ZEOLITIC IMIDAZOLATE FRAMEWORK 8 INCORPORATED DUAL LAYER HOLLOW FIBER MEMBRANE FOR NATURAL GAS PURIFICATION

MA XUEFENG

A thesis submitted in partial fulfilment of the
requirements for the award of the
Master of Gas Engineering And Management

School of Chemical and Energy Engineering
Faculty of Engineering
Universiti Teknologi Malaysia

JANUARY 2020

ACKNOWLEDGEMENT

I would like to express special gratitude to author's parents and siblings for continuous love, support and motivation toward completing the study. In preparing this thesis, I was in contact with many people, researchers, academicians, and practitioners. They have contributed towards my understanding and thoughts. In particular, I wish to express my sincere appreciation to my thesis supervisor, Assoc. Prof. Ts. Dr. Mohd Hafiz Dzarfan Othman, for encouragement, guidance, critics and friendship. I am also very thankful to my coordinator Dr. Farhana Aziz for guidance, advices and motivation. Without their continued support and interest, this thesis would not have been the same as presented here.

I am deep gratitude is addressed to Roziana kamaludin, Sumarni mansur, Zhong Sheng Tai, Wong Kar Chun, Zhi Chien Ng, and all the AMTEC laboratory personnel who have directly or indirectly assisted the authors in completing the research.

ABSTRACT

The main purpose of this work was studied the effect of ZIF-8 loading on the physical and chemical properties of dual-layer hollow fiber (DLHF) mixed matrix membranes (MMMs). In addition, the effect of the outer dope extrusion rate (DER) of the spinning on the selective layer thickness of the DLHF membrane was investigated. Finally, the gas separation performance of the coated DLHF membranes under different ZIF-8 loading and outer DER was evaluated. The recipe for the prepared DLHF membrane is: polysulfone (PSf) as polymer, N, N-dimethylacetamide (DMAc) and tetrahydrofuran (THF) as solvents, and at the same time, the metal organic framework (MOF) ZIF-8 Only added to the outer solution. Then, the solution was co-extruded through triple orifice spinneret in order form dual layer structure of membrane, where the inner layer was consists of pure PSf and the outer layer were the PSf and ZIF-8. Field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), Thermogravimetric analysis (TGA) and Scanning electron microscopy (SEM) were used to analyse the ZIF-8 material and to detect DLHF membranes. The main findings that obtained from this research are as below: (1) Zeolite imidazole framework8 (ZIF-8) nanoparticles were successfully synthesized in aqueous solution with a particle size of 86.25 nm. (2) Successfully prepared DLHF membrane with high heat resistance, good chemical stability and good interaction between polymer PSf and filler ZIF-8. (3) The optimal loading of ZIF-8 was 0.5wt%, and the CO_2 permeability increased dramatically by 61.19% compared to the neat membrane, and the selectivity of CO_2/CH_4 also improved significantly by 94.46%. (4) The experiment further concluded that when the outer DER was 1 ml/min, the prepared membrane was thin and no defects on the top skin layer. The good combination of ZIF-8 and PSf substrates and the appropriate outer DER explain the application and significance of the novel DLHF membrane.

ABSTRAK

Tujuan utama kerja ini adalah mengkaji kesan pemuatan ZIF-8 terhadap sifat-sifat fizikal dan kimia membran matriks bercampur dwi-serat rongga (DLHF). Di samping itu, kesan kadar penyemperitan dadah luar (DER) yang berputar pada ketebalan lapisan terpilih membran DLHF telah disiasat. Akhirnya, prestasi pemisahan gas membran DLHF bersalut di bawah pemuatan ZIF-8 yang berbeza dan DER luar telah dinilai. Resipi membran DLHF yang disediakan ialah polysulfone (PSf) sebagai polimer, N, N-dimetilacetamide (DMAc) dan tetrahydrofuran (THF) sebagai pelarut, dan pada masa yang sama, rangka organik logam (MOF) ZIF-8 kepada penyelesaian luar. Kemudian, larutan itu diekstrusi melalui tiga spinneret orifis untuk membentuk struktur lapisan dua lapisan membran, di mana lapisan dalaman terdiri daripada PSf tulen dan lapisan luar adalah PSf dan ZIF-8. Mikroskop elektron scanning emission field (FESEM), X-ray difraksi (XRD), analisis Thermogravimetric (TGA) dan Mikroskop elektron scanning (SEM) digunakan untuk menganalisis bahan ZIF-8 dan untuk mengesan membran DLHF. Penemuan utama yang diperolehi daripada penyelidikan ini adalah seperti berikut: (1) Rangka nanopartikel Zeolite8 (ZIF-8) berjaya disintesis dalam larutan berair dengan saiz zarah sebanyak 86.25 nm. (2) Membakar DLHF dengan berjaya dengan rintangan haba yang tinggi, kestabilan kimia yang baik dan interaksi yang baik antara polimer PSf dan pengisi ZIF-8. (3) Beban optimum ZIF-8 adalah 0.5%, dan kebolehtelapan CO_2 meningkat dengan ketara sebanyak 61.19% berbanding membran yang kemas, dan pemilihan CO_2/CH_4 juga bertambah baik dengan ketara sebanyak 94.46%. (4) Eksperimen selanjutnya menyimpulkan bahawa apabila DER luar adalah 1 ml / min, membran yang disediakan nipis dan tiada kecacatan pada lapisan atas kulit. Gabungan yang baik dari substrat ZIF-8 dan PSF dan DER luar yang sesuai menjelaskan aplikasi dan kepentingan membran DLHF novel.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

