ZEOLITIC IMIDAZOLATE FRAMEWORKS BLENDED POLYSULFONE HOLLOW FIBER MEMBRANES FOR NATURAL GAS PURIFICATION

IMRAN ULLAH KHAN

A thesis submitted in fulfilment of the requirements for the award of the degree of Doctor of Philosophy

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

NOVEMBER 2018
For my beloved late mother and father,
my wife, children and family.
ACKNOWLEDGEMENT

Alhamdulillah praised be to Allah for giving health, strength, and inspiration along the journey for completing this thesis. In preparing this thesis, I was in contact with many people, researchers, academicians, and the laboratory's staff. They have contributed towards my understanding and thoughts. In particular, I wish to express my sincere appreciation to my supervisors, Assoc. Prof. Dr. Mohd Hafiz Dzarfan Othman, Prof. Dr. Haslenda Hashim, and Assoc. Prof. Dr. Juhana Jaafar for encouragement, guidance, advice and motivation. Without their continued support and interest, this thesis proposal would not have been the same as presented here.

I am also indebted to acknowledge financial support from the UniversitiTeknologi Malaysia under the Research University Grant Tier 1 (Project number: Q. J130000.2546.12H25) and Nippon Sheet Glass Foundation for Materials Science and Engineering under Overseas Research Grant Scheme (Project number: R. J130000.7346.4B218). I also like to thank the Research Management Centre, Universiti Teknologi Malaysia for the technical support. Lastly, I would also like to thank the National University of Science and Technology (NUST), Pakistan for their scholarship under Faculty Development Programme (FDP).

My special thanks for all colleagues in Advanced Membrane Technology Research Centre (AMTEC) for their continuous support and help. Their direct and indirect involvement in this study really inspired my work. Unfortunately, it is not possible to list all of them in this limited space. Besides, I would like to thank my wife, kids and family for their non-conditional sacrifices and moral support during my PhD studies.
ABSTRACT

Mixed matrix membranes (MMMs) have received world-wide attention for natural gas purification due to their superior performance in terms of permeability and selectivity. In this study, zeolitic imidazole framework (ZIF) based polysulfone (PSf) hollow fiber membranes were fabricated for natural gas purification. A new micron-sized leaf-like ZIF (ZIF-L) and hexagonal nano-sized ZIF-8 were synthesized in an aqueous basic solution at room temperature with the same molar ratio of reagents (Zn^{2+}/Hmim = 8). Furthermore, various moles of triethylamine (TEA)/total moles ratio of reactants ranging from 0–0.006 were used. Both ZIF powders were characterized by field emission scanning electron microscopy, X-ray diffraction, CO₂ temperature programmed desorption, Fourier transform infrared spectroscopy, thermogravimetric analysis, transmission electron microscopy, and surface area and pores textural properties using nitrogen adsorption-desorption analysis. ZIF-8 particles have shown improved thermal stability, textural properties, basic sites and CO₂ adsorption capacity compared to ZIF-L. The neat PSf membrane and mixed matrix hollow fiber membranes incorporated with the various loading of ZIF-8 ranging from 0–1.25% were fabricated at bore fluid rate of 1.5 and 1.8 ml/min. The prepared membranes were further investigated with respect to their structural morphology, thermal stability, functional groups, surface roughness and finally gas separation performance. The gas permeation results at room temperature showed that fabricated MMM at 1.8 ml/min of bore fluid and loaded with 0.5 wt% of ZIF-8 showed 28% higher CO₂/CH₄ selectivity at 6 bar (g) feed pressure compared to neat PSf membrane. High loading of ZIF-8 ≥0.75 wt% deteriorated the separation performances. However, CO₂/CH₄ selectivity decreased at elevated pressure (8 and 10 bar) due to CO₂-induced plasticization. The amine modification of ZIF-8 particles with 25 ml ammonium hydroxide solution at room temperature was found to significantly improve textural properties, basic sites strength and CO₂ desorption capacity. MMM prepared at 1.8 ml/min of bore fluid rate and loaded with 0.25 wt% of amine modified ZIF-8 showed 18% increase in CO₂/CH₄ selectivity compared to unmodified ZIF-8 based membrane. The amine modification was proven to be a membrane’s anti-plasticization agent with superior gas separation performance at elevated pressure. In comparison to the neat PSf membrane, amine modified MMM prepared at the bore fluid rate of 1.8 ml/min has shown 50, 72 and 69% higher selectivity at 6, 8 and 10 bar (g) feed pressure respectively. Also, the selectivity of A-M₀.₂₅ was 18% higher than unmodified ZIF-8 based MMM at 6 bar (g) feed pressure. The permeance of both gases decreased at an acceptable level with an increase of selectivity at elevated pressure. Hence, the promising results obtained in this study has demonstrated the potential of amine modified ZIF-8 based MMMs for natural gas purification.
ABSTRAK

