Optimization of Fabrication Parameters of Polymer-Inorganic Mixed Matrix Membranes using Zeolitic Imidazolate Framework Nanofiller and 6FDA-Durene Polyimide.

By

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16074

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical)

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CERTIFICATION OF APPROVAL

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(Chemical)

Approved by:

____

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Project Supervisor

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

January 2015

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

CHEONG WENG LEONG

ABSTRACT

The presence of carbon dioxide in natural gas has greatly reduced the heating value of the gas and caused corrosion to the transport pipelines. Membrane technology is well-known in the oil and gas industry especially in the separation of carbon dioxide from natural gas due to its cheaper capital cost, smaller size and the ability to separate mixture of more than 20% carbon dioxide in it. Although mixed matrix membranes have been widely reported as a potential membrane material in separation of carbon dioxide from natural gas, there are still problems and challenges in the fabrication of defects free and particles-agglomeration free mixed matrix membrane. Therefore, in the present research, the parameters including the sonication and stirring duration in the fabrication of zeolitic imidazolate framework (ZIF-8) nanofiller and 6FDA-durene polyimide mixed matrix membrane was studied and optimized. The resultant mixed matrix membranes were characterized by using field emission scanning electron microscopy (FESEM), scanning electron microscopy (SEM) and also energy dispersive x-ray spectroscopy (EDX) in order to investigate its morphology and the agglomeration of the dispersed ZIF-8. It was shown in FESEM and SEM that ZIF-8 nanofiller is compatible with 6FDA-durene polymeric matrix. Thermogravimetric analysis (TGA) results showed that the MMM are stable up to 400 °C while differential scanning calorimetry (DSC) showed that the glass transition temperature, T_g of the resultant mixed matrix membrane is 15 °C higher than the pristine membrane. Lastly, permeation testing was carried out at 3.5 bar in order to test the performance of the resultant membrane in CO_2/CH_4 separation. Generally, the incorporation of ZIF-8 nanofillers in 6FDA-durene polymer membrane results in the increase in CO_2 and CH_4 permeability while a drop of CO_2/CH_4 selectivity is observed. MMM with the total stirring and sonication duration of 11 hours displayed the best separation performance as well as the most well dispersed ZIF-8 among the 7 sets of mixed matrix membrane fabricated.

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LIST OF ABBREVIATIONS

DCM	Di-Chloro Methane
DSC	Differential Scanning Calorimetry
EDX	Energy Dispersive X-ray
FESEM	Field Emission Scanning Electron Microscopy
MMM	Mixed Matrix Membrane
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric Analysis
XRD	X-ray Diffraction
ZIF	Zeolitic Imidazolate Framework

CHAPTER 1: INTRODUCTION

1.1 Background of Study

In search of greener technology, the world is working towards the renewable sources of energy and the natural gas is becoming more important as it is the cleanest of all fossil fuel used to generate energy. However, the presence of carbon dioxide in natural gas reduces the calorific value of the gas as well as makes the gas streams to become more acidic and corrosive, which might greatly affect the transportation system of the gas. Therefore, carbon dioxide has to be removed from natural gas in order to improve the heating value of the gas, and to prevent corrosion of the pipeline and other process equipment used (J.Hao, P.A.Rice, & S.A.Stern, 1993).

Membrane technology is a mechanical separation process in which it covers all engineering approaches for separating gaseous or liquid streams with the help of permeable membranes. Membrane separation is a technology which selectively separates the materials via pores or gaps in the molecular arrangement of the membrane. The examples of gas separation via membranes are shown in Figure 1 and Figure 2. Membrane separation can operate without the need of energy intensive process such as heating or vaporizing, and hence it uses far less energy than the conventional thermal separation processes such as distillation or crystallization. In addition to that, membrane separation technology also enables separations to take place with substances that are impossible to separate using normal thermal separation methods (mastmona, 2014).

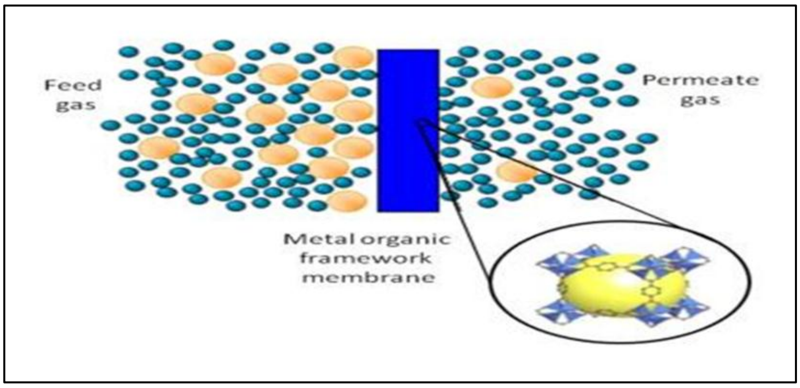

Figure 1: Membrane technology (Toon, 2010).

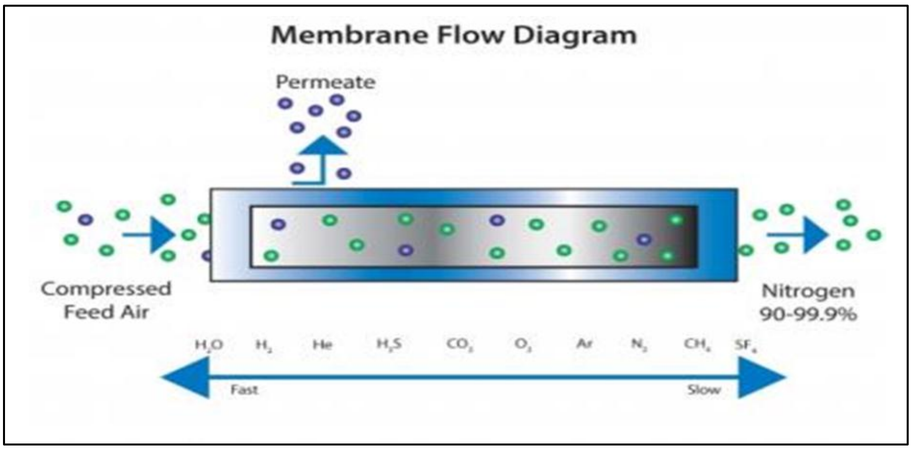

Figure 2: Membrane flow diagram (IGS, 2014).

Due to low capital cost, good reliability and high energy efficiency compared to other separation methods, membrane based gas separation had since gained its attention from the researches lately (Schell & Houston, 1983). However, it is always an issue for the researchers to concurrently improve the gas selectivity of the membrane along with a high permeability. Polymer based membranes are cost efficient and easy to fabricate but are limited by the trade-off between selectivity and permeability (Koros & Mahajan, 2000). On the other hand, inorganic membranes offer high selectivity and are thermally more stable than polymer based membranes. The trade-off of the inorganic membranes is the high fabrication cost and also poor mechanical properties. Therefore, a mixed matrix membrane which comprised of a porous inorganic materials dispersed in a polymeric membrane, can combine the favourable properties of both inorganic and polymer membranes. Figure 3 shows the examples of mixed matrix membranes used in gas separation.

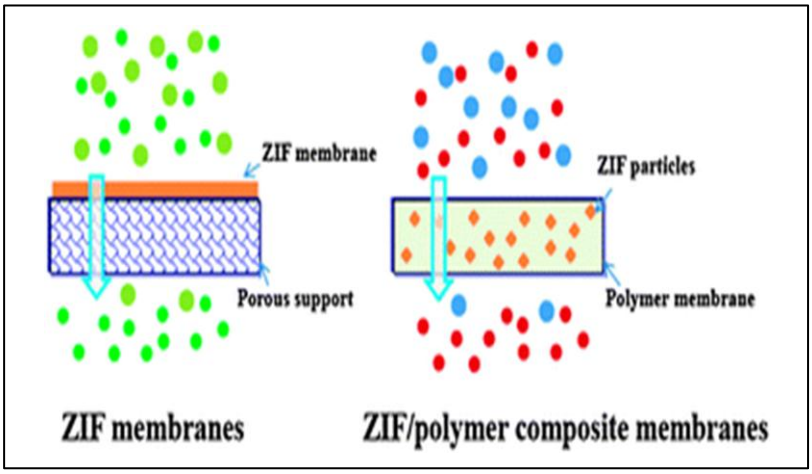

Figure 3: Mixed matrix membrane (Yao & Wang, 2014).

In the separation of CO_2 in CH_4, zeolitic imidazolate frameworks (ZIF) is used for its attractive possibility for carbon capture. ZIF is a chemically and thermally stable material as the porous little crystal can be heated to high temperatures without decomposing. ZIF-8 has good compatibility with polymers and often exhibit good performance in gas separation (Yao & Wang, 2014). The presence of imidazolate linkers in the metal organic frameworks make ZIF more hydrophobic than aluminosilicate zeolite, and therefore imply a better interfacial interactions between the sieve and the polymer (Askari & Chung, 2013). The smaller pore size of ZIF-8 at only 3.4 angstrom makes it a good candidate for CO_2 capture (Nafisi & Hägg, 2014). ZIF-8 which is used in this research project, display a high CO_2 permeances for equimolar mixtures of CO_2 and CH_4. On the other hand, hexafluoropropane diandydride (6FDA) and 2,3,5,6-tetramethyl-1,4-phenylenediamine (durene diamine) are synthesized to form 6FDA-durene polyimide and is used as the polymeric membrane as this polymer exhibits good gas transport properties and high selectivity for CO_2/CH_4 (Liu et al., 2001).

1.2 Problem Statement

It is known that the success of a mixed matrix membrane in the separation of each specific gas pair or group lies mainly on the proper selection of the combination of an inorganic filler and the polymeric material. However, apart from that, there are also a lot of other challenging issues in the process to fabricate a defect free mixed matrix membrane for the separation of a specific gas pair.

One of the challenges in the fabrication of a mixed matrix membrane that researches currently face is the distribution of inorganic filler in the polymeric matrix. Most of the time, the researchers could not obtain a well dispersed of inorganic filler in the polymer membrane, and hence agglomeration happens. In addition, it is also challenging to obtain a good interfacial contact between the continuous polymer phase and the inorganic filler, as a poor polymer and filler contact may cause defects and decrease the selectivity. Apart from that, the sizes of the inorganic filler as well as the loading of the inorganic filler in the polymer membrane also create a good research scope in fabrication of mixed matrix membrane. Nevertheless, high loading of inorganic fillers in the polymer matrix will lead to a brittle membrane and thus worsen the performance of the membrane in gas separation.

To the best of the author's knowledge, the optimization of the fabrication parameters of mixed matrix membrane is not well studied by worldwide researchers. There are also limited publications and research papers reported on the method to fabricate a defect free mixed matrix membrane. Hence, this field of study is still new and highly novel.

1.3 Objectives

The main goal of this research is to develop a defect free ZIF-8/6FDA-durene mixed matrix membrane that can optimize the separation between carbon dioxide and methane.

The objectives of this research project are:

1. To optimize the parameters including sonication and stirring duration in the fabrication of ZIF-8/6FDA-durene mixed matrix membrane.
2. To study the surface morphology and ZIF-8 agglomeration of the resultant mixed matrix membrane by using field emission scanning electron microscopy (FESEM) and energy-dispersive x-ray spectroscopy (EDX).
3. To test the performance of the resultant mixed matrix membranes in CO_2/CH_4 separation.

1.4 Scope of Studies

This research involves the synthesis of the inorganic filler, ZIF-8 and the fabrication of a few sets of ZIF-8/6FDA-durene mixed matrix membrane with different fabrication parameters. Prior to the start of laboratory work, various journals and research articles were reviewed. The different fabrication parameter (stirring and sonication duration) were varied based on reviewing the research by other researchers in the fabrication of similar type mixed matrix membrane. The findings of this research project were recorded, documented and used for postgraduate studies.

CHAPTER 2: LITERATURE REVIEW

2.1 Natural Gas and Reasons for CO_2/CH_4 Separation

In search of greener technology, the world is working towards the renewable sources of energy and the natural gas is becoming more important as it is the cleanest of all fossil fuel used to generate energy (Adewole et al., 2013; Schoots, Rivera-Tinoco, Verbong, & van der Zwaan, 2011). The use of natural gas over the other fossil fuels in the generation of energy produces far less amount of carbon dioxide, which is believed to be a major contributor to global warming (Adewole et al., 2013). Furthermore, natural gas makes a perfect balancing source to the renewable energy sources especially when the solar, wind or the hydro energy are not producing enough energy to supply the growing communities. According to a report by the United States Energy Information Administration in 2013, natural gas consumption is projected to increase from 3.2 trillion cubic meter per year in the 2010, to around 5.2 trillion cubic meter per year in the next thirty years. This makes the natural gas the fastest growing fossil fuel in the United States (Dudley, 2014; "International Energy Outlook 2013," 2013; Japip et al., 2014).

Natural gas is being produced in many countries around the world along with crude oils. Only a few countries produce just natural gas and no crude oil. Figure 4 shows the natural gas reserves around the world as of 2012. As illustrated in the figure, Russia got the most reserve of natural gas in the world and in general, the major supply of natural gas is in Eastern Europe and the Middle East.

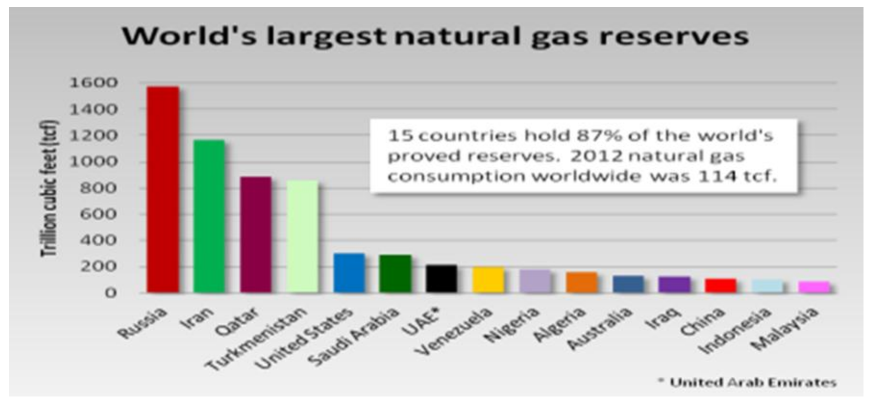

Figure 4: World’s largest natural gas reserves (White, 2012).

The Eastern European reserves are dominated by Russian gas reserves, which approaching 1600 trillion cubic feet (tcf). In the Middle East, the major reserves are in Iran, at almost 1200 tcf and Qatar, in a series of gas fields known as the “North Field”, has more than 900 tcf of proven reserves. Malaysia is the world’s 15th largest natural gas reserves and also the world’s 2nd largest exporter of liquefied natural gas (LNG) (EIA, 2014).

Natural gas is a mixture of gases, in which up to 90% of it is made up of methane, while the remaining are made up of other hydrocarbons such as ethane, propane and also natural gas such as nitrogen, oxygen and carbon dioxide (Naturalgas.org, 2013; Pierobon, 2013). Nature gas containing small volumes of impurities can still be used as fuel whereas it is not possible for nature gas which contains high volumes of impurities as it cannot be burned efficiently and safely ("Removal of CO2 from natural gas processing plant," n.d.). The presence of CO_2 in natural gas reduces the calorific value of the gas as well as makes the gas streams to become more acidic and corrosive, which might greatly affect the transportation system of the gas (Zhang et al., 2013). Therefore, CO_2 has to be removed from natural gas in order to improve the heating value of the gas, and to prevent corrosion of the pipeline and other process equipment used (J.Hao et al., 1993; Koch, Buchan, & Cnop, 2005).

The main problem when it comes to the exploration of new natural gas fields around the world is that up to 40% of the proven gas reserves are sour, which means the natural gas contains more than 10% CO_2 (Jahn, Bos, & Broeke, 2012). Pipeline specifications for transporting natural gas usually require a concentration of less than 2% CO_2 in the natural gas (Koch et al., 2005). Most of the natural gas produced in the United States of America contains more than 5% of CO_2. According to Natural Environment Research Council of British, the natural gas produced at the Sleipner field in the North Sea contains as much as 9% of CO_2. In Malaysia, the natural gas produced from Tangga Barat cluster fields of PETRONAS contains relatively high level of CO_2, at 32% of CO_2 in the natural gas, whereas the gas field such as in Bujang, Sepat, Noring and Inas of the peninsular Malaysia are all of high CO_2 concentration in the natural gas, ranging from 60% CO_2 and above (Darman & Harun, 2006). Therefore, it is essential to remove or reduce the level of CO_2 to an acceptable limit in the natural gas before the gas is being transported or processed (Adewole et al., 2013; Ahmad, Keong, & Shariff; Zhang et al., 2013).