GHG	-	Greenhouse Gases
MMM	-	Mixed Matrix Membrane
DLHF	-	Dual Layer Hollow Fiber
SLHF		Single Layer Hollow Fiber
ZIF-8	-	Zeolitic Imidazole Framework 8
SOD	-	Sodalite
DER	-	Dope Extrusion Rate
MOF		Metal-Organic Framework
XRD	-	X-ray Diffraction
TGA	-	Thermogravimetric Analysis
FTIR	-	Fourier Transform Infrared Spectroscopy
SEM	-	Scanning Electron Microscopy
FESEM		Field Emission Scanning Electron Microscopy
EDX		Energy-dispersive X-ray spectroscopy
TEA		Triethylamine
MEA		Ethanolamine
DEA		Diethanolamine
PSf		Polysulfone
DMAc		N, N-dimethylacetamide
THF		Tetrahydrofuran
PEO		Polyethylene Oxide

LIST OF SYMBOLS

D	-	Crystal size (nm)
β	-	line broadening at half the maximum intensity in radians
θ	-	Diffraction angle of the peak
λ	-	X-ray wavelength of Cu Kα (0.1542 nm)
P/L	-	Gas permeance
Qi	-	Volumetric flow rate
ΔP	-	Pressure difference
A	-	Effective area (cm^2)
$\propto_{A/B}$		Selectivity of CO_2/CH_4

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Background of study

Natural gas is a naturally occurring hydrocarbon gas mixture mainly consisting of methane (CH_4) and carbon dioxide (CO_2) which is the by-product of the natural compression process that take billions of years ago inside the small rock that are located beneath the ground surface several miles away. Natural gas is a fossil fuel preferable world's energy source provides energy for heating, used in combined heat and power, electricity generation and also as a fuel for vehicles but it requires purification from impurities. Therefore, before use by consumers, natural gas must undergo a pre-treatment process to remove impurities such as CO_2 and hydrogen sulfide (H_2S), nitrogen, mercury, and even water content. CO_2 is one of the main greenhouse gases (GHG), which is emitted into the atmosphere through the burning of fossil fuels such as coal, oil and natural gas. (Hosseini and Wahid, 2013). Therefore, the removal of CO_2 is the most critical and important step in the purification of natural gas, because its presence can lead to corrosion of the pipeline, reduce the heating value and increase the maintenance time.

In the past half century, the use of gas separation membranes in the industry represents only a small fraction of potential applications. Most recent applications involve purifying or separating non-condensable gases, Several polymer membrane-based gas separation modules operate around the world and can be divided into four main applications, including separation of nitrogen from air, separation of carbon dioxide from natural gas, hydrogen recovery and vapor recovery (Karimi et al.,2019). There are four types of technologies which are commercially available on an industrial scale for purification of natural gas. Adsorption, physical and chemical absorption, membrane separation and cryogenic technique. For example, chemical absorption gives high CH_4 concentration >99% with low operational costs but high investment costs and heat is required for regeneration of solvent (Chen et al., 2015). In addition, membrane technology is very economic and low cost of maintenance but for high purity multiple steps are required (Baker and Lokhandwala, 2008; Zhao and Leonhardt, 2010).

Membrane materials are at the heart of membrane separation technology. The quality of the membrane directly affects its application prospects. The permeability coefficient and selectivity of the material are controlled by the Robeson upper limit. That is, an increase in the permeability coefficient results in a decrease in selectivity and vice versa. Therefore, scientists are insisting on the study of membrane materials with stable physical and chemical properties, high selectivity and high permeability. These properties depend on the composition, structure and chemical properties of the membrane material. According to the type of membrane material, separation membranes are mainly divided into three categories: inorganic membranes, organic polymer membranes, and mixed matrix membranes. According to the transfer mechanism, the organic polymer membrane can be further divided into a common polymer membrane (breathable membrane) to promote the transfer membrane and the gas liquid membrane contactor (Adewole et al., 2013).

