PREPARATION OF ZEOLITIC IMMIDAZOLATE FRAMEWORK-8 (ZIF-8) MEMBRANE FOR QUALITY UPGRADING OF BIO-GAS

Wittawat Laipraditthagron

A Thesis Submitted in Partial Fulfillment of the Requirements for the
Degree of Master of Science in Biotechnology
Suranaree University of Technology
Academic Year 2017

การเตรียมเมมเบรน ซีโอลิติกอิมิดาโซเลตเฟรมเวิร์ค-แปด ในการปรับปรุงคุณภาพของแก๊สชีวภาพ

นายวิทวัส ลายประดิษฐกร

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาเทคโนโลยีชีวภาพ
มหาวิทยาลัยเทคโนโลยีสุรนารี
ปีการศึกษา 2560

PREPARATION OF ZEOLITIC IMMIDAZOLATE FRAMEWORK-8 (ZIF-8) MEMBRANE FOR QUALITY UPGRADING OF BIO-GAS

Suranaree University of Technology has approved this thesis submitted in partial fulfillment of the requirements for a Master's Degree.

Thesis Examining Committee

(Assoc. Prof. Dr. Panlada Tittabutr)
Chairperson

(Assoc. Prof. Dr. Apichat Boontawan)
Member (Thesis Advisor)

(Assoc. Prof. Dr. Sittipong Amnuyapanich)
Member

(Prof. Dr. Santi Maensiri)
Vice Rector for Academic Affairs
and Internationalization

(Prof. Dr. Neung Teaumroong)
Dean of Institute of Agricultural Technology

นายวิทวัส ลายประดิษฐกร : การเตรียมเมมเบรน ซีโอลิติกอิมิดาโซเลตเฟรมเวิร์ค-แปด ในการ
ปรับปรุงคุณภาพของแก๊สชีวภาพ (PREPARATION OF ZEOLITIC IMMIDAZOLATE
FRAMEWORK-8 (ZIF-8) MEMBRANE FOR QUALITY UPGRADING OF BIO-GAS)
อาจารย์ที่ปรึกษา : รองศาสตราจารย์ ดร.อภิชาติ บุญทาวัน, 94 หน้า.

แก็สชีวภาพเป็นพลังงานทดแทนที่ผลิตจากกระบวนการย่อยสลายของชีวมวล ซึ่งเหมาะสมในการทดแทนการใช้พลังงานจากฟอสซิล แต่อย่างไรก็ตามแก็สชีวภาพที่ได้จากการย่อยสลายโดยไม่ใช้อากาศจะมีความดันต่ำ ความถ่วงจำเพาะต่ำ และมีปริมาณแก็สรวมสูง ทำให้ไม่เหมาะสมแก่การใช้ประโยชน์โดยตรง จึงมีกระบวนการต่างๆ มาประยุกต์ใช้ในการปรังปรุงคุณภาพแก็สชีวภาพ ในงานวิจัยนี้ใช้เมมเบรนสำหรับแยกแก็ส เพื่อปรับปรุงคุณภาพของแก็สชีวภาพ โดยซีโอลิติกอิมิดาโซเลตเฟรมเวิร์ค-แปด ถูกใช้สำหรับเป็นชั้นในการแยกแก็ส ซีโอลิติกอิมิดาโซเลตเฟรมเวิร์ค เป็นหนึ่งในเมทัลออกานิคเฟรมเวิร์ค ซึ่งเป็นวัสดุที่มีความพรุนสูง และมีความโดดเด่นในด้านการทนทานความร้อนและทนสารเคมี ในการเตรียมอนุภาคของซีโอลิติกอิมิดาโซเลตเฟรมเวิร์ค-แปดนี้จะถูกเตรียมในสัดส่วนของทูเมททิลอิมิดาโซเลต และซิงค์ไนเตรตเฮกซะไฮเดรตที่ต่างกันคือ 12:1, 9:1, 6:1 และ 3:1 ในการสังเคราะห์เมมเบรนซีโอลิติกอิมิดาโซเลตเฟรมเวิร์ค-แปด ด้วยอนุภาคขนาดเล็กของซีโอลิติกอิมิดาโซเลตเฟรมเวิร์ค-แปด ในชั้นเลือกผ่านแก็สแสดงถึงความสำคัญในการเพิ่มประสิทธิภาพในการแยกแก็สคาร์บอนไดออกไซด์ที่ผ่านเมมเบรนและประสิทธิภาพในการเลือกผ่านของแก็สในกระบวนการทดสอบการแยกแก็ส อนุภาคของซีโอลิติกอิมิดาโซเลตเฟรมเวิร์ค-แปด ถูกวิเคราะห์ด้วยกล้องจุลทรรศน์แบบส่องกราด วิเคราะห์การเลี้ยวเบนของรังสีเอ็กซ์ และการดูดซับแก็สไนโตรเจน ผลจากการวิเคราะห์การดูดซับไนโตรเจนสามารถหาความพรุนของพื้นผิวได้ 1,882 ตารางเมตรต่อกรัม และขนาดอนุภาค 150 นาโนเมตร ในสัดส่วนของทูเมททิลอิมิดาโซเลท และซิงค์ไนเตรตเฮกซะไฮเดรต 12:1 ในกระบวนการสังเคราะห์เมมเบรนซีโอลิติกอิมิดาโซเลตเฟรมเวิร์ค-แปด ถูกสังเคราะห์ในวิธีซีดดิ้ง ซีดแบบทุติยภูมิ และซีดแบบดูดติดผิว ความสำคัญของการสังเคราะห์เมมเบรน ซีดแบบทุติยภูมิ และ ซีดแบบดูดติดผิว ประกอบไปด้วยการขัดผิวให้เรียบ และการสังเคราะห์สองขั้น เพื่อป้องกันการเกิดจุดบกพร่องของเมมเบรน และเป็นการเพิ่มประสิทธิภาพในการแยกแก็สของคาร์บอนไดออกไซด์ต่อมีเทน เมมเบรนซีโอลิติกอิมิดาโซเลตเฟรมเวิร์ค-แปดถูกวิเคราะห์ด้วยกล้องจุลทรรศน์แบบส่องกราด วิเคราะห์การเลี้ยวเบนของรังสีเอ็กซ์ และการทดสอบในการแยกแก็ส ในการทดสอบการแยกแก็สจะถูกทดสอบโดยใช้อุณหภูมิขณะทดสอบที่แตกต่างกันคือ 25, 35 และ 45 องศาเซลเซียส และความดันขาเข้าที่ต่างกัน ตั้งแต่ 500 ถึง 800 กิโลปาสคาล การเลือกผ่านของแก็สคาร์บอนไดออกไซด์ออกจากมีเทนสามารถทำได้สำเร็จโดยเมมเบรนซีโอลิติกอิมิดาโซเลตเฟรมเวิร์ค-แปด ที่ความดันขาเข้า 500 กิโลปาสคาล และอุณหภูมิขณะทดสอบ 25 องศาเซลเซียส การซึมผ่านของแก็สคาร์บอนไดออกไซด์ในวิธีซีดแบบทุติยภูมิ สามารถทำได้ ถึง 6.98×10^{-6} ที่อุณหภูมิและความดัน

มาตรฐานเซนติเมตรต่อตารางเซนติเมตรวินาทีเซนติเมตรปรอท และค่าการเลือกผ่านของแก๊สคาร์บอนไดออกไซด์ต่อมีเทนเท่ากับ 10.1

สาขาวิชาเทคโนโลยีชีวภาพ
ปีการศึกษา 2560

ลายมือชื่อนักศึกษา
ลายมือชื่ออาจารย์ที่ปรึกษา

WITTAWAT LAIPRADITTHAGRON : PREPARATION OF ZEOLITIC IMMIDAZOLATE FRAMEWORK-8 (ZIF-8) MEMBRANE FOR QUALITY UPGRADING OF BIO-GAS. THESIS ADVISOR : ASST. PROF. APICHAT BOONTAWAN, Ph.D., 94 PP.

MEMBRANE GAS SEPARATION/BIO-GAS/ZEOLITIC IMMIDAZOLATE FRAMEWORK-8/CARBON DIOXIDE REMOVAL

Zeolitic imidazolate frameworks (ZIFs) are one of the metal organic frameworks (MOFs) and highly porous material, known for their remarkable thermal and chemical stability. ZIF-8 membranes were prepared by seed ZIF-8 particles on a porous α-alumina surface via seeding, secondary seed growth and suction methods. Secondary seedings of ZIF were used to minimize defects in the membranes. The synthesized ZIF-8 membranes with small ZIF-8 particles in a selective layer showed significant improvement in CO_2 permeability and CO_2/CH_4 selectivity in mixed gas permeation tests. Subsequently, the ZIF-8 particles were characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD) and Brunauer Emmett Teller surface area (BET). In this study, various preparations of ZIF-8 particles were synthesized using different ratios of metal cations and imidazolate anions (12:1, 9:1, 6:1 and 3:1). The result showed that BET surface area and Mean crystal size were 1,882 m^2/g and 150 nm with 12:1 ratio of 2-methylimidazole: Zinc nitrate hexahydrate. The ZIF-8 membranes were analyzed using SEM, XRD and gas permeation tests at different operating temperatures (25°C, 35°C and 45°C). The permeation and selectivity tests of CO_2 and CH_4 on ZIF-8 membranes were measured at different pressures in the feed side (500-800 kPa). The quality of the ZIF-8 selective layer on the surface of α-alumina support was confirmed by XRD and SEM. The finished selectivity of CO_2 removal from CH_4

was improved via ZIF-8 membranes. On the feed pressure of 500 kPa at 25°C, the CO_2 permeance can reach 6.98×10^{-6} cm^3 (STP) $cm\cdot cm^{-2}\cdot s^{-1}\cdot cmHg^{-1}$ and the selectivity of CO_2 / CH_4 was 10.1.

School of Biotechnology — Student's Signature ____________

Academic Year 2017 — Advisor's Signature ____________

ACKNOWLEDGEMENTS

I would like to thank Suranaree University of Technology for financial and laboratory facilities supports during my study. I would like to express my sincere gratitude to my advisor, Assoc. Prof. Apichat Boontawan for his remarkable guidance, valuable advices, motivation, knowledge and other supports during this study, add considerably to my graduated experiment.

I deeply grateful to my co-advisor, Assoc. Prof. Sittipong Ammnuaypanich for his guidance, support and provided a valuable experience during I had studied in Khon Kaen University.

The special thank my fellow labmates (AB Lab), teachers, staffs and friends in Biotechnology school for familiarity, good environment, good support and for all the fun we have had together. I also thanks to my Khon Kaen partners (P’Santi, P’Tum, P’Ease, Mai and Mo) for their advised, support and giving points to fulfill of this report. Moreover, I also extend appreciate to Department of Chemistry, Faculty of Science, Khon Kaen University, CSTE staff from F10 and F11, School of Ceramic Engineering, SUT for their suggestion and official support.

Finally, I would like to thank my parent for their supports, encourage and faith. This work could not be achieved without their support. They have always been a great source of inspiration to take on any challenge in life.

Wittawat Laipraditthagron

CONTENTS

Page

ABSTRACT IN THAI I

ABSTRACT IN ENGLISH III

ACKNOWLEDGEMENTS V

CONTENTS VI

LIST OF TABLES X

LIST OF FIGURES XI

LIST OF ABBREVIATIONS XIV

CHAPTER

I INTRODUCTION 1

- 1.1 Significant of research 1
- 1.2 Research objectives 3
- 1.3 Research hypothesis 3
- 1.4 Scope of thesis 3
- 1.5 Expected results 4

II LITERATURE REVIEWS 5

- 2.1 Biogas 5
- 2.2 Application of Biogas 9
  - 2.2.1 Hydrogen production from biogas 10
  - 2.2.2 Electricity production 10
  - 2.2.3 Biogas injection into natural gas grids 11

CONTENTS (Continued)

Page

2.2.4 Biogas for the production of heat system 12
2.2.5 Bio-CBG as vehicular fuel 12
2.3 Biogas upgrading and purification technologies 14
2.3.1 Adsorption 15
2.3.1.1 Pressure swing adsorption (PSA) 15
2.3.1.2 Adsorbents 16
2.3.2 Absorption 18
2.3.2.1 High pressure water scrubbing (HPWS) 18
2.3.2.2 Organic physical scrubbing (OPS) 19
2.3.2.3 Chemical scrubbing process (CSP) 19
2.3.3 Membrane gas separation 21
2.3.4 Cryogenic separation 25
2.4 Type of membrane gas separation 25
2.4.1 Polymer membrane 26
2.4.2 Carbon membranes 26
2.4.3 Ceramic membrane 27
2.4.4 Mixed matrix membranes (MMMs) 28
2.5 Zeolitic imidazolate frameworks (ZIFs) 30
2.5.1 Important features in ZIF membrane synthesis 31
2.5.1.1 Effect of the substrate 31
2.5.1.2 Effect of surface modification 32
2.5.1.3 Effect of deprotonates 32

CONTENTS (Continued)

Page

2.5.1.4 Effect of the solvent 33

2.5.1.5 Effect of activation 33

2.5.1.6 Chemical and thermal stability 34

2.5.1.7 Effect of functionalization 35

2.5.2 ZIF membrane synthesis 35

2.5.2.1 *In situ* growth 35

2.5.2.2 Secondary growth 36

III MATERIAL AND METHOD 37

3.1 Materials 37

3.2 Methods 37

3.2.1 Preparation of ZIF-8 particles 38

3.2.2 Porous α-alumina support preparation 39

3.2.3 ZIF-8 membrane synthesis methods 41

3.2.3.1 Seeding method 41

3.2.3.2 Secondary seed growth method 42

3.2.3.3 Suction seeding method 43

3.3 Gas permeation measurements 44

3.4 Analytical methods 47

3.4.1 Scanning electron microscopy (SEM) 47

3.4.2 X-ray diffraction (XRD) 48

3.4.3 Nitrogen adsorption 49

CONTENTS (Continued)

Page

IV RESULTS AND DISCUSSION......50

4.1 ZIF-8 particles preparation......50

4.2 Porous α-alumina support structural characterization......53

4.3 The effect of seeding methods on ZIF-8 membrane properties......55

4.4 Gas separation property of ZIF-8 membranes......60

V CONCLUSION......72

REFERENCES......74

BIOGRAPHY......94

LIST OF TABLES

Table **Page**

2.1 The composed of Biogas produce from tapioca starch factory 8

2.2 Biogas impurities and their effects 15

3.1 The ratio of MeIM: Zinc nitrate hexahydrate for synthesize the ZIF-8 particles 39

4.1 The mean crystal size and BET surface area of synthesized ZIF-8 particles at different temperatures...52

4.2 Permeate and separation factors of CO_2/CH_4 mixtures (60:40 vol.%) on various ZIF- 8 membranes synthesized at difference feed pressure 25°C 67

4.3 Permeate and separation factors of CO_2/CH_4 mixtures (60:40 vol.%) on various ZIF- 8 membranes synthesized at difference feed pressure 35°C...68

4.4 Permeate and separation factors of CO_2/CH_4 mixtures (60:40 vol.%) on various ZIF- 8 membranes synthesized at difference feed pressure 45°C 69

4.5 The comparisons selectivity of gases mixtures on different synthesis methods and type of supports 71

LIST OF FIGURES

Figure **Page**

2.1 The biogas production in anaerobic digestion condition 6

2.2 Potential applications of biogas 11

2.3 Current technologies for biogas upgrading 14

2.4 Principle of membrane gas separation process 23

2.5 Schematic procedure for in situ growth and secondary growth methods for the synthesis of ZIF membranes under solvothermal conditions. 36

3.1 The overall of synthesis ZIF-8 membranes process for biogas upgrading 38

3.2 The dried kaolin powder and sieve (No.100, Retsch, Germany)..........................40

3.3 The sintering times of porous α-alumina support 40

3.4 45 mL Teflon lined stainless steel autoclave 42

3.5 Slip-coating on secondary seed growth method 43

3.6 The membrane synthesis via suction seeding method 44

3.7 The flow diagram of gas permeation testing...46

3.8 Experimental setup for membrane synthesis and permeation testing 47

3.9 Gold coating machine (Neo coater MP-19010 NCTR, JEOL, Japan) 48

3.10 X-ray diffractometer (XRD) (D2 phaser, Bruker AXS GmbH, Germany) 49

4.1 The synthesized ZIF-8 particles on various ratios (12:1, 9:1, 6:1 and 3:1) 51

4.2 SEM images of the ZIF-8 particles of the ZIF-8 particles using various different ratios of MeIM: Zinc nitrate hexahydrate: 12:1 (A), 9:1(B), 6:1(C) and 3:1(D)...52

LIST OF FIGURES (Continued)

Figure **Page**

4.3 XRD chromatograms of the ZIF-8 particles using various ratios different of MeIM/ Zinc nitrate hexahydrate: 12:1 (A), 9:1(B), 6:1(C) and 3:1(D)..........53

4.4 XRD chromatogram of the α-alumina support 54

4.5 SEM images surface (A) and cross-section (B) of the α-alumina support (C). 55

4.6 The ZIF-8 membrane synthesizes on seeding, secondary seed growth and suction method..........57

4.7 XRD chromatograms of ZIF-8 membranes on seeding (A), secondary seed growth (B) and suction seed methods (C) 58

4.8 SEM images surface of ZIF-8 membranes synthesized on seeding (A), secondary seed growth (B) and suction seed (C) methods..........59

4.9 SEM images cross section of ZIF-8 membranes synthesized on seeding methods (A), suction seed (B) and secondary seed growth (C) 60

4.10 Fluxes of CO_2 and CH_4 at different partial pressures differences under operation temperatures of (a) 25°C, (b) 35°C and (c) 45°C 62

4.11 The CO_2 permeate effect of various synthesized ZIF-8 membranes at differences operating times and feed pressures on mixed gas of CO_2/CH_4.......... 63

4.12 The CH_4 permeate effect of various synthesized ZIF-8 membranes at differences operating times and feed pressures on mixed gas of CO_2/CH_4..........64

LIST OF FIGURES (Continued)

Figure **Page**

4.13 The separation factor effect of various synthesized ZIF-8 membranes at differences operating times and feed pressure on mixed gas of CO_2/CH_4 70

LIST OF ABBREVIATIONS

°C = Degree Celsius

µm = Micrometer

2θ = Two theta

Å = Angstroms

A = Effective membrane area

AD = Anaerobic digestion

APTES = Aminopropyltriethox-ysilane

BET = Brunauer Emmett Teller

bio-CBG = bio-compressed biogas

CBG = Compressed biogas

CH_3OH = Methanol

CH_4 = Methane

CHP = Combined heat and power

cm = Centimeter

cm^3 = Cubic centimeter

cmHg = Centimeter mercury

CNG = Compressed Natural Gas

CO = Carbon monoxide

CO_2 = Carbon dioxide

CSP = Chemical scrubbing process

DEA = Diethanolamine

LIST OF ABBREVIATIONS (Continued)

DI = Deionized

g = Gram

GHGs = Greenhouse gases emission

H_2 = Hydrogen

H_2S = Hydrogen sulphide

HC = Hydrocarbon carbon

HPWS = High pressure water scrubbing

KJ/mol = Kilojoule per mole

l = Thickness of selective layer

LNG = Liquid natural gas

m^2 = Square meter

Mbar = Milli bar

MEA = Monoethanolamine

MeIM = 2-methylimidazole

min = Minuet

mL = Milliliters

mm = Millimeter

MMMs = Mixed Matrix Membranes

mmol = Milimole

MOFs = Metal organic frameworks

mol = Mole

MPa = Mega Pascal

LIST OF ABBREVIATIONS (Continued)

N_2 = Nitrogen

NH_3 = Ammonia

nm = Nanometer

NMP = N-methyl pyrrolidone

O_2 = Oxygen

OPS = Organic physical scrubbing

P = Permeability

Pa = Pascal

P_{CH4} = Methane permeable

P_{CO2} = Carbon dioxide permeable

ppf = Partial pressures at feed side

ppi = Partial pressures at permeate

ppm = Parts per million

PSf = Polysulfone

psi = Pounds per square inch

Q = Volumetric permeation rate

rpm = Revolutions per minute

s = Second

SEM = Scanning electron microscope

SOD = Sodalite

STP = Standard temperature and pressure

vol.% = Volume percent

LIST OF ABBREVIATIONS (Continued)

wt% = Weight percent

XRD = X-ray Powder Diffraction

ZIFs = Zeolitic midazolate frameworks

$Zn(NO_3)_2 \cdot 6H_2O$ = Zinc nitrate hexahydrate

ZnO = Zinc oxide

α-Al_2O_3 = Alpha aluminum oxide

$\alpha_{CO2/CH4}$ = Separation factors

CHAPTER I

INTRODUCTION

1.1 Significant of research

Recently, the world is changing with the environment and energy concern. Fossil fuels have contributed to the development of the world in an extensive way. However, mankind is always rereleased as a result of the exploration activities. The world is affected by oil spillage, global warming, acid rain, Greenhouse gases emission (GHGs), and many more (Dada *et al.*, 2017). As a result, bioenergy is gaining more and more significance as an attractive energy all around the world, especially biogas. Biogas presents to be a cleaner energy compared with other fossil fuels. Biogas has wide application such as heating, gas grid injection, fuel cells, compressed biogas (CBG) and power generation (Angelidaki *et al.*, 2018, Budzianowski *et al.,* 2017 and Augelletti *et al.*, 2017). Biogas contains mainly CH_4 and non-hydrocarbon components, especially CO_2. However, biogas produced from anaerobic digestion is of low pressure, large specific volume and unsuitable for energy storage (Abdeshahian *et al.,* 2016). The large volume of CO_2 present in biogas the lower its calorific value, flame velocity and flammability limits compared to natural gas and fossil fuels. Thus, CO_2 need to remove from biogas because it is a non- flammable gas resulting in a reduction of the heat and a corrosion of the pipelines (Bhide *et al.,* 1998).

Membrane gas separation technologies are promising alternatives for gas separation due to their low energy requirement, small carbon footprint and environmental friendliness (Ordonez *et al.,* 2010). It contains various applications such as hydrogen separation, nitrogen recovery, carbon dioxide removal, and biogas purification (Chung *et al.*, 2017).

Recently, metal organic frameworks (MOFs) showed the potential in CO_2 separation due to its high porosity, large surface areas and pores size (Amedi *et al.*, 2017). Meanwhile, zeolitic midazolate frameworks (ZIFs) is a subclass of MOFs. Unlike MOFs, ZIFs exceptionally exhibited the high stability due to the strong bonding between metal cations and imidazolate anions by a sodalite (SOD) topology forming (Li *et al.*, 2013, Nafisi and Hagg, 2014 and, Venna and Carreon, 2015). In among of ZIFs, ZIF-8 is one of the most study material for gas separation due to its high affinity towards CO_2, great chemical, hydrothermal stability and frameworks flexibility (Aceituno Melgar *et al.*, 2015, Fang *et al.*, 2015 and Hwang *et al.*, 2015). These porous, flexible, chemically, and thermally stable crystals (up to 400 °C) are promising materials for gas separation and storage, as well as for size and shape selective catalysis due to their pore size (less than 5 Å) with zinc metal center coordinated by imidazole-type of organic linkers (M. Shah *et al.*, 2012, K.S. Park *et al.*, 2006 and A. Phan *et al.*, 2010).

In this study, the ZIF-8 particles were synthesized at varies metal cations and imidazolate anions ratio. The properties of synthesized ZIF-8 particles and ZIF-8 membranes were analyzed using XRD, SEM and Nitrogen absorption. The varies methods for synthesizes ZIF-8 membranes were used for seed on the surface porous α-alumina supports. Gas permeability and membrane selectivity including CO_2 and CH_4 were determined. The effect of several factor such as temperature, pressure to membrane separation was analyzed as well.

1.2 Research objectives

1.2.1 To establish and upgrade the quality of biogas production by ZIF-8 membrane.

1.2.2 To study the appropriate ratio of metal cations and imidazolate anions for improving the absorption property of ZIF-8 particle.

1.2.3 To evaluate the relative feed pressure of membranes synthesis condition and operating temperature.

1.2.4 To design an efficient separation process for upgrading biogas using ZIF-8 membranes.

1.3 Research hypothesis

The ZIF-8 is one of the most study material for CO_2 removal due to its high affinity towards CO_2, great chemical, hydrothermal stability and frameworks flexibility. Membrane synthesized from ZIF-8 was applied to biogas upgrading process. The best relative feed pressure and temperature were obtained to upgrading biogas by ZIF-8 membrane. The ZIF-8 membrane is the most effective material for upgrading and remove CO_2 from biogas.

1.4 Scope of thesis

This research consists of two parts. The first part was focused on the effects of pore morphology on the absorption in ZIF-8 particles at varies metal cations and imidazolate anions ratio. The next part is to study the effects of gas separation on synthesis ZIF-8 membrane for biogas upgrading production. The gas separation on ZIF-8 membrane was compared by synthesis methods, feed pressure and operating temperature.

1.5 Expected results

The higher quality of biogas was obtained from ZIF-8 membrane. The absorption properties of ZIF-8 particles under the appropriate ratio of metal cations and imidazolate anions were obtained. The suitable relative feed pressure and temperature on membranes synthesis condition were achieved. High selectivity of CO_2/CH_4 was obtained using ZIF-8 membrane. This gas separation system was applied to the industrial scale production with the improving of CH_4 production.

CHAPTER II

LITERATURE REVIEWS

2.1 Biogas

Biogas is produced by the anaerobic digestion (AD) for treating organic waste. Biogas attractive for many reasons that involve economic such as environmental aspects. Anaerobic digestion is the collection of processes by which microorganisms break down biodegradable material in the absence of oxygen. It contains mostly three components, including methane (CH_4), carbon dioxide (CO_2) and nitrogen (N_2). However, another trace species exists such as hydrogen sulfide (H_2S), hydrogen (H_2), nitrogen (N_2), ammonia (NH_3), oxygen (O_2) and carbon monoxide (CO). Furthermore, typical biogas saturates with water, dust particles, siloxanes, aromatic and halogenated compounds (Andriani *et al,* 2014 and Rasi *et al,* 2006). There are basically four stages involve in the production of biogas from organic wastes by anaerobic digestion. Anaerobic digestion is mesophilic and thermophilic biological decomposition and stabilization of biodegradable wastes at controlled anaerobic conditions such as temperature, pH, retention time etc. The four stages for biogas production including at Hydrolysis, Acidogenesis, Acetogenesis and Methanogenesis. At each phase specific bacteria namely: Hydrolytic, Acidogenic, Acetogenic and Methanogenic, respectively are used to carry out the decomposition process. The process of anaerobic digestion is summarized in Figure 2.1.