2.2 Existing CO_2/CH_4 Separation Technology

Several separation technologies are commonly used in order to separate carbon dioxide from natural gas. The technologies mentioned above include cryogenic distillation, amine adsorption, absorbent liquid absorption and membrane separation (Y.-S. Bae et al., 2008; Chew, Ahmad, & Bhatia, 2010). Figure 5 shows the types of CO_2 separation techniques.

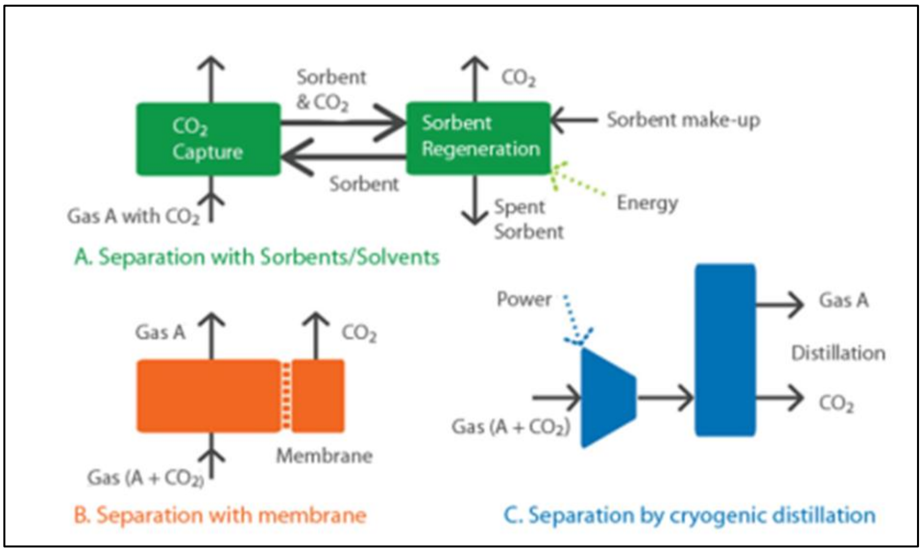

Figure 5: Types of CO_2 separation techniques ("Three basic methods to separate gases," 2008).

Amine absorption is the widely developed commercial technology used to separate CO_2 from natural gas. However, there are a number of issues by using amine type liquid absorbent to capture the CO_2. After the removal of CO_2 from the natural gas via amine absorption, an additional step is required in order to isolate and regenerate the solvent (Chew et al., 2010). This increases the operating cost as it requires high amount of energy in order to regenerate the solvent (Adewole et al., 2013; Chew et al., 2010). Furthermore, the equipment used in the process also tends to get corroded easily which further increase the cost of operation (Adewole et al., 2013; Ohlrogge, Wind, & Brinkmann, 2002).

Apart from using amine absorption to separate CO_2 from natural gas, adsorption is also used as a more cost effective separation process compared to the higher cost for amine absorption. Adsorption-based methods such as pressure swing adsorption are easy to control, good energy efficiency and low operating and capital investment costs (Y.-S. Bae et al., 2008). In the adsorption process, physical adsorbents based on carbons and zeolites are able to adsorb large amount of CO_2 at room temperature, but have its limitation such as reduced CO_2 adsorption capacity once the temperature becomes higher (Wang et al., 2014). Adsorption by solids has generally been economically practical to use, however only when the feed gas contained small amounts of CO_2 and it is required to substantially remove all the CO_2 presence in the feed gas (Holmes & Ryan, 1982).

Extractive distillation is one of the separation technologies that separate the CO_2 from natural gas by using distillation in the presence of relatively non-volatile solvent added into the distillation column. The addition of non-volatile components into the distillation system will break the azeotrope between light and heavy key components with low relative volatilities (Berstad, Nekså, & Anantharaman, 2012). An example of this is in the context of CO_2 removal from natural gas is the separation of CO_2 and ethane, where the obtainable CO_2 product purity would otherwise be constrained by a relatively pressure independent azeotrope if there is no addition of non-volatile components into the distillation system (Hong & Kobayashi, 1986). The advantages of using this separation technology are that the entrainer used is CO_2 selective, non-corrosive, and is effective for high CO_2 concentration feedstock (Torres-Ortega et al., 2014).

Lastly, membrane separation is an energy efficient technology and being widely investigated for the CO_2 separation currently (Chew et al., 2010). Membrane gas separation technology involves the separation of individual gas component based on the difference of their rate of permeation through a certain specific membrane (Kohl & Nielsen, 1997). The membrane technology for gas separation has been developed rapidly in the last two decades. Polymeric membranes have dominated the industrial application typically in gas separation as they are affordable and easier to scale up compared to inorganic membranes (Japip et al., 2014). However, polymeric membranes have low thermal stability and has its limitation in application of high temperature CO_2 separation (Chew et al., 2010). In the membrane separation process, feed gas enters the membrane system after pre-treatment to ensure efficient separation (Ahmad et al., n.d.).

2.3 Gas Separation via Membrane Separation over Other Separation Technologies

Among the gas separation technologies available and listed above, membrane is the most suitable for gas separation as the separation process is energy efficient and cost effective when compared to conventional separation technologies such as to remove CO_2 from natural gas by absorption with alkanolamines (Wu et al., 2015). The existing technologies such as adsorption, amine absorption or extractive distillation, used to separate CO_2 from natural gas are not able to separate mixtures which contained CO_2 content more than 20% in the mixture (Jusoh, Lau, Shariff, & Yeong, 2014). There come the advantages of using membrane technology for gas separation over aforementioned gas separation technologies, as membrane separation normally greatly reduced the capital and installation costs due to the simplicity of the operation and its modular design. It also requires lower energy consumption and a smaller size and weight (Schell & Houston, 1983). Figure 6 shows the CO_2/CH_4 separation via mixed matrix membrane.

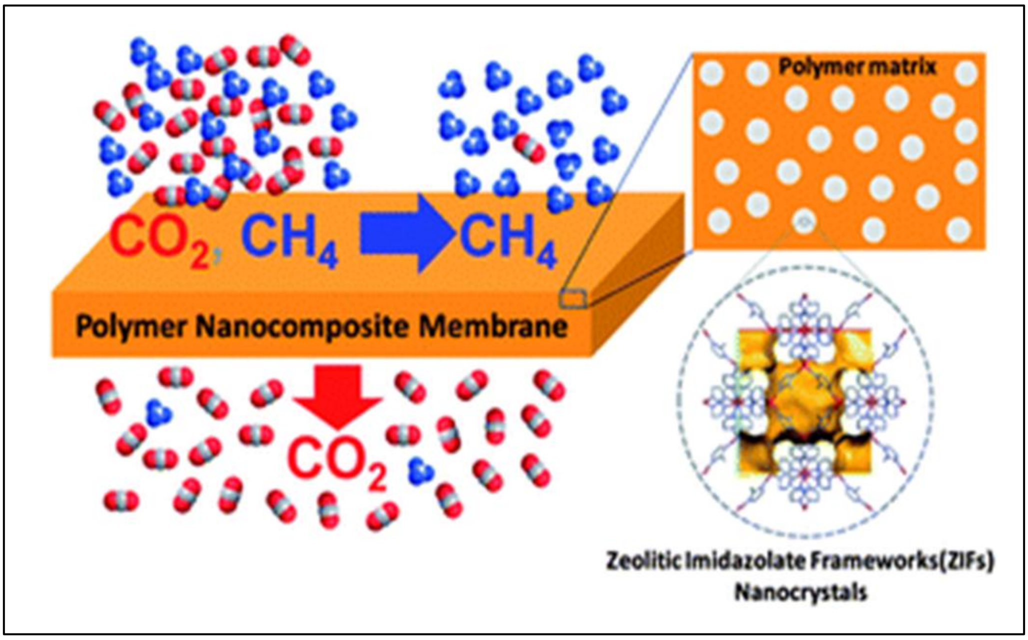

Figure 6: CO_2/CH_4 separation via mixed matrix membrane (Song et al., 2012).

2.4 Type of Membranes and its Advantages/Disadvantages

Generally, three types of membranes including inorganic membrane, polymeric membrane, as well as the mixed matrix membrane are being widely investigated for its potential used in CO_2 separation.

Inorganic membranes generally refer to the membranes which are made of materials such as silica, ceramic, carbon, metals and zeolite (Pabby, Rizvi, & Sastre, 2008). Inorganic membrane can be further classified into two major categories, which are the porous inorganic membranes and the dense inorganic membranes (Abedini & Nezhadmoghadam, 2010). Among the different type of inorganic membrane, zeolite membrane is used in the separation of CO_2 from natural gas as it has well-defined crystals micropores in the zeolite framework, which makes it has great potential to achieve high flux and selectivity (Maghsoudi & Soltanieh, 2014). In addition to that, the thermal and mechanical resistance are the positive inherent characteristics of zeolite membrane (Maghsoudi & Soltanieh, 2014). The advantages of using inorganic membranes include the long term stability of the membrane at high temperature, and its resistance to harsh environments and high pressure drop (Abedini & Nezhadmoghadam, 2010). On the other hand, the disadvantages of using inorganic membrane are the high capital cost to fabricate, brittleness of the membrane, low membrane surface per module volume and also difficulty in getting high selectivity in large scale micro porous membrane (Gallucci, Basile, & Hai, 2011).

The other type of membrane is polymeric membrane. Polymeric membranes are made from natural or synthetic polymer. Natural polymers consist of wool, rubber and cellulose whereas examples of synthetic polymers include polyamide, polystyrene and polytetrafluorothylene (Freeman & I.Pinnau, 1999). For the synthetic polymer, it is produced by the polymerisation of a monomer, or by the co-polymerisation of two different monomers. Polymeric membrane materials are further divided into polymers above the glass transition temperature (Rubbery) or polymers below the glass transition temperature (Glassy) (Rodriguez, Cohen, Ober, & Archer, 2003). These polymer membranes are known to have high selectivity but low permeability (Adewole et al., 2013). The advantages of using polymer membrane include the light weight of the membrane, lower cost of membrane fabrication, process-ability into thin films, porous beads, hollow fibres and composites, and huge variations in structure and properties (Bernardo, Drioli, & Golemme, 2009; Huang, Guan, Tan, Qiao, & Kulprathipanja, 2006). However, the efficiency of polymer membranes will decrease with time due to chemical degradation, fouling, thermal instability and the occurrence of swelling phenomenon (Souza & Quadri, 2013).

Mixed matrix membranes are composed of either porous or nonporous inorganic filler dispersed in a continuous polymer matrix (Cakal, Yilmaz, & Kalipcilar, 2012). Mixed matrix membranes combine the characteristics of both inorganic and organic polymer membranes (Souza & Quadri, 2013). The permeability of the mixed matrix membrane is largely influenced by the properties of the polymer and the inorganic filler, as well as the compatibility between the inorganic filler and the polymer (Cakal et al., 2012). One of the advantages of using a mixed matrix membrane over the organic membrane is the increase in gas permeability compared to the pure polymer membrane. It is shown that some hybrid membrane pair actually performed better with a higher gas permeability and similar or improved gas selectivity compared to the corresponding polymer only membrane, particularly at elevated temperature (J. H. Kim & Lee, 2001). An addition of an inorganic filler into the polymer yields performances similar to the best polymer membranes for the same gas separation (Jeazet, Staudt, & Janiak, 2012). Figure 7 shows the schematic diagram of a mixed matrix membrane consisting of a polymeric matrix and inorganic filler.

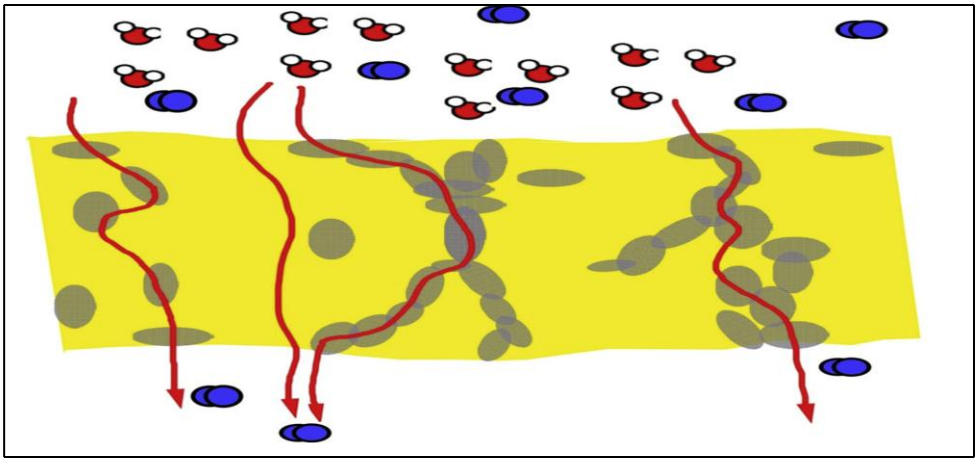

Figure 7: Schematic diagram of a MMM (Rezakazemi, Ebadi Amooghin, Montazer-Rahmati, Ismail, & Matsuura, 2014).

Tables 1, 2 and 3 show the performance of polymeric, inorganic and mixed matrix membranes in CO_2/CH_4 separation.

Table 1: Performance of polymeric membranes on CO_2/CH_4 separation

Polymeric membrane	**CO_2 Permeability (Barrer)**	**CH_4 Permeability (Barrer)**	**CO_2/CH_4 Selectivity**	**References**
6FDA-durene Polyimide	1468.3	65.0	22.6	(Nafisi & Hägg, 2014)
6FDA-durene/ DABA (9/1)	256.0	13.1	19.51	(Askari & Chung, 2013)
6FDA-durene/ DABA (7/3)	158.0	6.2	25.48	(Askari & Chung, 2013)
Matrimid®	6.2	0.22	28.2	(Abedini, Omidkhah, & Dorosti, 2014)
Polycarbonate	2.0	-	27.2	(Zhang et al., 2013)

Table 2: Performance of inorganic membranes on CO_2/CH_4 separation

Inorganic membrane	**CO_2 Permeance (GPU)**	**CO_2/CH_4 Selectivity**	**References**
SAPO-34 zeolite	268.95	49.0	(Li, Alvrada, Noble, & Falconer, 2005)
KY zeolite	2091.80	40.0	(Hasegawa et al., 2002)
Silica	204	71.5	(Raman & Brinker, 1995)
Carbonized	5.71	70.0	(Ogawa & Nakano, 2000)
DDR zeolite	209.18	400.0	(van den Bergh et al., 2008)

Table 3: Performance of mixed matrix membranes on CO_2/CH_4 separation

Polymeric membrane	**Inorganic filler**	**CO_2 Permeability (Barrer)**	**CO_2/CH_4 Selectivity**	**References**
6FDA-DAM	ZIF-90 (15%)	720	37.0	(T. H. Bae et al., 2010)
PSf	MCM-41 Silica (10%)	6.6	23.0	(S. Kim & Marand, 2008)
Matrimid®52 18	CMS (33%)	11.5	47.92	(Vu, Koros, & Miller, 2003)
6FDA-durene/DABA (9/1)	ZIF-8 (20%)	392	20.45	(Askari & Chung, 2013)
6FDA-durene	ZIF-8 (5%)	1695.0	22.70	(Nafisi & Hägg, 2014)

2.5 Fabrication of Mixed Matrix Membrane

Mixed matrix membranes were prepared by dispersing of the inorganic filler in a solvent before the addition of polymer to form the hybrid membrane (Thompson et al., 2014). Both the inorganic filler and the polymer membrane must be carefully selected to be selective for the same gas pair, as to create a mixed matrix membrane which can separate the gas pair well. In order to choose the dispersed and continuous phases properly, the transport mechanisms and the gas component preferentially transporting through the membrane must be taken into account (T.-S. Chung, Jiang, Li, & Kulprathipanja, 2007). The stirring and sonication duration are an important parameter in the fabrication of mixed matrix membrane. However, there is no standard approach for fabricating mixed matrix membrane reported by worldwide researches.

2.6 Material Selection

In the present work, zeolitic imidazolate frameworks (ZIF-8) will be selected as inorganic filler due to its attractive characteristic. ZIF-8 composes tetrahedrally coordinated transition metal ions connected by organic imidazole linkers. It is chemically and thermally stable material as the porous little crystal can be heated to high temperatures without decomposing (Yao & Wang, 2014). ZIF-8 as shown in

Figure 8, which is used in this research project, display high CO_2 permeances for equimolar mixtures of CO_2 and CH_4. It has demonstrated its high thermal stability, permanent porosity and also remarkable chemical resistance to boiling alkaline water and organic solvents (Park et al., 2006).