Polymer membrane is a commercial type widely used for gas and liquid separation, because it offers high-performance separation with lower operating cost. It is extensively used for different separation applications like wastewater treatment, gas separation, seawater desalination, distillation and much more (Fakult and Hussain, 2013). Despite the many advantages, polymer membranes are limited by the trade-off between permeability and selectivity (Robeson, 2008). The trade-offs characterized as high permeability membranes are accompanied by low selectivity properties and vice versa. This factor is often considered to be a major key factor hindering its potential application in the separation process.

Therefore, the researchers have found an opportunity to develop a new class of membrane called mixed matrix membrane (MMM) which consists of the polymers and inorganic nanoparticles as a dispersed phase. Ideally, separation performance significantly increased due to the dispersion of inorganic nanoparticles into the polymer matrix (Chung et al., 2007). The nanoparticles dispersed in the polymer improve gas separation performance by (1) providing a path to hinder macromolecular penetration (Hudiono et al., 2010), (2) molecular sieve principle (Kwon et al., 2011), and (3) destruction of polymer chains (Zornoza et al., 2011), Polymer-filler compatibility is often considered a challenge in MMM development because it directly reflects the morphology, performance, and size of the membrane and, therefore, requires more development to fully exploit its potential.

From the last few years, the fabrication of dual-layer hollow fiber (DLHF) membranes has largely investigated topic for gas separation (Li et al., 2002; Widjojo et al., 2008; Li et al., 2006). It is economical process employ high-performance polymers as an outer layer to form composite hollow fiber membrane (Strathmann, 2001);(McKelvey et al., 1997). It is composed of a thin selective outer layer and porous supporting inner layer. However, the gas separation is mainly achieved by the dense selective layer. The outer layer generally provides the Permeability and selectivity, while the inner layer provides the required mechanical and thermal support. Therefore, economical polymers with good mechanical and thermal properties can be used for it. Following morphological aspects are also very important for an ideal dual-layer hollow fiber membranes, such as (1) the outer and inner layers of the DLHF membrane should not be delaminated (Widjojo *et al.*, 2008), (2) the structural frame of the inner layer must be porous to minimize gas transport resistance through the inner layer (Li et al., 2002a).

Co-extrusion is a process of making a multilayer membrane in a single step in which two or more polymer solutions are extruded through a single die and joined together at the triple orifice. The DLHF membranes fabrication by the co-extrusion technology serves as an innovative idea in its research and development. Dual-layer hollow fiber membranes prepared by the co-extrusion technique retain all the advantages of conventional single-layer hollow fiber membranes: (1) high membrane area per unit membrane module volume, resulting in a higher productivity; (2) highly selective and permeable layer could be formed by deploy brittle materials; and (3) good flexibility and ease of handling during module fabrication and system operation; (4) the DLHF membrane can form not only a selective structure on the outer layer but also a porous support frame in the inner layer. Therefore, co-extrusion is more attractive than conventional hollow fiber membrane (Sun et al., 2010).

Selection of outer layer and inner layer materials are an equally crucial factor to develop high-performance dual-layer membrane. To avoid interfacial delamination, polysulfone (PSf) is chosen as the material for both outer and inner layers because of its high mechanical and thermal characteristics. In addition, synthesized zeolitic imidazole framework 8 (ZIF-8) nanoparticles will be chosen as additives in the outer dope solution. The presence of phenylene unit in PSf linked with isopropylidene, ether, and sulfone, provides the polymer with good chemical resistance, thermal stability, and mechanical strength. For CO_2/CH_4 separation, PSf has an excellent balance between permeability and selectivity to CO_2 and has high plasticizing pressure. (PPlasticization ~ 34 bar (Bos et al., 1999)) while a relatively cheaper material has compensated itself as preferable continuous phase.

The uniform dispersion of inorganic nanoparticles in a dual-layer membrane is a formidable challenge because the low compatibility of the polymer filler results in the formation of macromolecules, thereby reducing the selectivity of the gas (Jiang et al., 2005). Compared to other fillers, the metal-organic framework (MOF) has been shown to have good affinity for polymer matrices without surface modification. MOF is a crystalline compound having metal ions and organic ligands as repeating units and systematically arranged in a frame. The presence of organic ligands in their structure provides a good interaction with the polymer matrix, thus greatly reducing the disadvantages.