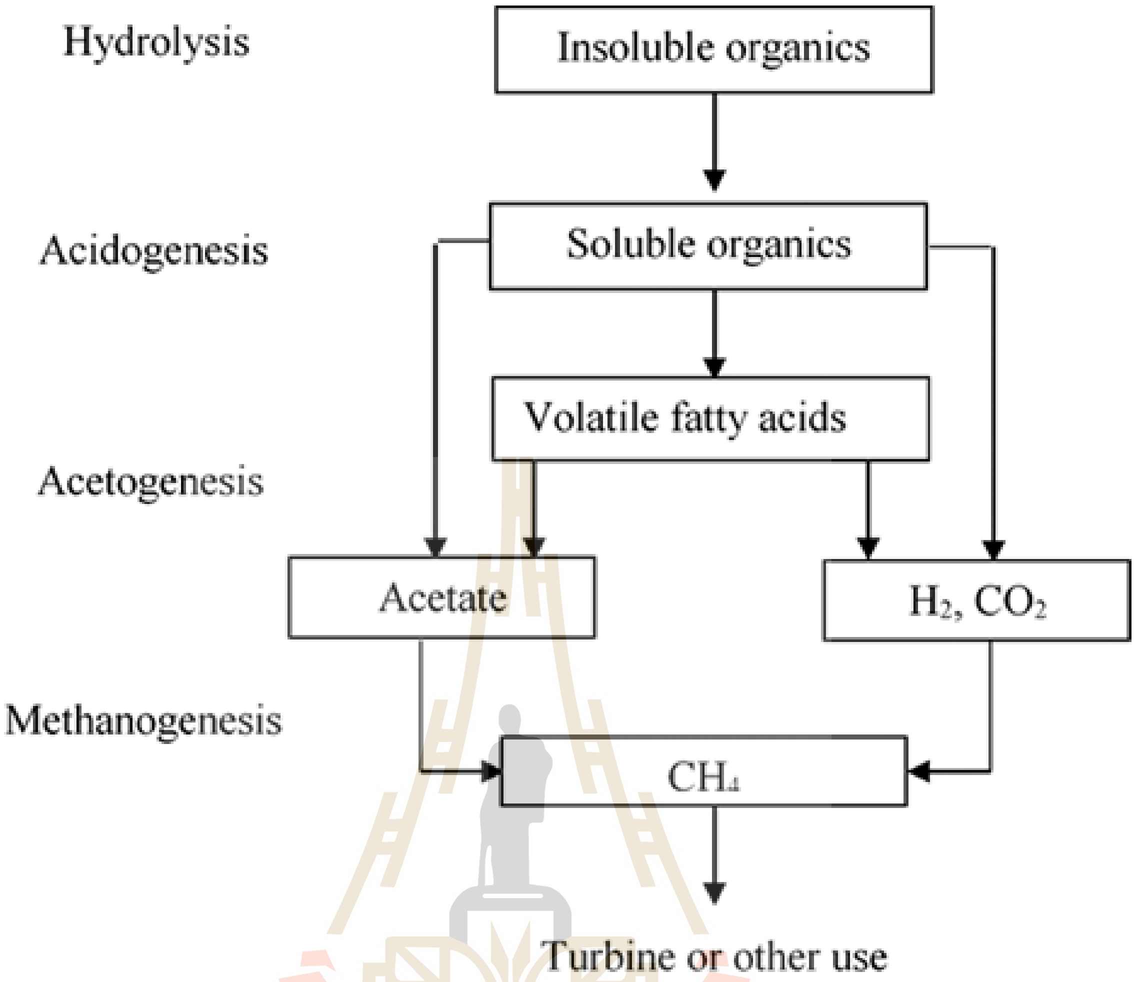

Figure 2.1 The biogas production in anaerobic digestion condition (Venko Beschkov *et al.*, 2017).

Hydrolysis stage: This stage involves the breaking down of large protein macromolecules, fats and carbohydrate polymers such as starch and cellulose to amino acids, long chain fatty acids and sugars. Acidogenesis stage: At this stage, the small organic molecules produced in the hydrolysis stage are fermented to from three, four and five volatile fatty acids such as lactic acid, butyric acid, propionic acid, valeric acid and low alcohols. Acetogenesis stage: At this stage, acetogenic bacteria consume the fermented products from the acidogenic stage to produce acetic acid, carbon dioxide and hydrogen. Methanogenesis stage: This is the final stage where methane is produced as a result of the consumption of acetate, hydrogen and carbon dioxide. Three biochemical pathways are used by methanogens to produce methane gas. The pathways along with the stoichiometries of overall chemical reactions are shown in equations (2.1, 2.2 and 2.3).

Acetotrophic methano genesis: $4CH_3COOH \rightarrow 4CO_2 + 4CH_4$ (2.1)

Hydrogennotrophic methanogenesis: $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ (2.2)

Methylotophic methanogenesis: $4CH_3OH + 6H_2 \rightarrow 3CH_4 + 2H_2O$ (2.3)

Biogas that produce from tapioca starch factory. The mainly component was show in Table 2.1. (Petersson *et al.*, 2009, Lems *et al.*, 2009). Methane is considered to be 25 times more effective at heat value than CO_2 (Guinée *et al.*, 2002). In biogas 1 m^3 composed of 60 mol% CH_4 energy values about 21 MJ/m^3 (Thailand institute of scientific and technological research, 2538). Therefore, even if biogas is released in small quantities, it is still a substance with a high contribution to global warming.

Biogas can play a major role in the developing market for renewable energy and it is estimated that biogas usage in the world was doubled in the coming years ranging from 14.5 gigawatts (GW) in 2012 to 29.5 GW in 2022 (Maroneze *et al*,2014 and Karaszova *et al.*,2015). The demand for renewable fuels is increasing with growing concern about environmental problems due to the high greenhouse gases (GHGs) emission from fossil fuel combustion (Hosseini *et al.*, 2013, Gonzalez *et al.*, 2017, Shane *et al.*, 2016 and Yang *et al.*, 2017). The purified biogas used directly as automotive fuel or power generation. Current biogas upgrading technologies consume less than about 20% of biogas energy for upgrading and compression purposes. Thus, purified biogas enables transforming more than about 80% of the energy content of raw biogas into the usable form of clean energy. In addition, purified biogas generates little or no low-grade heat and hence thermal losses are minimized. The purified biogas can therefore be competitive to raw biogas fed combined heat and power (CHP) systems. In CHP only about 35-40% of biogas energy is converted into useful electricity. The purified biogas is thus a dispatch able sustainable biofuel which can complement the performance of renewable energy systems rich in naturally fluctuating wind and solar power sources. The major uses of purified biogas include power-only production, CHP production, vehicle fuel and cooking fuel. These uses require grid injection, fuel tank injection or bottling all require compressed purified biogas (Wojciech *et al.*, 2017). In relation to gas compression, CO_2 separation brings benefits associated with reduced gas amount for compression having greater energy.

Table 2.1 The composed of Biogas produce from tapioca starch factory.

Biogas component	Percentage (%)
CH_4	35-65
Hydrocarbons	0
H_2	0
CO_2	65-35
N_2	>0.2
O_2	0
H_2S (ppm)	0-4000
NH_3 (ppm)	100
Heating value, kWh/Nm^3	6.5

(Petersson *et al.*, 2009, Lems *et al.*, 2009 and Thailand institute of scientific and technological research, 2538).

2.2 Application of Biogas

As mentioned previously, biogas has other impurities except for CO_2 that should be removed. The concentration of those impurities depends on the biogas source (Maroneze *et al.*, 2014). Therefore, the biogas is preferred to be upgraded before any utilization. In fact, the levels of biogas impurities should be controlled based on the requirements of each application as shown in Figure 2.2. Biogas can be used for different applications either as raw or upgraded. The selection of upgrading technologies relies on various factors, such as availability of resources, utilization of biogas and investment cost. The cheapest technology does not always mean the best solution if it is not able to meet the requirements for utilization (Loh *et al.*, 2017)

Currently, production and utilization of biogas has numerous environmental advantages: It is used as a renewable energy source, reduced the CH_4 emission to the environment, it can be used as a substitute for fossil fuels, it reduced the emission of CO_2 from combustion and used in natural gas appliances after upgrading. The utilization biogas including power generation in the combined heat and power (CHP) unit (Yang *et al.*, 2014, Beaudin *et al.*, 2010), vehicle fuel and cooking fuel (Grimsby *et al.*, 2016). Biogas is also used as fuel in boiler for steam production in different industrial applications. Burning biogas in a boiler is one of the most reliable technologies due to low quality of biogas can be used with pressure around 8–25 mbar (Yang *et al.*, 2014). Normally, biogas can be used in a boiler without upgrading, however, H_2S level below 1000 ppm should be considered to avoid corrosion of boiler (Sun *et al.*, 2015 and Baszaadeh *et al.*, 2012). After the removal of unwanted components from biogas to ≥ 97% CH_4, it can be converted into bio-compressed biogas (bio-CBG) at 20–25 MPa (2900–3600 psi) (Molino *et al.*, 2013 and Farzaneh *et al.*, 2011). Figure 2.2 shows the different potential applications of biogas after upgrading to the required level.

2.2.1 Hydrogen production from biogas

Reforming of biogas on supported catalysts is an interesting method to produce hydrogen. The used of biogas instead of CH_4 for the production of H_2 is also a promising way to reduce CO_2 emission (Shiga *et al.*, 1998 and Muradov *et al.*, 2008). Currently, the biogas derived H_2 is used in the field of the hydrogen-base fuel cell which efficiently converts the H_2 to electricity at a commercial level. The main drawback in there forming process is the formation of carbon monoxide (CO) as a gaseous by-product (Effendi *et al.*, 2005). It acts as a poison to the fuel cell in the 50 ppm range (Purwanto *et al.*, 2006). Therefore, the controlled steam reforming (Eqs. (2.4) and (2.5)) followed by CO shift reactions (high-temperature and low-temperature) (Eq. (2.6)) are proved to be the feasible and economical solution for CO reduction.

$$CH_4 + H_2O \rightarrow CO + 3H_2 \Delta H\ 298 = +206.2\ kJ/mol \tag{2.4}$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \Delta H\ 298 = +247.9\ kJ/mol \tag{2.5}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \Delta H\ 298 = -41\ kJ/mol \tag{2.6}$$

Also, there are various advantages of using biogas for the production of H_2: a domestic and local energy resource, a cheap feed which helps to decrease the end-use cost and considered as an environmentally, and friendly process.

2.2.2 Electricity production

A significant percentage of the global electricity demand is expected to be generated using biogas in the near future (Akinyele *et al.*, 2014). Biogas is an economical fuel for the generation of electricity and heat (Beaudin *et al.*, 2010). Internal combustion engines, gas turbines, micro-turbines, Stirling engines and fuel cells have been successfully generated electricity using biogas (Smith *et al.*, 2013 and Jiang *et al.*, 2009). Gas engines do not require high quality gas but it is preferred to condense the water vapors in raw gas to avoid condensation in gas lines. The required level of H_2S is below 250 ppm to avoid corrosion of boiler and gas engine in combined heat and power plants (CHPs) (Nielsen *et al.*, 2009). A low calorific value of biogas is one of the main barriers for its utilization in combined heat and power generation (Sun *et al.*, 2015).

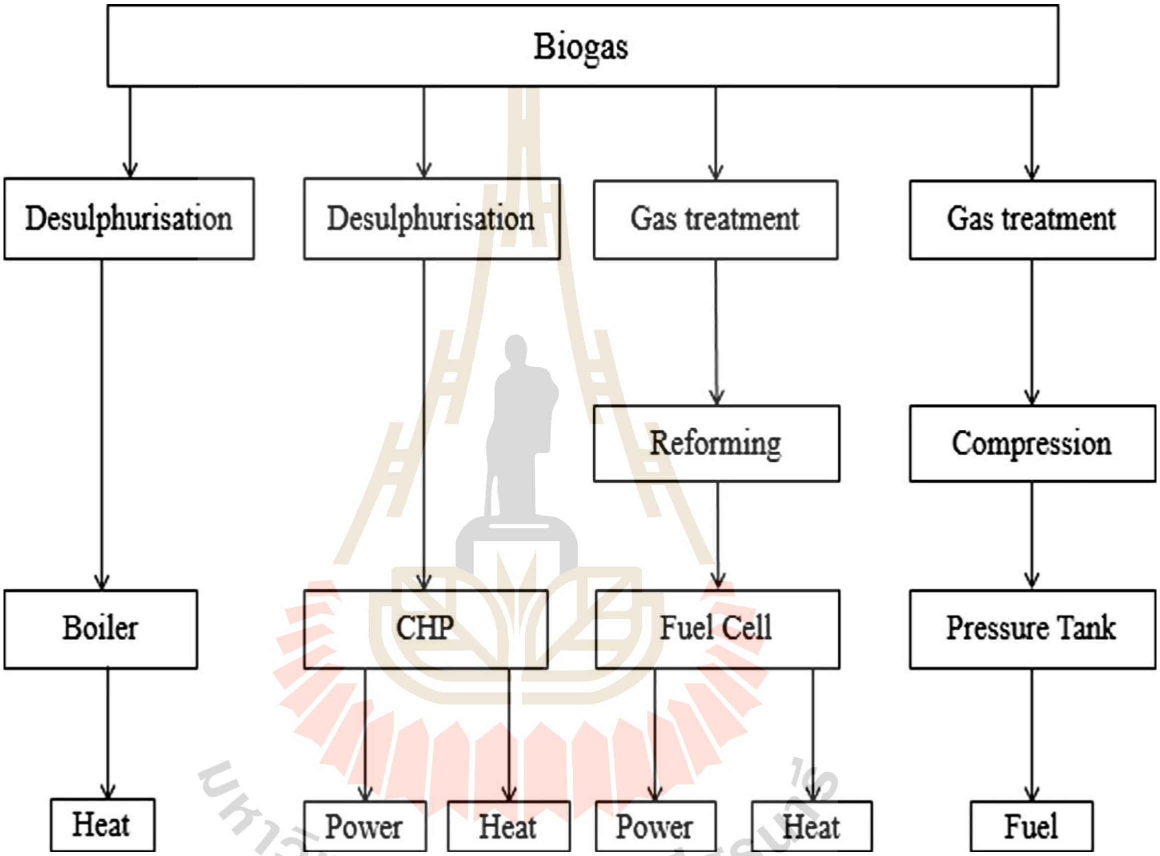

Figure 2.2 Potential applications of biogas. (Khan *et al.*, 2017).

2.2.3 Biogas injection into natural gas grids

Biogas utilization as a substitute of natural gas has gained significant importance in recent years due to depletion and low quality of natural gas resources. Purified biogas can be injected into the natural gas grids (Chandra *et al.*, 2011). Upgrading biogas as equal quality as natural gas by an efficient appropriate method is very important for its injection into the existing natural gas grids. These standards could be maintained using the existing biogas upgrading processes (Miltner *et al.*, 2008 and Petersson *et al.*, 2009).

2.2.4 Biogas for the production of heat system

In most developing countries, biogas is used for cooking and lighting (Grimsby *et al.*, 2016). Biogas is also used as fuel in the boiler for steam production in different industrial applications. Burning biogas in a boiler is one of the reliable technologies because low quality biogas can also be used with pressure around 8–25 mbar (Yang *et al.*, 2014). Normally, biogas can be used in a boiler without upgrading, however, H_2S level below 1000 ppm should be considered to avoid corrosion of boiler (Sun *et al.*, 2015 and Papong *et al.*, 2014).

2.2.5 Bio-CBG as vehicular fuel

Global warming, energy crisis, and the increasing cost of fossil fuels are the driving forces for the development of alternative vehicular fuels. The compressed biomethane, also called as bio-compressed biogas (bio-CBG), has the same properties as compressed natural gas CNG in terms of engine performance, gas consumption, and efficiency, when use as vehicular fuel (Lim *et al* 2015 and Jiang *et al* 2009). The CO_2 is one of the GHGs emission and important parameters for any fuel in view of global warming and climate changes. There is no significant difference in CO_2 emission level for both fuels, however, the emission levels of NOx, HC, and CO for bio-CBG are slightly higher than CNG when used as a vehicular fuel. After the removal of unwanted components from biogas to $\geq$ 97% CH_4, it can be converted into bio-CBG at 20-25 MPa (2900-3600 psi) (Molino *et al.*, 2013 and Farzaneh *et al.*, 2011). Subsequently, bio-CBG gives slightly higher CO emission when used as a vehicular fuel compared to CNG. The reason of high hydrocarbon carbon (HC) emission is also due to the incomplete combustion caused by poor oxidation at low temperature during warm up period. Bio-CBG contains a higher content of N_2 compared to CNG which favors the NOx formation during combustion. Furthermore, there is no significant difference in fuel economy between biogas (24.11 km/kg) and CNG (24.38 km/kg) (Subramanian *et al.,* 2013). Bio-CBG has a great potential for becoming one of the most sustainable, economical, and environmentally friendly vehicular fuels in the near future (Ryan *et al.*, 2010). The low density and high thermal efficiency of bio-CBG make it an economic vehicular fuel (Osorio *et al.*, 2009 and Vijay *et al.*, 2006). For heavy vehicles, the use of bio-CBG is very advantageous because it has higher calorific value and more environmentally friendly compared to any other fuels. There is a reduction of 63% in the emission of GHGs when bio-CBG is used instead of CNG for heavy vehicles (Uusitalo *et al.*, 2014 and Makareviciene *et al.*, 2013). Compression also reduces its storage volume with high energy and pressure (Kapdi *et al.*, 2005). Although compression at high pressure is very expensive, high heating value and highly valuable product of bio-CBG justify this cost (Krich *et al.*, 2005). Compression is a physical approach for the conversion of biogas to bio-CNG. Also, the properties of bio-CBG are the same as that of CBG. However, the logistical investigation is also important with biogas upgrading and compression techniques.

Also, it produces a less amount of dangerous and hazardous chemicals such as CO_2, sulphur, lead, and other heavy hydrocarbons into the atmosphere (Rapport *et al.,* 2011 and Held *et al.,* 2008). These countries have their own quality standards for biogas as a vehicular fuel. Although, the most important biogas quality indicators for vehicular fuel are the concentrations of CH_4 and CO_2, which should be $\geq$ 96% and<2.5%, respectively (Lim *et al.*, 2015, Hahn *et al.*, 2015 and Ryan *et al.*, 2010). These requirements for bio-CBG could also be taken as a quality standard for other developing countries such as Pakistan, India Malaysia, Indonesia and Thailand.

2.3 Biogas upgrading and purification technologies

Recently, the technologies are developed on the industrial scale for the upgrading of biogas include adsorption, absorption (physical and chemical), membrane separation, and cryogenic. These technologies are mainly used for CO_2 removal while the pre-upgrade stage is required to reduce the concentrations of contaminants gas. The components of contaminates in biogas were showed in Table 2.2. Further classification of these upgrading technologies is showed in Figure 2.3.

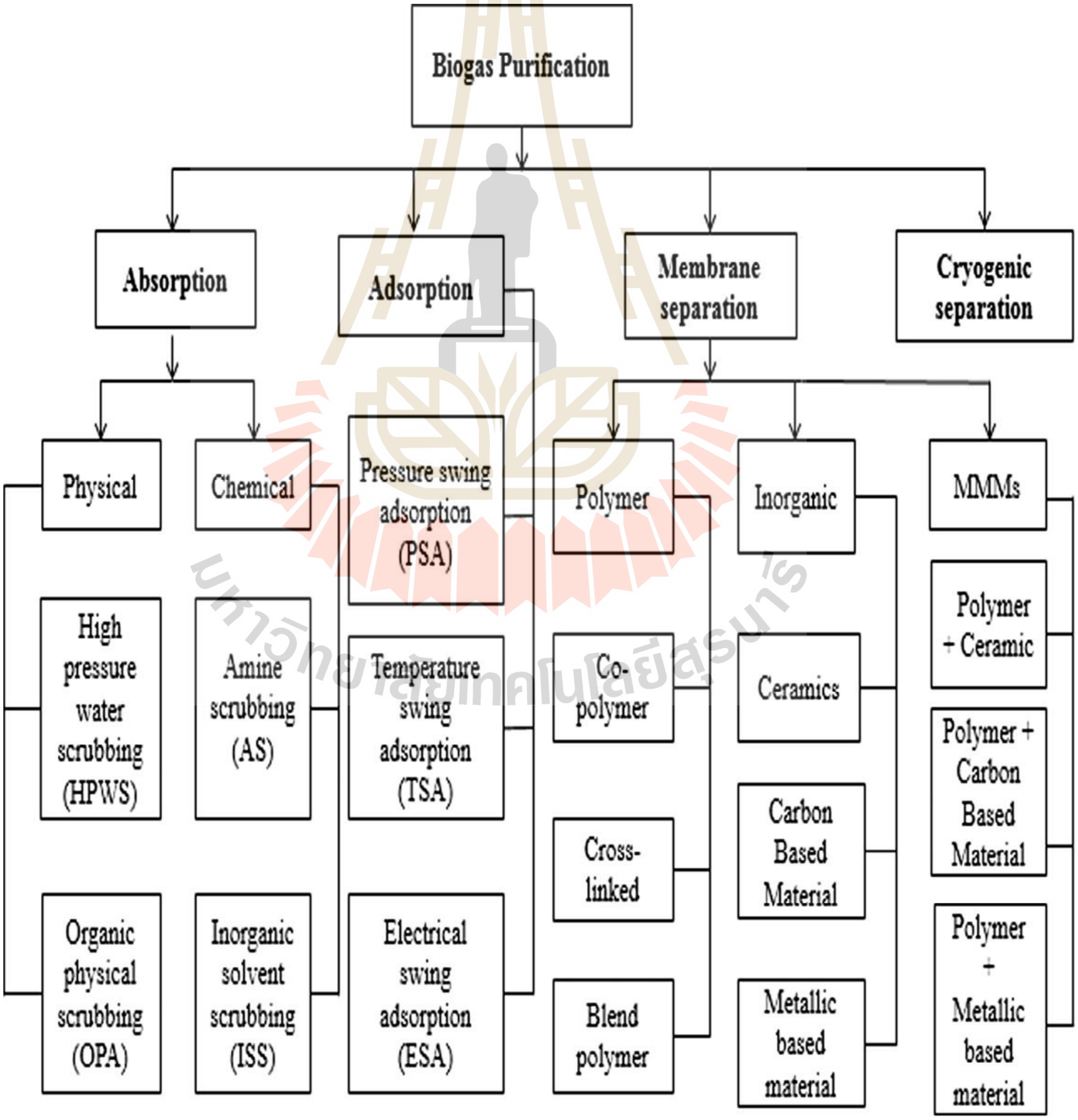

Figure 2.3 Current technologies for biogas upgrading (Khan *et al.*, 2017).

Table 2.2 Biogas impurities and their effects (Veijanen *et al.*, 2006 and Ryckebosch *et al.*, 2011).

Contaminates	**Effect**
Water	Corrosion in compressors, gas storage tanks and engines due to reaction with H_2S, NH_3, and to form acids. Accumulation of water in pipes. Condensation or freezing due to high pressure.
Dust	Clogging due to deposition in compressors and gas storage tanks.
Hydrogen sulfide	SO_2 and SO_3 are formed due to combustion, which are more toxic than H_2S and cause corrosion with water.
Carbon dioxide	Reduction in calorific value
Siloxanes	Formation of SiO_2 and microcrystalline quartz due to combustion; deposition at spark plugs, valves, and cylinder heads abrading the surface
Hydrocarbon	Corrosion in engines due to combustion
NH_3	Corrosive when dissolves in water leads to an increase in antiknock properties of engines; causes formation of NOx
O_2/air	Explosive mixtures due to high concentrations in biogas
Cl^-	Corrosion in combustion engines
F^-	Corrosion in combustion engines

2.3.1 Adsorption

2.3.1.1 Pressure swing adsorption (PSA)

Adsorption process involves the transfer of solute in the gas stream to the surface of an absorbent material due to physical or van der Waals forces. In pressure swing adsorption (PSA), some undesirable gases like

CO_2 are separated from biogas under elevated pressure using adsorbent materials. Later, the pressure is reduced to desorb the adsorbed gases (Cavenati *et al.*, 2005 and Ho *et al.*, 2008). In PSA, H_2S gas removing is a primary step because it is considered as toxic to the process and adsorption of this gas is normally irreversible (Hullu *et al.*, 2008). In this process, high methane concentration can be achieved (95–99%). However, this process needs an extensive process control and requires high investment and operational costs (Cavenati *et al.*, 2005 and Gomes *et al.*, 2002). Also, impurities in the raw biogas stream effect the efficiency of the process (Krich *et al.*, 2005). To reduce CH_4 losses in the desorbed gas, the system should be designed in such a way that desorbed gases recirculate to PSA process. Temperature swing adsorption (TSA) and electrical swing adsorption (ESA) are the other types of adsorption. The temperature in TSA enhanced at constant pressure, while in PSA, the pressure is reduced (Plaza *et al.*, 2010 and Mason *et al.*, 2011). TSA requires thermal energy to regenerate the adsorbent material while in PSA compression energy is used. Carbon cryogel microspheres (CCM) and carbon xerogel microspheres (CXM) have been identified as efficient absorbent materials for TSA process due to their highly porous and stable structure (Yamamoto *et al.*, 2004). In ESA, the regeneration is carried out by passing electricity through the saturated adsorbent and the heat generated by Joule effect facilitates the release of CO_2 (Moon *et al.*, 2006). Although, this process has the potential to reduce the cost of CO_2 capture compared to TSA and PSA, electrical conductivity is required for the absorbent used. Activated carbon has been developed as a new type of semiconductor adsorbent with large surface area and micropore volume (Grande *et al.*, 2009 and Feng *et al.*, 2011).