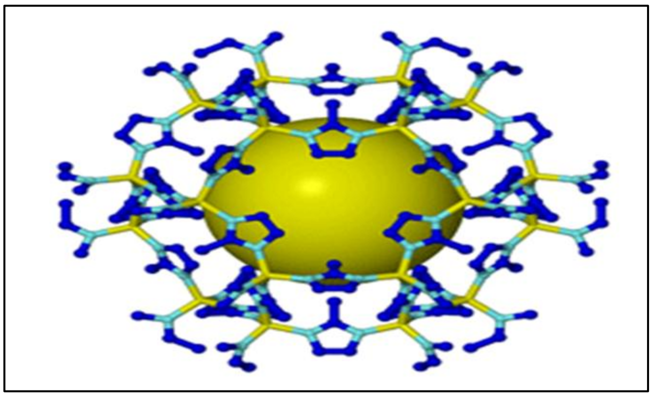

Figure 8: Chemical structure of ZIF-8 (Pan, Liu, Zeng, Zhao, & Lai, 2011).

6FDA-based polyimides exhibit good separation performance for various types of gas pair such as CO_2/N_2 and CO_2/CH_4. Among the 6FDA-based polyimides, 6FDA-durene is selected as the polymer matrix in this research project due to its high intrinsic gas separation performance, especially for its high gas permeability for carbon dioxide gas, as well as reasonable CO_2/CH_4 selectivity (Japip et al., 2014). 6FDA-durene in hollow fiber membranes is also proven to have impressive separation performance, despite the fact that the gas permeation flux decrease significantly by aging of the membrane (Lin & Chung, 2001).

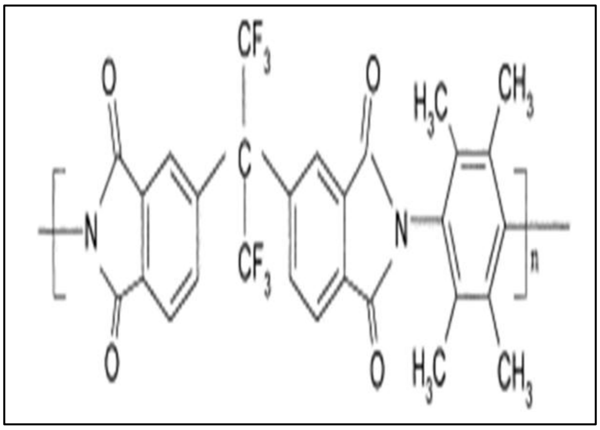

Figure 9: Chemical formula of 6FDA-durene (T. S. Chung & Shao, 2006).

CHAPTER 3: METHODOLOGY

3.1 Flowchart of Final Year Project

Figure 10 shows the overall activity flow chart of FYP.

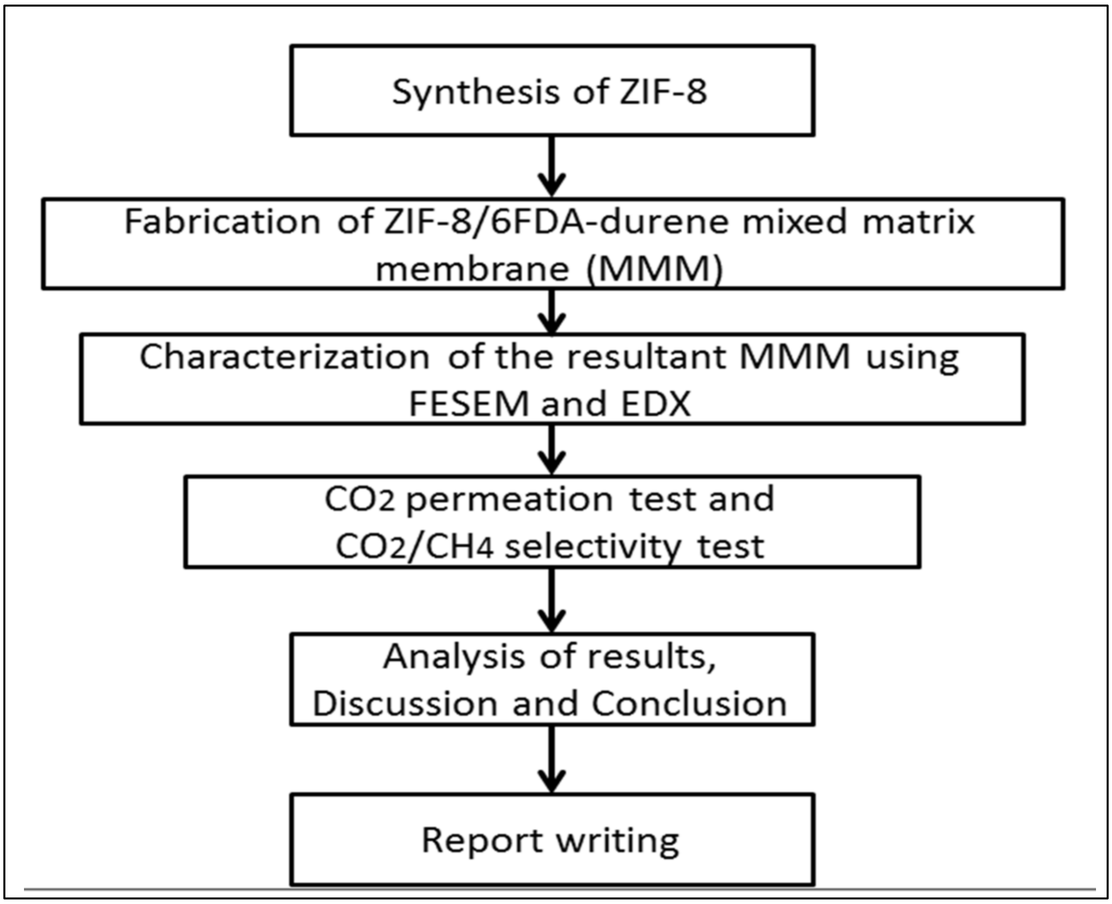

Figure 10: Activity flowchart of FYP

Laboratory work was commenced beginning from the synthesis of ZIF-8 nanoparticles. Research work was then continued in the fabrication of few sets of ZIF-8/6FDA-durene mixed matrix membranes by means of varying the parameters in the fabrication of the mixed matrix membranes. The resultant mixed matrix membranes were then characterized by using SEM, FESEM and EDX. Gas performance testing of CO_2/CH_4 separation of the resultant mixed matrix membranes were then carried out.

3.2 Experimental Procedures

Figure 11 shows the experimental procedures of the current research work.

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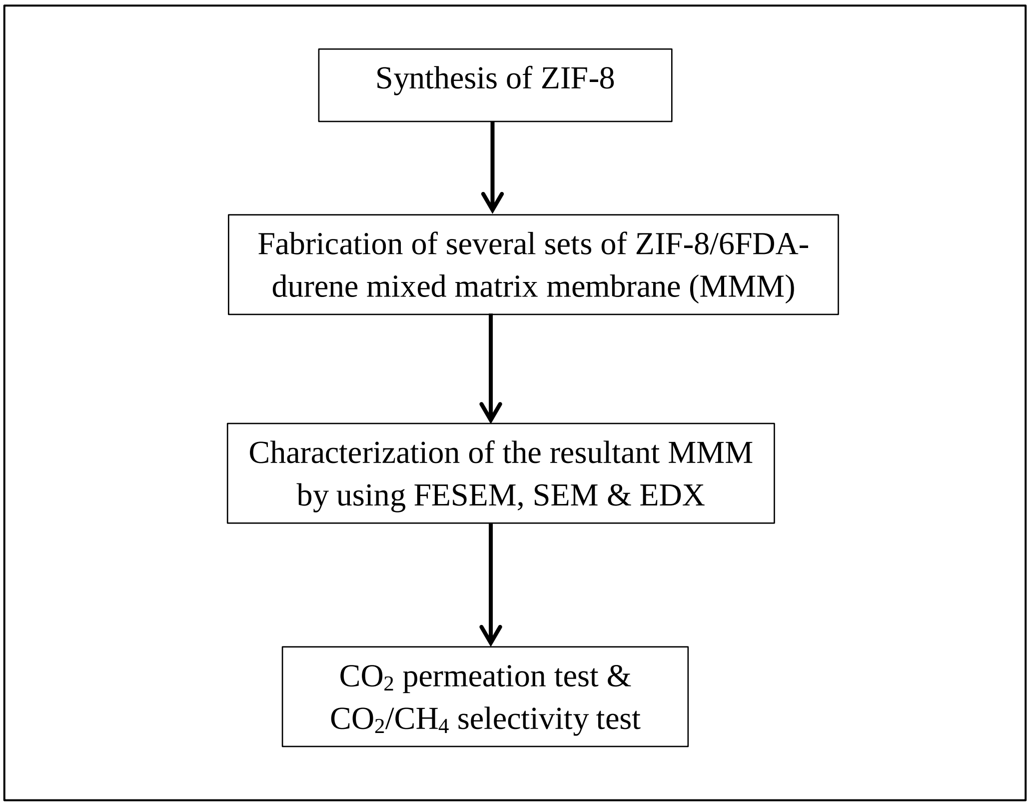


Figure 11: Flowchart of experimental procedures.

3.2.1 Synthesis of ZIF-8

1. A solution of 2-methyimidazole (6.489g, 79.04 mmol) is prepared and dissolved in 200 mL of methanol under stirring in a magnetic bar
2. A second solution of zinc nitrate hexahydrate, $Zn(NO_3)_2 \cdot 6H_2O$, (2.933 g, 9.87 mmol) is prepared and dissolved in 200mL of methanol
3. The prepared solution of zinc nitrate hexahydrate is then rapidly poured into the solution of 2-methyimidazole and stir with a magnetic bar for an hour.
4. The cloudy solution is then centrifuged using 7800 rpm for 5 minutes to separate the nanocrystals and the solution
5. The nanocrystals are washed with fresh methanol for 3 times and dried overnight at 85 °C in oven.

Figure 12 illustrates the steps for the synthesis of ZIF-8 nanoparticle.

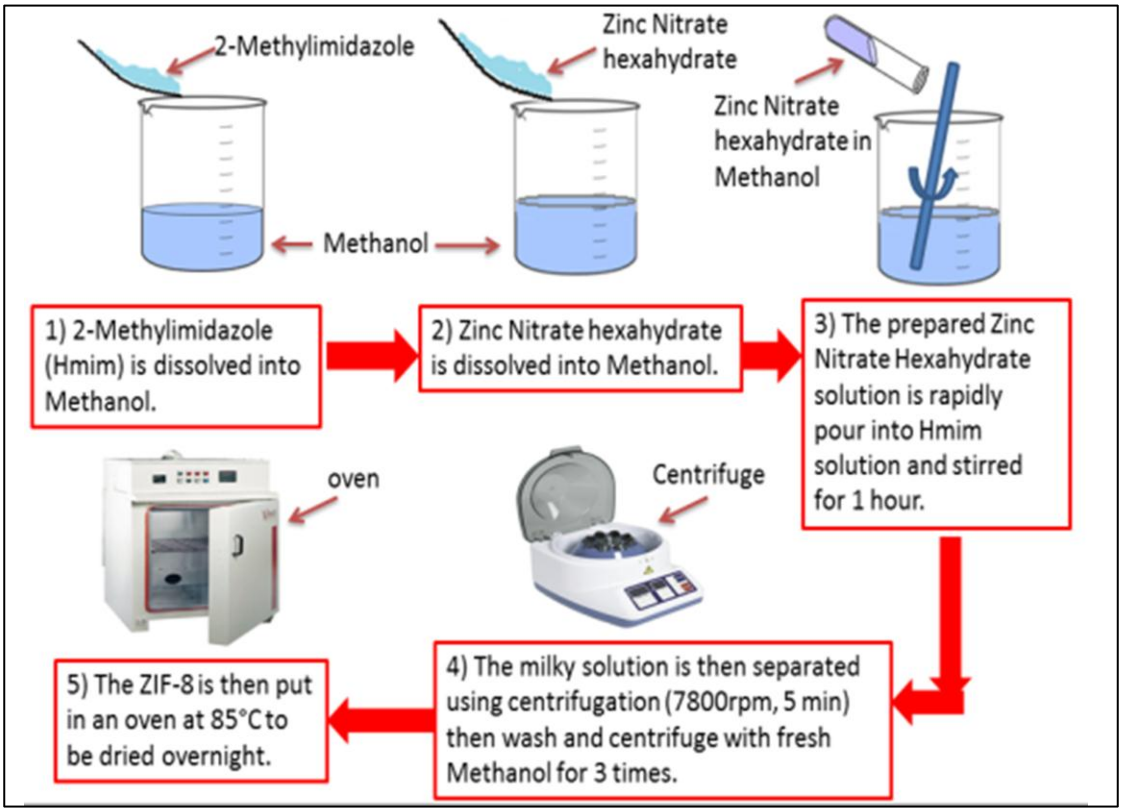


Figure 12: Synthesis of ZIF-8 nanoparticles.

3.2.2 Fabrication of ZIF-8/6FDA-durene MMM

Figure 13 shows the procedures to fabricate a ZIF-8/6FDA-durene mixed matrix membrane.

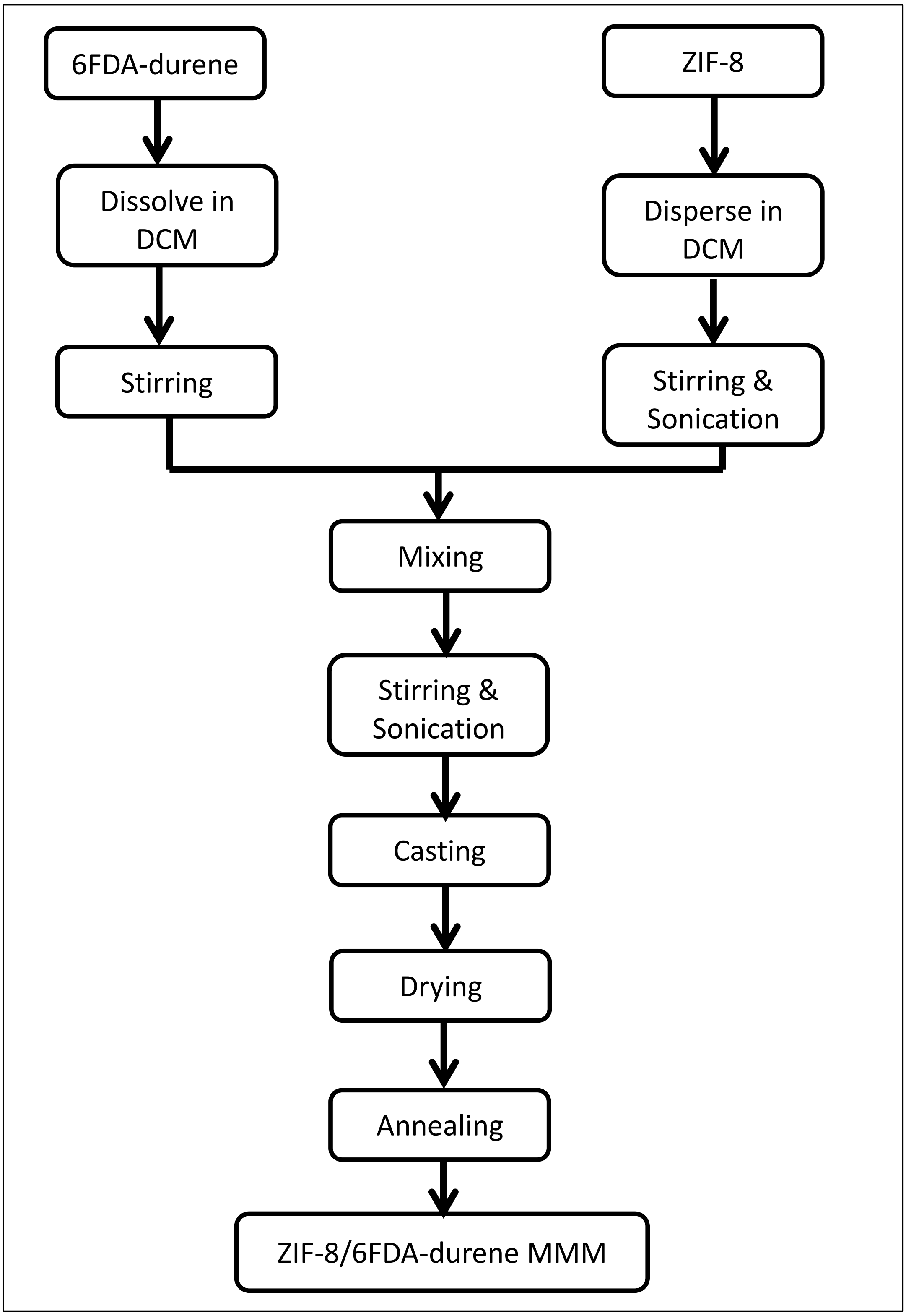


Figure 13: Fabrication of ZIF-8/6FDA-durene MMM

Steps to fabricate ZIF-8/6FDA-durene mixed matrix membrane:

1. 6FDA-durene polyimide and ZIF-8 were synthesized prior to the fabrication of mixed matrix membrane.
2. Both the ZIF-8 and 6FDA-durene were dispersed and dissolved in dichloromethane (DCM) respectively. The loading of ZIF-8 in DCM is fixed at 5 wt. %.
3. For the fabrication of MMMs, ZIF-8 in the solvent was stirred and sonicated based on the stirring and sonication duration in table 4.
4. After that in all sets except for set 5 and set 6, 10% of 6FDA-durene solution was added into ZIF-8 followed by 30 to 60 minutes of stirring and another 30 to 60 minutes of sonication.
5. The remaining 90% of the polymer solution was added into ZIF-8 solution, stirred and sonicated alternately for 30 to 60 minutes for twice.
6. Two membrane samples (Set 5 & Set 6) bypassed the priming stage and 100% of 6FDA-durene solution was directly added into ZIF-8 in DCM.
7. Table 4 summarized the experimental procedure in fabricating seven mixed matrix membrane samples with different stirring and sonication durations.