Zeolitic imidazole frameworks (ZIFs) are a subclass of MOF and ZIF-8 is one of the newly synthesized types of ZIFs. In particular, ZIF-8 is one of the most studied prototypes of ZIFs due to its potential functional application of gas storage (CO_2, H_2 and acetylene), catalysis and gas separation. The ZIF-8 has a large hole of 11.6 Å and has a hole diameter of 3.4 Å through a small hole. It has a cubic space group (I-43 nm) and a unit size of 16.32 Å. It has a pore size of the sodalite (SOD) zeolite type structure which is about twice that of the corresponding SOD zeolite. Due to its highly porous open frame structure, it is easy to enter the organically linked edge and face of the pore volume which is completely exposed. With a range of kinetic diameters of gas molecules, and high CO_2 adsorption capacity, ZIF-8 is an attractive application for gas separation. In addition, it has been shown that ZIF-8 is a chemically stable aromatic hydrocarbon such as benzene in the presence of water. Making this particular ZIF component may be useful for separating CO_2 from CH_4 (Venna and Carreon, 2010).

Recently, it is very less concern has been devoted to ZIF-8 loading and outer DER. Therefore, the purpose of this study is to develop a defect-free product with coating and ZIF-8 uniformly dispersed MMM, and based on the effect of ZIF-8 loading and external extrusion rate on the performance of DLHF membranes. Thus, the main objective of this study is to study the effect of outer dope extrusion rate (DER) and ZIF-8 loading on the morphology of DLHF membranes. X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and field emission scanning electron microscopy (FESEM) techniques were used to characterize the structural of ZIF-8 and the prepared DLHF membranes. Finally, the selected ZIF-8-based DLHF membrane was applied to a membrane contactor to detect the selectively and permeance.

1.2 Problem statement

To choose suitable membrane materials is a primary requirement to fabricate high performance defect-free membranes with low cost, high thermal stability and plasticization resistance at elevated pressure. Most of the inorganic fillers are not compatible with the polymer phase and cause the occurrence of non-selective interfacial voids that leads to reducing the gas separation performance due to unselective pathways at the filler interfaces. Hence, it is necessary to investigate the common problems such as filler size and loading, compatibility with polymers, and gas separation performance in the MMMs. However, the available ZIF-8 possesses large particle sizes (particle size of ~300nm) and this will become a huge challenge for the ZIF-8 filler defect-free dispersion in the thin outer layer of DLHF. ZIF-8 is considerably expensive, Sigma Aldrich, one of the MOFs marketing companies, announced the ZIF-8 cost of RM 25,733 for 500g, relatively expensive compared to synthesis materials used in this research such as 2-methylimidazole (RM 652/kg), zinc nitrate hexahydrate (RM 13,256/kg) and base-type additive triethylamine (RM 263/500ml). Dual-layer hollow fiber membranes provide a solution for a wide range of applications for high performance but expensive materials compared to single layer membranes, because it only uses them for the selective outer layer instead of the whole membranes. Therefore, the choice of co-extrusion dual-layer technology is undoubtedly the most economical and flexible way.

However, the fabricate based ZIF-8/PSf dual-layer hollow fiber membrane with desired morphology and separation performance is still an important work. The effects of spinning parameters, such as spinneret temperature, air gap, draw ratios, bore fluid rate, coagulant temperature. This research found that the co-extrusion rate between the outer and inner layer also play a major role in the thickness of dual-layer membrane. Therefore, it should carefully be taken into consideration to produce desired thickness delamination-free dual-layer membranes. Also, different shrinkage rates of the outer and inner layers are the main cause of delamination. Different methods to reduce substructure resistance between the outer and inner layers may result in delamination due to a different shrinkage rate of these two layers during precipitation and solvent exchange (Li *et al.,* 2002b). To achieve desired morphology of DLHF membrane, control of both inner and outer dope solutions concentration and varying the co-extrusion rate process is important (Jiang *et al.,* 2004).

Therefore, this study is aimed to fabricate MMMs for CO_2 separation using synthesized ZIF-8. Furthermore, the effect of the different loading of fillers and feed pressures on the gas separation performance of prepared MMMs is evaluated. Moreover, the co-extrusion rate of dope solution on thickness of prepared MMMs membrane is evaluated. To date, the incorporation of ZIF-8 particles has primarily been subjected to the preparation of flat sheet membranes, whereas studies on ZIF-8 based DLHF membranes are rarely investigated.