Membran matriks campuran (MMMs) telah mendapat perhatian seluruh dunia untuk penulenan gas asli kerana prestasi unggul dari segi kebolehtelapan dan selektiviti. Dalam kajian ini, membran gentian geronggang polisulfona (PSf) berasaskan rangka imidazolat ziolitik (ZIF) telah dihasilkan untuk penulenan gas asli. ZIF berbentuk daun (ZIF-L) bersaiz-mikron dan ZIF heksagonal (ZIF-8) bersaiz-nano yang baharu telah disintesis dalam larutan berair pada suhu blik dengan nisbah molar reagen yang sama (Zn^{2+}/Hmim = 8). Tambahan pula, pelbagai mol trietilamina (TEA)/jumlah mol ratio bahan tindak balas dari 0-0.006 telah digunakan. Kedua-dua serbuk ZIF ini dicirikan oleh analisis mikroskop elektron imbasan pelepasan medan, pembelauan sinar-X, penyahjerapan berprogram suhu CO\(_2\), spektroskopi infra merah transformasi Fourier, analisis termogravimetrik, mikroskop elektron penghantaran dan sifat luas permukaan dan liang tekstur menggunakan analisis penyahjerapan nitrogen. ZIF-8 menunjukkan peningkatan kestabilan terma, sifat-sifat struktur dan tekstur, tapak asas dan kapasiti penjerapan CO\(_2\) berbanding dengan ZIF-L. Membran PSf yang asas dan membran serat berongga matriks campuran yang digabungkan dengan pelbagai muatan ZIF-8 dari 0-1.25% telah dihasilkan pada kadar bendalir penebuk 1.5 dan 1.8 ml/min. Membran yang disediakan telah disiasat dengan lebih lanjut mengenai morfologi struktur, kestabilan terma, kumpulan fungsi, kekasaran permukaan dan akhirnya prestasi pemisahan gas. Hasil ketelapan gas pada suhu blik menunjukkan bahawa MMM yang dihasilkan pada 1.8 ml/min dengan bendalir penebuk dan dengan muatan 0.5 wt% daripada ZIF-8 menunjukkan selektiviti CO\(_2\)/CH\(_4\) 28% lebih tinggi pada tekanan suapan 6 bar (g) berbanding dengan membra PSf yang asas. Muatan tinggi ZIF-8 ≥0.75 wt% menjejaskan prestasi pemisahan. Walaubagaimanapun, CO\(_2\)/CH\(_4\) telah menunjukkan penurunan selektivity pada tekanan tinggi (8 dan 10 bar) akibat daripada pemplantakan teraruh CO\(_2\). Pengubahsuaian amina yang lebih lanjut pada zarah ZIF-8 dengan 25 ml larutan aminium hidroksida pada suhu blik didapati memperbaiki sifat-sifat struktur dan tekstur, kekuatan tapak asas dan kapasiti penjerapan CO\(_2\) dengan ketara. MMM yang disediakan pada kadar bendalir penebuk 1.8 ml/min dan dimuatkan dengan ZIF-8 terubahsuai dengan 0.25% amina menunjukkan peningkatan 18% dalam selektiviti CO\(_2\)/CH\(_4\) berbanding membran berasaskan ZIF-8 tanpa ubahsuai. Pengubahsuaian amina telah bertindak sebagai agent anti-pemplantakan membran dengan prestasi pemisahan gas unggul pada tekanan tinggi. Sebagai perbandingan dengan PSf yang asal, MMM diubahsuai amina yang disediakan pada kadar bendalir penebuk 1.8 ml/min telah menunjukkan selektiviti 50, 72 dan 69% lebih tinggi pada tekanan suapan masing-masing 6, 8 dan 10 bar (g). Juga, selektiviti A-Ma25 adalah 18% lebih tinggi daripada membran berasaskan ZIF-8 tanpa ubahsuai pada tekanan suapan 6 bar (g). Ketelapan bagi kedua-dua gas menurun pada tahap yang boleh diterima dengan peningkatan selektiviti pada tekanan tinggi. Oleh itu, keputusan utama yang diperoleh dalam kajian ini telah menunjukkan potensi penulenan gas asli bagi MMM yang berasaskan ZIF-8 diubahsuai amina.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>DECLARATION</td>
<td>ii</td>
<td></td>
</tr>
<tr>
<td>DEDICATION</td>
<td>iii</td>
<td></td>
</tr>
<tr>
<td>ACKNOWLEDGEMENT</td>
<td>iv</td>
<td></td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>v</td>
<td></td>
</tr>
<tr>
<td>ABSTRAK</td>
<td>vi</td>
<td></td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>vii</td>
<td></td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xiii</td>
<td></td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xv</td>
<td></td>
</tr>
<tr>
<td>LIST OF ABBREVIATIONS</td>
<td>xix</td>
<td></td>
</tr>
<tr>
<td>LIST OF SYMBOLS</td>
<td>xxii</td>
<td></td>
</tr>
<tr>
<td>LIST OF APPENDICES</td>
<td>xxiii</td>
<td></td>
</tr>
</tbody>
</table>

1 INTRODUCTION 1
1.1 Background of Study 1
1.2 Problem Statement 3
1.3 Objective of the Study 4
1.4 Scope and Limitations of the Study 5
1.5 Significance of the Study 6
1.6 Thesis Organization 7

2 LITERATURE REVIEW 9
2.1 General Gas Purification Processes 9
   2.1.1 Pressure Swing Adsorption (PSA) 11
2.1.2 Absorption
   2.1.2.1 High Pressure Water Scrubbing (HPWS) 14
   2.1.2.2 Organic Physical Scrubbing (OPS) 15
   2.1.2.3 Chemical Scrubbing Process (CSP) 17
2.1.3 Cryogenic Separation (CS) 18
2.1.4 Membrane Separation (MS) 20
2.2 Mixed Matrix Membrane (MMM)
   2.2.1 Progress in MMM Development 30
   2.2.2 Challenges in MMM 32
2.3 Promising Nanoparticles for Mixed Matrix Membranes 35
   2.3.1 Zeolitic Imidazolate Frameworks (ZIFs) 37
   2.3.2 Leaf-like Zeolitic Imidazolate Framework (ZIF-L) 39
   2.3.3 Zeolitic Imidazolate Framework-8 (ZIF-8) 41
   2.3.4 ZIF Based Filler in the Fabrication of MMM 43
   2.3.5 Challenges of ZIFs as Filler 44
   2.3.6 Overcoming ZIFs Limitations as Filler 45
   2.3.7 Overcoming MOF Limitation via Modification 45
2.4 Hollow Fiber Membrane (HF) 48
2.5 Membrane Fabrication Methods 51
   2.5.1 Thermally Induced Phase Separation (TIPS) 51
   2.5.2 Non-Solvent Induced Phase Separation (NIPS) 52
      2.5.2.1 Dry Process Phase Inversion 53
      2.5.2.2 Wet Process Phase Separation 54
      2.5.2.3 Dry-Wet Phase Inversion Process 54
   2.5.3 Electrospinning Method 55
2.6 Effect of Different Fabrication Parameters on MMM Morphology and Performance 57
   2.6.1 Polymer Solution Composition 58
   2.6.2 Viscosity of the Dope Solutions 59
   2.6.3 Spinning Parameters
      2.6.3.1 Spinneret Design 61
      2.6.3.2 Internal Coagulant (Bore Fluid) 61
2.6.3.3 Air Gap
2.6.3.4 Coagulation Bath
2.6.3.5 Spinneret Temperature
2.6.3.6 Extrusion Flow Rate
2.6.3.7 Elongational Draw Ratio
2.6.3.8 Drying Process
2.6.3.9 The Optimization of Hollow Fiber Spinning Process Parameters for High Performance

2.7 Concluding Remarks on the Literature Review

3 RESEARCH METHODOLOGY

3.1 Research Design and Procedure

3.2 Details of Materials
3.2.1 Polymer
3.2.2 Solvents
3.2.3 Filler

3.3 ZIF-L and ZIF-8 Synthesis
3.3.1 Materials
3.3.2 Synthesis Procedures
3.3.3 Amine Modification

3.4 Fabrication of Mixed Matrix Hollow Fiber Membrane
3.4.1 Polymer Dope Formulation and Preparation
3.4.2 Spinning of Hollow Fiber Membrane
3.4.3 Solvent Exchange Post Treatment
3.4.4 Membrane Coating Procedure