Table 4: Summary of the experimental procedure in MMM fabrication

Samples	**ZIF-8 in Dichloromethane (DCM)**		**ZIF-8 in 6FDA-durene**	
	Stirring (minutes)	**Sonication (minutes)**	**Stirring (minutes)**	**Sonication (minutes)**
1	30	30	**Add 10% of polymer into ZIF-8 in DCM**	
			30	30
			30	30
	30	30	**Add remaining polymer into ZIF-8 in DCM**	
			30	30
			30	30

2	30	30	**Add 10% of polymer into ZIF-8 in DCM**	
			30	30
			30	30
	30	30	**Add remaining polymer into ZIF-8 in DCM**	
			60	60
			60	60
3	60	60	**Add 10% of polymer into ZIF-8 in DCM**	
			30	30
			30	30
	60	60	**Add remaining polymer into ZIF-8 in DCM**	
			30	30
			30	30
4	60	60	**Add 10% of polymer into ZIF-8 in DCM**	
			30	30
			30	30
	60	60	**Add remaining polymer into ZIF-8 in DCM**	
			60	60
			60	60
5	30	30	No priming stage. 100% of polymer is added into ZIF-8 in DCM.	
	30	30		
	30	30		
6	60	60	No priming stage. 100% of polymer is added into ZIF-8 in DCM.	
	60	60		
	60	60		
7	30	30	**Add 10% of polymer into ZIF-8 in DCM**	
			30	30
			Add remaining polymer into ZIF-8 in DCM	
			30	30

Note: All the MMM solutions were stirred vigorously for 1 hours prior to casting.

3.3 Characterization

The field emission scanning electron microscopy (FESEM), scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDX) were used to investigate the cross section surface morphology, agglomeration of ZIF-8 in the resultant mixed matrix membranes. Table 5 summarized the characterization methods and its function.

Table 5: Characterization methods and its function

CHARACTERIZATION METHOD	**FUNCTION**
Field emission scanning electron microscope (FESEM)	• To study the surface morphology of the mixed matrix membrane (MMM)
Scanning electron microscope (SEM)	• To study the surface morphology of the mixed matrix membrane (MMM)
Energy dispersive x-ray (EDX)	• To study the agglomeration and dispersion of ZIF-8 in the MMM
Thermogravimetric analysis (TGA)	• To determine the thermal stability of the membrane
Differential Scanning Calorimetry (DSC)	• To determine the glass transition temperature of the membrane

3.4 Gas Permeation Test

The separation performance of the resultants membranes were evaluated by determining the CO_2 and CH_4 permeability as well as CO_2/CH_4 selectivity. The temperature of the study was fixed at 25 °C with pressure set at 3.5 bar. The permeability and selectivity of the membrane was calculated using the measured values for permeate flowrate which is obtained from the bubble flowmeter (Mohammadi, Moghadam, Saeidi, & Mahdyarfar, 2008) The permeability for pure gases was then calculated as below:

$$(P)_i = \frac{Q_i l}{A \Delta p} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

Where $(P)_i$ is defined as permeability for gas i in Barrer, Q_i is the volumetric flow rate of gas i, Δp is the pressure difference across membrane, A is the membrane effective surface area, l is the membrane skin thickness (Ismail & Lai, 2004). The permeability of the CH_4 and CO_2 are reported in the unit of Barrer (1 Barrer = 1×10^{-10} cm^3 (STP).cm/s.cm^2.cmHg).

The selectivity of the membrane for pure gas and negligible downstream pressure were then be obtained by dividing permeability of CO_2 over permeability of CH_4 (Hillock, Miller, & Koros, 2008) as follows:

$$\alpha_{CO_2/CH_4} = \frac{(P)_{CO_2}}{(P)_{CH_4}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

Where, $(P)_{CO_2}$ is the permeability of CO_2 and $(P)_{CH_4}$ is the permeability of CH_4

The performance test for the CO_2 permeation and CO_2/CH_4 selectivity was conducted using a permeation test rig as shown in Figure 14.

Figure 14: Permeability test rig.

3.5 Materials, Equipment and Apparatus used

ZIF-8 and the 6FDA-durene polyimide were synthesized in the laboratory of Universiti Teknologi PETRONAS prior to be used to fabricate the mixed matrix membranes. Zinc nitrate hexahydrate and 2-methyimidazole are purchased from Acros Organics and were used in the synthesis of ZIF-8. Methanol was used as solvent in the synthesis of ZIF-8. Dichloromethane was used as a solvent for ZIF-8 and also 6FDA-durene in the fabrication of mixed matrix membrane.

Equipment and apparatus such as beaker, hot plate stirrer, petri dish, tweezer, pestle & mortar, magnetic stirrer, measuring cylinder, stopwatch, vacuum oven, sonicator, and centrifuge are used in the synthesis of ZIF-8 and also the fabrication of ZIF-8/6FDA-durene mixed matrix membrane.

3.6 Gantt Chart

Table 6 shows the Gantt chart for FYP II.

Table 6: Gantt chart

No	**Week Description**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
1	Synthesis of ZIF-8 nanoparticles	■													
2	Fabrication of 6FDA-durene polymer membrane	■	■												
3	Fabrication of 7 sets of mixed matrix membranes			■	■	■	■								
4	Progress report preparation					■	■	■							
5	Characterization of membranes					■	■	■	■	■					
6	Membranes performance testing					■	■	■	■	■	■				
7	Pre-SEDEX preparation									■	■	■			
8	Technical paper preparation									■	■	■	■	■	
9	Final dissertation preparation												■	■	■
10	Meeting with FYP supervisor	■	■	■	■	■	■	■	■	■	■	■	■	■	■

3.7 Key Milestones

Table 7 shows key milestones for FYP II.

Table 7: Key milestones of FYP II

Milestones	**Week**
Synthesis of ZIF-8 nanoparticle	1
Fabrication of 6FDA-durene polymeric membrane	2
Fabrication of ZIF-8/6FDA-durene mixed matrix membranes	5
Characterization of resultant membranes	8
Progress report submission	8
Performance testing of resultant membranes	9
Pre-SEDEX	11
Technical paper submission	13
Oral presentation	14
Submission of hardbound	15

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Synthesis of ZIF-8 Nanocystal

Zeolitic imidazolate frameworks (ZIF-8) was synthesized in laboratory in the first term of final year project prior to the fabrication of the mixed matrix membrane. Figure 15 shows the picture of ZIF-8 nanocrystal formed prior to be grinded into fine powder form. Figure 16 shows the picture of ZIF-8 nanocrystal in fine white powder form.

Figure 15: ZIF-8 nanocrystal prior to grind

Figure 16: ZIF-8 nanocrystal in fine white powder form.

X-ray diffraction (XRD) was carried out to determine the crystalline structure of ZIF-8 sample. The XRD characteristic peaks obtained in the present work at 2θ values of 7.28°, 10.32°, 12.66°, 16.30° and 17.92° are consistent with those XRD peaks reported in the literatures for ZIF-8 structure (Yan, 2012; Zhu, Jasinski, & Carreon, 2012). Figure 17 shows the XRD pattern of the ZIF-8 sample synthesized in the present work. Surface morphology of the ZIF-8 crystal was examined by using the field emission scanning electron microscopy (FESEM). Figure 18 shows the FESEM image of the ZIF-8 obtained in the present work. The average particle size of the ZIF-8 formed is approximately 50 nm.

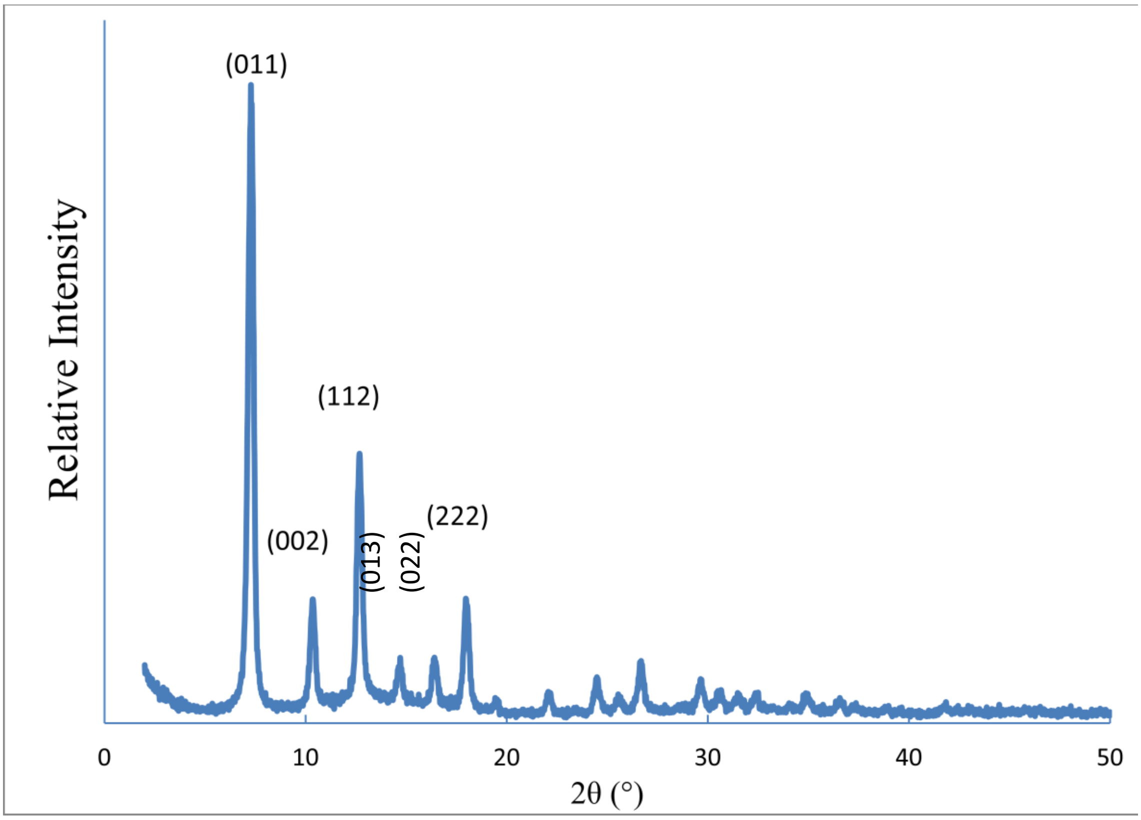


Figure 17: XRD result of ZIF-8 sample synthesized in the present work.

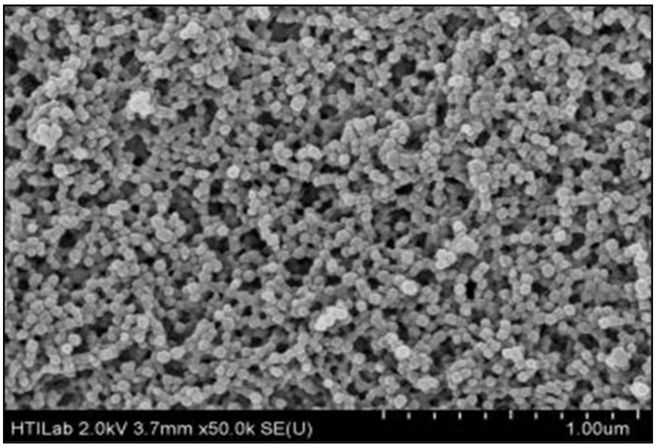


Figure 18: FESEM image of ZIF-8 sample synthesized in the present work.

4.2 Resultant Mixed Matrix Membranes

Total seven sets of ZIF-8/6FDA-durene mixed matrix membranes were synthesized according to different stirring and sonication duration to determine the optimum route to fabricate a defect free membrane. The physical appearance of the resultant MMMs are shown in Figure 19.

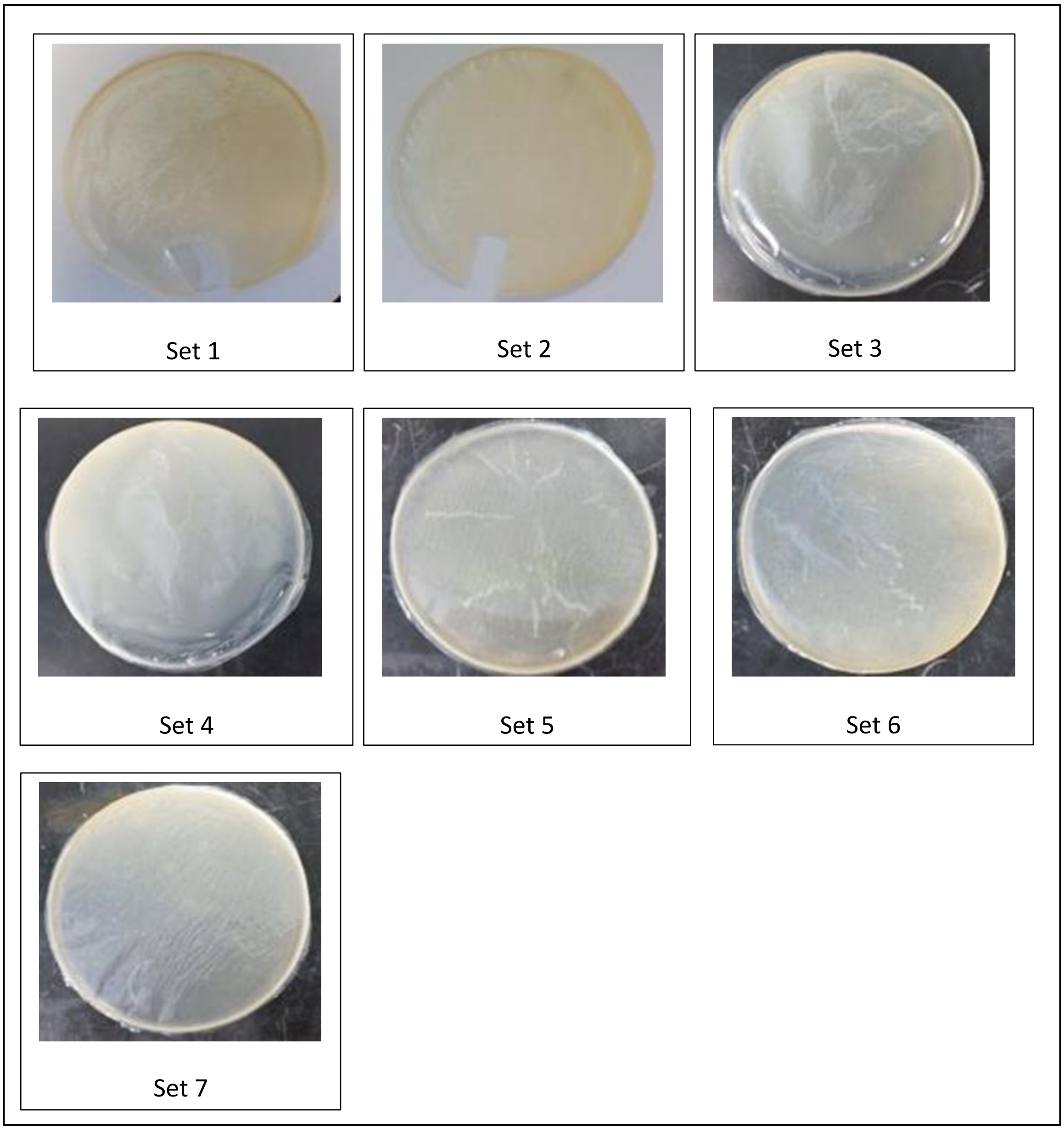


Figure 19: The Physical appearance of ZIF-8/6FDA-durene mixed matrix membranes fabricated in the present work.