2.3.1.2 Adsorbents

Physical and chemical adsorption can remove CO_2 , H_2S, moisture, and other impurities from biogas either selectively or simultaneously. The adsorbent materials are very important to achieve high selectivity of CO_2. Molecular sieve materials such as zeolites and activated carbon are commonly used adsorptive materials for biogas upgrading (Zhao *et al.*, 2010). The pores of these adsorbents are responsible for easy penetration of CO_2 while retaining CH_4 molecules. This is due to different sizes of CO_2 and CH_4 molecules and also their adsorption capacity (Grande *et al.*, 2007 and Ko *et al.*, 2003). Zeolites are commercially available adsorbents for biogas upgrading due to their small pores. Types of zeolites 4A and 5A, were reported in the literature to be used for the upgrading of biogas and in particular, for the separation of CO_2 from CH_4 (Vicario *et al.*, 2010 and Montanari *et al.*, 2011). Biogas can also be upgraded using silica, alumina, activated carbon, or silicates, which are also known as molecular sieves (Chaffee *et al.*, 2007). Zeolitic imidazolate frameworks (ZIFs), a sub class of metal organic frameworks (MOFs) have recently gained much attention to be used for the adsorption of CO_2 due to their intrinsic characteristics such as tunable pore size, large pore volumes, and large surface area (Betard *et al.*, 2012). The adsorbent materials used for biogas upgrading following on this process, the surface of the adsorbent should be basic so can be easily attracted by CO_2 acidic gas. These types of materials are known as equilibrium base adsorbents because main driving factor is the differences of interaction forces between CO_2 and CH_4 with the surface of the adsorbent. The pores of the adsorbent should be modified in such a way that CO_2 (kinetic diameter of 3.4 Å) can easily penetrate into their structure while larger CH_4 molecules (kinetic diameter of 3.8 Å) are constrained to pass through them. These materials have been reported as kinetic adsorbents since its main selectivity is due to diffusion constrain. Material should be easily regenerated or desorbed with low energy demand. It should have a good moisture removal capacity (Khan *et al.*, 2017).

2.3.2 Absorption

Absorption depends on the solubility of various gas components in a liquid solvent. Raw biogas fed pass to liquid in column, is fed with packing material to increase the contact area between gas and liquid. In biogas upgrading, CO_2 is more soluble than CH_4 in liquid, thus the gas that leaves the column has a high concentration of CH_4 while the liquid leaving the column has an increased concentration of CO_2. The chemical absorption involves reversible reaction between absorbed substances and solvent. The most common amines used as solvent for removing acidic gases (CO_2 and H_2S) are diethanolamine (DEA), monoethanolamine (MEA), and methyl diethanolamine (MDEA) (Chen *et al*., 2015). Organic physical scrubbing (OPS) were used as an organic solvent instead of water. Various organic solvents such as methanol (CH_3OH), N-methyl pyrrolidone (NMP), and polyethylene glycol ethers (PEG) were used to absorb CO_2 in raw biogas (Tock *et al*., 2010).

2.3.2.1 High pressure water scrubbing (HPWS)

High pressure water scrubbing (HPWS) is the most common and well-established technology used to remove CO_2 and H_2S from biogas since these gases are more soluble in H_2O than CH_4. The operating pressure of the HPWS was 10 bars (Cozma *et al*., 2014), where biogas is fed into the bottom of a packed column while water is fed counter-currently. The physical absorption of the gases have been governed by Henry's law, which states at a constant temperature. The amount of any dissolved gas is directly proportional to its partial pressure in the gas stream. It is also observed that solubility of CO_2 can be increased at low temperature (Petersson *et al*., 2009). This process is useful for the H_2S removal because it is more soluble than CO_2 in water (Abatzoglou *et al*., 2009). The learning water from bottom of the scrubber is saturated with CO_2 or H_2S and a small amount of CH_4 was regenerated and recirculated back to the absorption tower. Regeneration is accomplished by reduce the pressure or stripping with air in a desorption column. Stripping with air is not recommended with high H_2S concentration level is high since the water rapidly becomes polluted with elementary sulphur which causes corrosion and operational problems. It is preferable to use fresh water if the cheap source of water is available. Produced biomethane is saturated with water so the drying process is mandatory for final upgrading (Chandra *et al.*, 2012 and Nie *et al.*, 2013). When a high concentration of H_2S presented in the gas stream then pre-removing of H_2S is a mandatory step in water scrubbing process like in PSA (Sun *et al.*, 2015). Although, it is an eco-friendly and highly efficient process with no special chemicals requirement and high methane recovery (> 97%), high investment and operational cost require. In addition, high energy consumption required during water regeneration process, which leads to high costs (Eze *et al.*, 2010).

2.3.2.2 Organic physical scrubbing (OPS)

Organic physical scrubbing (OPS) has the same principle as water scrubbing, but an organic solvent instead of water is used. Various organic solvents such as methanol (CH_3OH), N-methyl pyrrolidone (NMP), and polyethylene glycol ethers (PEG) are applied for CO_2 absorption. The solubility of CO_2 is five times higher in PEG than in water for the same upgrading capacity (Tock *et al.*, 2010). Which resulted in lower organic solvent demand and less pumping requirement (Tippayawong *et al.*, 2010 and Bauer *et al.*, 2013). H_2S, H_2O, O_2, N_2, and halogenated hydrocarbons are also removed together with CO_2, but the prior removal of H_2S is recommended for this absorption process (Zhao *et al.*, 2010).

2.3.2.3 Chemical scrubbing process (CSP)

Chemical absorption composes of the reversible reaction between absorbed substances and solvent. The most common amines were used as solvent for acidic gases removing (CO_2 and H_2S) are diethanolamine (DEA), monoethanolamine (MEA), and methyl diethanolamine (MDEA) (Chen *et al.*, 2015). Nowadays, a mixture of MDEA and piperazine (PZ), called as activated MDEA (AMDEA), is commonly used in this process. The absorption capacity of AMDEA is significantly higher than MDEA. The possible reason is the presence of primary and secondary amines in PZ and the tertiary amine in MDEA that gives high reaction rate for CO_2 absorption. Typically, an amine scrubber system consists of an absorber, where the CO_2 is absorbed from the biogas and a stripper in which the CO_2 is separated from the waste amine solution by heating under reduced pressure (Kismurtono *et al.*, 2011). The operating pressure of the absorber is 1–2 bar. The liquid from the bottom of the absorber is pass through the heat exchanger and pumped to the top of the stripper column, which it is connected with the steam and CO_2 is released. The bottom part of the stripper column is equipped with a reboiler at 120–150 °C where amine solution is boiled. Reboiler provided the heat of reaction for the releasing of CO_2 from the waste amine solution and regenerated the amine solution. Highly concentrated CH_4 of>99% gas was obtained with low operational cost but high investment cost, and significantly a massive heat is required for the regeneration of amine solution (Krich *et al.*, 2005). If H_2S present in the raw biogas, it will be absorbed by amine solution and higher temperature needed for the regeneration to desorb H_2S. Therefore, the removing prior to the AS process. Another downside of this technology is the requirement to treat waste chemicals, corrosion, and contaminant build-up which makes the process more complex (Palma *et al.*, 2013). Inorganic solvent scrubbing (ISS) generally employs an aqueous solution of alkaline salts such as sodium, potassium, ammonium, and calcium hydroxides (Huang *et al.*, 2003). The absorption of CO_2 in this alkaline solution assisted by agitation. The turbulence in the solvent and the contact time between biogas and liquid increased the diffusion of CO_2 in the solvent (Chen *et al.*, 2015).

2.3.3 Membrane gas separation

During the last 40 years, the membrane-based gas separation process has become the part of market share and the principle was show in Fig 2.4 (Makaruk *et al.*, 2010, Harasimowicz *et al.*, 2007 and Deng *et al.*, 2010). The membrane acted as a permeable barrier that allows specific compounds to pass through differently and control their permeability based on the applied driving forces such as the difference in concentration, pressure, temperature, and electric charges of different species. Generally, two models were used to explain the membrane separation process such as solution-diffusion and pore-flow model (Jiang *et al.*, 2006). In the first model, permeates dissolved in the membrane material then diffuse through the membrane due to the concentration difference. Later in this process, permeate was separated by pressure-driven convective flow through small pores (Rongwong *et al.*, 2012). However, the solution-diffusion model was frequently used for gas transportations in polymeric membranes (Kentish *et al.*, 2008). For biogas upgrading, CO_2 permeates through the membrane while CH_4 retained on the inlet side as retentate. The membrane gas separation probably more benefic if the gas flow is low and the inlet CO_2 content is high. These considerations were suitable for a typical biogas upgrading plant (Baker *et al.*, 2008). It is a cheap process including low operating and capital costs, less demand for energy, simple and compact membrane equipment set up requirement (Basu *et al.*, 2010). Polymeric, inorganic, and mixed matrix membranes (MMMs) three different types of membrane used for biogas purification. Most of the commercial membranes are polymeric made from organic materials such as polysulfone (PSf), polyimide (PI), polycarbonate (PC), polydimethyl siloxane, and cellulose acetate (Robeson *et al.*, 1991 and Harasimowicz *et al.,* 2007). They have excellent mechanical strength, easy to fabricate with low cost, and high selective permeation. CA and PI based polymeric membranes are the mostly used commercial membranes for biogas separation. Polyvinyl amine/polyvinyl alcohol blend membrane was also tested and achieve 98% CH_4 purity (Deng *et al.*, 2010). CA membrane is the first polymeric membrane commercialized for biogas purification (Scholz *et al.,* 2013). CA is relatively inexpensive due to an abundant and renewable resource of cellulose with attractive separation properties. Therefore, CA membrane has been commercialized for over 30 years. However, CA membranes possess several limitations that restrict its use in gas separation membrane. CA membranes are susceptible plasticization (Plasticization = 8 bar) (Bos *et al.*, 1999). due to its -OH rich functional groups that easily dissolve CO_2 within the membrane matrix. PI, a highly crystalline material that attract for gas separation. It shows a high permeability, selectivity and mechanical/thermal stability. Matrimid® is commercially available PI with stiff polymer backbone. Furthermore, PSf also possesses the excellent mechanical in strength and high rigidity as well as acceptable gas pair selectivity and thus, becoming one of the most important polymeric membrane materials. Although, the separation properties of PSf are still lacking compared to PI based membrane, PSf is cheaper than high plasticization resistance (Plasticization = 34 bar) (Bos *et al.*, 1999). State of the art polymeric membranes are economically competitive in separating CO_2 and H_2S from the biogas compared to conventional technologies in both capital and operating costs (Chen *et al.,* 2015). However, the investigation of polymeric materials for gas separation has been challenged by the upper bound trade-off limit between permeability and selectivity. In fact, highly permeable membranes are commonly accompanied by low gas pair selectivity (Robeson *et al.*, 2008).

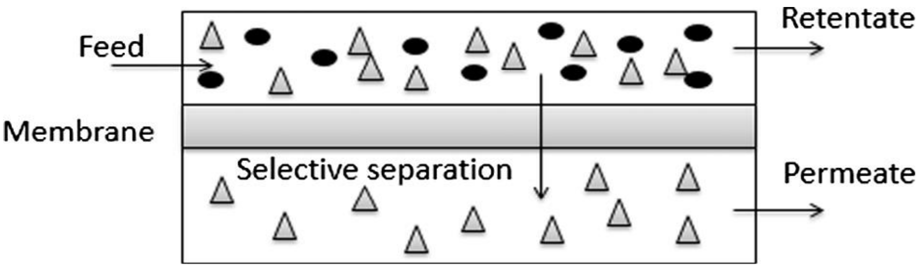

Figure 2.4 Principle of membrane gas separation process (Khan *et al.*, 2017).

Inorganic membranes are more advantageous compared to the conventional polymeric membrane as offer more mechanical strength, thermal stability, and resistance against any chemicals. Mostly, inorganic membranes facilitate permeability and selectivity, exceeding the Robeson upper bound. There are several classes of the inorganic membranes such as zeolite, activated carbon, silica, carbon nanotubes (CNT), and metal-organic framework (MOF). Developing continuous defect-free inorganic membranes, however is the most crucial step in inorganic membrane fabrication (Rezaei *et al.*, 2015). It is noted that the fabrication of inorganic membranes is a stringent process and requires continuous monitoring due to their fragile structure. For example, a carbon membrane derived from a polymer precursor is supported by alumina or quartz to provide a strengthens to the membrane before undergoing pyrolysis. The rigid porous materials like carbon molecular sieves and zeolites have difficulties to form continuous and defect free membranes for practical applications in spite of their superior gas separation properties (Jiang *et al.*, 2005, Barboiu *et al.*, 2009 and Rezaei *et al.*, 2014). It is clear that, both polymeric and inorganic membranes have limitations that motivate researchers to develop new membranes. The developments so far are focused on integrating both polymeric and inorganic membranes known as mixed matrix membranes (MMMs). MMMs are composite membranes consisting of polymeric materials as continuous phase with inorganic particle as dispersed phase. It is predicted that the resultant membranes have benefits owing to the combing advantages of both polymeric and inorganic materials and overcome the limitations of each individual phase (Rezaei *et al.*, 2016 and Aroon *et al.*, 2010). Significant improvement in MMMs properties is expected due to the superior separation performance of inorganic particles combined with high processability and moderate processing cost of base polymeric membranes. Excellent gas separation properties of MMMs are the main driving force in the development of the novel gas separation membranes (Chung *et al.*, 2007, Zornoza *et al.*, 2014 and Shao *et al.*, 2012). The embedment of inorganic filler into polymer matrix would introduce an additional mechanism to improve the membrane performances. For example, using zeolite as a filler for CO_2 removal membrane would provide a molecular sieving mechanism to further discriminate CH_4 while specific interaction with CO_2 provides an improved surface diffusion across the membrane. The presence of particles in the polymer matrix also increases the tensile strength and thermal stability of the membrane and membrane can be applied at harsh environment (Favre *et al.*, 2009, Rezaei *et al.*, 2014 and Zanganeh *et al.*, 2009). Thus, improvements in biogas separation factor are expected where MMMs are applied. However, more investigations should be performed to enhance filler dispersion and compatibility when it is incorporated into the polymeric phase. Pre-removal of H_2S from raw biogas is necessary because it can negatively affect the membrane performance. Besides, water, oil droplets, and aerosols are also needed to be removed by a filter before the gas enters the membrane unit (Persson *et al.*, 2006). There is a requirement of system development that separates CO_2/CH_4, H_2S/CH_4, and other traces impurities simultaneously from raw biogas using different membranes. Also, membrane separation process for biogas system should be further explored to facilitate easy operation with low energy demands using a multistage membrane that is more economical for biogas upgrading.

The multistage of membrane process had lower investment and operating costs with high CH_4 purity in comparison to the single stage process (Rezaei *et al.*, 2014).

2.3.4 Cryogenic separation

Cryogenic separation of biogas is based on the principle that various gases like CO_2 and H_2S liquefy under different pressure and temperature conditions. It operates under a very low temperature (-170 °C) and high pressure (80 bar) condition. The boiling point of CH_4 at 1 atm is -161.5 °C that is much lower than the boiling point of CO_2 which is -78.2 °C and thus allowing the separation of CO_2 from CH_4 by liquefying (Andriani *et al.*, 2014). These operating conditions are maintained using a series of compressors and heat exchangers (Zanganeh *et al.*, 2009). The purified gas is depressurized and can be used in various applications. This separation is regarded as new technology, which is still under development (Ryckebosch *et al.*, 2011 and Petersson *et al.*, 2009). Cryogenic separation used to produce liquefied biomethane and liquid natural gas (Krich *et al.*, 2005). It is advised to pre-separate H_2O and H_2S to avoid plugging of equipment due to the freezing of existed water in the raw biogas (Sun *et al.*, 2015). This phenomenon significantly reduces the operating pressure of the system (Mondal *et al.*, 2012).

2.4 Type of membrane gas separation

Membrane for gas separation is classified by materials such as organic, inorganic polymer, carbon and ceramics membrane. On the other hand, membrane for gas separation can be classified by porous membrane and non-porous membranes. Porous membrane consist of two layers, the first is supportive layer, and the second layer is coating with zeolite and this type of membrane has high selectivity thus this study uses non-porous membrane for separate CO_2 from biogas. The example types of membrane gas.

2.4.1 Polymer membrane

Polymer membrane are still one of the most common types of membrane normally used for gas separation, in which the transport takes place according to a solution-diffusion mechanism (Ghadimi *et al.*, 2012). Polymer membrane is alternative membrane gas separation and leading of industry market because they are very competitive performance and economics. A polymer is appropriate of characteristics for the intended application. Suitable polymer offer a low binding affinity for separate molecules and has to withstand the harsh cleaning conditions. It can be compatible with chosen membrane fabrication technology. The polymer is suitable and efficient membrane former in terms of its chains rigidity, chain interactions, stereo regularity, and polarity of its functional groups. The polymers can be forming at amorphous and semi crystalline structures that affecting to the membrane performance characteristics. The polymer has to be obtainable and reasonably priced to comply with the low cost criteria of membrane separation process.

2.4.2 Carbon membranes

Carbon membranes are emerging as promising candidates for gas separation applications. Thus, it has been demonstrated that the selectivity obtained with carbon membranes are much higher than those typically found with polymeric membranes. Depending on the separation mechanism, two types of carbon membranes can be distinguished: molecular sieve carbon membranes (MSCM) and adsorption-selective carbon membranes (ASCM). Carbon membranes is prepared by the carbonization of a phenolic resin film. Carbon membranes have been transformed into adsorption-selective carbon membranes by an additional short time air oxidation prior to or after carbonization. In this way, the separation properties of carbon membranes towards multi-component mixtures of hydrocarbons with and without N_2 can be tailored (Fuertes *et al.*, 2001 and Menendez *et al.*, 2002). The predominant transport mechanism of most carbon membranes is molecular sieving. Hollow fiber carbon molecular sieve membranes have been made via pyrolytic carbonization of organic polymers (Koresh *et al.*, 1987). Mixed carbon silica membranes with excellent gas separation properties have been prepared by the pyrolysis of imide-siloxane co-polymers at 600, 800, and 1000 °C (Park *et al.*, 2003). The separation of gas molecules by means of MSCM takes place via a molecular sieving mechanism. Since MSCM have microspores with sizes close to the dimensions of permanent gases (<4 Å), the diffusivity of these gases through the membrane changes abruptly with the molecular size and shape. This allows the separation of gases with similar molecular sizes. These membranes have demonstrated to be effective to separate gas mixtures, such as O_2/N_2, CO_2/N_2 and CO_2/CH_4 (Jones *et al*., 1994 and Hayashi *et al*., 1995). Gas separation by MSCM is limited to gases with molecular sizes smaller than 4.0–4.5 Å. However, MSCM are not suitable to separate gas mixtures, such as iso-butane/n-butane or gas–vapor mixtures.

2.4.3 Ceramic membrane

Ceramic membrane or zeolite membranes are generally formed on porous supports by hydrothermal synthesis. The pores in zeolite membranes are part of the crystal structure and, hence, have uniform dimensions. The size of the microspores, with molecular dimensions are generally less than 1 nm, can be varied by the crystal structure. Zeolites can separate molecules based on size, shape, polarity and degree of unsaturation, amongst other things. Many zeolites are thermally stable above 500 °C. Some are stable in alkaline environments and some are stable in acidic media. In the production of zeolite membranes, the ability to prepare reproducibly is very thin (<1.5

μm) and oriented zeolite layers with an almost complete absence of defects, as well as sufficient mechanical strength, has still to be reached. Elimination of small defects can be achieved by CVD. Major steps forward still have to be taken to render these highly selective porous membranes reliable and cheap enough to be produced on an industrial scale. Zeolite membranes offer good separation properties for gas molecules. At low temperatures, the permeation rate increases with molecular weight, being essentially zero for H_2. At high temperatures (about 500 °C), however, the trend is reversed, and permeation decreases with increasing molecular weight. At high temperatures the permeation rate for H_2 is higher than for hydrocarbons, making the membrane particularly useful for H_2 separation.in dehydrogenation reactions. The majority of zeolite membranes are of an MFI zeolite-type and show a CO_2/N_2 selectivity of the order of 10, CO_2 permeations being around 10^{-7} mol/m^2 Pa s in the temperature range of 30-150 °C. With a potassium-ion exchanged Y-type zeolite, a CO_2/N_2 selectivity of the order of 30, with CO_2 permeations being around 10^{-6} mol/ m^2 Pa s, has been achieved (Morooka *et al.*, 1999).

2.4.4 Mixed matrix membranes (MMMs)

Mixed matrix membranes are a well-known route to enhance the properties of polymeric membranes. Their microstructure consists of an inorganic material in the form of micro- or nanoparticles incorporated into a polymeric matrix. The application of two materials with different flux and selectivity provides the possibility to better design a gas separation membrane, allowing the synergistic combination of polymers, easily process ability and the superior gas separation performance of inorganic materials. In principle, the incorporation of the inorganic component can be seen as a relatively and easily modification of existing methods for fabricating large-surface area polymeric membrane; therefore, The MMMs possess an economic advantage over inorganic membranes. In addition, they may offer the enhanced physical, thermal, and mechanical properties for aggressive environments and could be a way to stabilize the polymer membrane against change in perm selectivity with temperature (Hu *et al.*, 1997). These membranes offer very interesting properties; however, it’s difficult for commercial scale manufacture, and brittleness remain important challenges. The successful development of MMMs depend on several factors, such as the proper selection of polymeric matrix and inorganic filler and the elimination of interfacial defects between the two phases. It is also important to filler concentration control, shape, and dimensions in order to reach the expected performance (Koros *et al.*, 1997 and Zimmerman *et al.*, 1997). For the formation of this, defect-free is mixed matrix structures as asymmetric membranes, several aspects are relevant: the rheological properties of the dope solutions, the spinning conditions, and the shape, size, and wettability of the particles. Several inorganic materials, porous and nonporous were considered for the preparation of MMMs. These inorganic particles can improve the separation (e.g., by molecular sieving mechanism) or increase the membrane free-volume (Merkel *et al.*, 2002). Molecular sieves were chosen to enhance selectivity for a given gas mixture by increasing the sorption of the desired gas component. In particular, zeolites were widely used in rubbery and glassy polymers (Duval *et al.*, 1993, Jia *et al.*, 1991 and Paul *et al.*, 1973). Polydimethylsiloxane and ethylene propylene diene rubber (EPDM) glassy flexible polymers, such as cellulose acetate (Kulprathipanja *et al.*, 1988) and polyvinyl acetate (PVAc). The flexibility of the rubbery polymers was suggested as the primary cause of good polymer-zeolite interaction and stress-free interfaces with the zeolite (Mahajan *et al.*, 2000). An adequate contact between the dispersed phase of the molecular sieve and the polymeric phase was generally observed using rubbery polymers as membrane matrix.

2.5 Zeolitic imidazolate frameworks (ZIFs)

Zeolitic imidazolate frameworks (ZIFs) are a subclass of Metal organic frameworks (MOFs). MOFs are materials of wide interests in recent years because of their interesting chemistry and potential applications. In separation science, researchers have extensively explored the use of MOFs for gas separation and water treatment. MOF membranes have attracted significant attentions in recent years because of their potentials in gas and liquid separations and other applications such as catalysis and chemical sensors, etc. (Lai *et al.*, 2018). Metal-organic frameworks (MOFs) are a class of materials consisting of inorganic blocs that form a textured structure with each other by organic linkers (Li *et al.*, 2015). These materials are currently getting an increasing interest due to their special properties, such as high surface area and pore volume, low density (Farha *et al.*, 2012 and Furukawa *et al.*, 2011), abundant adsorption sites, and different structures that promote various specific applications (Li *et al.*, 2015 and James *et al.*, 2003). Among these applications, separation and filtration were mostly explored, in which MOFs were incorporated into the membranes in different ways to improve their overall performance.

Zeolitic imidazolate frameworks are topologically similar to zeolites. ZIFs are composed of tetrahedrally coordinated transition metal ions (e.g. Fe, Co, Cu, Zn) by organic imidazole connect linkers. The three-dimensional structures in ZIFs consist of tetrahedral transition metal cations such as Co^{2+} and Zn^{2+}, which are linked to imidazole-based ligands by coordination bonds. The bond angle of M-Im-M is similar to the Si-O-Si bond angle in zeolites. In these structures, the tetrahedral metal centers are coordinated by nitrogen atoms in the 1, 3-positions of the imidazolate ligand (Tan *et al.*, 2010). These porous, flexible, chemically, and thermally stable crystals (up to 400 °C) are the promising materials for gas separation and storage, as well as size and shape of selective catalysis due to their pore size (Shah *et al.*, 2012, Park *et al.*, 2006 and Phan *et al.*, 2010). In addition, their surface area is similar to that of very porous MOFs and is attributed to the full exposition of imidazole-based ligand edges and faces (Park *et al.*, 2006 and Hee *et al.*, 2004). ZIFs also show framework flexibility with respect to gas adsorption and are stable under harsh conditions such as refluxing with organic solvents, water, and aqueous alkaline solutions (Park *et al.*, 2006).

2.5.1 Important features in ZIF membrane synthesis

Some of the most important features that high-performance ZIF membranes must exhibit are pore continuity (interconnectivity), defect-free structure, and good adherence to the substrate surface. Gas separation performance is affected by various factors such as the membrane orientation, chemical composition of the support, activation process, and membrane thickness (Gascon *et al.*, 2012). In this section, the relevant work related to the improvement of these factors was reviewed.

2.5.1.1 Effect of the substrate

The type of support is very important during ZIF membrane synthesis. Ceramic and polymeric supports have been used in the past for is of ZIF membranes synthesis, with ceramic supports comprising the most commonly used type of substrate. Ceramic supports exhibit excellent mechanical and thermal stability, which permit their use in processes that carried out at high temperatures. The types of ceramic support have been used for the synthesis of ZIF membranes include α-alumina (Liu *et al.*, 2010 and Shah *et al.*, 2013), titania (Bux *et al.*, 2009 and Pan *et al.*, 2012), YSC, ZnO (Dong *et al.*, 2012), and SiO_2 (Fan *et al.*, 2012). Titania is a substrate that promotes heterogeneous nucleation. On the other hand, α-alumina offers excellent mechanical stability, which permits wide use in ZIF membrane synthesis and for this reason is the most commonly preferred type of substrate. A support that combines the mechanical stability of α-alumina and the smooth layer of titanium has also been described. Another approach to promote heterogeneous nucleation is surface modification. Reports on the surface modification of α-alumina are available. In fact, a-alumina supports have been modified with ZIF organic ligands (McCarthy *et al.,* 2010).