1.3 Objectives of study

The major goal of this research was to produce dual layer mixed matrix hollow fiber membranes with ZIF-8 based materials as the filler via dry-wet phase inversion process with improve gas separation performance. The specific objectives of the study are as follows:

a) To investigate effect of ZIF-8 loading on the physical and chemical properties of dual-layer hollow fiber membrane.

b) To examine the influence of outer dope extrusion rate of the spinning on the DLHF membrane selective layer thickness.

c) To evaluate the gas separation performance of DLHF membrane at different ZIF-8 loading and outer dope extrusion rate.

1.4 Project Scope

The following research activities were selected as the scope of this study to achieve the above objectives:

a) Synthesizing ZIF-8 filler from zinc hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$,99% purity), 2-methylimidazole (Hmim, 99% purity) and triethylamine (TEA, 99.5% purity).

b) Analyzing the structure of ZIF-8 by X-ray diffraction (XRD), and field emission scanning electron microscopy (FESEM).

c) Preparing the polymer solution by mixing polysulfone (PSf, 28%), N, N-dimethylacetamide (DMAc, 37%), tetrahydrofuran (THF, 35%), while varying ZIF-8 loading range from 0-1% by weigh.

d) Fabricating high performance DLHF membrane by varying the outer DER from 0-2 cm^3/min.

e) The membranes were externally coated using 3 wt% of Pebax dissolved in ethanol.

f) Characterizing the membrane properties using Scanning Electron Microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDX), Fourier Transform Infrared Spectroscopy (FTIR) and Thermogravimetric Analysis (TGA).

g) Evaluating the gas separation performance of the produced mixed matrix DLHF membranes was evaluated using pure gases (CO_2 and CH_4).

1.5 Significance of study

The importance of this process is emphasized by the formation of ZIF-8 particles under deionized water conditions. In particular, this method allows the metal framework and the organic ligand to be rapidly combined, since the base additive TEA is capable of inducing deprotonation of the organic ligand. And other synthetic methods such as solvothermal synthesis, hydrothermal synthesis, ion thermal synthesis, acoustic synthesis. In contrast, the alternatives provided in this study are very economical, environmentally friendly, non-polluting, with improved morphology and gas separation performance.

Compared with traditional single-layer hollow fiber membranes, ZIF-8/PSf based double-layer hollow mixed matrix membranes have obvious advantages, such as (1) significantly saves inorganic materials cost; (2) highly selective and permeable layer; (3) good flexibility and ease of handling during module fabrication and system operation; (4) the DLHF membrane has a thinner selective outer layer and a good support structure for the inner layer.

REFERENCE

Aaron, D. and Tsouris, C., 2005. Separation of CO 2 from Flue Gas: A Review. *Separation Science and Technology*, 40(1–3), pp.321–348.

Adewole, J.K., Ahmad, A.L., Ismail, S. and Leo, C.P., 2013. Current challenges in membrane separation of CO2 from natural gas: A review. *International Journal of Greenhouse Gas Control*, 17, pp.46–65.

Anastasiou, S. et al., 2018. Metal-organic framework/graphene oxide composite fillers in mixed-matrix membranes for CO 2 separation. *Materials Chemistry and Physics*, 212, pp.513–522.

Anderson, M. and Lin, Y.S., 2010. Carbonate – ceramic dual-phase membrane for carbon dioxide separation. *Journal of Membrane Science*, 357(1–2), pp.122–129.

Baker, R. and Lokhandwala, K., 2008. Natural gas processing with membranes: an overview. *Industrial & Engineering Chemistry Research*, 47(7), pp.2109–2121.

Bastani, D., Esmaeili, N. and Asadollahi, M., 2013. Polymeric mixed matrix membranes containing zeolites as a filler for gas separation applications: A review. *Journal of Industrial and Engineering Chemistry*, 19(2), pp.375–393.

Bhowmick, K. et al., 2013. Co-Extrusion of Multilayer Glass Fiber-Optic Preforms : Prediction of Layer Dimensions in the Extrudate. , 124, pp.118–124.

Bos, A., Pünt, I., Wessling, M. and Strathmann, H., 1999. CO 2-induced plasticization phenomena in glassy polymers. *Journal of Membrane Science*, 155(1), pp.67–78.

Bux, H. et al., 2009. Zeolitic imidazolate framework membrane with molecular sieving properties by microwave-assisted solvothermal synthesis. *Journal of the American Chemical Society*, 131(44), pp.16000–16001.

Castro-Muñoz, R. and Fíla, V., 2018. Progress on incorporating zeolites in matrimid® 5218 mixed matrix membranes towards gas separation. *Membranes*, 8(2), pp.1–23.