3.5 Characterization Techniques
3.5.1 Field Emission Scanning Electron Microscopy (FESEM)
3.5.2 Atomic Force Microscopy (AFM)
3.5.3 X-ray Diffraction (XRD) Analysis
3.5.4 Differential Scanning Calorimeter (DSC)
3.5.5 Thermogravimetric Analysis (TGA)
3.5.6 Nitrogen Adsorption-Desorption Analysis
3.5.7 Transmission Electron Microscopy (TEM) 84
3.5.8 Fourier Transform Infrared Spectroscopy (FTIR) 84
3.5.9 CO₂-Temperature Programmed Desorption (CO₂-TPD) 85

3.6 Membrane Performance Evaluation 86
3.6.1 Preparation of hollow Fiber Membrane Module for Gas Performance Test 86
3.6.2 Gas Permeation Test 86

4 SYNTHESIS AND CHARACTERISATION OF LEAF-LIKE ZEOLITIC IMIDAZOLE FRAMEWORKS 88
4.1 Introduction 88
4.2 Results and Discussion 89
  4.2.1 Crystal and Physical Structure of ZIF-L 89
  4.2.2 Thermal Stability 93
  4.2.3 Functional Groups 94
  4.2.4 Pore Textural Properties 95
  4.2.5 Desorption of CO₂ 98
4.3 Conclusions 99

5 STRUCTURAL TRANSITION FROM TWO DIMENSIONAL ZIL-L TO THREE DIMENSIONAL ZIF-8 WITH IMPROVED BASICITY 100
5.1 Introduction 100
5.2 Results and Discussion 101
  5.2.1 Structural and Surface Properties 101
  5.2.2 Thermal Stability Analysis 105
  5.2.3 Functional Groups 108
  5.2.4 Pore Textural Properties 109
  5.2.5 CO₂ Temperature Programmed Desorption (CO₂-TPD) 113
5.3 Conclusions 115
6 PREPARATION OF PSF/ZIF-8 HOLLOW FIBER MEMBRANES USING VARIOUS LOADING OF ZIF-8 FOR CO2/CH4 SEPARATION

6.1 Introduction 116
6.2 Results and Discussion 117
   6.2.1 Effect of Various Loading of ZIF-8 on Morphology of Membrane 117
   6.2.2 Thermal Stability Analysis 124
   6.2.3 Functional Groups 128
   6.2.4 Surface Analysis of MMMs 129
   6.2.5 Gas Separation Performance of MMMs 133
   6.2.6 Comparison with Literature 138
6.4 Conclusions 139

7 IMPROVEMENT OF CO2/CH4 SEPARATION PERFORMANCE OF PSF/A-ZIF-8 MIXED MATRIX HOLLOW FIBER MEMBRANE BY USING AMINE MODIFIED FILLER

7.1 Introduction 141
7.2 Results and Discussion 142
   7.2.1 Characterization of Amine Modified ZIF-8 (A-ZIF-8) 142
   7.2.2 Characterization of Amine Modified ZIF-8 Based Hollow Fiber Membranes (A-M) 148
      7.2.2.1 Effect of Amine Modification of ZIF-8 on Membrane Morphology 148
      7.2.2.2 Functional Groups on Amine Modified ZIF-8 Based Hollow Fiber Membranes (A-M) 151
      7.2.2.3 Thermal Stability of Amine Modified ZIF-8 Based Hollow Fiber Membranes (A-M) 152
      7.2.2.4 Surface Analysis of Amine Modified ZIF-8 Based Hollow Fiber Membranes (A-M) 156
      7.2.2.5 Gas Separation Performance of Amine Modified ZIF-8 Based Hollow Fiber Membranes (A-M) 159
7.3 Conclusions 162