2.5.1.2 Effect of surface modification

Heterogeneous nucleation is difficult to achieve on bare supports. One strategy to promote nucleation is surface modification, various methodologies have been proposed. For instance, imidazole-based ligands have been used to modify the substrates and obtained strong covalent bonds between the organic ligand and the substrate (McCarthy *et al.,* 2010). In addition, 3-aminopropyltriethoxysilane (APTES) has also been used in order to modify ceramic substrates. APTES has been reported in order to act as a binder between the membrane layer and the support and anchor the crystals in ZIF-22 membranes (Huang *et al.,* 2010). APTES acts as a covalent linker between the membrane and the support because the ethyl groups of APTES react with the surface hydroxyl groups of the Al_2O_3 supports. As a result, nucleation and crystal growth can occur in sites where linkers present. APTES has also been reported in development of continuous layers on the substrate by providing enough heterogeneous nucleation sites. In another work, a layer of ZnO deposited on a tubular substrate to act as a Zn^{2+} source, provide a smooth support layer, and promote homogeneous nucleation (Zhang *et al.*, 2013).

2.5.1.3 Effect of deprotonates

Well-intergrown ZIF crystals required to obtain pore continuity in membranes. To achieve such ZIF crystals, bases are usually included in the membrane precursor solution in order to increase the pH of the solution and promote the completely deprotonation of imidazole-based ligands, which in turn permits the growth of ZIF membranes in all directions. Sodium formate is the most commonly used deprotonator, and its use was first proposed by McCarthy *et al.*, 2010.

2.5.1.4 Effect of the solvent

The three popularly used solvents in the synthesis of ZIF membranes include dimethylformamide (DMF), methanol, and water. Choosing and establishing are the most suitable solvent for synthesizing the desired type of ZIF membranes successfully is a challenging task. The use of cost effective and benign solvents such as water is preferred for health and environmental reasons; however, to date, only ZIF-8 membranes have been synthesized successfully with water as the solvent in the precursor solution (Yao *et al.*, 2013). In addition to solvent toxicity, molecular size should also be taken into consideration for further activation. It is worth mentioning that, the smaller the solvent molecule, the easier the activation can take place, and the more the ZIF structure integrity can be preserved. Efforts to synthesize ZIF membranes using water as the solvent should be made a priority not only because of the benefit to subsequent activation and reduction of toxic waste, but also because the degree of deprotonation of the organic ligand can be promoted as well. As demonstrated in their synthesis of ZIF-8 membranes, 2-methylimidazole exhibits a higher degree of deprotonation in water than in organic solvents (Pan *et al.*, 2012).

2.5.1.5 Effect of activation

The activation step is very critical for ZIF membrane synthesis. Activation consists of removing the occluded solvent molecules from the ZIF structure and is usually done by solvent exchange with a solvent of smaller molecular size (e.g. methanol). The solvent exchange unit operation is usually conducted in pure methanol. Considering the fact that the concentration of occluded solvent molecules in pure methanol is zero, a high concentration gradient will exist and therefore, the mass transfer rate will high. This high mass transfer rate provoke the fast transport of occluded molecules to the high methanol concentration phase, consequently damaging the ZIF structure and leading to poor gas separation performance. In order to prevent high mass transfer rates, DMF and methanol solution used at different compositions for the activation of ZIF-78 membranes to decrease the diffusion rate of DMF. Specifically, they suggested starting the activation by immersing the membranes in a DMF-methanol solution with low methanol composition in order to reduce the concentration gradient of DMF. The composition of methanol in the activation solution increased successively until pure methanol is used at the end of the activation process. Drying is the next step after solvent exchange and is much easier to perform with highly volatile solvents. Methods for ZIF membranes synthesis that simultaneously reduce the amount of occluded solvent in the structures are constantly sought after. Indeed, by reducing the amount of occluded solvent, activation can occur easier and high quality of the ZIF membranes can be preserved. Recently, electrospray deposition has been introduced ZIF-7 and ZIF-8 synthesis (Aceituno *et al.,* 2015) membranes. It was demonstrated that this technique permits the full activation of the membranes by simultaneously synthesis and activating the ZIF membranes.

2.5.1.6 Chemical and thermal stability

In spite of the fact that the chemical and thermal stability of ZIF crystals was studied. For instance, Liu and his colleague synthesized c-oriented ZIF-69 membranes that were stable under boiling methanol. The same group synthesized APTES-functionalized ZIF-90 membranes that showed excellent thermal and hydro-thermal stability with outstanding separation performance. They also synthesized ZIF-95 membranes that showed hydrothermal stability (Xie *et al.,* 2012). In their studies, the highest temperature at which gas separation tests were conducted using

ZIF membranes was 325 °C. Identifying the extreme temperature conditions in which the membranes can operate (where they are chemically and thermally stable at this temperature range) is important because most of the exhaust or flue gases to be treated, separated, or enriched from industrial processes are present at high temperatures. Such stability will ensure reliability and reproducibility in the separation performance of ZIF membranes, which are necessary for industrial applications.

2.5.1.7 Effect of functionalization

Materials with rigid structures are preferred for the synthesis of membranes to guarantee that the pore size remains unchanged throughout the process (Gascon *et al.*, 2012). Membranes with rigid structures can be obtained through post-synthetic modification and functionalization. Post-synthetic functionalization has been accomplished by imine and APTES functionalization. Excellent gas separation performance has also been observed in membranes that were synthesized by following this strategy, with improvement of the membrane microstructure documented as well.

2.5.2 ZIF membrane synthesis

Conventionally, ZIF membranes have been synthesized by *in situ* growth and secondary growth as shown in Figure 2.5 In this section, different synthesis methodologies of ZIF membranes, were presented and divided into three groups: *In situ* growth, secondary growth, and innovative techniques.

2.5.2.1 *In situ* growth

In situ growth comprises the growth of a ZIF membrane on a porous support that not contain any crystals attached (seeded) to its surface. This technique is accomplished by immersing the support in a precursor solution. After sufficient amount time is given at an elevated temperature, nucleation begins to proceed where the ZIF starts to grow on the support, and the membrane is eventually formed. In this type of synthesis, nucleation, growth, and intergrowth of the crystals are not decoupled, occurring instead during the same step for an extended period of time. *In situ* growth can be conducted using both unmodified and modified supports (Manuel *et al.*, 2015).

2.5.2.2 Secondary growth

Secondary or seeded growth is related to the synthesis of ZIF membranes on supports that contain attached seeding crystals (Figure 2.5). Such seeding crystals can be attached by means of physical or chemical treatment. Unlike *in situ* synthesis, crystal nucleation, growth, and intergrowth not occur simultaneously in secondary growth synthesis. Moreover, the layer growth is independent of the substrate. Depending on the manner in which the crystals are seeded on the supports, this type of synthesis can be classified as secondary growth on supports with physically and chemically attached seeds. ZIF membranes have been synthesized using secondary growth with prior seeding, which is accomplished via rubbing, dip-coating, slip-coating, electro-spinning, and microwave radiation (Manuel *et al.*, 2015).

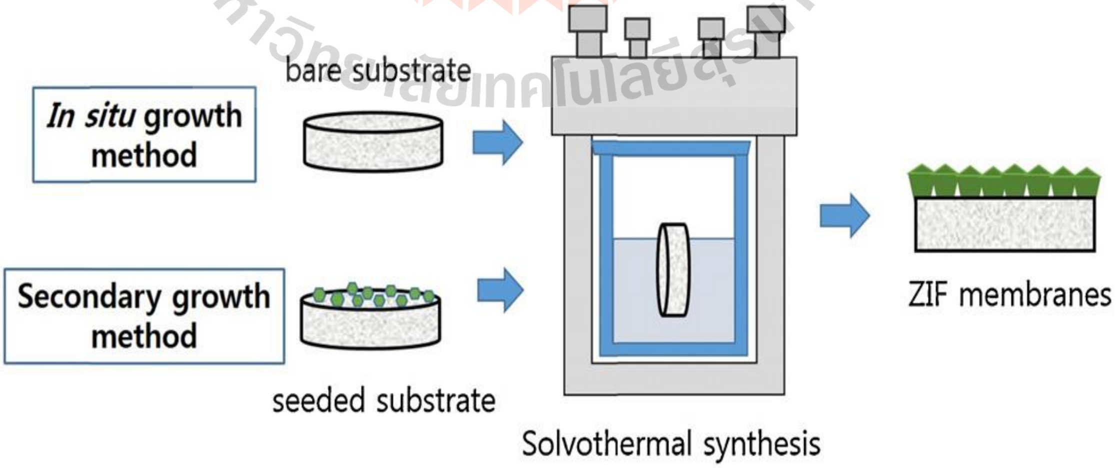

Figure 2.5 Schematic procedure for in situ growth and secondary growth methods for the synthesis of ZIF membranes under solvothermal conditions.

CHAPTER III

MATERIAL AND METHOD

3.1 Materials

Zinc nitrate hexahydrate [Zn $(NO_3)_2 \cdot 6H_2O$] was purchased from Ajax Finechem Pty Ltd. (New Zealand). 2-methylimidazole (MeIM) was obtained from RIC Labscan, Thailand. Methanol (99.99%) was purchased from Merck (Germany). All other chemicals are analytical grade, and were used as received. Gas mixture of CO_2/CH_4 was purchased from Sung Neon Oxygen (Thailand). Kaolin originating from Ranong province for α-alumina support preparation was obtained from School of Ceramic Engineering, SUT.

3.2 Methods

In this study the ZIF-8 membrane was produced via seeded ZIF-8 particles on α-alumina support as selective layer for upgrade biogas quality. Figure 3.1 was presented the overall process in this study.

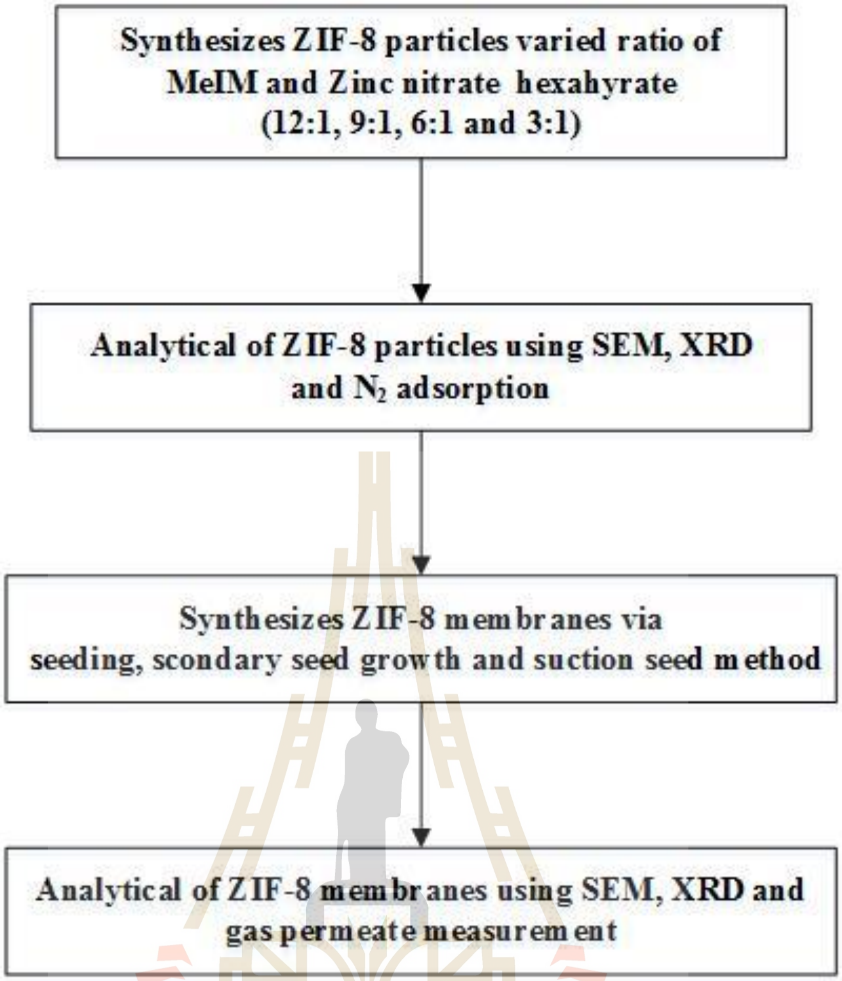

Figure 3.1 The overall of synthesis ZIF-8 membranes process for biogas upgrading.

3.2.1 Preparation of ZIF-8 particles

To synthesize ZIF-8 particles, the absorbed moister of precursors must be removed, hence, initially a predetermined number of precursors (MeIM and Zinc nitrate hexahydrate) powders were placed in oven for about 2-3 hours in 70°C. An optimal condition sample with molar ratio of MeIM/ Zinc nitrate hexahydrate of 12:1 was synthesized using 6.94g (85 mmol) of MeIM and 0.54g (1.8 mmol) of Zinc nitrate hexahydrate. Other molar ratios of precursors (MeIM/ Zinc nitrate hexahydrate: 9:1, 6/1 and 3:1) were also applied in synthesis of ZIF-8 particles using 3.47g, 1.73g and 0.87g of MeIM for 0.54 gram of Zinc nitrate hexahydrate (Table 3.1), respectively according to the following procedure: Each precursor was dissolved in 12 mL of methanol for 1 hour. Two prepared solutions were mixed and stirred at 70°C in oil bath under cover with aluminum foil for 30 min, followed by sonication for 1 min. The obtained ZIF-8 was centrifuged to hasten the sedimentation at 7,000 rpm for 15 min and washed several times with methanol (Jomekian *et al.*, 2017). The prepared sample (deposited ZIF-8 powder) was placed in petri dish in ambient temperature for 24 h to dry. The properties of ZIF-8 particles were analyzed via XRD and SEM. The surface area and adsorption-desorption isotherm measurements were carried out on Bel Japan Inc, Belsorp mini-II.

Table 3.1 The ratio of 2-methylimidazole: Zinc nitrate hexahydrate for synthesize the ZIF-8 particles.

Ratio	2-methylimidazole (g)	Zinc nitrate hexahydrate (g)
12:1	6.94	0.54
9:1	3.47	0.54
6:1	1.73	0.54
3:1	0.87	0.54

3.2.2 Porous α-alumina support preparation

The α-alumina support (ceramic) was used as a support due to its thermal resistant and long term used. The porous α-alumina support was prepared by cleaning the kaolin 2 times using DI water and then filtered through filter paper. The wet kaolin was dried at 100°C overnight using hot air oven (Memmert, Germany). The dried kaolin was milled and sieved (No.100, Retsch, Germany) (Figure 3.2). Afterward, support was formed using 5 g of dried kaolin then pressed at 10,000 pounds using a hydraulic pressing machine. The diameter of support was 4 mm at 0.3 mm thickness. The formed support was sintered at 1200°C for 2 hours (ramp up and down at 4°C per min) according to Figure 3.3.

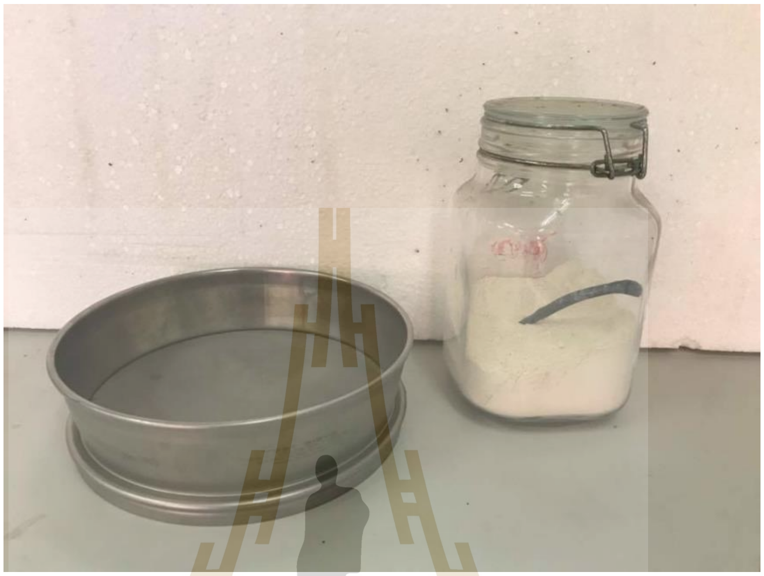

Figure 3.2 The dried kaolin powder and sieve (No.100, Retsch, Germany).

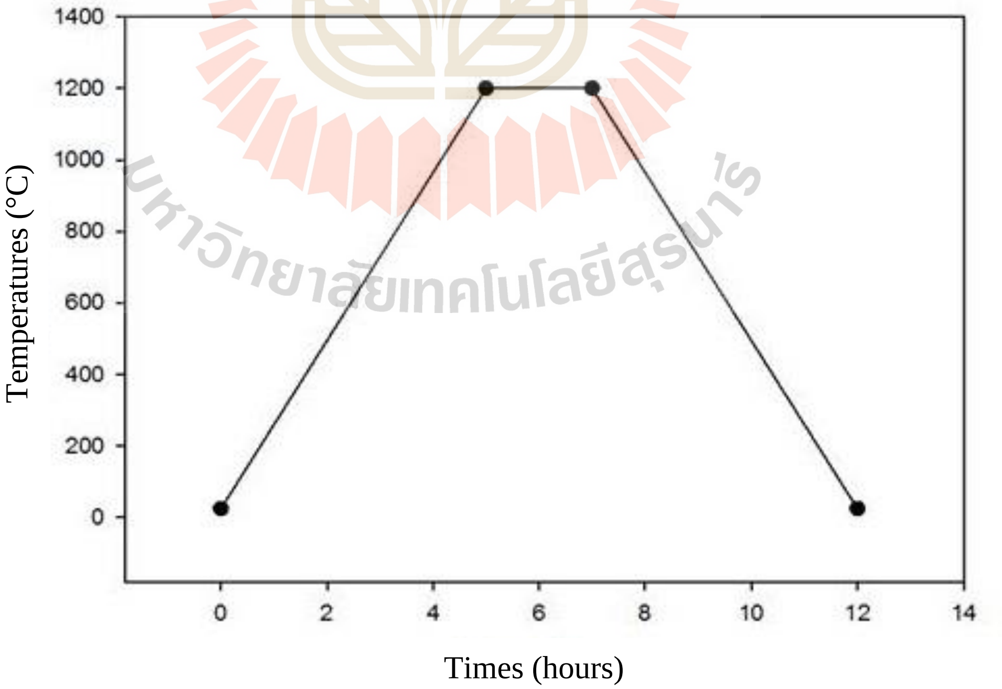

Figure 3.3 The sintering times of porous α-alumina support (ramp up and down at 4°C per min).

3.2.3 ZIF-8 membrane synthesis methods

The porous α-alumina support 4 mm at 0.3 mm thickness diameter were applied to each method. The several synthesis methods prior to gas permeate analysis were seeded as follow:

3.2.3.1 Seeding method

The α-alumina disk was finely polished with an abrasive paper (no. 1000 silicon carbide, Nash, Thailand) in order to smooth the surface. The support disks were then sonicated for 10 min with 20 mL deionized water, and subsequently washed with fresh methanol several times for impurities removal. The supporting disk was subsequently dried in oven at 100°C for 12 hour and cooled down until room temperature before using. After that, the support was placed horizontally in a 45 mL Teflon lined stainless steel autoclave (Figure 3.4) filled with the seed solution (hydrothermal synthesis). The solution was prepared by mixing Zinc nitrate hexahydrate and MeIM (from optimal condition ratio) in 30 mL methanol. The membrane synthesis was incubated at 70°C from 6 hours. After synthesis the ZIF-8 membrane disks were taken out and rinsed several times with fresh methanol. Finally, seeding membrane was dried under ambient conditions for 24 hours and used for further analytical method.

Figure 3.4 45 mL Teflon lined stainless steel autoclave.

3.2.3.2 Secondary seed growth method

ZIF-8 seed solution was prepared according to Chi *et al.* 2015. The 0.54g of Zinc nitrate hexahydrate and 1.477g of MeIM were separately dissolved in 12 mL of methanol for 1 hour. Two prepared solutions were mixed, and stirred at 70°C in oil bath, and with aluminum foil cover (solvothermal treatment) for 30 min, following by 1 min sonication. The obtained ZIF-8 particles were collected by centrifugation at 7,000 rpm for 15 min and were washed several times with fresh methanol. The particles were dried overnight at 70°C and dispersed into fresh methanol to form a 0.1 wt% seed solution. The coating side of the α-alumina disk was finely polished with an abrasive paper in order to smooth the surface. The supporting disk was then sonicated for 10 min in 20 mL of deionized water, and subsequently washed with fresh methanol several times for impurities removal. The disk was subsequently dried in oven at 100°C for 12 hour and cooled down to room temperature. The supporting disk was undergone a simple slip-coating, the polished side of α- alumina disk was half immersed two times in the above prepared seed solution for about 20 s then carefully slid away (Figure 3.5) and the support was dried at room temperature for 1 hour. The support after slip-coating was hydrothermal synthesized in accordance with seeding method.

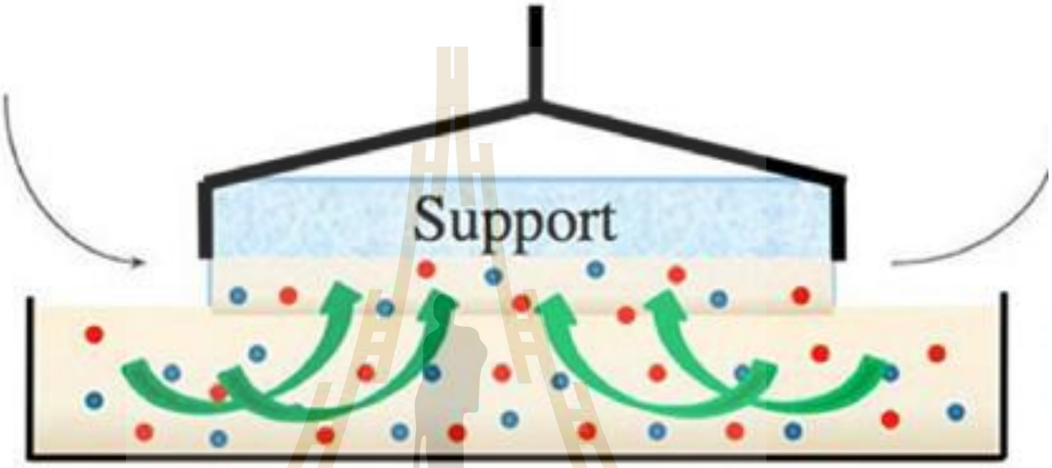

Figure 3.5 Slip-coating on secondary seed growth method (Melgar *et al.*, 2015).

3.2.3.3 Suction seeding method

The porous α-alumina support was fixed in the vacuum flask and connected to the vacuum pump (Figure 3.6). Then, 5 mL of 1 wt% of seed solution was poured into support. The ZIF-8 particle (from optimal condition ratio) and methanol were prepared for suction seed solution mixing and sonicating for 10 min. After suction, the suction seeding membrane was dried at 70°C in hot air oven overnight. The support after suction was hydrothermal synthesized in accordance with seeding method.

Figure 3.6 The membrane synthesis via suction seeding method.

3.3 Gas permeation measurements

The flow diagram and experiment setup for gas permeation measurement were shown in Figure 3.7 and Figure 3.8. Firstly, the ZIF-8 membrane was loaded into self-made stainless steel module housing sealed with a silicon o-ring to prevent the leakage of gas. At the side of stainless steel module housing temperature probe, pressure gauge and safety valve were also installed. The stainless steel module housing was placed on hotplate stirrer for heating up. The feed pressure was adjusted accordingly with the total pressure difference ranging from 500 kPa to 800 kPa. The permeate side was maintained at atmospheric pressure. The feed temperature was also varied at 3 different values 25°C, 35°C and 45°C. The synthesis gas used in this study were contained 60 vol.% CO_2 and 40 vol.% CH_4. After attaining steady state condition, the permeate side was connected with bubble flow meter for measuring the gas flow rate. The collected gas was analyzed by a gas detector (Geotech Biogas 5000, U.K.). The permeation results for each membrane were collected from 3 distinct samples of that membrane by the same procedures, and the average errors were reported. The permeabilities of mixed gas tests were directly calculated from the gas flux data measured by gas bubble meter using the Eq. (3.1) as follow;

$$P_i = \frac{Q \times l}{A \times (P_{fi} - P_{pi})} \tag{3.1}$$

Where, Pi is permeability coefficient (cm^3 (STP) $\cdot cm \cdot cm^{-2} \cdot s^{-1} \cdot cmHg^{-1}$) of the component i, Qi is the volumetric permeation rate of component i ($cm^3\ s^{-1}$), l is the thickness of selective layer (cm), A is the effective membrane area (cm^2) for gas permeation, and pfi and ppi are partial pressures of component i at feed and permeate side (cmHg), respectively (Jomekian *et al*., 2016).

The separation factors $\alpha_{CO2/CH4}$ was defined as the gas permeability ratio of more permeable gas (P_{CO2}) to the less permeable gas (P_{CH4}) as shown in Eq. (3.2);

$$\propto_{CO_2/CH_4} = \frac{P_{CO_2}}{P_{CH_4}} \tag{3.2}$$

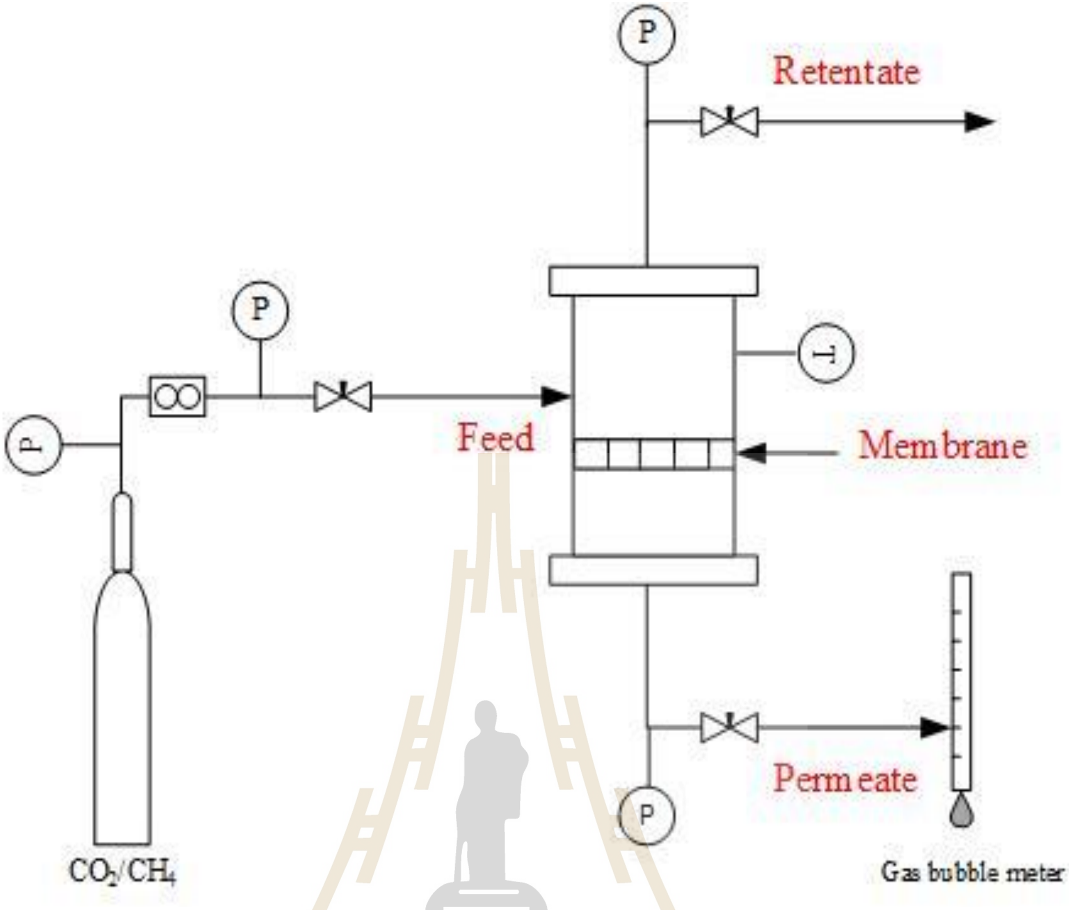

Figure 3.7 The flow diagram of gas permeation testing.