4.3 Characterization of Resultant Membranes

4.3.1 Scanning electron microscopy (SEM) and Energy dispersive x-ray (EDX)

The cross section morphology of the pure 6FDA-durene polymer membrane and ZIF-8/6FDA-durene mixed matrix membranes were characterized using SEM.

Energy dispersive x-ray (EDX) was used to study the agglomeration and dispersion of ZIF-8 nanoparticles in the resultant mixed matrix membranes. Figure 20 shows the SEM image of the 7 sets of resultant membrane at 10k magnification.

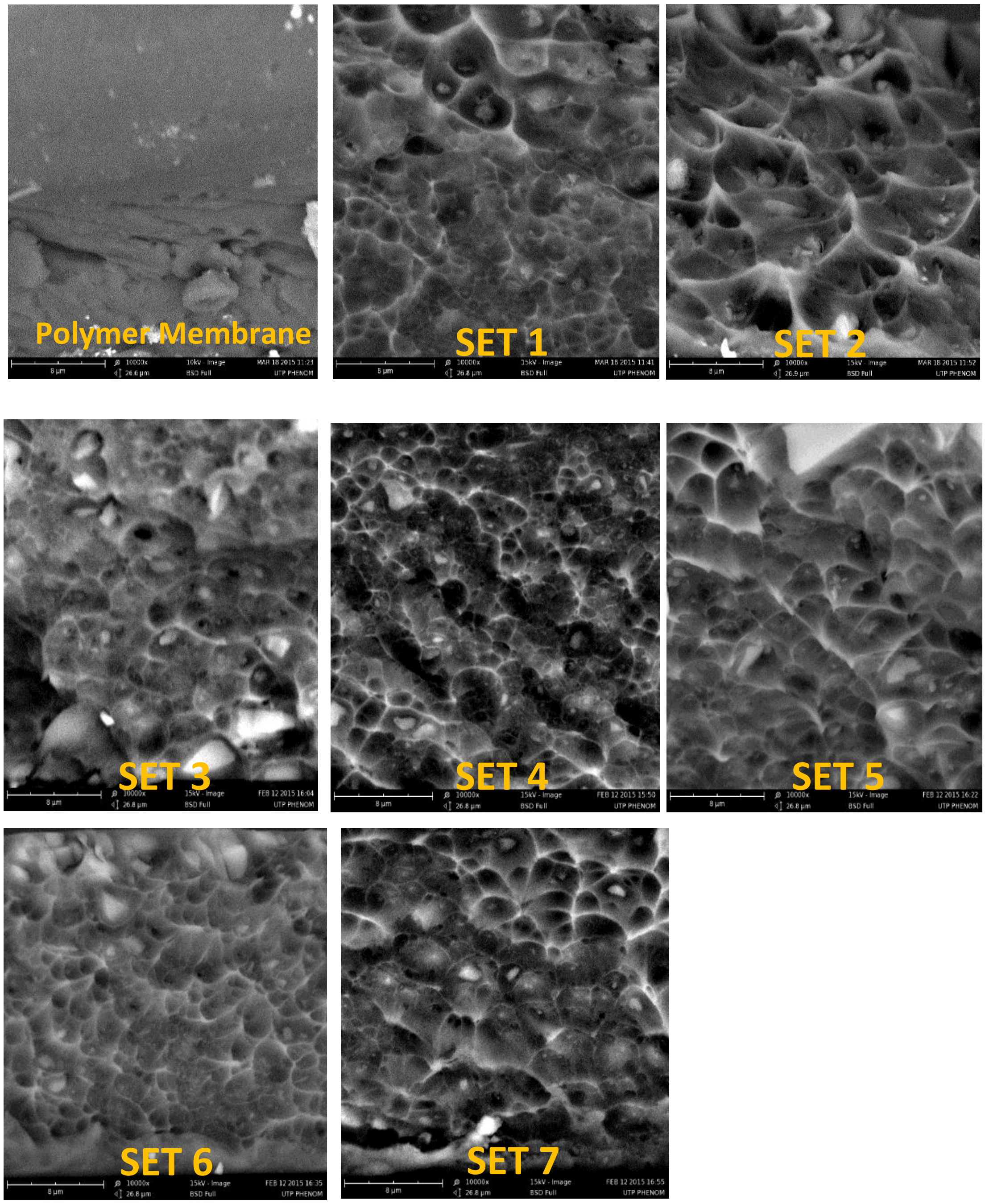


Figure 20: SEM cross-sectional images of pure polymer membrane and MMM set 1 to MMM set 7 at 10k magnification.

It can be seen from the SEM images in Figure 20 that ZIF-8 generally mixed well with 6FDA-durene polyimide in all of the seven sets of MMM fabricated in the present work. This indicates that ZIF-8 is compatible with 6FDA-durene. A homogeneous dispersion of particles were seen in all the 7 sets of MMM at 10k magnification.

4.3.2 Field emission scanning electron microscopy (FESEM) and Energy dispersiveX-ray (EDX)

The cross section morphology of the seven sets of mixed matrix membranes were also studied using FESEM while Energy dispersive x-ray (EDX) was used to study the agglomeration and dispersion of ZIF-8 nanoparticles in the resultant membranes. Figure 21 & 22 shows the FESEM images of the cross section morphology of the resultant membranes at 50k and 100k magnification respectively.

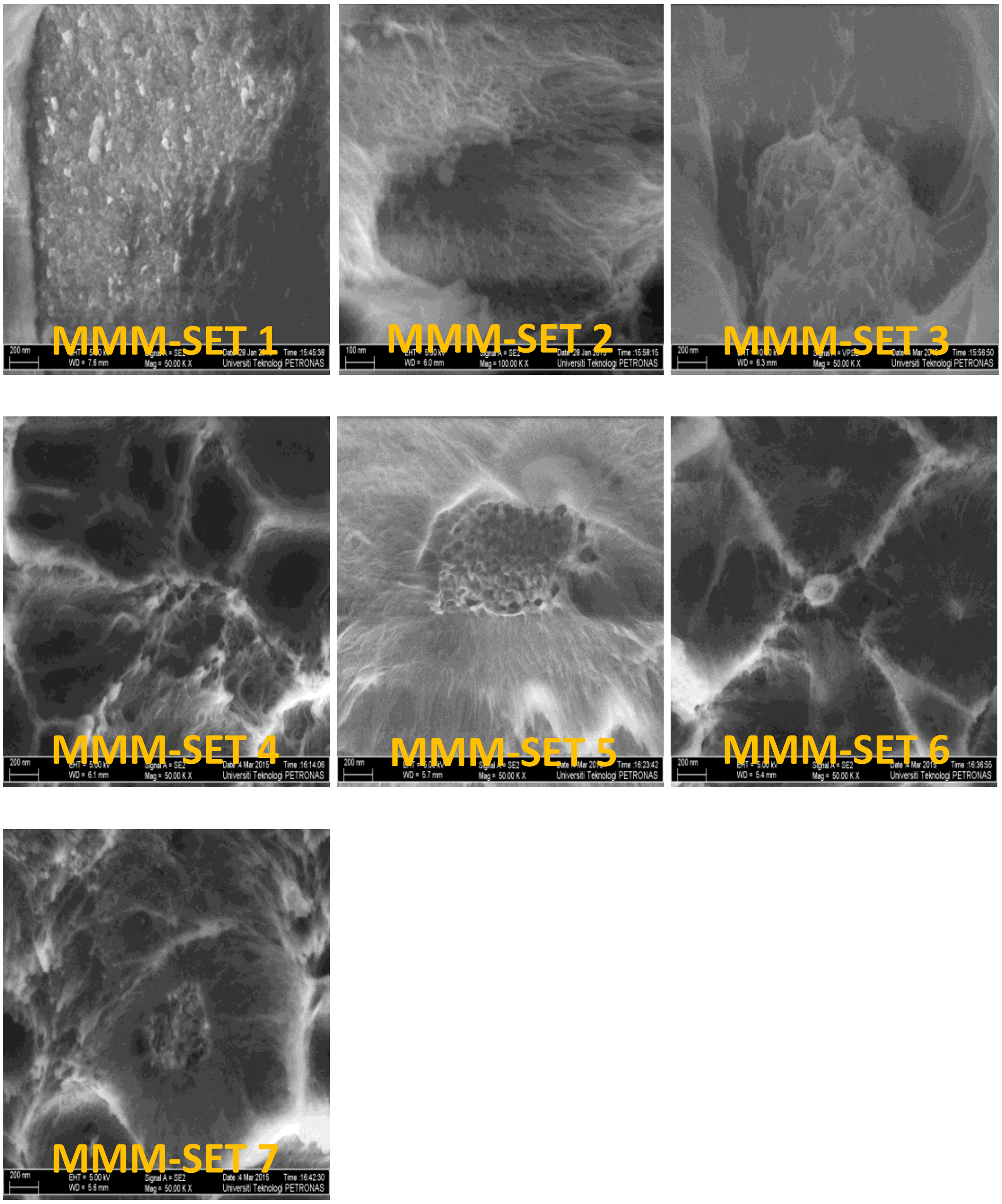


Figure 21: FESEM images of MMMs at 50k magnification.

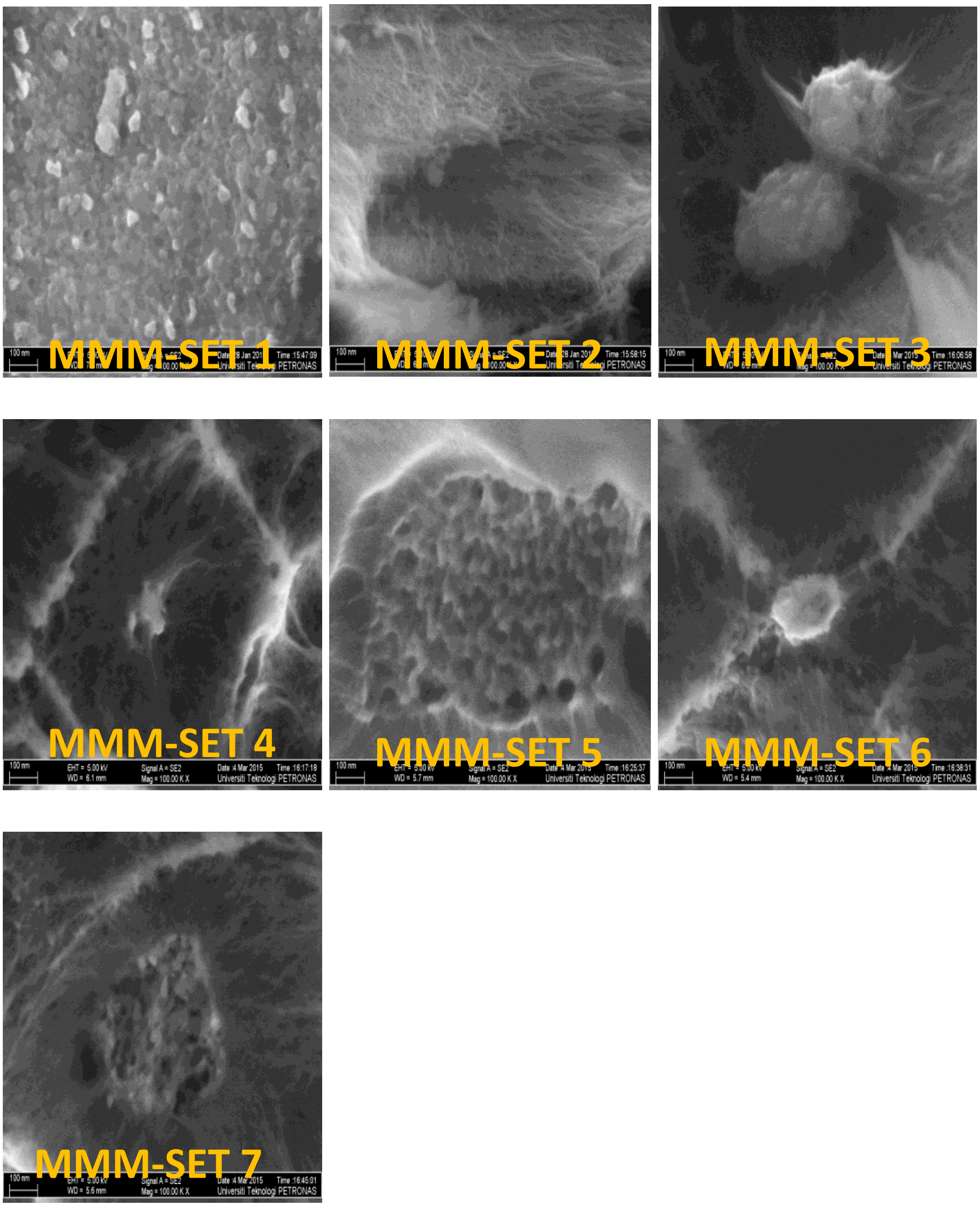


Figure 22: FESEM images of MMMs at 100k magnification.

It can be seen clearly in Figure 21 and 22 that agglomeration of ZIF-8 nanoparticles occurred in set 1, set 3, set 5, set 6 and set 7. In MMM set 1, a huge agglomeration of ZIF-8 nanoparticles (Ostwald ripening) was observed whereas smaller agglomeration were observed in MMMs Set 3, Set 5, Set 6 and Set 7. As reported by Thompson et al. (2014), priming step which was not used in MMMs Set 5 andS 6, eventually produced agglomeration of ZIF-8 nano-fillers in the polymeric matrix. Therefore, it is essential to apply the priming step in order to produce a well dispersed particles in the MMMs containing ZIF materials. In MMMs Set 2 and Set 4, ZIF-8 nanoparticles were found to disperse well and did not agglomerate. From all of the FESEM images, it can be seen that ZIF-8 nanoparticles are compatible with 6FDA-durene polyimide. This could be due to the same type of solvent is used for both ZIF-8 and 6FDA-durene solutions. The uniform dispersion of ZIF-8 nanoparticles in 6FDA-durene was later confirmed again by mapping the zinc element with the use of energy dispersive X-ray spectroscopy (EDX). Due to the reason that zinc element only exists in ZIF-8 nanoparticles, therefore it can be used as an indicator to determine the dispersion of ZIF-8 nanoparticles in the MMMs. Figure 23-24 show the FESEM-EDX mapping for Zinc from the cross sectional area of seven sets of MMMs with various stirring and sonication duration.