Chen, X. et al., 2015. Membrane gas separation technologies for biogas upgrading. *RSC Adv.*, 5(31), pp.24399–24448.

Chung, T., Jiang, L., Li, Y. and Kulprathipanja, S., 2007. Mixed matrix membranes (MMMs) comprising organic polymers with dispersed inorganic fillers for gas separation. *Progress in Polymer Science*, 32(4), pp.483–507.

Constantinou, A., Barrass, S. and Gavriilidis, A., 2014. CO 2 Absorption in Polytetra fl uoroethylene Membrane Microstructured Contactor Using Aqueous Solutions of Amines.

Díaz, K., López-González, M., Del Castillo, L.F. and Riande, E., 2011. Effect of zeolitic imidazolate frameworks on the gas transport performance of ZIF8-poly(1,4-phenylene ether-ether-sulfone) hybrid membranes. *Journal of Membrane Science*, 383(1–2), pp.206–213.

Dzinun, H. et al., 2015. Morphological study of co-extruded dual-layer hollow fiber membranes incorporated with different TiO2 loadings. *Journal of Membrane Science*, 479, pp.123–131.

Eykens, L. et al., 2017. MEMBRANE SYNTHESIS FOR MEMBRANE DISTILLATION : A REVIEW. *Separation and Purification Technology*.

Faculty, T.A., Kosuri, M.R. and Fulfillment, I.P., 2009. Polymeric Membranes for Super Critical Carbon Dioxide (scCO 2) Separations Polymeric Membranes for Super Critical Carbon Dioxide (scCO 2) Separations. , (May).

Fakult, D.T. and Hussain, M., 2013. Mixed Matrix Membranes for Gas Separation (Mixed-Matrix-Membranen Zur Gastrennung).

Faramawy, S., Zaki, T. and Sakr, A.A.E., 2016. Natural gas origin, composition, and processing: A review. *Journal of Natural Gas Science and Engineering*, 34, pp.34–54.

Ferreira, A.F.P., Ribeiro, A.M., Kulaç, S. and Rodrigues, A.E., 2014. Methane puri fi cation by adsorptive processes on MIL-53 (Al). , 53.

Hafiz, M. et al., 2010. Single-step fabrication and characterisations of electrolyte / anode dual-layer hollow fibres for micro-tubular solid oxide fuel cells. *Journal of Membrane Science*, 351(1–2), pp.196–204.

Hayes, R.A. and Manos, P., 1992. United States Patent (19). , (19).

He, M. et al., 2014. Microporous and Mesoporous Materials Facile synthesis of zeolitic imidazolate framework-8 from a concentrated aqueous solution. *Microporous and Mesoporous Materials*, 184, pp.55–60.

He, T., Mulder, M.H. V, Strathmann, H. and Wessling, M., 2002. Preparation of composite hollow fiber membranes : co-extrusion of hydrophilic coatings onto porous hydrophobic support structures. , 207, pp.143–156.

Hosseini, S. and Wahid, M., 2013. Feasibility study of biogas production and utilization as a source of renewable energy in Malaysia. *Renewable and Sustainable Energy Reviews*, 19, pp.454–462.

Hudiono, Y., Carlisle, T. and Bara, J., 2010. A three-component mixed-matrix membrane with enhanced CO 2 separation properties based on zeolites and ionic liquid materials. *Journal of Membrane …*, 350(1)(117–123).

Hwang, S. et al., 2015. Hollow ZIF-8 nanoparticles improve the permeability of mixed matrix membranes for CO2/CH4 gas separation. *Journal of Membrane Science*, 480, pp.11–19.

Ismail, A.F. and Lai, P.Y., 2003. Effects of phase in v ersion and rheological factors on formation of defect-free and ultrathin-skinned asymmetric polysulfone membranes for gas separation. , 33, pp.127–143.

Jian, M. et al., 2015. Water-based synthesis of zeolitic imidazolate framework-8 with high morphology level at room temperature. *RSC Advances*, 5(60), pp.48433–48441.

Jiang, L., Chung, T. and Li, D., 2004. Fabrication of Matrimid/polyethersulfone dual-layer hollow fiber membranes for gas separation. *Journal of Membrane Science*, 240(1), pp.91–103.

Jiang, L.Y. et al., 2005. Fundamental understanding of nano-sized zeolite distribution in the formation of the mixed matrix single- and dual-layer asymmetric hollow fiber membranes. *Journal of Membrane Science*, 252(1–2), pp.89–100.