8 CONCLUSION AND RECOMMENDATIONS 164
8.1 General Conclusion 164
8.2 Recommendations 166

REFERENCES 167
List of Publications 199
Appendix A-D 201-209
<table>
<thead>
<tr>
<th>TABLE NO.</th>
<th>TITLE</th>
<th>PAGE NO</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Typical composition of raw natural gas</td>
<td>10</td>
</tr>
<tr>
<td>2.2</td>
<td>Advantages and disadvantages of different purification technologies</td>
<td>23</td>
</tr>
<tr>
<td>2.3</td>
<td>The performance of different polymeric membranes for CO2/CH4 separation</td>
<td>25</td>
</tr>
<tr>
<td>2.4</td>
<td>The performance of different inorganic membranes for CO2/CH4 separation</td>
<td>27</td>
</tr>
<tr>
<td>2.5</td>
<td>Comparison of polymeric, inorganic, and MMM properties</td>
<td>30</td>
</tr>
<tr>
<td>2.6</td>
<td>The performance of different MOF-based MMMs in CO2/CH4 separation</td>
<td>37</td>
</tr>
<tr>
<td>2.7</td>
<td>MOF modification strategies</td>
<td>48</td>
</tr>
<tr>
<td>2.8</td>
<td>Membrane fabrication techniques: fabrication parameters with their performances</td>
<td>57</td>
</tr>
<tr>
<td>3.1</td>
<td>Polysulfone (PSf) properties</td>
<td>73</td>
</tr>
<tr>
<td>3.2</td>
<td>Characteristics of solvents used in the present study</td>
<td>74</td>
</tr>
<tr>
<td>3.3</td>
<td>ZIF-L and ZIF-8 properties</td>
<td>75</td>
</tr>
<tr>
<td>3.4</td>
<td>Different moles of TEA/total moles ratio, yield and time for the synthesized samples</td>
<td>77</td>
</tr>
<tr>
<td>3.5</td>
<td>Various spinning conditions for fabricating ZIF based hollow fiber membrane</td>
<td>80</td>
</tr>
<tr>
<td>3.6</td>
<td>Coating solution preparation composition</td>
<td>81</td>
</tr>
<tr>
<td>4.1</td>
<td>Structural properties of the synthesized ZIF-L samples</td>
<td>92</td>
</tr>
<tr>
<td>4.2</td>
<td>Pore textural properties of the synthesized ZIF-L samples</td>
<td>96</td>
</tr>
<tr>
<td>4.3</td>
<td>Amounts of the basic surface sites of synthesized ZIF-L samples</td>
<td>98</td>
</tr>
<tr>
<td>5.1</td>
<td>Structural properties of synthesized ZIF-L and ZIF-8 samples</td>
<td>105</td>
</tr>
</tbody>
</table>
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>FIGURE NO.</th>
<th>TITLE</th>
<th>PAGE NO</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Current technologies available for natural gas purification</td>
<td>10</td>
</tr>
<tr>
<td>2.2</td>
<td>Process flow diagram of pressure swing adsorption process</td>
<td>11</td>
</tr>
<tr>
<td>2.3</td>
<td>Process flow diagram of high pressure water scrubbing</td>
<td>15</td>
</tr>
<tr>
<td>2.4</td>
<td>Process flow diagram of an organic solvent scrubber</td>
<td>16</td>
</tr>
<tr>
<td>2.5</td>
<td>Process flow diagram of an amine scrubber</td>
<td>18</td>
</tr>
<tr>
<td>2.6</td>
<td>Process flow diagram of a cryogenic separation</td>
<td>19</td>
</tr>
<tr>
<td>2.7</td>
<td>Scheme of membrane gas separation process</td>
<td>21</td>
</tr>
<tr>
<td>2.8</td>
<td>Robeson trade-off limit between gas permeability and gas pair selectivity</td>
<td>26</td>
</tr>
<tr>
<td>2.9</td>
<td>Process flow diagram of membrane separation process</td>
<td>28</td>
</tr>
<tr>
<td>2.10</td>
<td>Schematic of a mixed matrix membrane (MMM)</td>
<td>29</td>
</tr>
<tr>
<td>2.11</td>
<td>Schematic representations of the general classification of porous solids and a typical construction procedure of MOF</td>
<td>35</td>
</tr>
<tr>
<td>2.12</td>
<td>(a) The structure of ZIF-L showing the location and approximate shape of the cavity (yellow) (b) top view image showing the leaf-like shape and (c) side view image showing the crystal thickness</td>
<td>40</td>
</tr>
<tr>
<td>2.13</td>
<td>Crystal structure of ZIF-L</td>
<td>40</td>
</tr>
<tr>
<td>2.14</td>
<td>The ZIF-8 simulation cell (left) and a closer view of the relevant 6 membered window openings (right)</td>
<td>42</td>
</tr>
<tr>
<td>2.15</td>
<td>Schematic diagram for the formation of nascent HF membrane during phase inversion</td>
<td>55</td>
</tr>
<tr>
<td>2.16</td>
<td>Apparatus used for electrospinning method</td>
<td>56</td>
</tr>
<tr>
<td>2.17</td>
<td>Influence of coagulation temperature on the formation of macrovoids (Matrimid/Polyetherimide (PEI)</td>
<td>64</td>
</tr>
<tr>
<td>2.18</td>
<td>Influence of spinneret temperature on the cross-sectional morphology of (Matrimid/PEI) membrane structure</td>
<td>65</td>
</tr>
</tbody>
</table>
2.19 Effect of draw ratio and take-up speed for macrovoids formation (Matrimid/PEI) membrane structure

3.1 Research operational framework

4.1 XRD pattern of the synthesized ZIF-L samples with different moles of TEA/total moles ratio: A0 (0), A1 (0.0002), A2 (0.0003), and A3 (0.0005)

4.2 FESEM images of the synthesized ZIF-L samples at different moles of TEA/total moles ratio: (a) A0 (0), (b) A1 (0.0002), (c) A2 (0.0003), (d) A3 (0.0005), and A4 (0.0006)

4.3 Size, width, and thickness measurements of ZIF-L from FESEM image

4.4 TEM images of the synthesized ZIF-L samples at various moles of TEA/total moles ratio: (a) A0 (0), and (b) A3 (0.0005)

4.5 (a) Thermal stability of the synthesized ZIF-L samples with weight loss profile at various temperatures with different moles of TEA/total moles ratio (b) Derivative of weight losses profile

4.6 ATR-IR spectrum analysis of the synthesized ZIF-L samples with different moles of TEA/total moles ratio

4.7 Nitrogen sorption isotherms of the synthesized ZIF-L samples at 100 °C with different moles of TEA/total moles ratio

4.8 Nitrogen sorption isotherms of the synthesized ZIF-L samples at 200 °C with different moles of TEA/total moles ratio

4.9 CO2-TPD spectra recorded for various synthesized ZIF-L samples with different moles of TEA/total moles ratio

5.1 XRD pattern of the synthesized ZIF-L, transition stage and ZIF-8 samples with different moles of TEA/total moles ratio: A3 (0.0005), A4 (0.0006), A5 (0.0009), A6 (0.001), A7 (0.002), A8 (0.003), A9 (0.004), and A10 (0.006)

5.2 FESEM images of the synthesized ZIF-L, transition stage and ZIF-8 samples at various moles of TEA/total moles ratio: (a) A3 (0.0005), (b) A4 (0.0006), (c) A5 (0.0009), (d) A6 (0.001), (e) A7 (0.002), (f) A8 (0.003), (g) A9 (0.004), and (h) A10 (0.006)

5.3 TEM images of the synthesized ZIF-L and ZIF-8 samples with different moles of TEA/total moles ratio

5.4 (a) Thermal stability of the synthesized ZIF-L, transition stage and ZIF-8 samples with weight loss profile at various temperatures with different moles of TEA/total moles ratio (b) Derivative of weight loss profile
The XRD pattern of ZIF-8 sample A7 (0.002) heated at 600 °C for 12 hours and 24 hours

Photographs of the ZIF-8 sample A7 (0.002): (a) As-synthesized, (b) 600 °C for 12 hours, and (c) 600 °C for 24 hours

ATR-IR spectrum analysis of the synthesized ZIF-L and ZIF-8 samples with different moles of TEA/total moles ratio

Nitrogen sorption isotherms of the synthesized ZIF-L and ZIF-8 samples at 100 °C with different moles of TEA/total moles ratio

Nitrogen sorption isotherms of the synthesized ZIF-L and ZIF-8 samples at 250 °C with different moles of TEA/total moles ratio

CO₂-TPD spectra recorded for various synthesized ZIF-L and ZIF-8 samples with different moles of TEA/total moles ratio

Cross sectional and surface images of membrane prepared at bore fluid of 1.5 ml/min with various ZIF-8 loading

Cross sectional and surface images of membrane prepared at bore fluid of 1.8 ml/min with various ZIF-8 loading