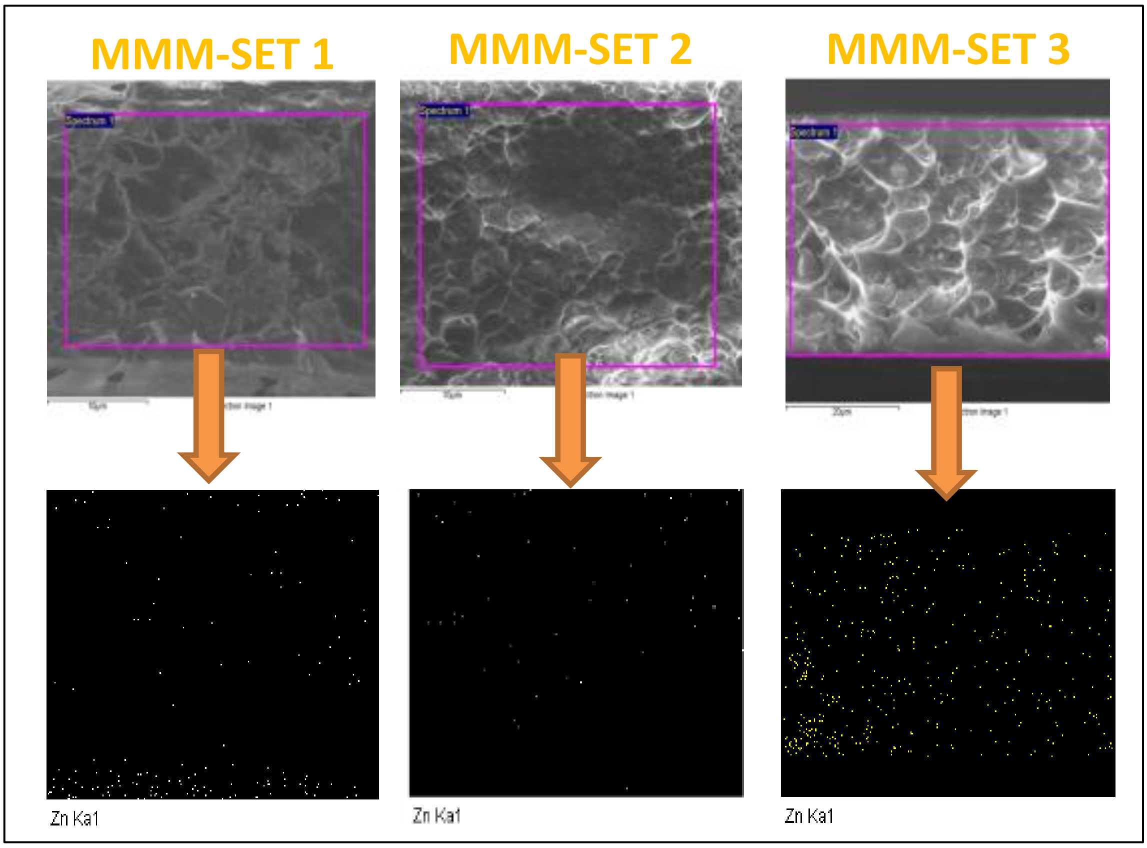


Figure 23: FESEM-EDX mapping for Zn element for MMM Set 1-3

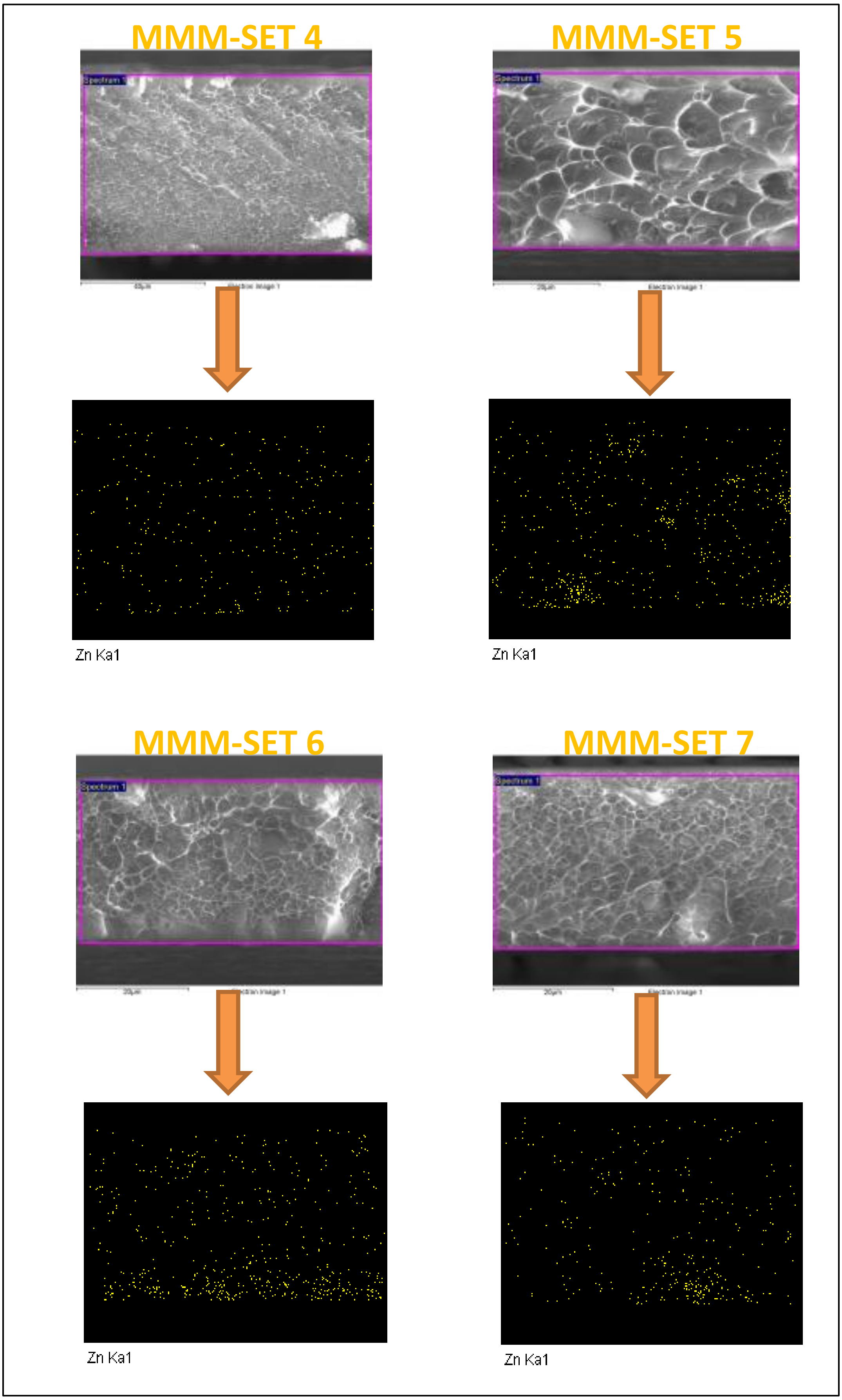


Figure 24: FESEM-EDX mapping for Zn element for MMM Set 4-7

FESEM-EDX mapping for Zn element in Figure 23 and 24 had shown that ZIF-8 nanoparticles in MMM Set 2 and set 4 were dispersed evenly in the mixed matrix membrane as compared to the other five sets of MMMs. The amount of ZIF-8 shown in Figure 26 for MMM Set 2 was significantly less compared to the other six sets of MMMs. This could be due to the ZIF-8 nanoparticles being allocated in another area of the membrane and hence could possibly indicate agglomeration on the other side of the membrane. MMM Set 5 showed the worst agglomeration among the other sets probably due to the least time allocated in stirring and sonicating of the ZIF-8 nanoparticles in DCM before being added to the polymer and cast. It should be noted also that MMM Set 5 did not undergo priming step prior to cast. Sedimentation of ZIF-8 nanoparticles were observed in MMMs Set 1 and Set 6.

4.3.3 Thermogravimetric analysis (TGA)

The thermal stability of the resultant MMMs as well as the pure 6FDA-durene and pure ZIF-8 were characterized by using Thermogravimetric analysis (TGA) in order to determine the decomposition temperature and the weight loss of the membranes as a function of temperature. TGA was done in the laboratory under nitrogen environment, operating at a heating rate of 10°C per minute. Figure 28 shows the thermogravimetric analysis result for pure 6FDA-durene polymer membrane.

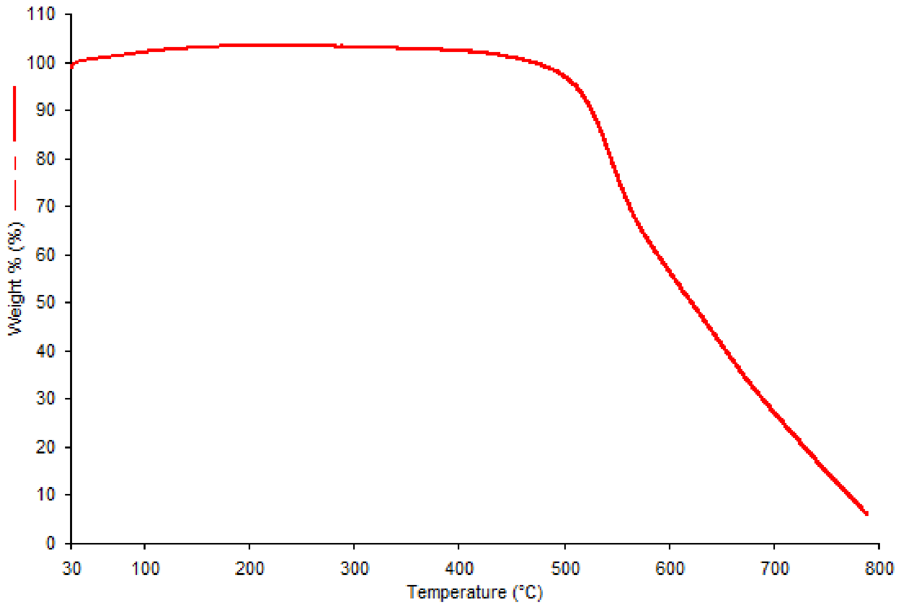


Figure 25: TGA result of 6FDA-durene polymer membrane

Figure 26 shows the thermogravimetric analysis (TGA) results for all the seven sets of mixed matrix membrane together with the TGA result of pure 6FDA-durene and of pure ZIF-8. No weight loss was observed below 400 °C for the pure 6FDA-durene as well as the seven sets of mixed matrix membrane. This could be due to the process of drying to completely remove all the moisture trapped in the membranes and also the residual DCM solvent. All of the seven sets of MMMs and the pure 6FDA-durene as well as ZIF-8 showed good thermal stability up to 500 °C.

From Figure 26, ZIF-8 showed higher decomposition stability and 30 wt % remained at 800°C, whereas the pure 6FDA-durene and MMM set 1 and set 2 have only less than 10 wt % at 800 °C. It can then be concluded that ZIF-8 nano-filler is not well dispersed in MMM set 1 and set 2 due to the close resemblance of TGA curve with the curve of the pure 6FDA-durene. MMMs Set 3 - Set 7 on the other hand, showed a better dispersion of ZIF-8 nano-filler in the membrane. The decompose stage at around 450 °C for the MMMs could be due to the onset of ZIF-8 decomposition in the MMMs, which was agreed with the decomposition of the pure ZIF-8 nano-filler.

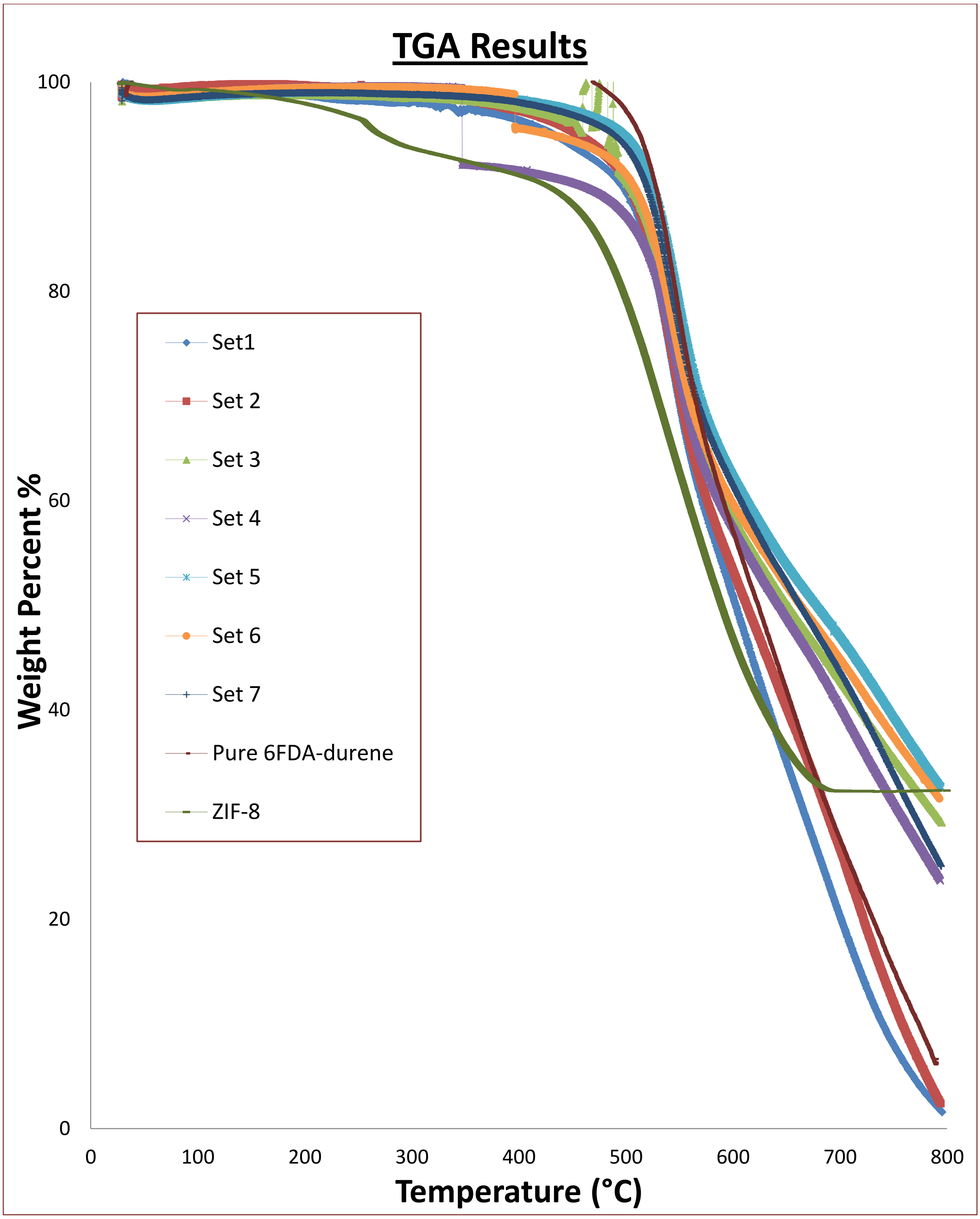


Figure 26: TGA of pure 6FDA-durene, pure ZIF-8, seven sets of 5wt% ZIF-8/6FDA-durene mixed matrix membrane

4.3.4 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) was carried out to determine the glass transition temperature, T_g, of the resultant mixed matrix membranes in order to investigate the interaction between the polymer and the inorganic filler used. The DSC was conducted using the DSC equipment from Mettler Toledo, operated under nitrogen atmosphere, heating from 40°C to 450°C at a heating rate of 10°C per minute. Two heating cycles were performed and the glass transition temperature for each of the membranes was obtained in the second cycle of the heating. Table 8 shows the DSC results of pure 6FDA-durene membrane and ZIF-8/6FDA-durene MMM Set 4.

Table 8: DSC results for pure 6FDA-durene & ZIF-8/6FDA-durene MMM Set 4

Membrane	**Glass Transition Temperature, T_g from experiment**	**Glass Transition Temperature, T_g reported from** (Nafisi & Hägg, 2014)
Pure 6FDA-durene	423.15 °C	416.62 °C
5 wt% ZIF-8/6FDA-durene (Set 4)	438.13 °C	423.87 °C

The DSC results for the pure 6FDA-durene and MMM Set 4 are comparable to the T_g result as reported by Nafisi & Hagg (2014). The glass transition temperature of 5 wt % of ZIF-8 nanoparticles in the MMM as reported by literature was 423.87 °C whereas thermal decomposition of the MMM starts at 496°C (Nafisi & Hägg, 2014). From Table 8, it was observed that the addition of 5 wt% of ZIF-8 into 6FDA-durene under the stirring and sonication duration specified for MMM Set 4, had increased the glass transition temperature of 15°C T_g from 423.15 °C to 438.13 °C. This showed good interactions between ZIF-8 nan-fillers and 6FDA-durene polyimide. As reported by Ahmad & Hagg (2013), the increased in T_g could be due to the H-bonding between the ZIF-8 nano-fillers and the polymeric matrix.

4.4 Gas Permeability and Selectivity of Resultant Membranes

The resultant mixed matrix membranes and the pure 6FDA-durene membrane were tested for gas separation performance using CH_4 and CO_2. The permeability of the resultant mixed matrix membranes were measured at 25 °C and at 3.5 bar. In the present work, the permeability of the 6FDA-durene membrane was found to be 671.49 barrer for CO_2 and 59.78 barrer for CH_4 with a CO_2/CH_4 selectivity of 11.23 at 3.5 bar. Table 9 summarizes the permeability and selectivity for the pure 6FDA-durene membrane and the seven sets of mixed matrix membranes.