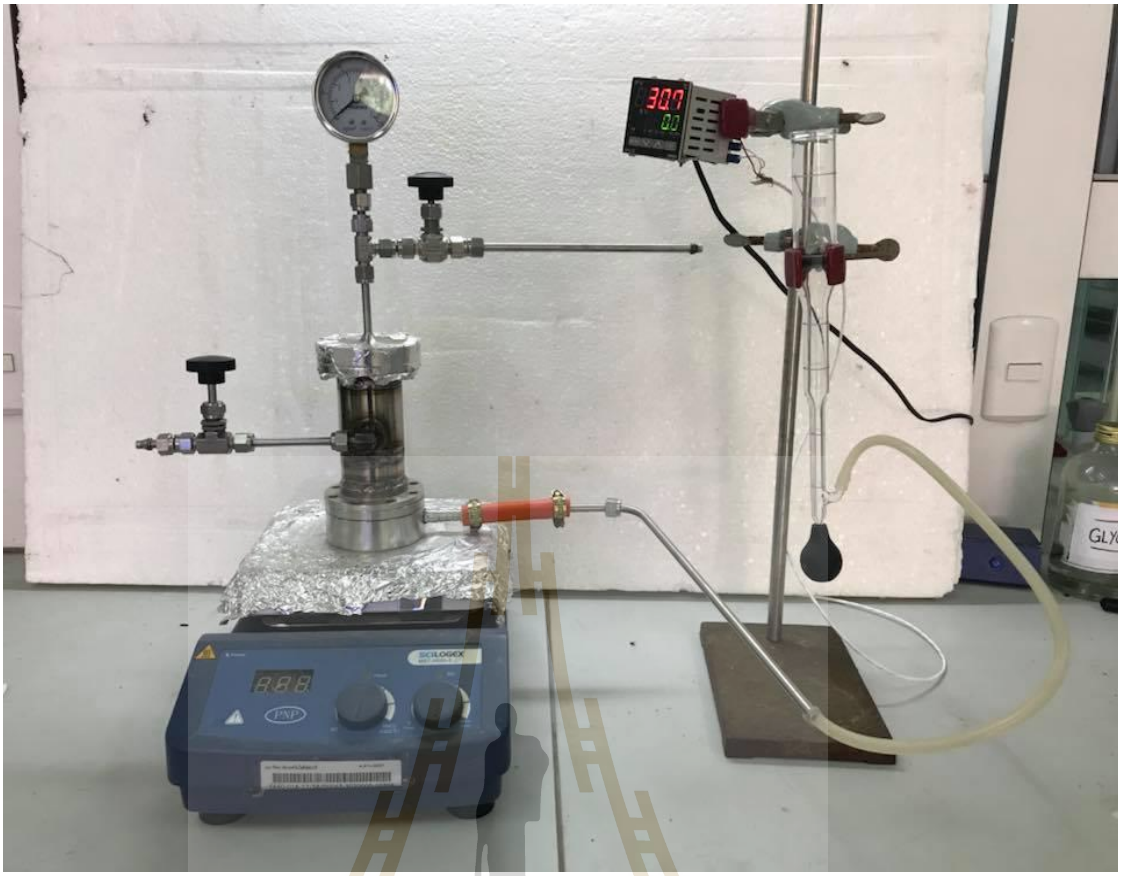

Figure 3.8 Experimental setup for membrane synthesis and permeation testing.

3.4 Analytical methods

3.4.1 Scanning electron microscopy (SEM)

The ZIF-8 membrane surface and fractured cross-section were analyzed by SEM (JEOL JSM-6010LV, Japan). The synthesized membrane samples were broken into a small piece and then coated with gold as a conductive material using coating machine (JEOL Neo coater MP-19010 NCTR, Japan) (Figure 3.9). The morphology including arrangement of crystal as well as the thickness of coated layer were observed on the top view and the cross-sectional view of the membrane, respectively.

Figure 3.9 Gold coating machine (Neo coater MP-19010 NCTR, JEOL, Japan).

3.4.2 X-ray diffraction (XRD)

The characterization of ZIF-8 seeds power and ZIF-8 membrane synthesized as well as the non-synthesized support were carried out by a D2 phaser X-ray diffractometer (XRD) from Bruker AXS GmbH, Germany (Figure 3.10) with CuKα diffraction (λ=1.5406°A) operating at 30 kV and 10 mA with a graphite monochromator in the diffracted beam path. The ZIF-8 particles were slightly pressed into sample holder with 25.4 mm diameter and 3 mm thickness in a powder sample holder. The ZIF-8 membranes were attached on the surface of a sample holder. The data were collected in the range of 5-60° 2θ by the step time and step size were selected 0.025 s^{-1} and 0.02°, respectively.

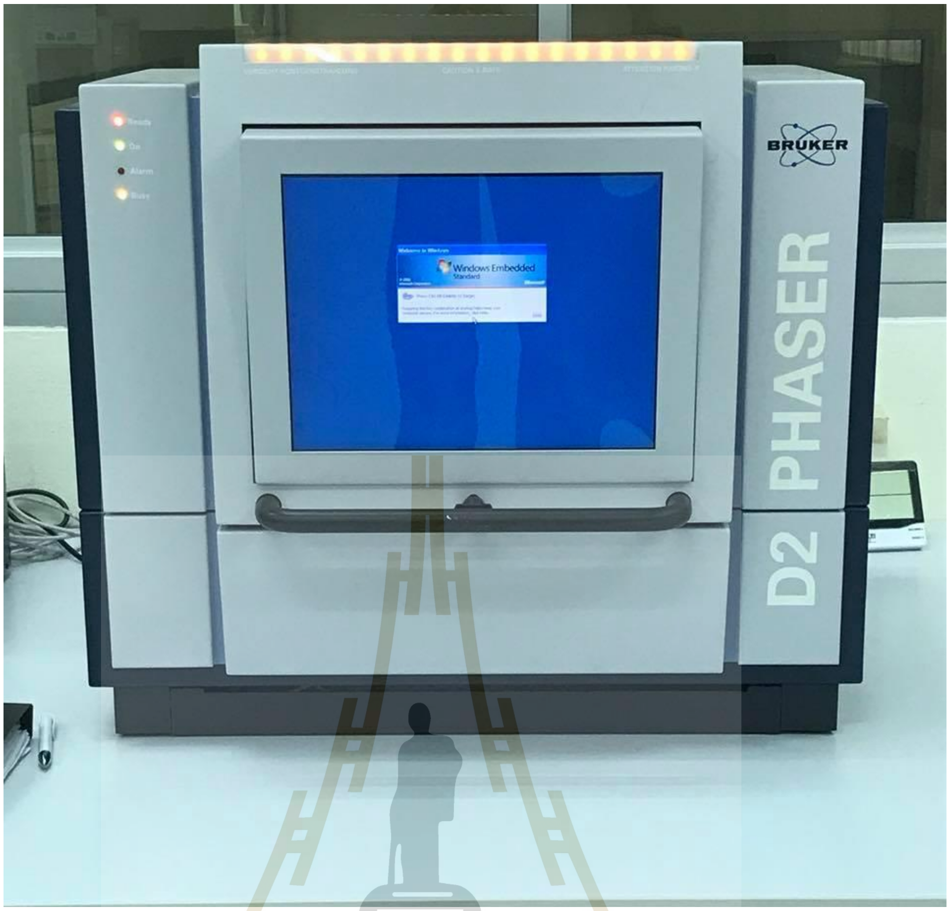

Figure 3.10 X-ray diffractometer (XRD) (D2 phaser, Bruker AXS GmbH, Germany).

3.4.3 Nitrogen adsorption

The ZIF-8 particles were characterized for the structural porous properties by nitrogen adsorption at 77 K using an automated adsorption apparatus (Bel Japan Inc, Belsorp mini-II). In this experiment, 200 mg of sample was used; the system was degassed at 423 K under vacuum for 24 hours under nitrogen flow and then the adsorption isotherm for nitrogen at 77 K was measured. The BET surface area (S_{BET}) and the total pore volume were calculated from the nitrogen adsorption isotherms. Pore size distribution of carbon was also determined by the application of the density functional theory (DFT) to the isotherm data.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 ZIF-8 particles preparation

The ZIF-8 particles were successfully synthesized on four samples via control MeIM and Zinc nitrate hexahydrate ratios. The aim of ZIF-8 particles analysis was to determine the appropriate hydrothermal condition as well as the chemicals formulation to obtain the pure ZIF-8 particle (Figure 4.1). The ZIF-8 particles powder was synthesized in different ratio of MeIM and Zinc nitrate hexahydrate. The morphology of ZIF-8 particles from varies ratio of MeIM and Zinc nitrate hexahydrate were illustrated in Figure 4.2 A, B, C and D. The results from SEM showed that all ratios of MeIM and Zinc nitrate hexahydrate were completely crystallinity. However, the size particles of each ratio were different. Moreover, the ZIF-8 particles crystallinity was further confirmed by XRD (Figure 4.3A, B, C and D). The XRD results exhibited peaks at $2\theta =$ 7.30°, 10.35°, 12.70°, 14.80°, 16.40° and 18.00° which confirms the typical ZIF-8 sodalite structure (Bux *et al.*, 2009). The observed well-defined sharp peaks revealed the high crystallinity of the ZIF-8 particles. The calculated BET surface areas of ZIF-8 particles ratios 12:1, 9:1, 6:1 and 3:1 were approximately 1,882, 1,752, 1,548 and 1,449 m^2/g, respectively (Table 4.1), which are comparable to the referenced values reported for ZIF-8 such as 1,630 m^2/g (Liu *et al.*, 2012), 1,781 m^2/g (He *et al.*, 2012), and 1,947 m^2/g (Park *et al.* 2006)). This result suggested that high to low surface area was obtained on ratios 12:1, 9:1, 6:1 and 3:1. The calculated pore size distributions of the four particles ratios were different, as shown in Table 4.1. The highest N_2 adsorption and, BET surface area were obtained at ratio 12:1 of MeIM and Zinc nitrate hexahydrate. Chi *et al.*, (2015) reported the small particles of ZIF-8, the higher CO_2 removal rate of the membrane. In this study, ZIF-8 particles from different ratios were not only intrinsically difference in pore structures but also difference in size. The MeIM and Zinc nitrate hexahydrate ratio 12:1 was chosen as the best ZIF-8 particle to synthesis membrane selective layer due to its smallest crystal size and largest BET surface area.

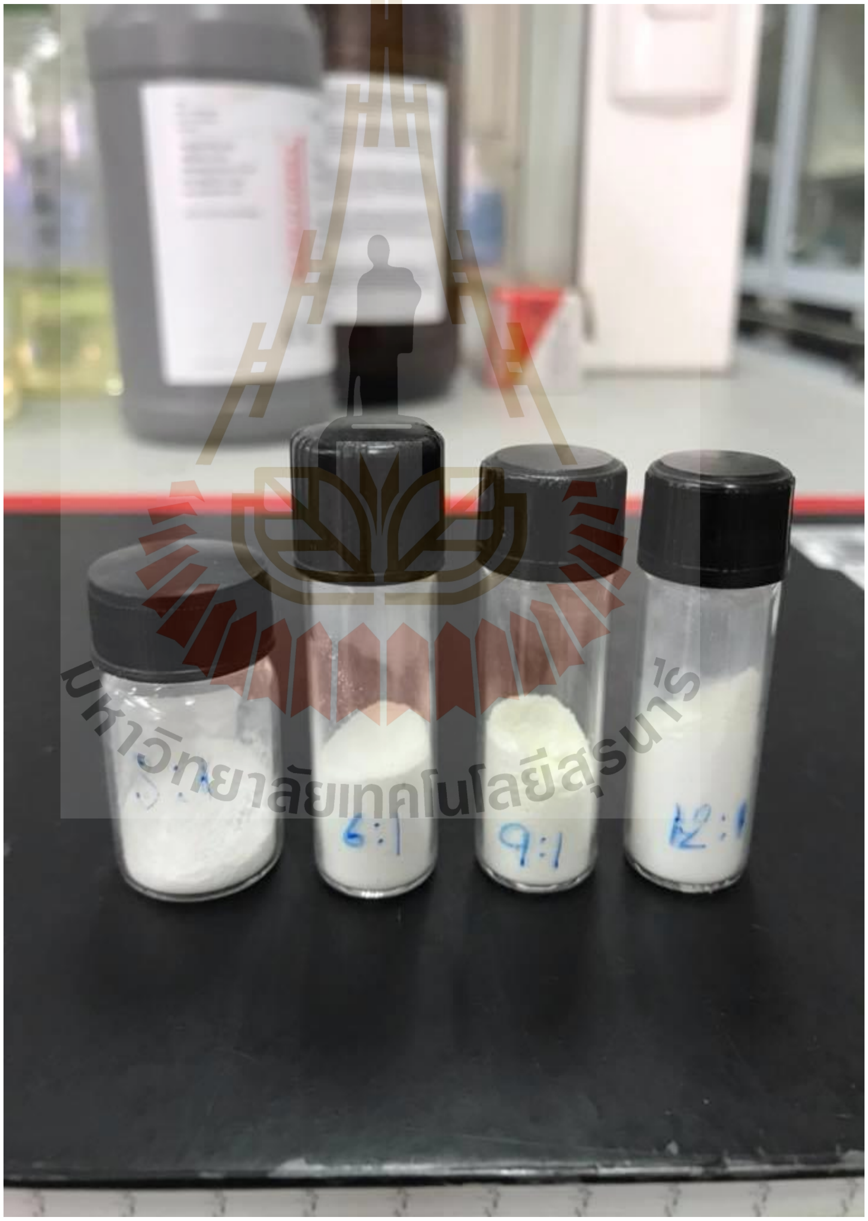

Figure 4.1 The synthesized ZIF-8 particles on various ratios (12:1, 9:1, 6:1 and 3:1).

Table 4.1 The mean crystal size and BET surface area of synthesized ZIF-8 particles a different temperatures.

Ratios of MeIM: Zinc nitrate hexahydrate	12:1	9:1	6:1	3:1
Mean crystal size (nm)	150	250	300	350
Total pore volume (cm^3/g)	1.352	1.344	1.117	1.182
Mean pore diameter (nm)	3.298	3.314	3.329	3.316
BET surface area (m^2/g)	1,882	1,752	1,548	1,449

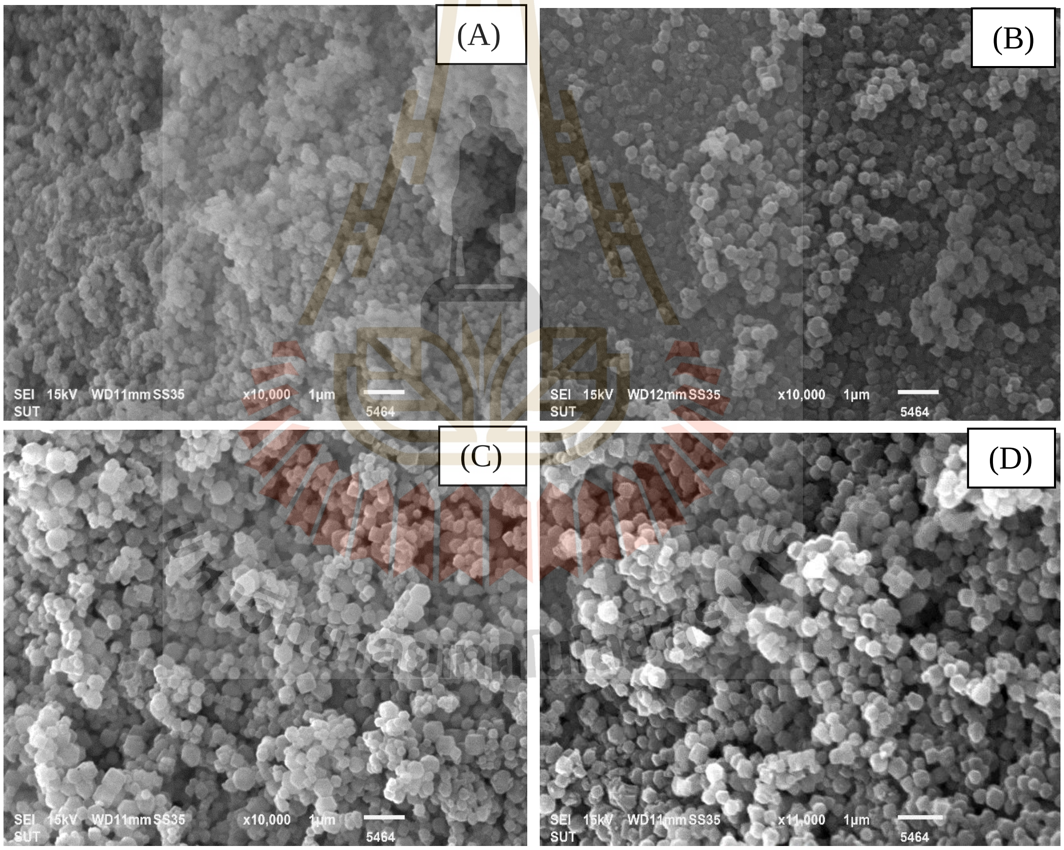

Figure 4.2 SEM images of the ZIF-8 particles of the ZIF-8 particles using various different ratios of MeIM: Zinc nitrate hexahydrate: 12:1 (A), 9:1(B), 6:1(C) and 3:1(D).

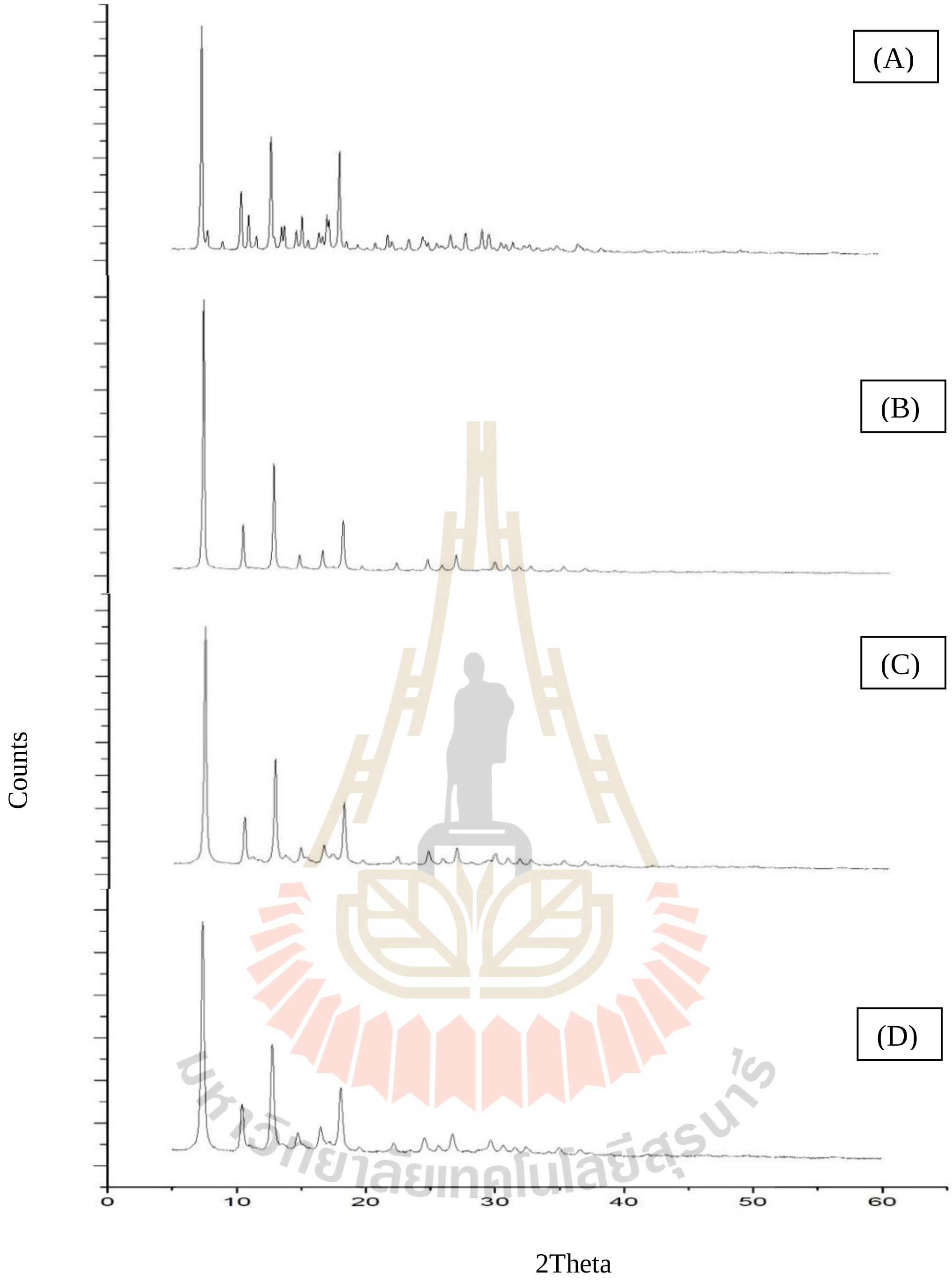

Figure 4.3 XRD chromatograms of the ZIF-8 particles using various ratios different of MeIM/ Zinc nitrate hexahydrate: 12:1 (A), 9:1(B), 6:1(C) and 3:1(D).

4.2 Porous α-alumina support structural characterization

In this study, the α-alumina supports after preparing, the morphology and crystallinity were characterization by using SEM and XRD, respectively. The α-alumina support were typically used in the past for the synthesis of ZIF membranes. The α-alumina supports exhibit excellent mechanical and thermal stability, which permit their use in processes that were carried out at high temperatures. The α-alumina supports in gas separation was also according to several authors (Hara *et al.*, 2014, Xu *et al.*, 2011 and Tao *et al.*, 2013). Figure 4.5 A, B and C illustrated the surface and cross-section of the support from pure kaolin. The present of porous α- alumina supports are high porosity on the surface when investigated with SEM. The average pore size of the α-alumina support was approximately 1-2 μm. The crystallinity of the support was observed using XRD (Figure 4.4).

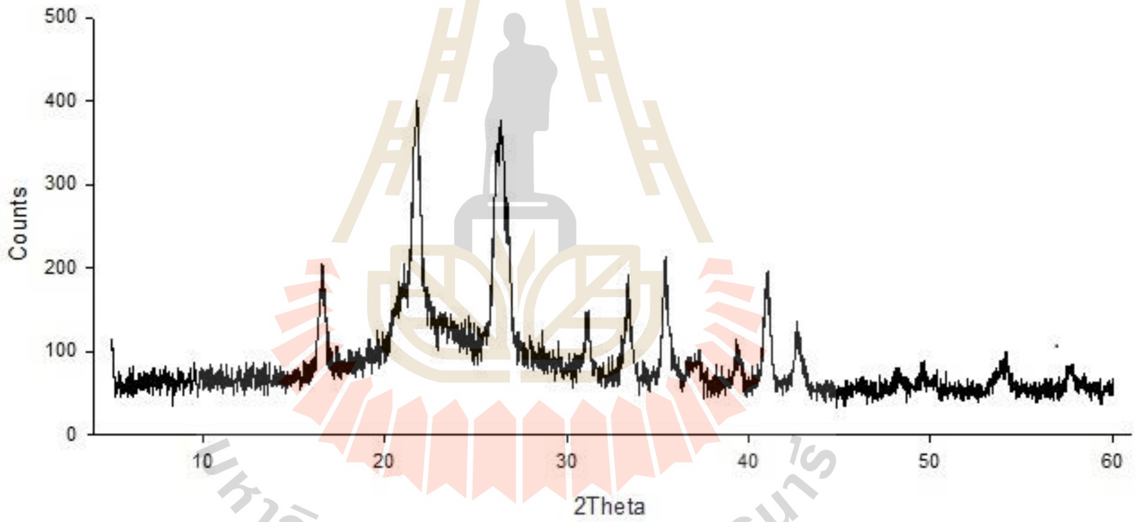

Figure 4.4 XRD chromatogram of the α-alumina support.