EDX surface analysis of neat PSf and PSf/ZIF-8 hollow fiber membranes: (a) M_{Neat}, (b) M_{0.25}, (c) M_{0.5}, (d) M_{0.75}, (e) M_{1}, and (f) M_{1.25}

(a) Thermal stability of the prepared membranes with weight loss profile at various temperature and loading of ZIF-8 (b) Thermal stability of the prepared membranes with derivative of weight loss profile at various temperature and loading of ZIF-8

Influence of various ZIF-8 loading on glass transition temperature (T_g) of prepared membranes (red colour: heating cycles, black colour: cooling cycles)

FTIR analysis of prepared neat PSf and PSf/ZIF-8 hollow fiber membranes

AFM images of the surfaces of neat PSf and PSf/ZIF-8 hollow fiber membranes fabricated at various ZIF-8 loading and bore fluid rate: (a) M_{Neat}, (b) M_{0.25}, (c) M_{0.5}, (d) M_{0.75}, (e) M_{1}, and (f) M_{1.25}

The effects of various loading of ZIF-8 and bore fluid rate on the membrane selectivity at 6 bar (g) feed pressure

The effects of various feed pressure on the gas permeation properties: (a) membrane samples prepared at bore fluid rate of 1.5 ml/min, (b) membrane samples prepared at bore fluid rate of 1.8 ml/min.
7.1 XRD pattern of the synthesized and amine modified ZIF-8 samples with different volume of ammonium hydroxide solution: A9 (0 ml), A925ml (25 ml), and A930ml (50 ml)

7.2 FESEM images of the amine modified ZIF-8 samples with different volume of ammonium hydroxide solution: (a) A925ml (25 ml), and (b) A930ml (50 ml)

7.3 FTIR spectrum analysis of the synthesized and amine modified ZIF-8 samples with different volume of ammonium hydroxide solution

7.4 (a) Thermal stability of the synthesized and amine modified ZIF-8 samples with weight loss profile at various temperatures with different volume of ammonium hydroxide solution (b) Derivative of weight losses profile

7.5 Nitrogen sorption isotherms of the synthesized and amine modified ZIF-8 samples with different volume of ammonium hydroxide solution

7.6 CO2-TPD spectra recorded for the synthesized and amine modified ZIF-8 samples with different volume of ammonium hydroxide solution

7.7 Cross sectional and surface images of membrane prepared at bore fluid of 1.5 ml/min with various A-ZIF-8 loading

7.8 Cross sectional and surface images of membrane prepared at bore fluid of 1.8 ml/min with various A-ZIF-8 loading

7.9 EDX surface analysis of amine modified (A-ZIF-8) based hollow fiber membrane: (a) A-M0.25, and (b) A-M0.5

7.10 FTIR analysis of prepared neat, PSf/ZIF-8 and PSf/A-ZIF-8 hollow fiber membranes

7.11 (a) Thermal stability of the prepared membranes with weight loss profile at various temperature and loading of ZIF-8 and A-ZIF-8 (b) Derivative of weight losses profile

7.12 Influence of various ZIF-8 and A-ZIF-8 loading on glass transition temperature (Tg) of prepared membranes (red colour: heating cycles, black colour: cooling cycles)

7.13 AFM images of the surfaces of neat, PSf/ZIF-8 and PSf/A-ZIF-8 hollow fiber membranes fabricated at two various bore fluid rates: (a) M_Neaf, (b) M_0.25, (c) M_0.5, (d) A-M_0.25, and (e) A-M_0.5