Table 9: Gas Permeability and CO_2/CH_4 Selectivity of the MMMs

Membrane	**CO_2 Permeability (Barrer)**	**CH_4 Permeability (Barrer)**	**CO_2/CH_4 Selectivity**
Pure 6FDA-durene membrane	671.49	59.78	11.23
MMM-Set 1	708.53	159.39	4.45
MMM-Set 2	895.76	235.71	3.80
MMM-Set 3	200.81	125.20	1.60
MMM-Set 4	779.61	107.67	7.24
MMM-Set 5	759.78	260.75	2.91
MMM-Set 6	805.35	205.43	3.92
MMM-Set 7	765.53	165.30	4.63

Generally, the incorporation of ZIF-8 nanoparticles into the 6FDA-durene polymer matrix showed an increase in CO_2 permeability as compared to the pristine 6FDA-durene membrane in most of the resultant sets of MMMs. MMM Set 3 on the other hand showed a decrease in CO_2 permeability and CH_4 permeability with a CO_2/CH_4 selectivity of only 1.60. This clearly showed that MMM Set 3 is a defect set. MMM Set 4 on the other hand showed the best CO_2/CH_4 selectivity among all of the MMM sets. This could be due to the longest duration of stirring and sonication in the preparation of the MMM. The CO_2 and CH_4 permeability in MMM Set 4 showed an increment of 16.10 % and 80.11 % respectively as compared to the pure 6FDA-durene membrane, but the ideal selectivity dropped 35% from 11.23 to 7.24. Generally, the addition of ZIF-8 nano-filler in the polymeric matrix showed an increase in the CO_2 and CH_4 permeability but decrease in the CO_2/CH_4 selectivity. This could be due to the reason that the increased in T_g (Table 8) as observed in the mixed matrix membrane which implied the increase in free volume of the membrane and thus, increases the separation performance of the MMM.

CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The present work focused on the optimization of the fabrication parameters including the stirring and sonication duration in the fabrication of a defect free ZIF-8/6FDA-durene mixed matrix membrane. ZIF-8 was synthesized by using zinc nitrate hexahydrate and 2-methlyimidazole where the synthesised ZIF-8 nanocrystals were then dissolved in dichloromethane (DCM) and the stirring and sonication durations were varied. After mixing the 6FDA-durene solution with ZIF-8 solution, and again the stirring and sonication durations were varied to study the effect of these parameters towards the fabrication of defects-free mixed matrix membrane. The resultant membranes were characterized by using scanning electron microscope (SEM), field emission scanning electron microscope (FESEM) and energy dispersive X-ray (EDX) to study the surface morphology, dispersion of ZIF-8 and ZIF-8 agglomeration in the resultant mixed matrix membranes. The SEM and FESEM images showed that ZIF-8 is compatible with 6FDA-durene. It was found that MMM Set 4 displayed the best dispersion of ZIF-8 nanoparticles among the resultant mixed matrix membranes as shown in FESEM images and also EDX mapping of Zn element. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to determine the thermal stability and find the glass transition temperature, T_g of the resultant mixed matrix membranes. The T_g of the MMM was found to be 15 °C more than the pure 6FDA-durene membrane. Lastly, CO_2 and CH_4 gas permeation testing at 3.5 bar was conducted to test the performance of the resultant membrane in CO_2/CH_4 separation. MMM Set 4 displayed the best separation performance among the resultant mixed matrix membranes which increased the permeability of CO_2 and CH_4 over the pristine membrane while offering the least dropped in selectivity as compared to other sets of MMMs.

5.2 Recommendations

For future expansion of this research project, it is suggested to increase the weight percentage of ZIF-8 nanofillers to be 10 wt%, 20 wt% and 30 wt%, in the 6FDA-durene polymeric matrix to further investigate the effect of the proposed stirring and sonication duration in the fabrication of a defect free mixed matrix membrane at higher loading. It is also recommended to increase the stirring and sonication duration of the mixed matrix membranes for a total stirring and sonication time of more than 12 hours to further investigate the effect of stirring and sonicating duration in fabricating a defect free membrane. Lastly, it is recommended to increase the number of times of stirring and sonication after priming step from two times to three times.

REFERENCES

Abedini, R., & Nezhadmoghadam, A. (2010). Application of Membrane in Gas Separation Processes: Its Suitability and Mechanisms.

Abedini, R., Omidkhah, M., & Dorosti, F. (2014). Highly permeable poly(4-methyl-1-pentyne)/NH2-MIL 53 (Al) mixed matrix membrane for CO2/CH4 separation. *RSC Advances, 4*(69), 36522-36537. doi: 10.1039/C4RA07030E

Adewole, J. K., Ahmad, A. L., Ismail, S., & Leo, C. P. (2013). Current challenges in membrane separation of CO2 from natural gas: A review. *International Journal of Greenhouse Gas Control, 17*(0), 46-65. doi: http://dx.doi.org/10.1016/j.ijggc.2013.04.012

Ahmad, F., Keong, L. L., & Shariff, A. Removal of CO2 from Natural Gas using Membrane Process: Design, Fabrication and Parametric study

Askari, M., & Chung, T.-S. (2013). Natural gas purification and olefin/paraffin separation using thermal cross-linkable co-polyimide/ZIF-8 mixed matrix membranes. *Journal of Membrane Science, 444*(0), 173-183. doi: http://dx.doi.org/10.1016/j.memsci.2013.05.016

Bae, T. H., Lee, J. S., Qiu, W., Koros, W. J., Jones, C. W., & Nair, S. (2010). A high performance gas separation membrane containing submicrometer sized metal-organic Framework Cystals. *Angewandte Chemie International Edition, 49*.

Bae, Y.-S., Mulfort, K. L., Frost, H., Ryan, P., Punnathanam, S., Broadbelt, L. J., . . . Snurr, R. Q. (2008). Separation of CO2 from CH4 using mixed-ligand metal-organic frameworks.

Bernardo, P., Drioli, E., & Golemme, G. (2009). Membrane Gas Separation: A Review/State of the Art. *Ind. Eng. Chem. Res., 48*(10), 4638-4663.

Berstad, D., Nekså, P., & Anantharaman, R. (2012). Low-temperature CO2 Removal from Natural Gas. *Energy Procedia, 26*(0), 41-48. doi: http://dx.doi.org/10.1016/j.egypro.2012.06.008

Cakal, U., Yilmaz, L., & Kalipcilar, H. (2012). Effect of feed gas composition on the separation of CO2/CH4 mixtures by PES-SAPO 34-HMA mixed matrix membranes. *Journal of Membrane Science, 417–418*(0), 45-51. doi: http://dx.doi.org/10.1016/j.memsci.2012.06.011

Chew, T.-L., Ahmad, A. L., & Bhatia, S. (2010). Ordered mesoporous silica (OMS) as an adsorbent and membrane for separation of carbon dioxide (CO2). *Advances in Colloid and Interface Science, 153*(1–2), 43-57. doi: http://dx.doi.org/10.1016/j.cis.2009.12.001

Chung, T.-S., Jiang, L. Y., Li, Y., & Kulprathipanja, S. (2007). Mixed matrix membranes (MMMs) comprising organic polymers with dispersed inorganic fillers for gas separation. *Progress in Polymer Science, 32*(4), 483-507. doi: http://dx.doi.org/10.1016/j.progpolymsci.2007.01.008

Chung, T. S., & Shao, L. (2006). Polyimide membranes: Google Patents.

Darman, N. H., & Harun, A. R. B. (2006). Technical Challenges and Solutions on Natural Gas Development in Malaysia.

Dudley, B. (2014). BP Energy Outlook 2035 (4th ed.).

EIA. (2014). Malaysia: Country Analysis.

Freeman, B. D., & I.Pinnau. (1999). *Polymer Membranes for Gas and Vapor Separation* (Vol. 733).

Gallucci, F., Basile, A., & Hai, F. I. (2011). Introduction- A review of membrane reactors.

Hasegawa, Y., Tanaka, T., Watanabe, K., Jeong, B., H, Kusakabe, K., & Morooka, S. (2002). Separation of CO2-CH4 and CO2-N2 systems using ion-exchanged FAU-type zeolite membranes with different Si/Al ratios. *Korean Journal of Chemical Engineering*(19).

Hillock, A. M. W., Miller, S. J., & Koros, W. J. (2008). Crosslinked mixed matrix membranes for the purification of natural gas: Effects of sieve surface modification. *Journal of Membrane Science, 314*(1–2), 193-199. doi: http://dx.doi.org/10.1016/j.memsci.2008.01.046

Holmes, A. S., & Ryan, J. M. (1982). Solidification prevention: Google Patents.

Hong, J. H., & Kobayashi, R. (1986). To Break an Azeotrope. 1. The use of n-pentane to break the carbon dioxide-ethane azeotrope, for carbon dioxide EOR gas processing. *Ind. Eng. Chem. Process Des.*, *25*(3), pp 736-741.

Huang, Z., Guan, H.-m., Tan, W. l., Qiao, X.-Y., & Kulprathipanja, S. (2006). Pervaporation study of aqueous ethanol solution through zeolite-incorporated multilayer poly(vinyl alcohol) membranes: Effect of zeolites. *Journal of Membrane Science, 276*(1–2), 260-271. doi: http://dx.doi.org/10.1016/j.memsci.2005.09.056

IGS, G. (2014). HOLLOW FIBER MEMBRANE : How Membranes Work – Separation of Nitrogen from the Air. from http://igs-global.com/about-igs/our-technologies-includes-comparison/hollow-fiber-membrane/

International Energy Outlook 2013. (2013). *U.S. Energy Information Administration*

Ismail, A. F., & Lai, P. Y. (2004). Development of defect-free asymmetric polysulfone membranes for gas separation using response surface methodology. *Separation and Purification Technology, 40*(2), 191-207. doi: http://dx.doi.org/10.1016/j.seppur.2004.02.011

J.Hao, P.A.Rice, & S.A.Stern. (1993). Membrane Processes for the removal of acid gases from natural gas. II. Effects of operating conditions, economic parameters, and membrane properties. *Journal of Membrane Science, 81*(3).

Jahn, J., Bos, P. V. D., & Broeke, L. J. V. D. (2012). *Evaluation of Membrane Processes for Acid Gas Treatment.* Paper presented at the SPE International Production and Operations Conference & Exhibition, Doha, Qatar.

Japip, S., Wang, H., Xiao, Y., & Shung Chung, T. (2014). Highly permeable zeolitic imidazolate framework (ZIF)-71 nano-particles enhanced polyimide membranes for gas separation. *Journal of Membrane Science, 467*(0), 162-174. doi: http://dx.doi.org/10.1016/j.memsci.2014.05.025

Jeazet, H. B. T., Staudt, C., & Janiak, C. (2012). Metal-organic frameworks in mixed-matrix membranes for gas separation. *Dalton Trans.*(46).

Jusoh, N., Lau, K. K., Shariff, A. M., & Yeong, Y. F. (2014). Capture of bulk CO2 from methane with the presence of heavy hydrocarbon using membrane process. *International Journal of Greenhouse Gas Control, 22*(0), 213-222. doi: http://dx.doi.org/10.1016/j.ijggc.2014.01.001

Kim, J. H., & Lee, Y. M. (2001). Gas permeation properties of poly(amide-6-b-ethylene oxide)–silica hybrid membranes. *Journal of Membrane Science, 193*(2), 209-225. doi: http://dx.doi.org/10.1016/S0376-7388(01)00514-2

Kim, S., & Marand, E. (2008). High permeability nano-composite membranes based on mesoporous MCM-41 nanoparticles in a polysulfone matrix. *Microporous and Mesoporous Materials, 114*(1–3), 129-136. doi: http://dx.doi.org/10.1016/j.micromeso.2007.12.028

Koch, D. R., Buchan, W. R., & Cnop, T. (2005). Proper pretreatment systems reduce membrane replacement element costs and improve reliability.

Kohl, A. L., & Nielsen, R. (1997). *Gas Purification* (fifth edition ed.).

Koros, W. J., & Mahajan, R. (2000). Pushing the limits on possibilities for large scale gas separation: which strategies? *Journal of Membrane Science, 175*(2), 181-196. doi: http://dx.doi.org/10.1016/S0376-7388(00)00418-X

Li, S., Alvrada, G., Noble, R. D., & Falconer, J. L. (2005). Effects of impurities on CO2/CH4 separations through SAPO-34 membranes. *Journal of Membrane Science, 251*.

Lin, W.-H., & Chung, T.-S. (2001). Gas permeability, diffusivity, solubility, and aging characteristics of 6FDA-durene polyimide membranes. *Journal of Membrane Science, 186*(2), 183-193. doi: http://dx.doi.org/10.1016/S0376-7388(01)00333-7

Liu, S. L., Wang, R., Liu, Y., Chng, M. L., & Chung, T. S. (2001). The physical and gas permeation properties of 6FDA-durene/2,6-diaminotoluene copolyimides. *Polymer, 42*(21), 8847-8855. doi: http://dx.doi.org/10.1016/S0032-3861(01)00439-6

Maghsoudi, H., & Soltanieh, M. (2014). Simultaneous separation of H2S and CO2 from CH4 by a high silica CHA-type zeolite membrane. *Journal of Membrane Science, 470*(0), 159-165. doi: http://dx.doi.org/10.1016/j.memsci.2014.07.025

mastmona. (2014). Membrane Technology.

Mohammadi, T., Moghadam, M. T., Saeidi, M., & Mahdyarfar, M. (2008). Acid Gas Permeation Behavior Through Poly(Ester Urethane Urea) Membrane. *Industrial & Engineering Chemistry Research, 47*(19), 7361-7367. doi: 10.1021/ie071493k

Nafisi, V., & Hägg, M.-B. (2014). Gas separation properties of ZIF-8/6FDA-durene diamine mixed matrix membrane. *Separation and Purification Technology, 128*(0), 31-38. doi: http://dx.doi.org/10.1016/j.seppur.2014.03.006

Naturalgas.org. (2013). Background of Natural Gas. from http://naturalgas.org/overview/background/

Ogawa, M., & Nakano, Y. (2000). Separation of CO2/CH4 mixture through carbonized membrane prepared by gel modification. *Journal of Membrane Science, 173*.

Ohlrogge, K., Wind, J., & Brinkmann, T. (2002). Membrane Technology for Natural Gas Processing. *SPE Gas Technology Symposium*.

Pabby, A. K., Rizvi, S. S. H., & Sastre, A. M. (2008). *Handbook of Membrane Separations. Chemical, Pharmaceutical, Food, and Biotechnological Applications*: CRC Press.

Pan, Y., Liu, Y., Zeng, G., Zhao, L., & Lai, Z. (2011). Rapid synthesis of zeolitic imidazolate framework-8 (ZIF-8) nanocrystals in an aqueous system. *Chemical Communications, 47*(7), 2071-2073. doi: 10.1039/C0CC05002D

Pierobon, J. (2013). Fugitive Methane Emissions: The Achilles' Heel of the Natural Gas Push? , from http://theenergycollective.com/jimpierobon/238831/fugitive-methane-emissions-achilles-heal-natural-gas-push

Raman, N., K, & Brinker, C., J. (1995). Organic 'template' approach to molecular sieving silica membranes. *Journal of Membrane Science, 105*.

Removal of CO2 from natural gas processing plant. (n.d.). Retrieved November 5, 2014, from http://www.bgs.ac.uk/discoveringGeology/climateChange/CCS/RemovalCO2NaturalGas.html

Rezakazemi, M., Ebadi Amooghin, A., Montazer-Rahmati, M. M., Ismail, A. F., & Matsuura, T. (2014). State-of-the-art membrane based CO2 separation using mixed matrix membranes (MMMs): An overview on current status and future directions. *Progress in Polymer Science, 39*(5), 817-861. doi: http://dx.doi.org/10.1016/j.progpolymsci.2014.01.003

Rodriguez, F., Cohen, C., Ober, C. K., & Archer, L. (2003). *Principles of Polymer Systems* (fifth edition ed.): CRC Press.

Schell, W. J., & Houston, C. D. (1983). Membrane Gas Separations forChemical Processes and Energy Applications (Vol. 223, pp. 125-143): American Chemical Society.