Karimi, S., Firouzfar, E. and Khoshchehreh, M.R., 2019. Assessment of gas separation properties and CO2 plasticization of polysulfone/polyethylene glycol membranes. *Journal of Petroleum Science and Engineering*, 173(June 2018), pp.13–19.

Kida, K. et al., 2013. Formation of high crystalline ZIF-8 in an aqueous solution. *CrystEngComm*, 15(9), pp.1794–1801.

Ko, D., Siriwardane, R. and Biegler, L.T., 2003. Optimization of a Pressure-Swing Adsorption Process Using Zeolite 13X for CO 2 Sequestration . *Industrial & Engineering Chemistry Research*, 42(2), pp.339–348.

Kwon, Y., Im, H. and Kim, J., 2011. Effect of PMMA-graft-silica nanoparticles on the gas permeation properties of hexafluoroisopropylidene-based polyimide membranes. *Separation and purification technology*, 78(3)(281–289).

Li, D.F., Chung, T.S., Wang, R. and Liu, Y., 2002a. Fabrication of fluoropolyimide/polyethersulfone (PES) dual-layer asymmetric hollow fiber membranes for gas separation. *Journal of Membrane Science*, 198(2), pp.211–223.

Li, D.F., Chung, T.S., Wang, R. and Liu, Y., 2002b. Fabrication of fluoropolyimide/polyethersulfone (PES) dual-layer asymmetric hollow fiber membranes for gas separation. *Journal of Membrane Science*, 198(2), pp.211–223.

Li, Yi, Chung, T., Huang, Z. and Kulprathipanja, S., 2006. Dual-layer polyethersulfone (PES)/ BTDA-TDI / MDI co-polyimide (P84) hollow fiber membranes with a submicron PES – zeolite beta mixed matrix dense-selective layer for gas separation. , 277, pp.28–37.

Li, Y, Chung, T., Huang, Z. and Kulprathipanja, S., 2006. Dual-layer polyethersulfone (PES)/BTDA-TDI/MDI co-polyimide (P84) hollow fiber membranes with a submicron PES–zeolite beta mixed matrix dense-. *Journal of membrane science*, 277, pp.28–37.

Li, Y. and Chung, T.S., 2010. Molecular-level mixed matrix membranes comprising Pebax® and POSS for hydrogen purification via preferential CO_2 removal. *International Journal of Hydrogen Energy*, 35(19), pp.10560–10568.

Malysheva, G. V, Akhmetova, E.S. and Marycheva, A.N., 2014. Estimation of Glass Transition Temperature of Polysulfone Modified Epoxy Binders. , 40(5), pp.543–548.

McKelvey, S., Clausi, D. and Koros, W., 1997. A guide to establishing hollow fiber macroscopic properties for membrane applications. *Journal of membrane science*, 124(2), pp.223–232.

Nordin, N.A.H.M. et al., 2014. The impact of ZIF-8 particle size and heat treatment on CO_2/CH_4 separation using asymmetric mixed matrix membrane. *RSC Advances*, 4(94), pp.52530–52541.

Nordin, N.A.H.M. et al., 2015. Utilizing low ZIF-8 loading for an asymmetric PSf/ZIF-8 mixed matrix membrane for CO<inf>2</inf>/CH<inf>4</inf> separation. *RSC Advances*, 5(38), pp.30206–30215.

Online, V.A., Ramirez, A.A., Rodrigue, D. and Kaliaguine, S., 2015. *RSC Advances*,

Ordoñez, M.J.C., Balkus, K.J., Ferraris, J.P. and Musselman, I.H., 2010. Molecular sieving realized with ZIF-8/Matrimid® mixed-matrix membranes. *Journal of Membrane Science*, 361(1–2), pp.28–37.

Pan, Y. et al., 2011. Tuning the crystal morphology and size of zeolitic imidazolate framework-8 in aqueous solution by surfactants. *CrystEngComm*, 13(23), p.6937.

Park, K.S. et al., 2006. ZIFs - first synthesis. *Proceedings of the National Academy of Sciences*, 103(27), pp.10186–10191.

Reid, B.D. et al., 2001. Gas permeability properties of polysulfone membranes containing the mesoporous molecular sieve MCM-41. *Chemistry of Materials*, 13(7), pp.2366–2373.

Rezakazemi, M. et al., 2014. State-of-the-art membrane based CO 2 separation using mixed matrix membranes (MMMs): An overview on current status and future directions. *Progress in Polymer Science*, 39(5), pp.817–861.

Robeson, L., 2008. The upper bound revisited. *Journal of Membrane Science*, 320, pp.390–400.

