weight Percentage

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CHAPTER 1

INTRODUCTION

1.0 Research Background

The significant increase in emissions of greenhouse gases in the atmosphere especially carbon dioxide (CO_2) has contributed towards the global warming. Generally, CO_2 emission was mostly cause by the combustion of fossil fuels for energy and industrial processes that will increase the acidic gases in the atmosphere (Adewole *et al.*, 2013). Thus, further action is required to overcome this matter by implement a technology that cost effective and energy efficient. One of the solutions for addressing this issue is by capturing acidic gases, which requires adoption of advanced technologies, such as membrane technology.

Since the 1980s, the research community has realized the potential of utilizing membrane technology in the industrial and environmental field as it possesses the ability to separate acidic gases such as carbon monoxide (CO), carbon dioxide (CO_2) and hydrogen (H_2). Generally, membranes are favorable for its low-cost production, reduction of equipment size and no hazardous chemicals been applied (such as solvent absorption technology). These unique properties make them practically attractive for separation of carbon dioxide (Kenarsari *et al.*, 2013).

Polymer membrane has been widely used around the world for various applications such as beverage processing, water purification, gas separation and medical devices. In the industry, most processes are applied at high operating temperature and pressure which is not a suitable condition for polymer membranes as they are commonly poor in chemical and thermal resistance (Bhuwania *et al.*, 2014;

Rodrigues *et al.*, 2014). Thus, there is a need to seek alternative membrane technology and carbon membrane was one of the candidate that has superior thermal and chemical resistance, which is applicable for gas separation with high operating conditions. Carbon membrane was discovered by Koresh and Suffer in the 1980s shows the potential of this inorganic porous type of membrane, along with ways to improve and enhance its performance (Ismail and David, 2001).

Carbon membrane which is fabricated by carbonizing polymer precursor beyond its decomposition temperature is one of the promising membrane that can give high performance in terms of its selectivity as proved from the Robeson "upper bound" line. Favvas *et al*., (2007) stated that carbon membrane exhibits high thermal and chemical stability and have great performance characteristics compared to polymeric membranes. The amorphous structure and pores formed from packing imperfections and an idealized pore structure gives a massive effect to the carbon membrane morphological structure (Bhuwania *et al.*, 2014; Hosseini *et al.*, 2014). The parameters controlled during the carbonization process (atmosphere, temperature, heating rate and gas flow) play the most crucial part in fabricating the carbon membrane.

The advantage of carbon membranes which can operate in a harsh environment, has drawn attention of industrial practitioners as it is one of the inorganic membranes that shows outstanding role in gas separation. The molecular sieving capability of carbon membranes is derived from an ultra micropore structure with dimensions close to the permeating gas molecules which contributes towards accomplishing the selectivity requirement (Li *et al.*, 2014).

1.1 Problem Statement

The polymeric solution that is directly coated on the supporting material tend to penetrate within the alumina pores and affect the gas performance of the carbon membrane as it increases the mass transfer resistance of the gas flow through the membrane. One of the option to minimize the deep penetration in the porous alumina supporting material is by adopting an intermediate layer. These intermediate layers lessen the penetration of polymeric solution and at the same time reduce the formation of defects on the membrane surface (Tseng *et al.*, 2016). The essential part employing intermediate layer is to concern about the compatibility of the intermediate layer towards the membrane layer and supporting material. In this study, alumina powder, carbon molecular sieve (CMS) and carbon pencil were utilized as the intermediate layer for carbon membrane preparation. The compatibility of the intermediate layer was determined based on the morphological structure and gas separation performance.

Achieving thin defect-free polymer coatings on the porous support is a prerequisite to produce thin carbon membranes that exhibit both high gas permeances and selectivity. Air spray with one-step spray coating-carbonization was applied as it can produce an ultra-thin selective layer which can provide high selectivity without deteriorating the gas permeability. Furthermore, it is convinced that the spray coating method have a high potential for reproducibility of a thin and uniform carbon membrane layer (Acharya and Foley, 1999). The concentration of the polymeric solution affect the distribution of the polymeric membrane on the supporting material. Thus, the polymer precursor weight percentage composition was study to produce smooth surface layer of the polymeric membrane.

Carbonization conditions is one of the essential parameters that give a massive impact on the morphological structure of the carbon membrane. Centeno *et al.*, (2004) stated that every increment of the temperature change, influenced the pores structure of the carbon membrane. Generally, the carbon membrane pores start to change when 500 °C to 600 °C of carbonization temperature applied (Zainal *et al.*, 2017). Further increase of carbonization temperature at 700 °C to 800 °C, enlarges the pores size. While at 900 °C to 1000 °C, the pores start to narrow down and vanish as the carbonization temperature increase. However, this carbonization temperature depends on the polymer precursor properties as it gives the consequences towards the morphological structure of the carbon membrane. Hence, the effect of the carbonization temperature was investigated to obtain the optimum conditions for the carbon membrane fabrication.

1.2 Objective of Study

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

1. To select the best intermediate layer for the carbon membrane based on the SEM images and gas permeation performance of the disk-supported carbon membrane.
2. To study the effect of polymer compositions towards gas permeation performance of the disk-supported polymeric and carbon membrane based on morphological and thermal analysis.
3. To examine the effect of carbonization temperature on gas permeation performance and thermal analysis of the disk-supported carbon membrane.

1.3 Scope of Study

In order to accomplish the above-mentioned objectives, the following scope of work was carried out:

i) Fabricating intermediate layers (alumina powder, CMS and carbon pencil) on the porous alumina surface by rubbing the materials using rubber gloves.
ii) Preparing a dope solution with various polymer compositions of 6 wt%, 9 wt%, 12 wt% and 15 wt%.

iii) Fabricating a disk-supported membrane via spray coating technique at 1 bar and a room temperature. The distance of the nozzle and alumina disk was 20 cm.

iv) Preparing the disk-supported carbon membrane by a heat treatment process at various carbonization temperatures (600, 700, 800 and 900 °C) under nitrogen (N_2) atmosphere.

v) Characterizing the fabricated polymer and carbon membrane properties by using Thermal Gravimetric Analysis (TGA), Elemental Analysis, Fourier Transform Infrared (FTIR), X-ray Diffraction (XRD), N_2 adsorption (BET) and Scanning Electron Microscopy (SEM).

vi) Conducting a pure gas permeation test using carbon dioxide (CO_2), methane (CH_4) and nitrogen (N_2).

1.4 Significance of Study

The carbon membrane was studied due to its superior gas separation performance compared to other membrane technologies as proved in the Robeson Chart 2010 upper bound line. The disk supported carbon membrane was introduced in this study via one-time spray coating-carbonization method. This coating method will give high effect to the adhesion mechanism of the carbon membrane and its supporting material. Moreover, the defect on the supporting material can be reduce by utilizing spray coating and at the same time obtain good gas separation performance. Therefore, this study has focused in gas separation of CO_2 which gives unpleasant effects towards the environment, equipment and human health. The data obtained from this research will be beneficial for CO_2 capturing. It is hoped that this finding can serve as a scientific platform for researchers and engineers to develop a viable and practical carbon membrane for gas separation processes in the future.

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