7.14 The effects of various feed pressure on the gas permeation properties: (a) ZIF-8 and A-ZIF-8 based membranes prepared at bore fluid rate of 1.5 ml/min, (b) ZIF-8 and A-ZIF-8 membranes prepared at bore fluid rate of 1.8 ml/min
## LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>AMDEA</td>
<td>Activated methyl diethanolamine</td>
</tr>
<tr>
<td>AS</td>
<td>Amine scrubbing</td>
</tr>
<tr>
<td>ATBC</td>
<td>Acetyl tributyl citrate</td>
</tr>
<tr>
<td>ATR-IR</td>
<td>Attenuated total reflectance infrared</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>CA</td>
<td>Cellulose acetate</td>
</tr>
<tr>
<td>CCM</td>
<td>Carbon cryogel microspheres</td>
</tr>
<tr>
<td>CM</td>
<td>Carbon membrane</td>
</tr>
<tr>
<td>CMS</td>
<td>Carbon molecular sieve</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon nanotubes</td>
</tr>
<tr>
<td>CS</td>
<td>Cryogenic separation</td>
</tr>
<tr>
<td>CSP</td>
<td>Chemical scrubbing process</td>
</tr>
<tr>
<td>CXM</td>
<td>Carbon xerogel microspheres</td>
</tr>
<tr>
<td>DEA</td>
<td>Diethanol amine</td>
</tr>
<tr>
<td>DEF</td>
<td>Diethylformamide</td>
</tr>
<tr>
<td>DER</td>
<td>Dope extrusion rate</td>
</tr>
<tr>
<td>DMAc</td>
<td>Dimethylacetamide</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl sulfoxide</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimeter</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive X-ray spectrometer</td>
</tr>
<tr>
<td>EIPS</td>
<td>Evaporation-induced phase separation</td>
</tr>
<tr>
<td>ESA</td>
<td>Electrical swing adsorption</td>
</tr>
<tr>
<td>FAU</td>
<td>Faujasite</td>
</tr>
<tr>
<td>FESEM</td>
<td>Field emission scanning electron microscopy</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>----------------------------------</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transmission infrared</td>
</tr>
<tr>
<td>GHG</td>
<td>Greenhouse gas</td>
</tr>
<tr>
<td>GS</td>
<td>Gas separation</td>
</tr>
<tr>
<td>HD</td>
<td>Hemodialysis</td>
</tr>
<tr>
<td>HF</td>
<td>Hollow fiber</td>
</tr>
<tr>
<td>Hmim</td>
<td>2-methylimidazole</td>
</tr>
<tr>
<td>HPWS</td>
<td>High pressure water scrubbing</td>
</tr>
<tr>
<td>ISS</td>
<td>Inorganic solvent scrubbing</td>
</tr>
<tr>
<td>JS</td>
<td>Jet strength</td>
</tr>
<tr>
<td>LBM</td>
<td>Liquefied biomethane</td>
</tr>
<tr>
<td>LNG</td>
<td>Liquid natural gas</td>
</tr>
<tr>
<td>MDEA</td>
<td>Methyl diethanol amine</td>
</tr>
<tr>
<td>MEA</td>
<td>Monoethanol amine</td>
</tr>
<tr>
<td>MF</td>
<td>Microfiltration</td>
</tr>
<tr>
<td>MMM</td>
<td>Mixed matrix membrane</td>
</tr>
<tr>
<td>MOF</td>
<td>Metal-organic framework</td>
</tr>
<tr>
<td>MS</td>
<td>Membrane separation</td>
</tr>
<tr>
<td>NIPS</td>
<td>Nonsolvent induced phase separation</td>
</tr>
<tr>
<td>NMP</td>
<td>N-methyl pyrrolidone</td>
</tr>
<tr>
<td>NYT</td>
<td>Neapolitan yellow tuff</td>
</tr>
<tr>
<td>OPS</td>
<td>Organic physical scrubbing</td>
</tr>
<tr>
<td>PC</td>
<td>Polycarbonate</td>
</tr>
<tr>
<td>PDMS</td>
<td>Polydimethyl siloxane</td>
</tr>
<tr>
<td>PEG</td>
<td>Polyethylene glycol</td>
</tr>
<tr>
<td>PEI</td>
<td>Polyetherimide</td>
</tr>
<tr>
<td>PI</td>
<td>Polyimide</td>
</tr>
<tr>
<td>PSA</td>
<td>Pressure swing adsorption</td>
</tr>
<tr>
<td>PSf</td>
<td>Polysulfone</td>
</tr>
<tr>
<td>PVDF</td>
<td>Polyvinylidene difluoride</td>
</tr>
<tr>
<td>PZ</td>
<td>Piperazine</td>
</tr>
<tr>
<td>RO</td>
<td>Reverse osmosis</td>
</tr>
<tr>
<td>SAPO-34</td>
<td>Silicoaluminophosphate-34</td>
</tr>
<tr>
<td>SBU</td>
<td>Secondary building units</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>SOD</td>
<td>Sodalite</td>
</tr>
<tr>
<td>STP</td>
<td>Standard temperature and pressure</td>
</tr>
<tr>
<td>TEA</td>
<td>Triethylamine</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>TIPS</td>
<td>Thermally induced phase separation</td>
</tr>
<tr>
<td>TPD</td>
<td>Temperature programmed desorption</td>
</tr>
<tr>
<td>TSA</td>
<td>Temperature swing adsorption</td>
</tr>
<tr>
<td>UF</td>
<td>Ultrafiltration</td>
</tr>
<tr>
<td>VIPS</td>
<td>Vapor induced phase separation</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>ZIF-L</td>
<td>Leak-like zeolitic imidazolate framework</td>
</tr>
<tr>
<td>ZIFs</td>
<td>Zeolitic imidazolate frameworks</td>
</tr>
<tr>
<td>ZSM-5</td>
<td>Zeolite socony mobil-5</td>
</tr>
</tbody>
</table>
### LIST OF SYMBOLS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( (P_i/l) )</td>
<td>Pressure-normalized flux or permeance</td>
</tr>
<tr>
<td>( P_i )</td>
<td>Permeability of gas ( i )</td>
</tr>
<tr>
<td>( P_j )</td>
<td>Permeability of gas ( j )</td>
</tr>
<tr>
<td>( Q_i )</td>
<td>Volumetric gas flow rate of gas ( i )</td>
</tr>
<tr>
<td>( \varepsilon )</td>
<td>Euro</td>
</tr>
<tr>
<td>( \Delta )</td>
<td>Change</td>
</tr>
<tr>
<td>( 2D )</td>
<td>Two dimensional</td>
</tr>
<tr>
<td>( 3D )</td>
<td>Three dimensional</td>
</tr>
<tr>
<td>( A )</td>
<td>Effective membrane area</td>
</tr>
<tr>
<td>( \AA )</td>
<td>Angstroms</td>
</tr>
<tr>
<td>( B )</td>
<td>Full-width at half maximum of the peak in radian</td>
</tr>
<tr>
<td>( D )</td>
<td>Crystal size, nm</td>
</tr>
<tr>
<td>( Da )</td>
<td>Molecular weight</td>
</tr>
<tr>
<td>( P_{\text{plasticization}} )</td>
<td>Plasticization pressure</td>
</tr>
<tr>
<td>( R_a )</td>
<td>Average roughness, nm</td>
</tr>
<tr>
<td>( R_{\text{rms}} )</td>
<td>Root mean squared roughness, nm</td>
</tr>
<tr>
<td>( T_c )</td>
<td>Crystallization temperature</td>
</tr>
<tr>
<td>( T_g )</td>
<td>Glass-transition temperature</td>
</tr>
<tr>
<td>( T_p )</td>
<td>Derivative peak of temperature</td>
</tr>
<tr>
<td>( V_m )</td>
<td>Molar volume</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>Gas pair selectivity</td>
</tr>
<tr>
<td>( \Delta P )</td>
<td>Pressure difference</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>X-ray wavelength</td>
</tr>
<tr>
<td>( \phi )</td>
<td>Elongational draw ratio</td>
</tr>
<tr>
<td>( \theta )</td>
<td>Diffraction angle</td>
</tr>
</tbody>
</table>
### LIST OF APPENDICES

<table>
<thead>
<tr>
<th>APPENDIX</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Calculations of moles of reactants during synthesis of ZIF-L and ZIF-8</td>
<td>201</td>
</tr>
<tr>
<td>B</td>
<td>Calculations of dope solution compositions</td>
<td>203</td>
</tr>
<tr>
<td>C</td>
<td>Calculations of crystal size</td>
<td>205</td>
</tr>
<tr>
<td>D</td>
<td>Calculations of permeance and selectivity</td>
<td>207</td>
</tr>
</tbody>
</table>
CHAPTER 1

INTRODUCTION

1.1 Background of Study

Natural gas is formed due to decomposition of plants and animal materials by heat and high pressure under the surface of the earth over millions of centuries. It is usually composed of hydrocarbon gas mixtures mainly consisting of methane (CH$_4$) and carbon dioxide (CO$_2$) (Baker and Lokhandwala, 2008). CH$_4$ is a world’s energy source that provides energy for heating, electricity generation, cooking and also as a fuel for vehicles but it requires purification from impurities. Furthermore, environmental problems have become a big issue due to the greenhouse gas (GHG) emission as the result of fossil fuel combustion (Hosseini and Wahid, 2013). Among impurities, the removal of CO$_2$ is more crucial and important due to its corrosive nature. In addition, the uncontrolled CO$_2$ emission to the atmosphere has become great concern worldwide that would lead to climate change, flooding, acid rain, hazards for human health and many undesirable effects (Permpool and Gheewala, 2017, Sun et al., 2015 and Nojedehi et al., 2016). There are several technologies that were commercially available on an industrial scale for purification of natural gas to ensure the elimination of CO$_2$. Adsorption, absorption, membrane separation and cryogenic technique were well-established processes with their own advantages and disadvantages. In general, membrane-based gas separation technique offers various advantages over the conventional processes such as: 1) Simple operation with easy maintenance (Karászová et al., 2015). 2) An economical process with low capital investment cost (Bekkering et al., 2010). 3) Low energy demands with minimal
space and supervision requirement (Samarasinghe et al., 2018), and 4) Environmentally friendly process.