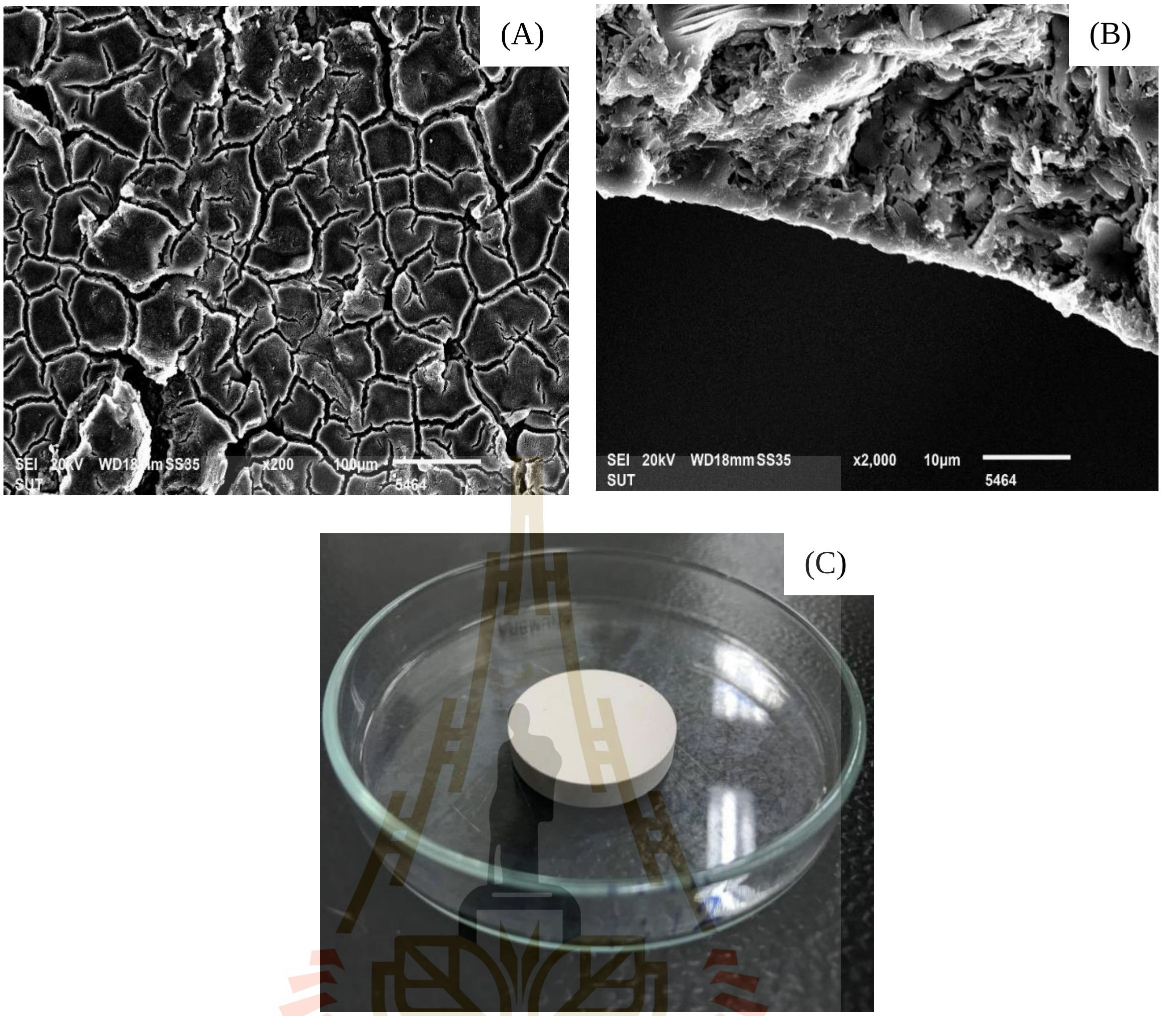

Figure 4.5 SEM images surface (A) and cross-section (B) of the α-alumina support (C).

4.3 The effect of seeding methods on ZIF-8 membrane properties

The ZIF-8 was successfully crystallized on the surface of the α-alumina support. Moreover, the seeding method was affected to the membranes separation process including total flux and selectivity. The different methods including, seeding, secondary seed growth and suction were carried out in this study (Figure 4.6). The seed method is *in situ* growth, comprises the growth of a ZIF-8 on α-alumina support whilst does not contain any crystals attached (seeded) to its surface. This technique is accomplished by immersing the support in a precursor solution. After a sufficient amount of time is given at an elevated temperature, nucleation begins to proceed where the ZIF starts to grow on the support, and the membrane is eventually formed. In this type of synthesis, nucleation, growth, and intergrowth of the crystals are not decoupled, occurring instead during the same step for an extended period of time. The secondary seed growth and suction seed method were a deposition of ZIF-8 crystals on surface of support before the hydrothermal synthesis, caused of the formation of regularly arrangement of the ZIF-8 crystal. In other words, the applying of secondary growth (secondary seed growth and suction seed) on the α-alumina support surface provided a better control of the membrane formation process by dip coating, reactive seeding, and microwave-induced thermal deposition (MITD) (Li *et al.*, 2010 and Shah *et al.*, 2012). The seeding, secondary seed growth and suction seed methods were successfully seeded on the surface of the α-alumina support (Figure 4.6). The ZIF-8 seed layer on support was observed using XRD chromatograms (Figure 4.7). The result from XRD presented that both peaks of ZIF-8 and α-alumina support was achieved. The SEM images surface of the synthesized membranes seeding, secondary seed growth and suction seed methods were illustrated in Figure 4.8. On the secondary seed growth and suction seed method, ZIF-8 was the completely crystallized on α-alumina support. However, the ZIF-8 layers on seeding method was found some defect, during when observing by SEM. The thickness of secondary seed growth, suction seed and seeding membranes were 5, 4.5 and 2 μm, respectively were shown in Figure 4.9. Higher total flux of membrane preparation process was achieved at thinner support layer, vice versa. From the results, the thickness of the ZIF-8 selective layer around 2-5 μm was also agreeable to studies of Hara *et al.*, (2014), Li *et al.*, (2013), Dong *et al.*, (2012) and Pan *et al.*, (2011).

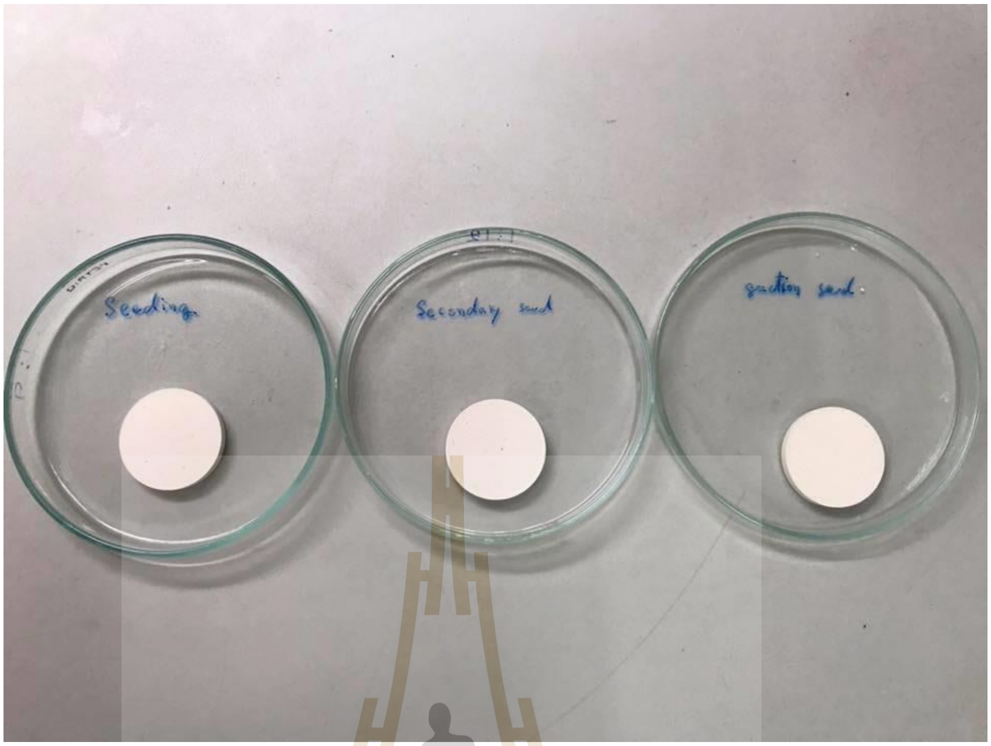

Figure 4.6 The ZIF-8 membrane synthesizes on seeding, secondary seed growth and suction method.

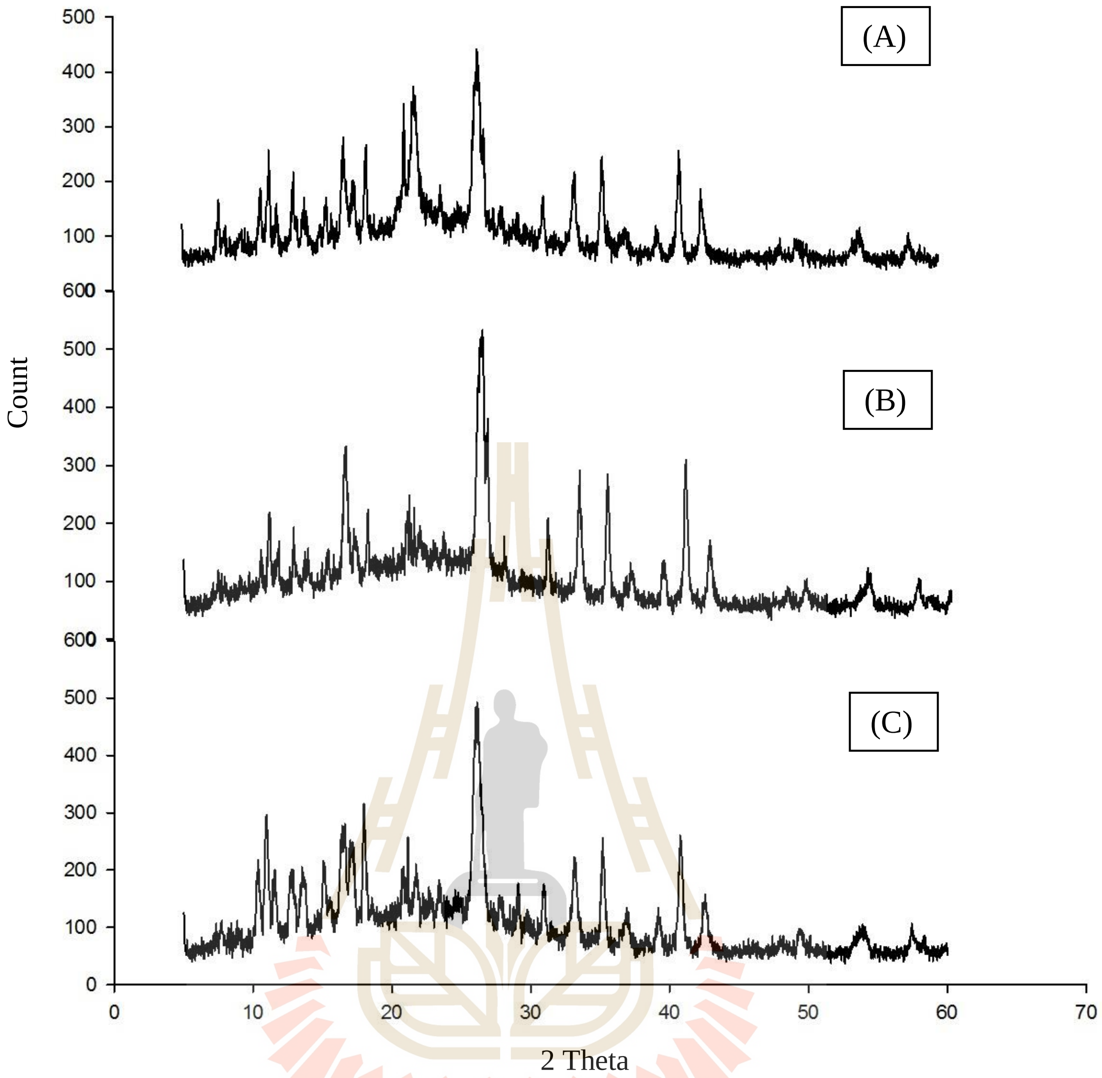

Figure 4.7 XRD chromatograms of ZIF-8 membranes on seeding (A), secondary seed growth (B) and suction seed methods (C).

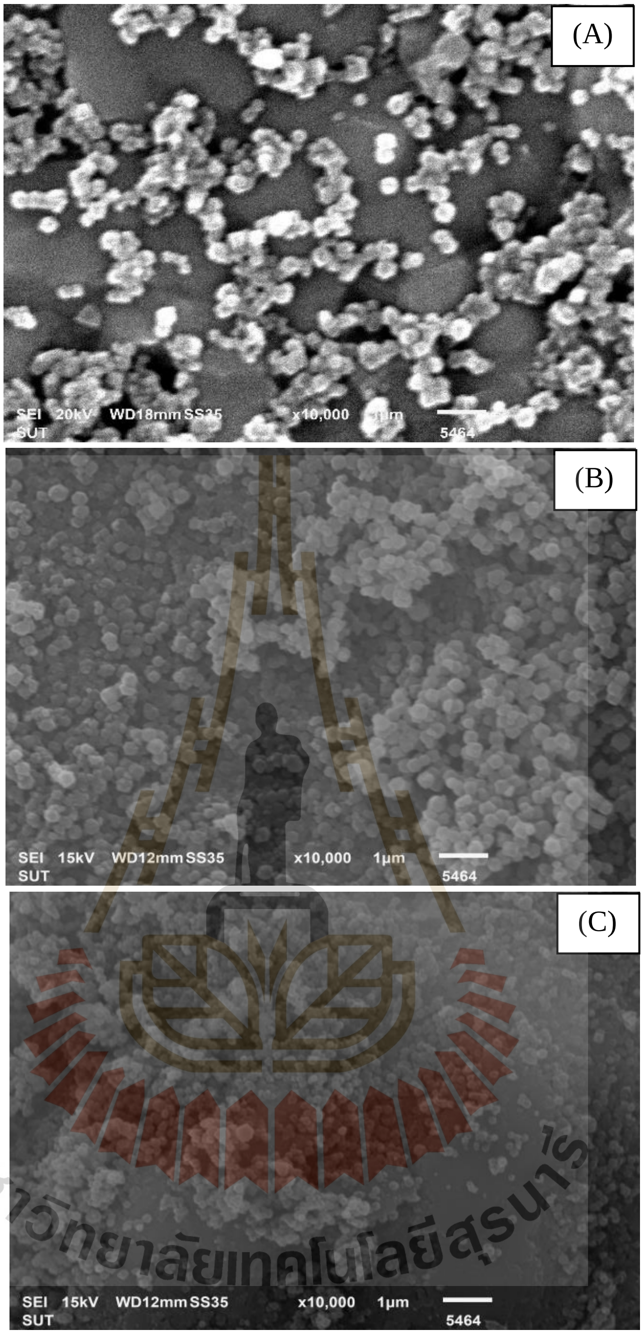

Figure 4.8 SEM images surface of ZIF-8 membranes synthesized on seeding (A), secondary seed growth (B) and suction seed (C) methods.

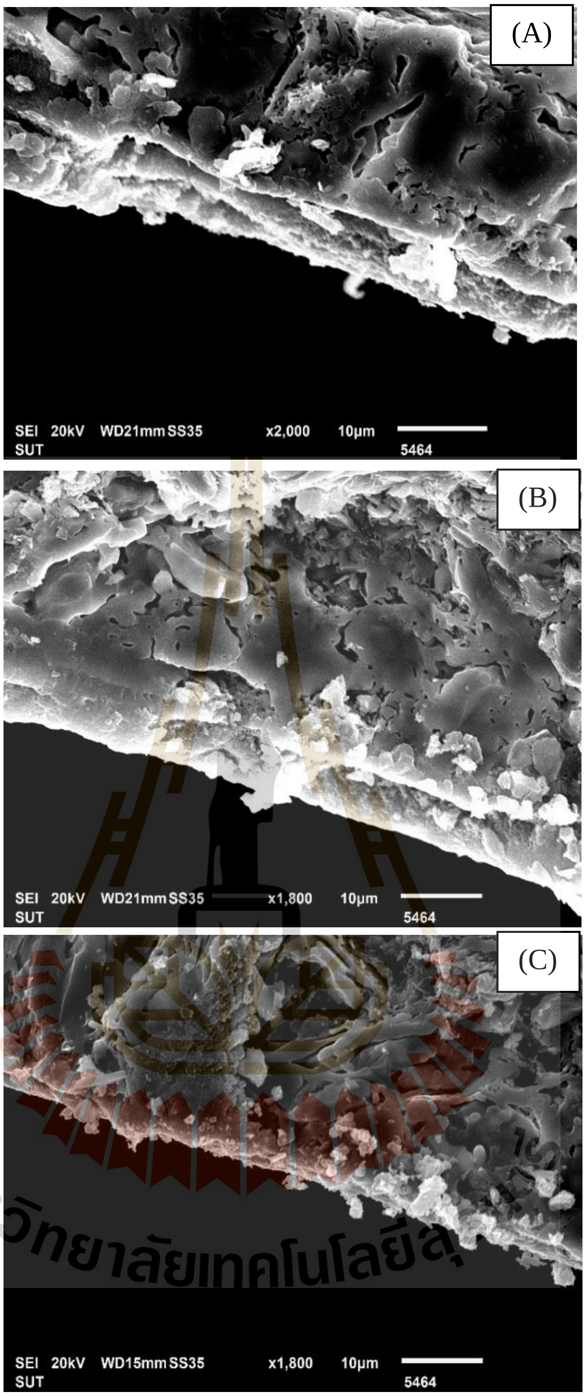

Figure 4.9 SEM images cross section of ZIF-8 membranes synthesized on seeding methods (A), suction seed (B) and secondary seed growth (C).

4.4 Gas separation property of ZIF-8 membranes

In this study, the ZIF-8 membranes using various seeding methods were tested under different conditions including feed pressures (500-800 kPa) and operating temperature (25°C, 35°C and 45°C). Firstly, the results of total flux gases at different feed pressure analyzed under temperature of 25°C, 35°C and 45°C were shown on Figure 4.10 (A), (B) and (C), respectively. The increasing of pressure was resulted in increasing of total flux of ZIF-8 membranes. The maximum total flux was achieved at high feed pressure using seeding method followed by secondary seed and suction seed methods. It can be seen from Figure 4.10 the results fluxes of gases were increase with the increasing pressure differences. Moreover, Figure. 4.11 shows the effect of pressures on CO_2 permeation over ZIF-8 membrane using various synthesized methods at different temperature of 25°C, 35°C and 45°C, respectively. Pressure was effected to the gas permeation of membrane process. Gas permeation was decreased with increasing of feed pressure at all different operating temperatures (Figure 4.11). Higher CO_2 permeation was obtained at low temperature. At 25°C, the maximum CO_2 permeate was $6.98\times10^{-6}\cdot cm^3$ (STP)$\cdot cm\cdot cm^{-2}\cdot s^{-1}\cdot cmHg^{-1}$ using secondary seed growth method, followed by $6.59\times10^{-6}\cdot cm^3$ (STP)$\cdot cm\cdot cm^{-2}\cdot s^{-1}\cdot cmHg^{-1}$ and $6.39\times10^{-6}\cdot cm^3$ (STP)$\cdot cm\cdot cm^{-2}\cdot s^{-1}\cdot cmHg^{-1}$, respectively. As reported by Bux *et al.*, 2010, CO_2 gas permeation on ZIF-8 membrane is adsorption controlled rather than diffusion controlled. Therefore, when the temperature increased, reduction of CO_2 coverage on the surface of ZIF-8 membrane is more prominent than the increase in gas diffusivity across the membrane. In the other hand, on CH_4 permeation over ZIF-8 membrane were shown the opposite result with CO_2 permeation (Figure 4.12). The CH_4 permeation result on all synthesized methods were shown slightly increasing trend when the temperature increases from 25°C, 35°C and 45°C, respectively.

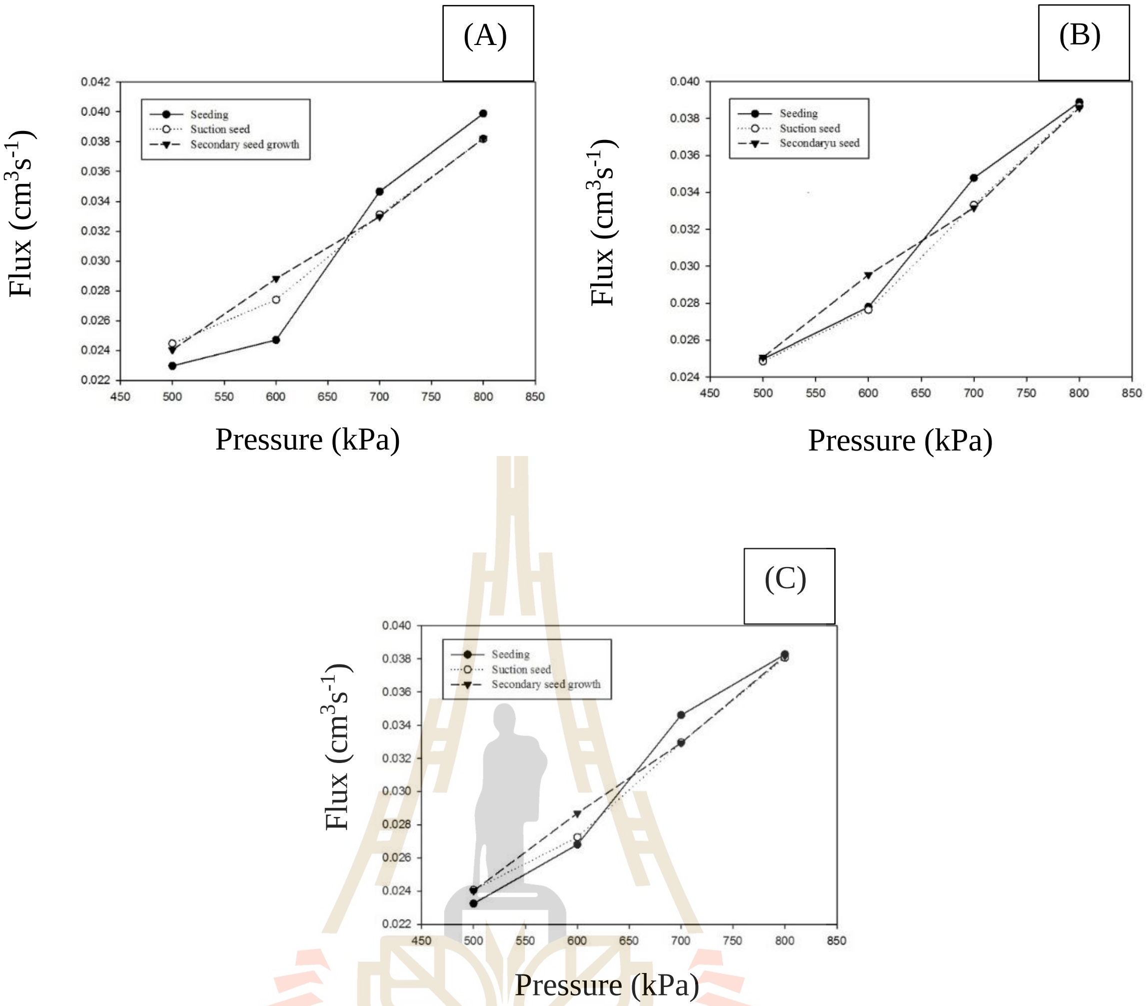

Figure 4.10 Fluxes of CO_2 and CH_4 at different partial pressure differences under operation temperature of (A) 25°C, (B) 35°C and (C) 45°C.

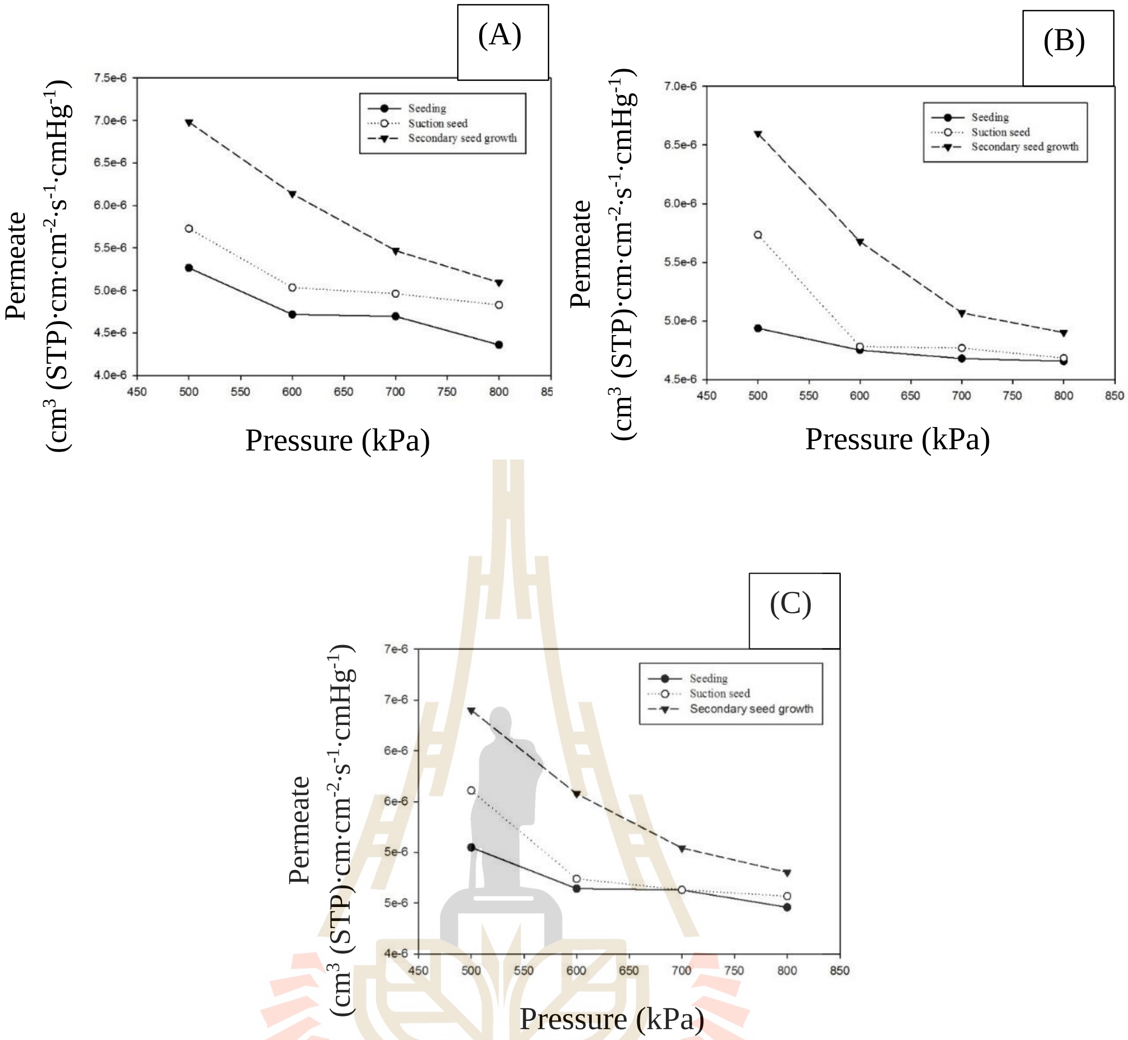

Figure 4.11 The CO_2 permeate effect of various synthesized ZIF-8 membranes at differences operating temperature (25°C (A), 35°C (B) and 45°C (C)) and feed pressure on mixed gas of CO_2/CH_4.