Saeid, S., Peng, N. and Shung, T., 2010. Gas separation membranes developed through integration of polymer blending and dual-layer hollow fiber spinning process for hydrogen and natural gas enrichments. , 349, pp.156–166.

Samarasinghe, S.A.S.C., Chuah, C.Y., Yang, Y. and Bae, T.H., 2018. Tailoring CO_2/CH_4 separation properties of mixed-matrix membranes via combined use of two- and three-dimensional metal-organic frameworks. *Journal of Membrane Science*, 557(April), pp.30–37.

Strathmann, H., 2001. Membrane separation processes: Current relevance and future opportunities. *AIChE Journal*, 47(5), pp.1077–1087.

Sun, S.P. et al., 2010. Novel polyamide-imide/cellulose acetate dual-layer hollow fiber membranes for nanofiltration. *Journal of Membrane Science*, 363(1–2), pp.232–242.

Tan, J.C., Bennett, T.D. and Cheetham, A.K., 2010. Chemical structure, network topology, and porosity effects on the mechanical properties of Zeolitic Imidazolate Frameworks. *Proceedings of the National Academy of Sciences*, 107(22), pp.9938–9943.

Thompson, J.A. et al., 2014. Mixed-linker zeolitic imidazolate framework mixed-matrix membranes for aggressive CO_2 separation from natural gas. *Microporous and Mesoporous Materials*, 192, pp.43–51.

Tsai, C.W. and Langner, E.H.G., 2016. The effect of synthesis temperature on the particle size of nano-ZIF-8. *Microporous and Mesoporous Materials*, 221, pp.8–13.

Ullah Khan, I. et al., 2018. Status and improvement of dual-layer hollow fiber membranes via co-extrusion process for gas separation: A review. *Journal of Natural Gas Science and Engineering*, 52, pp.215–234.

Venna, S.R. and Carreon, M.A., 2010. Highly Permeable Zeolite Imidazolate Framework-8 Membranes for CO 2 / CH 4 Separation. , pp.76–78.

Vinoba, M. et al., 2017. Recent progress of fillers in mixed matrix membranes for CO_2 separation: A review. *Separation and Purification Technology*, 188, pp.431–450.

Wade, J.L., Lackner, K.S. and West, A.C., 2007. Transport model for a high temperature , mixed conducting CO 2 separation membrane. , 178, pp.1530–1540.

Wahab, M.F.A., Ismail, A.F. and Shilton, S.J., 2012. Studies on gas permeation performance of asymmetric polysulfone hollow fiber mixed matrix membranes using nanosized fumed silica as fillers. *Separation and Purification Technology*, 86, pp.41–48.

Wang, Y., Hong, S., Shung, T. and Na, P., 2009. Polyamide-imide / polyetherimide dual-layer hollow fiber membranes for pervaporation dehydration of C1 – C4 alcohols. , 326, pp.222–233.

Widjojo, N., Chung, T.S. and Kulprathipanja, S., 2008. The fabrication of hollow fiber membranes with double-layer mixed-matrix materials for gas separation. *Journal of Membrane Science*, 325(1), pp.326–335.

Wiebcke, M. et al., 2009. Rapid Room-Temperature Synthesis and Characterization of Nanocrystals of a Prototypical Zeolitic Imidazolate Framework. *Chemistry of Materials*, 21(8), pp.1410–1412.

Wong, S. and Bioletti, R., 1999. Carbon Dioxide Separation Technologies = POP ×.

Yao, J. and Wang, H., 2014. Zeolitic imidazolate framework composite membranes and thin films: Synthesis and applications. *Chemical Society Reviews*, 43(13), pp.4470–4493.

Ying, L., Shung, T. and Kulprathipanja, S., 2006. An investigation to revitalize the separation performance of hollow fibers with a thin mixed matrix composite skin for gas separation. , 276, pp.113–125.

Zhang, Z., 2016. Comparisons of various absorbent effects on carbon dioxide capture in membrane gas absorption (MGA) process. *Journal of Natural Gas Science and Engineering*, 31, pp.589–595.

Zhao, Q. and Leonhardt, E., 2010. Purification technologies for biogas generated by anaerobic digestion. *CSANR Research*.

Zornoza, B. et al., 2013. Metal organic framework based mixed matrix membranes: An increasingly important field of research with a large application potential. *Microporous and Mesoporous Materials*, 166, pp.67–78.

Zornoza, B., Téllez, C. and Coronas, J., 2011. Mixed matrix membranes comprising glassy polymers and dispersed mesoporous silica spheres for gas separation. *Journal of Membrane Science*, 368(1)(100–109).