Metal-organic framework (MOF) has shown to have an excellent affinity towards many polymer matrices even without surface modification (Wen et al., 2009). MOF is a crystalline compound with metal ions and organic ligands as a repetitive unit arranged systematically as a framework (Samarasinghe et al., 2018). The organic ligands within its structure offers exceptional interaction with polymer matrices, hence minimize the interfacial defects. Zeolitic imidazolate frameworks (ZIFs), a subclass of MOFs are emerging as a new family of molecular sieves with low cost, and highly diversified and tunable structural properties (Lee et al., 2015, Wang et al., 2008). Therefore, leaf-like zeolitic imidazolate framework (ZIF-L) and zeolitic imidazolate framework 8 (ZIF-8) particles are synthesized and characterized. The selection of polymer and dispersed phase are very important factor to produce defect free and high-performance mixed matrix membrane (MMM). Hence, current research is concentrated on the fabrication of MMM having polysulfone (PSf) as a continuous phase and ZIF based inorganic filler as a dispersed phase. The basic objective is to improve gas separation performance of the existing pristine PSf membrane. PSf is the best option as polymer phase due to its advantages such as: (1) High mechanical and thermal strength (Nordin et al., 2014). (2) One of the most studied polymer membrane materials due to its low cost compared to other polyimide materials (Julian and Wenten, 2012). (3) Excellent equilibrium between permeability and selectivity towards CO\textsubscript{2} with high plasticization pressure (P_{plasticization} = 34 bar) (Bos et al., 1999). (4) Reasonably high separation factor for gas separations (Intrinsic CO\textsubscript{2}/CH\textsubscript{4} selectivity = 28.1 (Chern and Koros, 1985), and (5) good stability against environmental oxidation due to its high glass-transition temperature (T_g) approximately 185°C (Kesting et al., 1990).
1.2 Problem Statement

Membrane technology has proven to have numerous advantages over commercial adsorption and absorption processes. But, recent developments in this field are still at the experimental stage and long-term stability at elevated pressure has rarely been investigated in the literature. Selection of suitable membrane materials is a major 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, modification and gas separation performance in the MMM. However, the ZIF-L is still not commercially produced and available ZIF-8 possesses large particle sizes (particle size of ~500nm) and this would rise as challenges to incorporate the particles within the thin-selective layer of membrane. In addition, ZIF-8 is considerably expensive and would certainly increase the cost of prepared membrane. Nordin et al. (2015) has reported the cost of ZIF-8 particles around RM 25,551.87 for 500g, relatively expensive compared to synthesis materials provided by Sigma Aldrich in this research such as 2-methylimidazole (RM 852/kg), zinc nitrate hexahydrate (RM 802/kg) and base-type additive triethylamine (RM 361/500ml). Hence, research to produce smaller ZIFs particle with economical method would be of special interest to this study. The addition of base-type additives such as triethylamine (TEA) during synthesis process is beneficial in various ways such as minimizing the usage of organic ligands, shorter time of synthesis due to rapid deprotonation of organic ligands which further reduce the particles size. Though ZIF-L and ZIF-8 are compatible with different polymer materials but their intrinsic separation factor is not satisfactory. The intrinsic CO₂/CH₄ selectivity of ZIF-L and ZIF-8 is 7.2 (Chen et al., 2013) and 5 (Chen et al., 2014; He et al., 2014; Yao et al., 2013) respectively which is significantly lower than zeolite (CO₂/CH₄ = 80 (Yeo et al., 2014)) and carbon membrane (CO₂/CH₄ = 80 (Salleh and Ismail, 2011)). It is essential to modify the filler surface to enhance CO₂ adsorption capacity. Furthermore, ZIFs based membranes have low plasticization resistance at elevated
operating pressure. Hence, amine modification of ZIFs particles is used to improve its functional properties and compatibility with polymer. Subsequently, reducing the segmental mobility of polymer matrix and improve the plasticization resistance. So, these factors can be regarded as the main hindrances to the potential application of ZIFs based MMM for gas separation. Unless these limitations are addressed, the advantages offered by ZIF based MMM are likely to be neglected.

Therefore, this study is aimed to fabricate MMMs for CO₂ separation using various loading of synthesized and amine modified ZIFs nanoparticles. Furthermore, the effect of the different loading of fillers and feed pressures on the gas separation performance of prepared MMM is evaluated. Moreover, to date, the incorporation of ZIFs particles has primarily been subjected to the preparation of flat sheet membranes, whereas studies on ZIFs based hollow fiber membranes are rarely investigated.

1.3 Objective of the Study

The major goal of this research was to produce asymmetric mixed matrix hollow fiber membranes with ZIF based materials as the filler via dry-wet phase inversion process with high gas separation performance and improved plasticization resistance. Therefore, based on the above mentioned challenges and issues, the specific objectives of this research are as follows

i. To synthesize and characterize the ZIF-L and ZIF-8 particles with various moles of TEA/total moles ratio of the reactants with the aim to evaluate their potential for the use as filler in the fabrication of MMMs.

ii. To investigate the effect of different loading of selected ZIF based filler on the resultant mixed matrix hollow fiber membrane gas separation performance at various feed pressures.

iii. To evaluate the effect of amine modification of selected ZIF based filler on CO₂/CH₄ selectivity and plasticization resistance at various feed
pressures of gas permeation operations of the mixed matrix hollow fiber membranes.