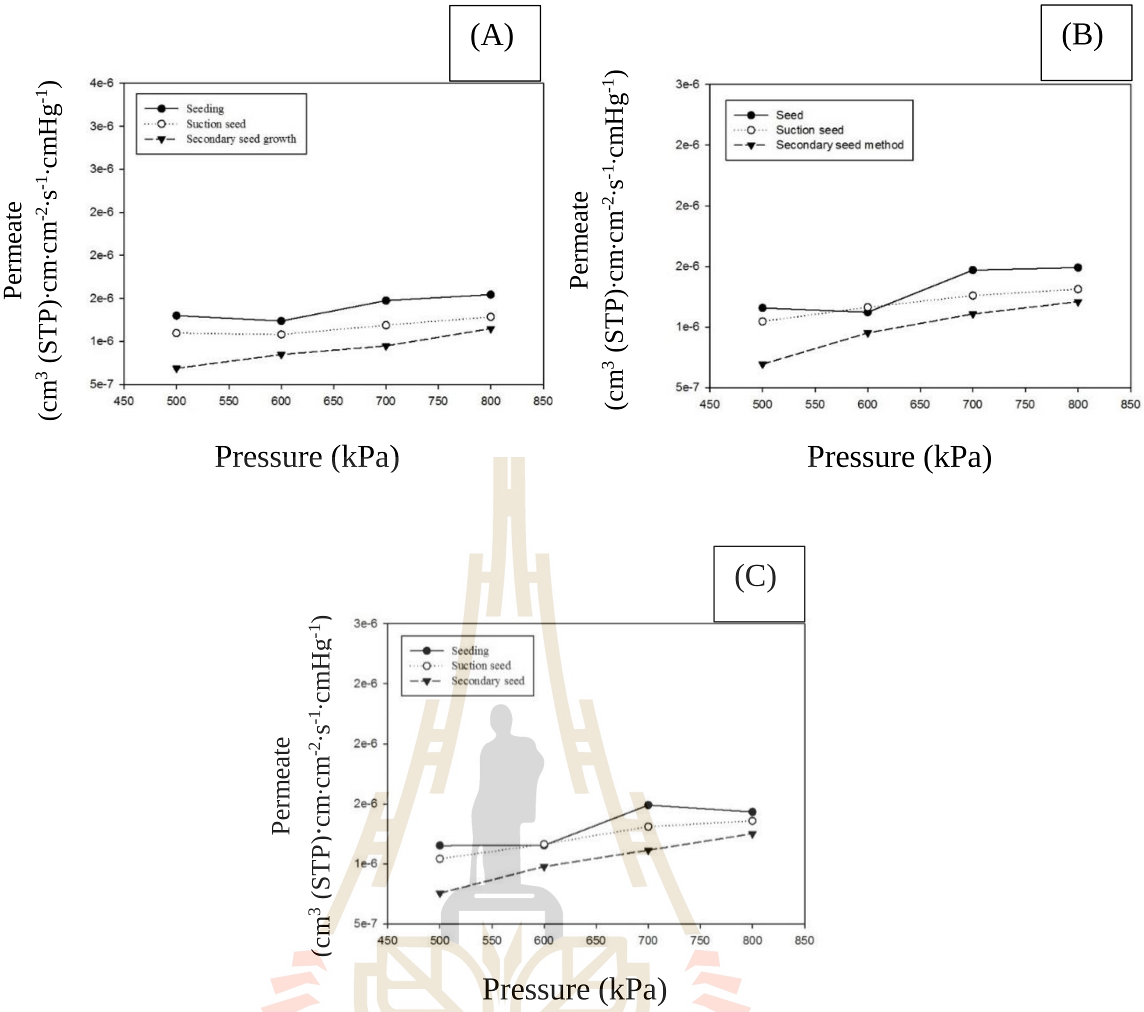

Figure 4.12 The CH_4 permeate effect of various synthesized ZIF-8 membranes at differences operating temperature (25°C (A), 35°C (B) and 45°C (C)) and feed pressure on mixed gas of CO_2/CH_4.

The effect of various seeding techniques on the separation performance including gas permeation and selectivity were shown in Table 4.2, 4.3 and 4.4. From results the highest CO_2 permeation and separation factor were obtained on lowest feed pressure (500 kPa) and lowest operating temperature (25°C). On the other hand, the lowest CO_2 permeation and separation factor were found on higher feed pressure (800 kPa) and higher operating temperature (45°C). The best CO_2 permeation and separation factor were presented on secondary seed method, suction seed method and seeding method, respectively. Figure. 4.14 shown the separation factor results of various synthesized ZIF-8 membranes on CO_2/CH_4 gas separation at different operate temperatures (25°C, 35°C and 45°C). Separation factor was decreased when the pressure was increased from 500 kPa to 800 kPa for both three methods. It was found that the decreasing trend of selectivity is similar to the CO_2 gas permeation as shown on Figure. 4.12. This is mainly due to higher temperature to increasing the diffusivity of CO_2 across the membrane and at the same time decreased its adsorbed coverage gradient (Li *et al.*, 2005). Overall, CO_2 permeance was decreased with the increasing in temperature, which attributed to the domination of adsorption compared to diffusion across the ZIF-8 membrane. The better membranes permeation was achieved $6.98\times10^{-6}\cdot cm^3$ (STP) $cm\cdot cm^{-2}\cdot s^{-1}\cdot cmHg^{-1}$. The optimal operation control was chosen at 500 kPa 25°C.

The selectivity of gas mixture in this study was achieved at 10.14±0.44 (CO_2/CH_4) using secondary seed growth method at synthesized times 6 hours, whilst using the same method at different temperature (130°C), the selectivity of Jame *et al.*, (2016) was reported 3.7 (CO_2/CH_4), lower than this study. Beside, several researcher studied about the modify type of the support such as Xie *et al.*, (2012), Huang *et al.*, (2014) and Zhang *et al.*, (2013). However, the results on selectivity were not comparable to this work (7.2, 7.3 and 4.7, respectively).

In this study, there were several methodologies of ZIF-8 membrane cloud be used to synthesis membrane such as *in situ* growth, secondary growth and innovative techniques were discussed. The synthesis methods and conditions, type of supports, and gas separation performance of the synthesized ZIF membranes were summarized in Tables 4.5. *In situ* growth is not containing any seeded on support surface. This method is completed by immersing the support in a seeded solution. After a sufficient amount of time was given at an elevated temperature, nucleation begins to proceed where the ZIF starts to grow on the support, and the membrane was formed. In this type of synthesis, nucleation, growth, and intergrowth of the crystals were not decoupled, occurring instead during the same step for an extended period of time. *In situ* growth could be conducted using both unmodified and modified supports (Manuel *et al.*, 2010). *In situ* growths were used for the growth of a ZIF membrane on a porous support (Venna *et al.*, 2016, Lai *et al.*, 2016, Xie *et al.*, 2012 and Huang *et al.*, 2014). Moreover secondary growth is related to the synthesis of ZIF membranes on supports that contain be attached by means of physical or chemical attached seeding crystals. Unlike *in situ* synthesis, crystal nucleation, growth, and intergrowth do not occur simultaneously in secondary growth synthesis. Moreover, the layer growth is independent of the substrate. Depending on the manner in which the crystals are seeded on the supports, this type of synthesis can be classified as secondary growth on supports with chemically attached seeds. ZIF membranes have been synthesized using secondary growth with prior seeding, which is accomplished via rubbing, dip coating, slip coating, electro-spinning, and microwave radiation (Ge *et al.*, 2012 and Melga *et al.*, 2015).

Table 4.2 Permeate and separation factors of CO_2/CH_4 mixtures (60:40 vol.%) on various ZIF- 8 membranes synthesized at difference feed pressure 25°C.

Synthesis methods	**Feed pressures (kPa)**	**Permeate ($\times10^{-6}\cdot cm^3$ (STP) $cm\cdot cm^{-2}\cdot s^{-1}\cdot cmHg^{-1}$)**		**Separation factor**
		CO_2	**CH_4**	
Seeding	500	3.88	0.826	4.7±0.055
	600	3.61	0.866	4.1±0.145
	700	3.58	0.965	3.7±0.048
	800	3.36	0.995	3.3±0.097
Suction seed	500	5.73	1.1	5.2±0.076
	600	5.03	1.08	4.6±0.068
	700	4.96	1.19	4.1±0.320
	800	4.83	1.29	3.7±0.092
Secondary seed growth	500	6.98	0.689	10.1±0.441
	600	6.14	0.849	7.2±0.336
	700	5.47	0.949	5.7±0.241
	800	5.09	1.150	4.4±0.159

Table 4.3 Permeate and separation factors of CO_2/CH_4 mixtures (60:40 vol.%) on various ZIF- 8 membranes synthesized at difference feed pressure 35°C.

Synthesis methods	**Feed pressures (kPa)**	**Permeate ($\times 10^{-6} \cdot cm^3$ (STP) $\cdot cm \cdot cm^{-2} \cdot s^{-1} \cdot cmHg^{-1}$)**		**Separation factor**
		CO_2	**CH_4**	
Seeding	500	3.57	0.83	4.2±0.037
	600	3.61	0.85	4.2±0.127
	700	3.55	0.96	3.6±0.100
	800	3.33	1.01	3.2±0.048
Suction seed	500	5.73	1.05	5.4±0.235
	600	4.78	1.16	4.1±0.016
	700	4.77	1.26	3.7±0.033
	800	4.68	1.31	3.5±0.086
Secondary seed growth	500	6.60	0.69	9.5±0.583
	600	5.68	0.95	5.9±0.453
	700	5.07	1.11	4.5±0.306
	800	4.90	1.21	4.0±0.119

Table 4.4 Permeate and separation factors of CO_2/CH_4 mixtures (60:40 vol.%) on various ZIF- 8 membranes synthesized at difference feed pressure 45°C.

Synthesis methods	**Feed pressures (kPa)**	**Permeate ($\times 10^{-6} \cdot cm^3$ (STP) $\cdot cm \cdot cm^{-2} \cdot s^{-1} \cdot cmHg^{-1}$)**		**Separation factor**
		CO_2	**CH_4**	
Seeding	500	3.67	0.83	4.3±0.106
	600	3.54	0.88	4.0±0.106
	700	3.53	0.99	3.5±0.106
	800	3.29	1.06	3.1±0.106
Suction seed	500	5.61	1.04	5.3±0.318
	600	4.74	1.16	4.0±0.008
	700	4.63	1.31	3.5±0.009
	800	4.57	1.36	3.3±0.119
Secondary seed growth	500	6.4	7.57	8.5±1.410
	600	5.58	9.78	5.7±0.631
	700	5.04	1.11	4.5±0.317
	800	4.8	1.25	3.8±0.100

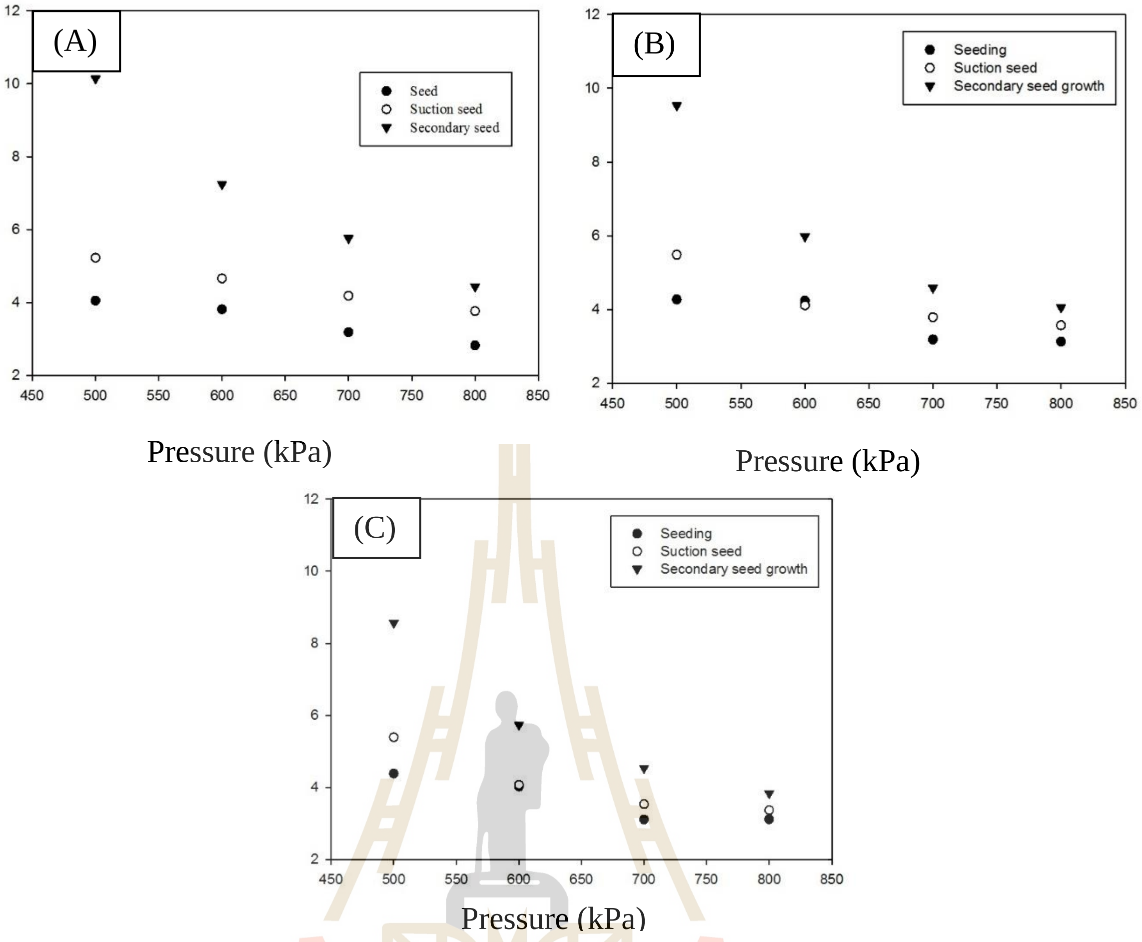

Figure 4.13 The separation factor effect of various synthesized ZIF-8 membranes at differences operating temperature (25°C (A), 35°C (B) and 45°C (C)) and feed pressure on mixed gas of CO_2/CH_4.

Table 4.5 The comparisons selectivity of gases mixtures on different synthesis method and type of supports.

Membrane	Type of support	Synthesis method	Selectivity	Ref.
ZIF-8	α-alumina tubes	In situ solvent thermal at 25-200 ºC for 5 h.	7.1 (H_2/CO_2)	Venna *et al.*, 2016
ZIF-8	α-alumina disks	In situ solvent thermal at 140ºC for 5 h	5.07 (CO_2/CH_4)	Lai *et al.*, 2016
ZIF-8	α-alumina disks	Secondary seeded growth at 130 °C for 6.5 h.	3.7 (CO_2/CH_4)	James *et al.*, 2016
ZIF-8	α-alumina disks	Secondary seed growth at 70 °C for 6 h.	10.1 ± 0.4 (CO_2/CH_4)	This study
ZIF-8	α-alumina tubes	Rubbing seeding followed by hydrothermal growth at 150 ºC for 5 h	4-7 (CO_2/CH_4)	Yao *et al.*, 2013
ZIF-22	APTES-modified TiO_2 disks	In situ solvent thermal conditions at 150 ºC for 72 h	7.2 (H_2/CO_2)	Xie *et al.*, 2012
ZIF-90	APTES-modified α-alumina disks	In situ solvent thermal conditions at 100 ºC for 18 h	7.3 (H_2/CO_2)	Huang *et al.*, 2014
ZIF-7	α-alumina disks	Dip-coating seeding followed by microwave-assisted solvent thermal growth at 100 ºC for 3 h	6.48 (H_2/CO_2)	Li *et al.*, 2010
ZIF-69	α-alumina disks	Dip-coating seeding followed by solvent thermal growth at 100 ºC for 72 h	2.7 (CO_2/CH_4)	Li *et al.*, 2010
ZIF-7	α-alumina disks	Dip-coating seeding with PEI followed by microwave-assisted secondary growth at 100 ºC for 2 h	6 (H_2/CO_2)	Pan *et al.*, 2012
ZIF-90	APTES-modified α - alumina disks	APTES functionalization by refluxing methanol and APTES solution at 110 ºC for 0.5 h	4.7 CO_2/CH_4	Zhang *et al.*, 2013

CHAPTER V

CONCLUSION

In this study, ZIF-8 particles have been synthesized using different ratios of MeIM and Zinc nitrate hexahydrate (12:1, 9:1, 6:1 and 3:1). The SEM and XRD results showed the complete of crystallinity for all ratios. The largest surface area of ZIF-8 particles was 1,882 m^2/g at ratio 12:1 while at ratio 3:1, surface area was obtained of 1,449 m^2/g when observed with N_2 absorption and BET surface area due to its particles size, the ZIF-8 particles synthesized from ratios MeIM: Zinc nitrate hexahydrate 12:1 was chosen as the optimal ratio to produce selective layer on ZIF-8 membranes. Moreover, the ZIF-8 membrane has been synthesized via several methods including seeding, secondary seed growth and suction seed methods. Various methods were seeded ZIF-8 on the surface of a porous α-alumina supports as a selective layer. The significant of secondary seed and suction seed methods, including a polishing and a second times synthesis were used to avoid holes or defects in the ZIF-8 membranes and improve the quality of ZIF-8 membranes for CO_2/CH_4 separation. The CO_2/CH_4 separation behaviors of the ZIF-8 membrane were studied at different operating conditions, including operating temperature ranged 25°C, 35°C and 45°C and total feed pressure difference ranged from 500 kPa to 800 kPa. At different feed pressure and operating temperature, the total flux and separation factor were changed under various seeding methods. The ZIF-8 membranes using secondary seed growth was performed as a comparable CO_2/CH_4 separation, the results exhibiting the highest CO_2/CH_4 separation factor of 10.1 and CO_2 permeate

6.98×10^{-6} $\mathrm{cm^3}$ (STP) $\cdot\mathrm{cm}\cdot\mathrm{cm^{-2}}\cdot\mathrm{s^{-1}}\cdot\mathrm{cmHg^{-1}}$ for a gas mixture of CO_2/CH_4 at pressure of 500 kPa and temperature of 25°C.

REFERENCES

REFERENCES

Abatzoglou, N., and Boivin, S. (2009). A review of biogas purification processes. **Biofuels, Bioproducts and Biorefining**. 3(1): 42-71.

Akinyele, D., and Rayudu, R. (2014). Review of energy storage technologies for sustainable power networks. **Sustainable Energy Technologies and Assessments**. 8: 74-91.

Alonso-Vicario, A., Ochoa-Gómez, J. R., Gil-Río, S., Gómez-Jiménez-Aberasturi, O., Ramírez-López, C., Torrecilla-Soria, J., and Domínguez, A. (2010). Purification and upgrading of biogas by pressure swing adsorption on synthetic and natural zeolites. **Microporous and Mesoporous Materials**. 134(1-3): 100-107.

Amedi, H. R., and Aghajani, M. (2017). Aminosilane-functionalized ZIF-8/PEBA mixed matrix membrane for gas separation application. **Microporous and Mesoporous Materials**. 247: 124-135.

An, H., Feng, B., and Su, S. (2011). CO_2 capture by electrothermal swing adsorption with activated carbon fibre materials. **International Journal of Greenhouse Gas Control**. 5(1): 16-25.

Andriani, D., Wresta, A., Atmaja, T. D., and Saepudin, A. (2014). A review on optimization production and upgrading biogas through CO_2 removal using various techniques. **Applied biochemistry and biotechnology**. 172(4): 1909-1928.

Aroon, M., Ismail, A., Matsuura, T., and Montazer-Rahmati, M. (2010). Performance studies of mixed matrix membranes for gas separation: a review. **Separation and purification Technology**. 75(3): 229-242.

Augelletti, R., Conti, M., and Annesini, M. C. (2017). Pressure swing adsorption for biogas upgrading. A new process configuration for the separation of biomethane and carbon dioxide. **Journal of Cleaner Production**. 140: 1390-1398.

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

Barboiu, C., Sala, B., Bec, S., Pavan, S., Petit, E., Colomban, P., Sanchez, J., De Perthuis, S., and Hittner, D. (2009). Structural and mechanical characterizations of microporous silica–boron membranes for gas separation. **Journal of Membrane Science**. 326(2): 514-525.

Basu, S., Khan, A. L., Cano-Odena, A., Liu, C., and Vankelecom, I. F. (2010). Membrane-based technologies for biogas separations. **Chemical Society Reviews**. 39(2): 750-768.

Bauer, F., Persson, T., Hulteberg, C., and Tamm, D. (2013). Biogas upgrading–technology overview, comparison and perspectives for the future. **Biofuels, Bioproducts and Biorefining**. 7(5): 499-511.

Beschkov, V. (2017). Biogas, Biodiesel and Bioethanol as Multifunctional Renewable Fuels and Raw Materials **Frontiers in Bioenergy and Biofuels:** InTech.

Bétard, A., and Fischer, R. A. (2011). Metal–Organic Framework Thin Films: From Fundamentals to Applications. **Chemical reviews**. 112(2): 1055-1083.

Bos, A., Pünt, I., Wessling, M., and Strathmann, H. (1999). CO_2-induced plasticization phenomena in glassy polymers. **Journal of Membrane Science**. 155(1): 67-78.

Budzianowski, W. M., Wylock, C. E., and Marciniak, P. A. (2017). Power requirements of biogas upgrading by water scrubbing and biomethane compression: comparative analysis of various plant configurations. **Energy Conversion and Management**. 141: 2-19.

Bux, H., Liang, F., Li, Y., Cravillon, J., Wiebcke, M., and Caro, J. r. (2009). Zeolitic imidazolate framework membrane with molecular sieving properties by microwave-assisted solvothermal synthesis. **Journal of the American Chemical Society**. 131(44): 16000-16001.

Cavenati, S., Grande, C. A., and Rodrigues, A. E. (2005). Upgrade of methane from landfill gas by pressure swing adsorption. **Energy & fuels**. 19(6): 2545-2555.

Chae, H. K., Siberio-Perez, D. Y., Kim, J., Go, Y., Eddaoudi, M., Matzger, A. J., O'keeffe, M., and Yaghi, O. M. (2004). A route to high surface area, porosity and inclusion of large molecules in crystals. **Nature**. 427(6974): 523.

Chaffee, A. L., Knowles, G. P., Liang, Z., Zhang, J., Xiao, P., and Webley, P. A. (2007). CO2 capture by adsorption: materials and process development. **International Journal of Greenhouse Gas Control**. 1(1): 11-18.

Chen, X. Y., Vinh-Thang, H., Ramirez, A. A., Rodrigue, D., and Kaliaguine, S. (2015). Membrane gas separation technologies for biogas upgrading. **RSC Advances**. 5(31): 24399-24448.

Chi, W. S., Hwang, S., Lee, S.-J., Park, S., Bae, Y.-S., Ryu, D. Y., Kim, J. H., and Kim, J. (2015). Mixed matrix membranes consisting of SEBS block copolymers and size-controlled ZIF-8 nanoparticles for CO_2 capture. **Journal of Membrane Science**. 495: 479-488.

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

Cozma, P., Ghinea, C., Mămăligă, I., Wukovits, W., Friedl, A., and Gavrilescu, M. (2013). Environmental impact assessment of high pressure water scrubbing biogas upgrading technology. **CLEAN–Soil, Air, Water**. 41(9): 917-927.

Dada, O., and Mbohwa, C. (2017). Biogas upgrade to biomethane from landfill wastes: a review. **Procedia Manufacturing**. 7: 333-338.

De Hullu, J., Maassen, J., Van Meel, P., Shazad, S., Vaessen, J., Bini, L., and Reijenga, J. (2008). Comparing different biogas upgrading techniques. **Eindhoven University of Technology**. 3.

Deng, L., and Hägg, M.-B. (2010). Techno-economic evaluation of biogas upgrading process using CO_2 facilitated transport membrane. **International Journal of Greenhouse Gas Control**. 4(4): 638-646.

Dong, X., Huang, K., Liu, S., Ren, R., Jin, W., and Lin, Y. (2012). Synthesis of zeolitic imidazolate framework-78 molecular-sieve membrane: defect formation and elimination. **Journal of Materials Chemistry**. 22(36): 19222-19227.

Drage, T. C., Arenillas, A., Smith, K. M., and Snape, C. E. (2008). Thermal stability of polyethylenimine based carbon dioxide adsorbents and its influence on selection of regeneration strategies. **Microporous and Mesoporous Materials**. 116(1-3): 504-512.

Effendi, A., Hellgardt, K., Zhang, Z.-G., and Yoshida, T. (2005). Optimising H_2 production from model biogas via combined steam reforming and CO shift reactions. **Fuel**. 84(7-8): 869-874.

Eze, J., and Agbo, K. (2010). Maximizing the potentials of biogas through upgrading. **Am. J. Sci. Ind. Res**. 1(3): 604-609.

Fan, L., Xue, M., Kang, Z., Li, H., and Qiu, S. (2012). Electrospinning technology applied in zeolitic imidazolate framework membrane synthesis. **Journal of Materials Chemistry**. 22(48): 25272-25276.

Fang, M., Wu, C., Yang, Z., Wang, T., Xia, Y., and Li, J. (2015). ZIF-8/PDMS mixed matrix membranes for propane/nitrogen mixture separation: experimental result and permeation model validation. **Journal of Membrane Science**. 474: 103-113.