Schoots, K., Rivera-Tinoco, R., Verbong, G., & van der Zwaan, B. (2011). Historical variation in the capital costs of natural gas, carbon dioxide and hydrogen pipelines and implications for future infrastructure. *International Journal of Greenhouse Gas Control, 5*(6), 1614-1623. doi: http://dx.doi.org/10.1016/j.ijggc.2011.09.008

Song, Q., Nataraj, S. K., Roussenova, M. V., Tan, J. C., Hughes, D. J., Li, W., . . . Sivaniah, E. (2012). Zeolitic imidazolate framework (ZIF-8) based polymer nanocomposite membranes for gas separation. *Energy & Environmental Science, 5*(8), 8359-8369. doi: 10.1039/C2EE21996D

Souza, V. C., & Quadri, M. G. N. (2013). Organic-Inorganic hybrid membranes in separation processes: a 10-year review. *Braz. J. Chem. Eng, 30*(4).

Thompson, J. A., Vaughn, J. T., Brunelli, N. A., Koros, W. J., Jones, C. W., & Nair, S. (2014). Mixed-linker zeolitic imidazolate framework mixed-matrix membranes for aggressive CO2 separation from natural gas. *Microporous and Mesoporous Materials, 192*(0), 43-51. doi: http://dx.doi.org/10.1016/j.micromeso.2013.06.036

Three basic methods to separate gases. (2008). Retrieved 6 November, 2014, from http://www.co2captureproject.org/

Toon, J. (2010). Energy Efficient Separations: Researchers Use Computational Modeling to Deisng Improved Membrane Technology. from http://www.gtresearchnews.gatech.edu/energy-efficient-separations/

Torres-Ortega, C. E., Segovia-Hernández, J. G., Gómez-Castro, F. I., Hernández, S., Bonilla-Petriciolet, A., Rong, B. G., & Errico, M. (2014). Optimization of Alternative Distillation Sequences for Natural Gas Sweetening. In P. S. V. Jiří Jaromír Klemeš & L. Peng Yen (Eds.), *Computer Aided Chemical Engineering* (Vol. Volume 33, pp. 1201-1206): Elsevier.

van den Bergh, J., Zhu, W., Kapteijn, F., Moulijn, J., A, Yajima, K., Nakayama, K., . . . Yoshida, S. (2008). Separation of CO2 and CH4 by a DDR membrane. *Research on Chemical Intermediates, 34*.

Vu, D. Q., Koros, W. J., & Miller, S. J. (2003). Effect of condensable impurity in CO2/CH4 gas feeds on performance of mixed matrix membranes using carbon molecular sieves. *Journal of Membrane Science*(221).

Wang, J., Huang, L., Yang, R., Zhang, Z., Wu, J., Gao, Y., . . . Zhong, Z. (2014). Recent advances in solid sorbents for CO2 capture and new development trends. *Energy & Environmental Science, 7*(11), 3478-3518. doi: 10.1039/C4EE01647E

White, B. (2012). Can gas-to-liquids technology get traction? , from http://www.arcticgas.gov/can-gas-liquids-technology-get-traction

Wu, T., Diaz, M. C., Zheng, Y., Zhou, R., Funke, H. H., Falconer, J. L., & Noble, R. D. (2015). Influence of propane on CO2/CH4 and N2/CH4 separations in CHA zeolite membranes. *Journal of Membrane Science, 473*(0), 201-209. doi: http://dx.doi.org/10.1016/j.memsci.2014.09.021

Yan, M. P. (2012). *Crystal growth of the metal-organic framework ZIF-8.* (Doctor of Philosophy), University of Manchester.

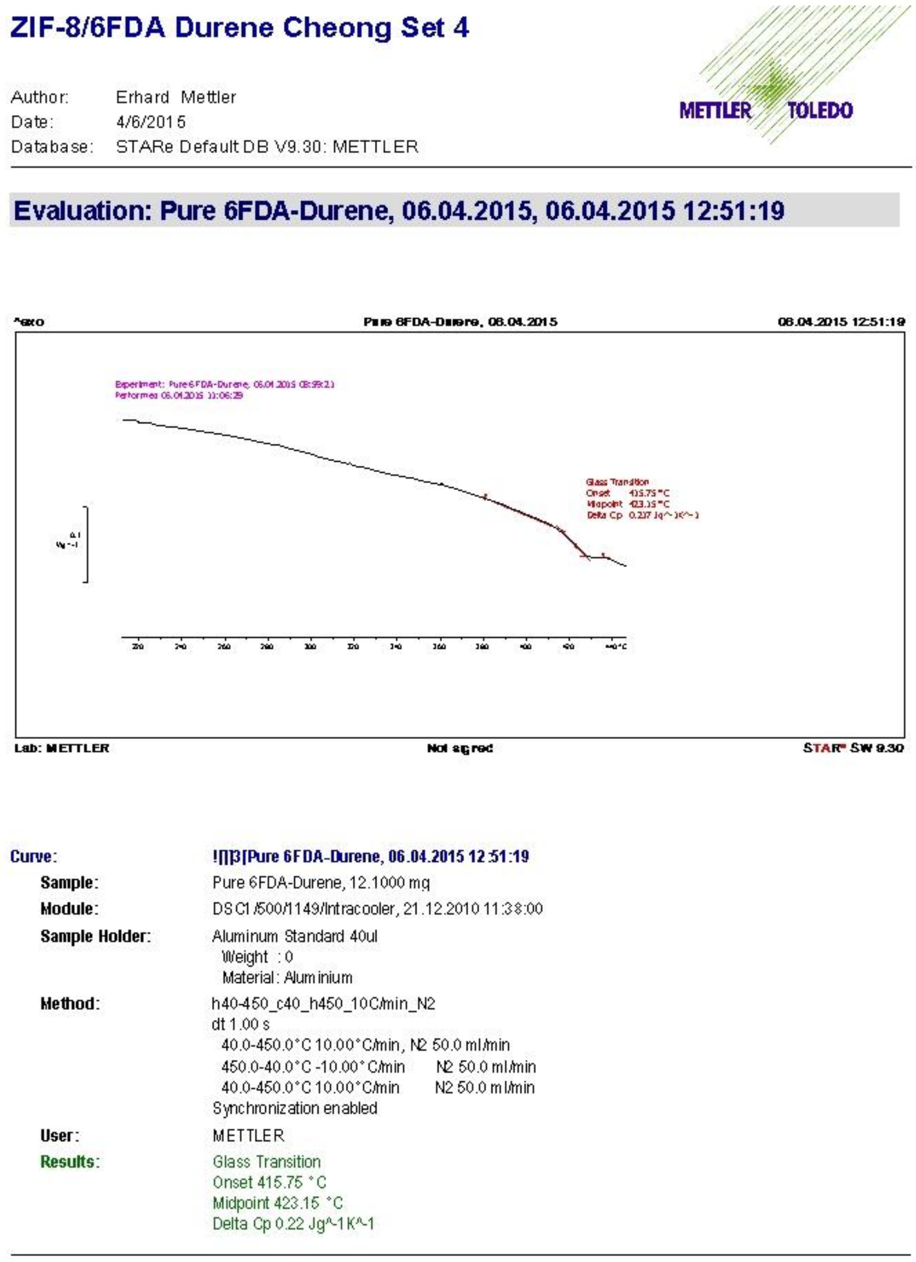
Yao, J., & Wang, H. (2014). Zeolitic imidazolate framework composite membranes and thin films: synthesis and applications. *Chemical Society Reviews, 43*(13), 4470-4493. doi: 10.1039/C3CS60480B

Zhang, Y., Sunarso, J., Liu, S., & Wang, R. (2013). Current status and development of membranes for CO2/CH4 separation: A review. *International Journal of Greenhouse Gas Control, 12*(0), 84-107. doi: http://dx.doi.org/10.1016/j.ijggc.2012.10.009

Zhu, M., Jasinski, J. B., & Carreon, M. A. (2012). Growth of Zeolitic Imidazolate Framework-8 cyrstals from the Solid-liquid interface. *The Royal Society of Chemistry*.

APPENDICES

DSC result for pure 6FDA-durene membrane



ZIF-8/6FDA Durene Cheong Set 4

Author: Erhard Mettler
Date: 4/6/2015
Database: STARe Default DB V9.30: METTLER

Evaluation: Pure 6FDA-Durene, 06.04.2015, 06.04.2015 12:51:19

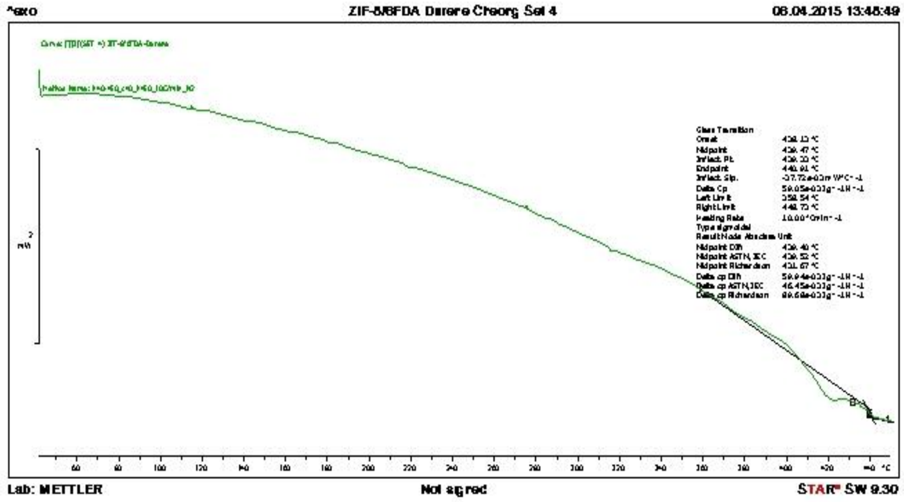
Curve:	**!∏3[Pure 6FDA-Durene, 06.04.2015 12:51:19**
Sample:	Pure 6FDA-Durene, 12.1000 mg
Module:	DSC1/500/1149/Intracooler, 21.12.2010 11:38:00
Sample Holder:	Aluminum Standard 40ul Weight : 0 Material: Aluminium
Method:	h40-450_c40_h450_10C/min_N2 dt 1.00 s 40.0-450.0°C 10.00°C/min, N2 50.0 ml/min 450.0-40.0°C -10.00°C/min N2 50.0 ml/min 40.0-450.0°C 10.00°C/min N2 50.0 ml/min Synchronization enabled
User:	METTLER
Results:	Glass Transition Onset 415.75 °C Midpoint 423.15 °C Delta Cp 0.22 Jg^-1K^-1

DSC result for ZIF-8/6FDA-durene mixed matrix membrane (Set 4)

ZIF-8/6FDA Durene Cheong Set 4

Author: Erhard Mettler
Date: 4/6/2015
Database: STARe Default DB V9.30: METTLER

Evaluation: ZIF-8/6FDA Durene Cheong Set 4, 06.04.2015 13:48:49



Curve: [1]3[(SET 4) ZIF-8/6FDA-Durene, 06.04.2015 13:48:49

Sample: (SET 4) ZIF-8/6FDA-Durene, 12.5000 mg

Module: DSC1/500/1149/Intracooler, 21.12.2010 11:38:00

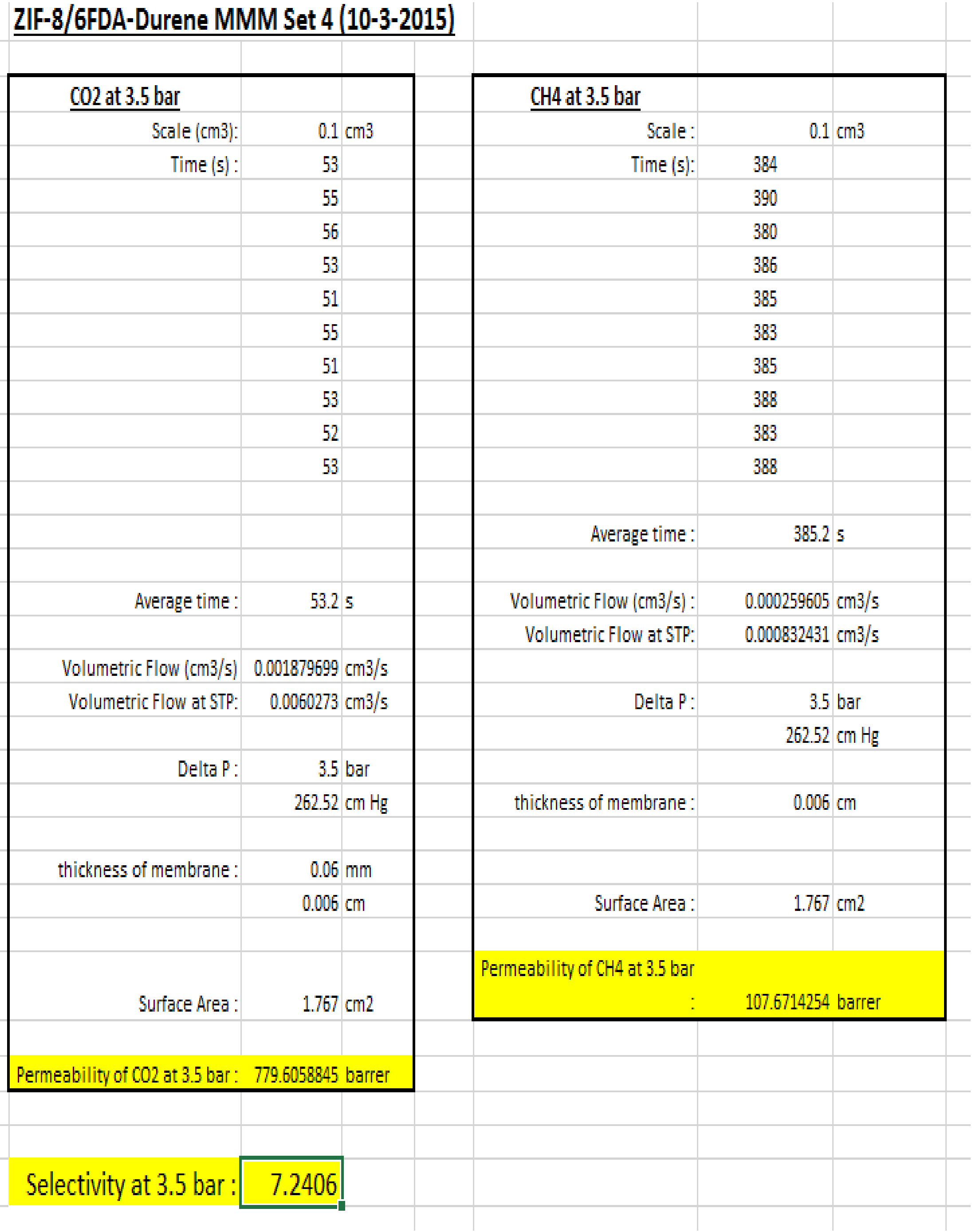
Sample Holder: Aluminum Standard 40ul
Weight : 0
Material: Aluminium

Method: h40-450_c40_h450_10C/min_N2
dt 1.00 s
40.0-450.0°C 10.00°C/min, N2 50.0 ml/min
450.0-40.0°C -10.00°C/min N2 50.0 ml/min
40.0-450.0°C 10.00°C/min N2 50.0 ml/min
Synchronization enabled

User: METTLER

Results: Glass Transition
Onset 438.13 °C
Midpoint 439.47 °C
Inflect. Pt. 439.33 °C
Endpoint 440.91 °C
Inflect. Slp. -37.72e-03 mW°C^-1
Delta Cp 59.05e-03 Jg^-1K^-1

Sample of excel spreadsheet to calculate permeability and selectivity



ZIF-8/6FDA-Durene MMM Set 4 (10-3-2015)

CO2 at 3.5 bar		
Scale (cm3):	0.1	cm3
Time (s) :	53	
	55	
	56	
	53	
	51	
	55	
	51	
	53	
	52	
	53	
Average time :	53.2	s
Volumetric Flow (cm3/s)	0.001879699	cm3/s
Volumetric Flow at STP:	0.0060273	cm3/s
Delta P :	3.5	bar
	262.52	cm Hg
thickness of membrane :	0.06	mm
	0.006	cm
Surface Area :	1.767	cm2
Permeability of CO2 at 3.5 bar :	779.6058845	barrer

CH4 at 3.5 bar		
Scale :	0.1	cm3
Time (s):	384	
	390	
	380	
	386	
	385	
	383	
	385	
	388	
	383	
	388	
Average time :	385.2	s
Volumetric Flow (cm3/s) :	0.000259605	cm3/s
Volumetric Flow at STP:	0.000832431	cm3/s
Delta P :	3.5	bar
	262.52	cm Hg
thickness of membrane :	0.006	cm
Surface Area :	1.767	cm2
Permeability of CH4 at 3.5 bar :	107.6714254	barrer

Selectivity at 3.5 bar : 7.2406