1.4 Scope of the Study

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

i. Investigating the effect of moles of TEA/total moles ratio ranging from 0–0.006 in the formation of ZIF-L and ZIF-8 at room temperature.

ii. Characterizing the ZIF-L and ZIF-8 particles by X-ray diffraction (XRD) analysis, transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM), Fourier transmission infrared (FTIR), Attenuated total reflectance infrared (ATR-IR), thermogravimetric analysis (TGA), surface area using the Brunauer-Emmett-Teller (BET) equation and CO₂ temperature programmed desorption (CO₂-TPD).

iii. Formulating polymer dope solutions comprised of polysulfone (Udel® P–1700, 30%), N, N-dimethylacetamide (DMAc, 35%), tetrahydrofuran (THF, 35%) with the various loading of selected filler ranging from 0 wt% to 1.25 wt%.

iv. Fabricating mixed matrix hollow fiber membranes using bore fluid rate of 1.5 and 1.8 ml/min.

v. The potted fibers were externally coated using 3 wt% of PDMS dissolved in n-hexane.

vi. Amine modification of selected filler by using 25 and 50 ml ammonium hydroxide solution.

vii. Characterizing the membranes using atomic force microscopy (AFM), energy dispersive X-ray spectrometer (EDX), and differential scanning calorimeter (DSC), FESEM and TGA.
Evaluating the gas separation performance and plasticization resistance of the fabricated mixed matrix hollow fiber membranes using pure gases (CO$_2$ and CH$_4$) at three different pressure (6, 8 and 10 bar).

1.5 Significance of the Study

The recent formation of ZIF-L and ZIF-8 particles through aqueous condition has emphasized the significance of this process. Particularly, this method gives rapid reaction between metal source and an organic ligand, promote yield due to the presence of base type additive TEA. Till date, aqueous condition synthesis needed high metal to solvent ratio but TEA induce the deprotonation of the organic ligand, subsequently reduce the excessive solvent usage and synthesis time. This alternative method offered in this research is very productive, environmentally friendly and economical with improved morphology and gas separation performance compared to other available methods.

Generally, one common problem encountered during fabrication of MMMs is filler-polymer incompatibilities that affect the gas separation performance. The unique advantage of incorporating ZIFs over many nonporous materials is its organic components that enhanced the filler-polymer compatibilities and also improved the separation performance and plasticization resistance of resulted membranes. Furthermore, amine modification of ZIFs particles is carried out to improve its functional properties before being dispersed into PSf. Therefore, MMMs with high gas separation performance and plasticization resistance at elevated pressure is expected to produce for natural gas purification. The gas separation performances of the amine modified MMMs explores the new perspective of membrane for natural gas purification. The CO$_2$ plasticization phenomena was yet to be investigated for MMMs. The incorporation of amine modified ZIFs nanoparticles into polymer matrix has offered superior gas separation performance with improved plasticization resistance compared to the virgin ZIFs based and neat membrane. This research contribution will offer guidelines to future researchers to select suitable organic and
inorganic membrane materials for high performance mixed matrix membranes with economical, safer and environmentally friendly unit operation.

1.6 Thesis Organization

This thesis consisted of eight chapters which describe original and novel research on mixed matrix membranes for natural gas purification. Chapter 1 briefly explores the ideas of membrane separation processes. The research background of membrane technology and the issues that lead to the current study were discussed. The four research objectives were identified, followed by the scopes of study used to attain these objectives. Chapter 2 describes the scientific literature review of all available separation processes with focused on membrane technology for gas separation. All basic principles of gas separation through hollow fiber membranes, the materials selection, morphology, spinning parameters and various fabrication techniques were critically reviewed and explained. The concepts and development of novel MMM were comprehensively explained. Also, advantages and limitations of ZIFs nanoparticles for membrane application were described in detail. Finally, different pre and post treatment methods for synthesized nanoparticles and MMM were discussed in detail. Chapter 3 provides the methodology for the fabrication of PSf and ZIFs mixed matrix membranes, procedures for material synthesis, modification, characterization techniques and finally gas separation performance. Also, complete research operational framework was provided in this chapter. Chapter 4 explains the synthesis of ZIF-L at aqueous room temperature with various concentrations of TEA in the synthesis mixture. The effect of various concentration of TEA on the yield, particle size, crystal growth, microposity, CO$_2$ desorption performance and thermal stability were investigated and discussed in detail. Chapter 5 elaborates on the determination of the critical loading of TEA that was used for intermediate structure between ZIF-L and ZIF-8 during the synthesis process. Chapter 6 aims to fabricate and characterize the defect-free high performance hollow fiber membranes using various loading of ZIF-8 nanoparticles and bore fluid rate. The effect of the different loading of ZIF-8, bore fluid rate and feed pressure on the
gas separation performance was evaluated. Chapter 7 has investigated the effect of amine modification on the structural, thermal, pore textural and desorption properties of ZIF-8 nanoparticles. Defect-free high performance hollow fiber membranes using various loading of amine modified ZIF-8 nanoparticles and bore fluid rate has been fabricated and characterized. Also, it further explains the plasticization effects of CO₂ using amine modified ZIF-8 nanoparticles as dispersed phase into PSf polymer matrices at high feed pressures. The plasticization reduction with high gas separation performance is the major objective of this chapter. The gas separation performances of the amine modified ZIF-8 based membranes are evaluated and compared with ZIF-8-based membranes reported in the previous chapter (Chapter 6). Finally, Chapter 8 presents the general conclusions from present work and providing a list of some recommendations for future researches.
REFERENCES


and C 3) transport properties of co-polyimides synthesized from 6FDA and 1, 5-NDA (naphthalene)/Durene diamines. Journal of Membrane Science, 218(1), 235–245.


Choi, S., Watanabe, T., & Bae, T. (2012). Modification of the Mg/DOBDC MOF with amines to enhance CO\textsubscript{2} adsorption from ultradilute gases. The Journal of Physical Chemistry Letters, 3(9), 1136–1141.


Ekiner, O., & Vassilatos, G. (2001). Polyamide hollow fibers for H₂/CH₄


Harasimowicz, M., Orluk, P., Zakrzewska-Trznadel, G., & Chmielewski, a. G.


Li, J., Ma, Y., McCarthy, M., & Sculley, J. (2011). Carbon dioxide capture-related
gas adsorption and separation in metal-organic frameworks. Coordination Chemistry Reviews, 255(15), 1791–1823.


Ren, J., Chung, T., Li, D., Wang, R., & Liu, Y. (2002). Development of asymmetric 6FDA-2, 6 DAT hollow fiber membranes for CO₂/CH₄ separation: 1. The


synthesis of zeolitic imidazolate frameworks from stoichiometric metal and ligand precursor aqueous solutions at room temperature. CrystEngComm, 15(18), 3601.


INTERNATIONAL CONFERENCE