Farha, O. K., Eryazici, I., Jeong, N. C., Hauser, B. G., Wilmer, C. E., Sarjeant, A. A., Snurr, R. Q., Nguyen, S. T., Yazaydın, A. O. z. r., and Hupp, J. T. (2012). Metal–organic framework materials with ultrahigh surface areas: is the sky the limit? **Journal of the American Chemical Society**. 134(36): 15016-15021.

Farzaneh-Gord, M., and Branch, S. (2011). Real and ideal gas thermodynamic analysis of single reservoir filling process of natural gas vehicle cylinders. **J. Theor. Appl. Mech. Sofia**. 41(2): 21-36.

Favre, E., Bounaceur, R., and Roizard, D. (2009). Biogas, membranes and carbon dioxide capture. **Journal of Membrane Science**. 328(1-2): 11-14.

Furukawa, H., Cordova, K. E., O'Keeffe, M., and Yaghi, O. M. (2013). The chemistry and applications of metal-organic frameworks. **Science**. 341(6149): 1230444.

Gascon, J., Kapteijn, F., Zornoza, B., Sebastian, V., Casado, C., and Coronas, J. (2012). Practical approach to zeolitic membranes and coatings: state of the art, opportunities, barriers, and future perspectives. **Chemistry of Materials**. 24(15): 2829-2844.

Ge, L., Zhou, W., Du, A., and Zhu, Z. (2012). Porous polyethersulfone-supported zeolitic imidazolate framework membranes for hydrogen separation. **The Journal of Physical Chemistry C**. 116(24): 13264-13270.

Gomes, V. G., and Yee, K. W. (2002). Pressure swing adsorption for carbon dioxide sequestration from exhaust gases. **Separation and purification Technology**. 28(2): 161-171.

González, M. O. A., Gonçalves, J. S., and Vasconcelos, R. M. (2017). Sustainable development: Case study in the implementation of renewable energy in Brazil. **Journal of Cleaner Production**. 142: 461-475.

Grande, C. A., Ribeiro, R. P., Oliveira, E. L., and Rodrigues, A. E. (2009). Electric swing adsorption as emerging CO_2 capture technique. **Energy Procedia**. 1(1): 1219-1225.

Grande, C. A., and Rodrigues, A. E. (2007). Biogas to fuel by vacuum pressure swing adsorption I. Behavior of equilibrium and kinetic-based adsorbents. **Industrial & Engineering Chemistry Research**. 46(13): 4595-4605.

Grimsby, L. K., Rajabu, H. M., and Treiber, M. U. (2016). Multiple biomass fuels and improved cook stoves from Tanzania assessed with the Water Boiling Test. **Sustainable Energy Technologies and Assessments**. 14: 63-73.

Guerrero, V. V., Yoo, Y., McCarthy, M. C., and Jeong, H.-K. (2010). HKUST-1 membranes on porous supports using secondary growth. **Journal of Materials Chemistry**. 20(19): 3938-3943.

Hahn, H., Hartmann, K., Bühle, L., and Wachendorf, M. (2015). Comparative life cycle assessment of biogas plant configurations for a demand oriented biogas supply for flexible power generation. **Bioresource technology**. 179: 348-358.

Hara, N., Yoshimune, M., Negishi, H., Haraya, K., Hara, S., and Yamaguchi, T. (2014). Diffusive separation of propylene/propane with ZIF-8 membranes. **Journal of Membrane Science**. 450: 215-223.

Harasimowicz, M., Orluk, P., Zakrzewska-Trznadel, G., and Chmielewski, A. (2007). Application of polyimide membranes for biogas purification and enrichment. **Journal of Hazardous Materials**. 144(3): 698-702.

He, Y., Krishna, R., and Chen, B. (2012). Metal–organic frameworks with potential for energy-efficient adsorptive separation of light hydrocarbons. **Energy & Environmental Science**. 5(10): 9107-9120.

Ho, M. T., Allinson, G. W., and Wiley, D. E. (2008). Reducing the cost of CO_2 capture from flue gases using pressure swing adsorption. **Industrial & Engineering Chemistry Research**. 47(14): 4883-4890.

Holm-Nielsen, J. B., Al Seadi, T., and Oleskowicz-Popiel, P. (2009). The future of anaerobic digestion and biogas utilization. **Bioresource technology**. 100(22): 5478-5484.

Hosseini, S. E., and Wahid, M. A. (2013). Feasibility study of biogas production and utilization as a source of renewable energy in Malaysia. **Renewable and Sustainable Energy Reviews**. 19: 454-462.

Huang, A., Bux, H., Steinbach, F., and Caro, J. (2010). Molecular-sieve membrane with hydrogen permselectivity: ZIF-22 in LTA topology prepared with 3-aminopropyltriethoxysilane as covalent linker. **Angewandte Chemie International Edition**. 49(29): 4958-4961.

Huang, A., Dou, W., and Caro, J. r. (2010). Steam-stable zeolitic imidazolate framework ZIF-90 membrane with hydrogen selectivity through covalent functionalization. **Journal of the American Chemical Society**. 132(44): 15562-15564.

Huang, A., Liang, F., Steinbach, F., and Caro, J. (2010). Preparation and separation properties of LTA membranes by using 3-aminopropyltriethoxysilane as covalent linker. **Journal of Membrane Science**. 350(1-2): 5-9.

Huang, A., Liu, Q., Wang, N., and Caro, J. (2014). Highly hydrogen permselective ZIF-8 membranes supported on polydopamine functionalized macroporous stainless-steel-nets. **Journal of Materials Chemistry A**. 2(22): 8246-8251.

Huang, H., Chang, S.-G., and Dorchak, T. (2002). Method to regenerate ammonia for the capture of carbon dioxide. **Energy & fuels**. 16(4): 904-910.

Hwang, S., Chi, W. S., Lee, S. J., Im, S. H., Kim, J. H., and Kim, J. (2015). Hollow ZIF-8 nanoparticles improve the permeability of mixed matrix membranes for CO2/CH4 gas separation. **Journal of Membrane Science**. 480: 11-19.

James, J. B., and Lin, Y. (2017). Thermal stability of ZIF-8 membranes for gas separations. **Journal of Membrane Science**. 532: 9-19.

Jiang, L. Y., Chung, T. S., and Kulprathipanja, S. (2006). An investigation to revitalize the separation performance of hollow fibers with a thin mixed matrix composite skin for gas separation. **Journal of Membrane Science**. 276(1-2): 113-125.

Jiang, Y.-H., Xiong, S.-S., Shi, W., He, W.-H., Zhang, T., Lin, X.-K., Gu, Y., Lv, Y.-D., Qian, X.-J., and Ye, Z.-Y. (2009). Research of biogas as fuel for internal combustion engine. Paper presented at the **Power and Energy Engineering Conference, 2009. APPEEC 2009. Asia-Pacific.**

Jomekian, A., Bazooyar, B., Behbahani, R. M., Mohammadi, T., and Kargari, A. (2017). Ionic liquid-modified Pebax® 1657 membrane filled by ZIF-8 particles for separation of CO_2 from CH_4, N_2 and H_2. **Journal of Membrane Science**. 524: 652-662.

Jomekian, A., Behbahani, R. M., Mohammadi, T., and Kargari, A. (2016). CO2/CH4 separation by high performance co-casted ZIF-8/Pebax 1657/PES mixed matrix membrane. **Journal of Natural Gas Science and Engineering**. 31: 562-574.

Kapdi, S., Vijay, V., Rajesh, S., and Prasad, R. (2005). Biogas scrubbing, compression and storage: perspective and prospectus in Indian context. **Renewable energy**. 30(8): 1195-1202.

Kárászová, M., Sedláková, Z., and Izák, P. (2015). Gas permeation processes in biogas upgrading: A short review. **Chemical Papers**. 69(10): 1277-1283.

Kentish, S. E., Scholes, C. A., and Stevens, G. W. (2008). Carbon dioxide separation through polymeric membrane systems for flue gas applications. **Recent Patents on Chemical Engineering**. 1(1): 52-66.

Khan, I. U., Othman, M. H. D., Hashim, H., Matsuura, T., Ismail, A., Rezaei-DashtArzhandi, M., and Azelee, I. W. (2017). Biogas as a renewable energy fuel–a review of biogas upgrading, utilisation and storage. **Energy Conversion and Management**. 150: 277-294.

Kismurtono, M. (2011). Upgrade biogas purification in packed column with chemical absorption of CO_2 for energy alternative of small industry (UKM-Tahu). **Int. J. Eng. Technol**. 11: 83-86.

Krich, K., Augenstein, A., Batmale, J., Benemann, J., Rutledge, B., and Salour, D. (2005). Upgrading dairy biogas to biomethane and other fuels. **Biomethane from dairy waste-A sourcebook for the production and use of renewable natural gas in California. California: Clear Concepts**: 47-69.

Lai, L. S., Yeong, Y. F., Chew, T. L., Lau, K. K., and Azmi, M. S. (2016). CO2 and CH4 gas permeation study via zeolitic imidazolate framework (ZIF)-8 membrane. **Journal of Natural Gas Science and Engineering**. 34: 509-519.

Lai, Z. (2018). Development of ZIF-8 membranes: opportunities and challenges for commercial applications. **Current Opinion in Chemical Engineering**. 20: 78-85.

Li, L., Yao, J., Chen, R., He, L., Wang, K., and Wang, H. (2013). Infiltration of precursors into a porous alumina support for ZIF-8 membrane synthesis. **Microporous and Mesoporous Materials**. 168: 15-18.

Li, T., Pan, Y., Peinemann, K.-V., and Lai, Z. (2013). Carbon dioxide selective mixed matrix composite membrane containing ZIF-7 nano-fillers. **Journal of Membrane Science**. 425: 235-242.

Li, W., Zhang, Y., Li, Q., and Zhang, G. (2015). Metal− organic framework composite membranes: Synthesis and separation applications. **Chemical Engineering Science**. 135: 232-257.

Li, Y., Liang, F., Bux, H., Yang, W., and Caro, J. (2010). Zeolitic imidazolate framework ZIF-7 based molecular sieve membrane for hydrogen separation. **Journal of Membrane Science**. 354(1-2): 48-54.

Li, Y. S., Bux, H., Feldhoff, A., Li, G. L., Yang, W. S., and Caro, J. (2010). Controllable synthesis of metal–organic frameworks: From MOF nanorods to oriented MOF membranes. **Advanced Materials**. 22(30): 3322-3326.

Li, Y. S., Liang, F. Y., Bux, H., Feldhoff, A., Yang, W. S., and Caro, J. (2010). Molecular sieve membrane: supported metal–organic framework with high hydrogen selectivity. **Angewandte Chemie**. 122(3): 558-561.

Lim, C., Kim, D., Song, C., Kim, J., Han, J., and Cha, J.-S. (2015). Performance and emission characteristics of a vehicle fueled with enriched biogas and natural gases. **Applied Energy**. 139: 17-29.

Liu, C., Sun, F., Zhou, S., Tian, Y., and Zhu, G. (2012). Facile synthesis of ZIF-8 nanocrystals in eutectic mixture. **CrystEngComm**. 14(24): 8365-8367.

Liu, Q., Wang, N., Caro, J. r., and Huang, A. (2013). Bio-inspired polydopamine: a versatile and powerful platform for covalent synthesis of molecular sieve membranes. **Journal of the American Chemical Society**. 135(47): 17679-17682.

Liu, Y., Hu, E., Khan, E. A., and Lai, Z. (2010). Synthesis and characterization of ZIF-69 membranes and separation for CO_2/CO mixture. **Journal of Membrane Science**. 353(1-2): 36-40.

Loh, S., Nasrin, A., Azri, S. M., Adela, B. N., Muzzammil, N., Jay, T. D., Eleanor, R. S., Lim, W., Choo, Y., and Kaltschmitt, M. (2017). First report on Malaysia’s experiences and development in biogas capture and utilization from palm oil mill effluent under the economic transformation programme: current and future perspectives. **Renewable and Sustainable Energy Reviews**. 74: 1257-1274.

Makareviciene, V., Sendzikiene, E., Pukalskas, S., Rimkus, A., and Vegneris, R. (2013). Performance and emission characteristics of biogas used in diesel engine operation. **Energy Conversion and Management**. 75: 224-233.

Makaruk, A., Miltner, M., and Harasek, M. (2010). Membrane biogas upgrading processes for the production of natural gas substitute. **Separation and purification Technology**. 74(1): 83-92.

Mao, Y., Cao, W., Li, J., Liu, Y., Ying, Y., Sun, L., and Peng, X. (2013). Enhanced gas separation through well-intergrown MOF membranes: seed morphology and crystal growth effects. **Journal of Materials Chemistry A**. 1(38): 11711-11716.

Mason, J. A., Sumida, K., Herm, Z. R., Krishna, R., and Long, J. R. (2011). Evaluating metal–organic frameworks for post-combustion carbon dioxide capture via temperature swing adsorption. **Energy & Environmental Science**. 4(8): 3030-3040.

McCarthy, M. C., Varela-Guerrero, V., Barnett, G. V., and Jeong, H.-K. (2010). Synthesis of zeolitic imidazolate framework films and membranes with controlled microstructures. **Langmuir**. 26(18): 14636-14641.

Melgar, V. M. A., Ahn, H., Kim, J., and Othman, M. R. (2015). Highly selective micro-porous ZIF-8 membranes prepared by rapid electrospray deposition. **Journal of Industrial and Engineering Chemistry**. 21: 575-579.

Melgar, V. M. A., Kim, J., and Othman, M. R. (2015). Zeolitic imidazolate framework membranes for gas separation: A review of synthesis methods and gas separation performance. **Journal of Industrial and Engineering Chemistry**. 28: 1-15.

Miltner, M., Makaruk, A., and Harasek, M. (2008). **Application of gas permeation for biogas upgrade-operational experiences of feeding biomethane into the Austrian gas grid: na.**

Molino, A., Migliori, M., Ding, Y., Bikson, B., Giordano, G., and Braccio, G. (2013). Biogas upgrading via membrane process: modelling of pilot plant scale and the end uses for the grid injection. **Fuel**. 107: 585-592.

Montanari, T., Finocchio, E., Bozzano, I., Garuti, G., Giordano, A., and Pistarino, C. (2010). Purification of landfill biogases from siloxanes by adsorption: a study of silica and 13X zeolite adsorbents on hexamethylcyclotrisiloxane separation. **Chemical engineering journal**. 165(3): 859-863.

Moon, S.-H., and Shim, J.-W. (2006). A novel process for CO2/CH4 gas separation on activated carbon fibers—electric swing adsorption. **Journal of colloid and interface science**. 298(2): 523-528.

Muradov, N., Smith, F., and Ali, T. (2008). Hydrogen production by catalytic processing of renewable methane-rich gases. **International Journal of Hydrogen Energy**. 33(8): 2023-2035.

Nafisi, V., and Hägg, M.-B. (2014). Development of dual layer of ZIF-8/PEBAX-2533 mixed matrix membrane for CO2 capture. **Journal of Membrane Science**. 459: 244-255.

Nan, J., Dong, X., Wang, W., Jin, W., and Xu, N. (2011). Step-by-step seeding procedure for preparing HKUST-1 membrane on porous α-alumina support. **Langmuir**. 27(8): 4309-4312.

Nie, H., Jiang, H., Chong, D., Wu, Q., Xu, C., and Zhou, H. (2013). Comparison of water scrubbing and propylene carbonate absorption for biogas upgrading process. **Energy & fuels**. 27(6): 3239-3245.

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

Osorio, F., and Torres, J. (2009). Biogas purification from anaerobic digestion in a wastewater treatment plant for biofuel production. **Renewable energy**. 34(10): 2164-2171.

Palma, V., Barba, D., and Ciambelli, P. (2013). Biogas purification by selective partial oxidation of H_2S on V_2O_5-CeO_2 catalysts. **Brazilian J Chem Eng**. 21: 5-6.

Pan, Y., Li, T., Lestari, G., and Lai, Z. (2012). Effective separation of propylene/propane binary mixtures by ZIF-8 membranes. **Journal of Membrane Science**. 390: 93-98.

Pan, Y., Wang, B., and Lai, Z. (2012). Synthesis of ceramic hollow fiber supported zeolitic imidazolate framework-8 (ZIF-8) membranes with high hydrogen permeability. **Journal of Membrane Science**. 421: 292-298.

Papong, S., Rotwiroon, P., Chatchupong, T., and Malakul, P. (2014). Life cycle energy and environmental assessment of bio-CNG utilization from cassava starch wastewater treatment plants in Thailand. **Renewable energy**. 65: 64-69.

Park, K. S., Ni, Z., Côté, A. P., Choi, J. Y., Huang, R., Uribe-Romo, F. J., Chae, H. K., O'Keeffe, M., and Yaghi, O. M. (2006). Exceptional chemical and thermal stability of zeolitic imidazolate frameworks. **Proceedings of the National Academy of Sciences**. 103(27): 10186-10191.

Persson, M., Jönsson, O., and Wellinger, A. (2006). Biogas upgrading to vehicle fuel standards and grid injection. Paper presented at the **IEA Bioenergy task.**

Petersson, A., and WeLLInGer, A. (2009). Biogas upgrading technologies–developments and innovations. **IEA bioenergy**. 20: 1-19.

Phan, A., Doonan, C. J., Uribe-Romo, F. J., Knobler, C. B., O'keeffe, M., and Yaghi, O. M. (2010). Synthesis, structure, and carbon dioxide capture properties of zeolitic imidazolate frameworks. **Acc. Chem. Res**. 43(1): 58-67.

Plaza, M. G., García, S., Rubiera, F., Pis, J., and Pevida, C. (2010). Post-combustion CO_2 capture with a commercial activated carbon: comparison of different regeneration strategies. **Chemical engineering journal**. 163(1-2): 41-47.

Privalova, E., Rasi, S., Mäki-Arvela, P., Eränen, K., Rintala, J., Murzin, D. Y., and Mikkola, J.-P. (2013). CO_2 capture from biogas: absorbent selection. **RSC Advances**. 3(9): 2979-2994.

Purwanto, H., and Akiyama, T. (2006). Hydrogen production from biogas using hot slag. **International Journal of Hydrogen Energy**. 31(4): 491-495.

Raboni, M., and Urbini, G. (2014). Production and use of biogas in Europe: a survey of current status and perspectives. **Revista ambiente & agua**. 9(2): 191-202.

Rapport, J. L., Zhang, R., Jenkins, B. M., Hartsough, B. R., and Tomich, T. P. (2009). Modeling the performance of anaerobic phased solids digester system for biogas energy production. Paper presented at the **2009 Reno, Nevada, June 21-June 24, 2009.**

Rezaei-DashtArzhandi, M., Ismail, A., Ghanbari, M., Bakeri, G., Hashemifard, S., Matsuura, T., and Moslehyani, A. (2016). An investigation of temperature effects on the properties and CO_2 absorption performance of porous PVDF/montmorillonite mixed matrix membranes. **Journal of Natural Gas Science and Engineering**. 31: 515-524.

Rezaei, M., Ismail, A., Bakeri, G., Hashemifard, S., and Matsuura, T. (2015). Effect of general montmorillonite and Cloisite 15A on structural parameters and performance of mixed matrix membranes contactor for CO_2 absorption. **Chemical engineering journal**. 260: 875-885.

Rezaei, M., Ismail, A., Hashemifard, S., and Matsuura, T. (2014). Preparation and characterization of PVDF-montmorillonite mixed matrix hollow fiber membrane for gas–liquid contacting process. **Chemical Engineering Research and Design**. 92(11): 2449-2460.

Robeson, L. M. (1991). Correlation of separation factor versus permeability for polymeric membranes. **Journal of Membrane Science**. 62(2): 165-185.

Rongwong, W., Boributh, S., Assabumrungrat, S., Laosiripojana, N., and Jiraratananon, R. (2012). Simultaneous absorption of CO_2 and H_2S from biogas by capillary membrane contactor. **Journal of Membrane Science**. 392: 38-47.

Ryan, F., and Caulfield, B. (2010). Examining the benefits of using bio-CNG in urban bus operations. **Transportation Research Part D: Transport and Environment**. 15(6): 362-365.

Ryckebosch, E., Drouillon, M., and Vervaeren, H. (2011). Techniques for transformation of biogas to biomethane. **Biomass and bioenergy**. 35(5): 1633-1645.

Scholz, M., Melin, T., and Wessling, M. (2013). Transforming biogas into biomethane using membrane technology. **Renewable and Sustainable Energy Reviews**. 17: 199-212.

Shah, M., McCarthy, M. C., Sachdeva, S., Lee, A. K., and Jeong, H.-K. (2012). Current status of metal–organic framework membranes for gas separations: promises and challenges. **Industrial & Engineering Chemistry Research**. 51(5): 2179-2199.

Shah, M. N., Gonzalez, M. A., McCarthy, M. C., and Jeong, H.-K. (2013). An unconventional rapid synthesis of high performance metal–organic framework membranes. **Langmuir**. 29(25): 7896-7902.

Shane, A., and Gheewala, S. H. (2017). Missed environmental benefits of biogas production in Zambia. **Journal of Cleaner Production**. 142: 1200-1209.

Shao, P., Dal-Cin, M., Kumar, A., Li, H., and Singh, D. P. (2012). Design and economics of a hybrid membrane–temperature swing adsorption process for upgrading biogas. **Journal of Membrane Science**. 413: 17-28.

Shiga, H., Shinda, K., Hagiwara, K., Tsutsumi, A., Sakurai, M., Yoshida, K., and Bilgen, E. (1998). Large-scale hydrogen production from biogas. **International Journal of Hydrogen Energy**. 23(8): 631-640.

Smith, A. D., Mago, P. J., and Fumo, N. (2013). Benefits of thermal energy storage option combined with CHP system for different commercial building types. **Sustainable Energy Technologies and Assessments**. 1: 3-12.

Subramanian, K., Mathad, V. C., Vijay, V., and Subbarao, P. (2013). Comparative evaluation of emission and fuel economy of an automotive spark ignition vehicle fuelled with methane enriched biogas and CNG using chassis dynamometer. **Applied Energy**. 105: 17-29.

Sun, Q., Li, H., Yan, J., Liu, L., Yu, Z., and Yu, X. (2015). Selection of appropriate biogas upgrading technology-a review of biogas cleaning, upgrading and utilisation. **Renewable and Sustainable Energy Reviews**. 51: 521-532.

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

Tao, K., Kong, C., and Chen, L. (2013). High performance ZIF-8 molecular sieve membrane on hollow ceramic fiber via crystallizing-rubbing seed deposition. **Chemical engineering journal**. 220: 1-5.

Tippayawong, N., and Thanompongchart, P. (2010). Biogas quality upgrade by simultaneous removal of CO_2 and H_2S in a packed column reactor. **Energy**. 35(12): 4531-4535.

Tock, L., Gassner, M., and Maréchal, F. (2010). Thermochemical production of liquid fuels from biomass: Thermo-economic modeling, process design and process integration analysis. **Biomass and bioenergy**. 34(12): 1838-1854.

Uusitalo, V., Havukainen, J., Manninen, K., Höhn, J., Lehtonen, E., Rasi, S., Soukka, R., and Horttanainen, M. (2014). Carbon footprint of selected biomass to biogas production chains and GHG reduction potential in transportation use. **Renewable energy**. 66: 90-98.

Venna, S. R., and Carreon, M. A. (2009). Highly permeable zeolite imidazolate framework-8 membranes for CO2/CH4 separation. **Journal of the American Chemical Society**. 132(1): 76-78.

Venna, S. R., and Carreon, M. A. (2015). Metal organic framework membranes for carbon dioxide separation. **Chemical Engineering Science**. 124: 3-19.

Vijay, V. K., Chandra, R., Subbarao, P. M., and Kapdi, S. S. (2006). Biogas purification and bottling into CNG cylinders: producing Bio-CNG from biomass for rural automotive applications. Paper presented at the **The 2nd Joint International**

Conference on "Sustainable Energy and Environment.

Xie, Z., Yang, J., Wang, J., Bai, J., Yin, H., Yuan, B., Lu, J., Zhang, Y., Zhou, L., and Duan, C. (2012). Deposition of chemically modified α-Al_2 O_3 particles for high performance ZIF-8 membrane on a macroporous tube. **Chemical communications**. 48(48): 5977-5979.

Xu, G., Yao, J., Wang, K., He, L., Webley, P. A., Chen, C.-s., and Wang, H. (2011). Preparation of ZIF-8 membranes supported on ceramic hollow fibers from a concentrated synthesis gel. **Journal of Membrane Science**. 385: 187-193.

Yamamoto, T., Endo, A., Ohmori, T., and Nakaiwa, M. (2004). Porous properties of carbon gel microspheres as adsorbents for gas separation. **Carbon**. 42(8-9): 1671-1676.

Yang, L., Ge, X., Wan, C., Yu, F., and Li, Y. (2014). Progress and perspectives in converting biogas to transportation fuels. **Renewable and Sustainable Energy Reviews**. 40: 1133-1152.

Yang, L., Wang, J., and Shi, J. (2017). Can China meet its 2020 economic growth and carbon emissions reduction targets? **Journal of Cleaner Production**. 142: 993-1001.

Yao, J., Li, L., Wong, W. H. B., Tan, C., Dong, D., and Wang, H. (2013). Formation of ZIF-8 membranes and crystals in a diluted aqueous solution. **Materials Chemistry and Physics**. 139(2-3): 1003-1008.

Zanganeh, K. E., Shafeen, A., and Salvador, C. (2009). CO_2 capture and development of an advanced pilot-scale cryogenic separation and compression unit. **Energy Procedia**. 1(1): 247-252.

Zhang, X., Liu, Y., Kong, L., Liu, H., Qiu, J., Han, W., Weng, L.-T., Yeung, K. L., and Zhu, W. (2013). A simple and scalable method for preparing low-defect ZIF-8 tubular membranes. **Journal of Materials Chemistry A**. 1(36): 10635-10638.

Zhao, Q., Leonhardt, E., MacConnell, C., Frear, C., and Chen, S. (2010). Purification technologies for biogas generated by anaerobic digestion. **Compressed Biomethane, CSANR, Ed**.

Zornoza, B., Martinez-Joaristi, A., Serra-Crespo, P., Tellez, C., Coronas, J., Gascon, J., and Kapteijn, F. (2011). Functionalized flexible MOFs as fillers in mixed matrix membranes for highly selective separation of CO_2 from CH_4 at elevated pressures. **Chemical communications**. 47(33): 9522-9524.

Zornoza, B., Téllez, C., and Coronas, J. (2011). Mixed matrix membranes comprising glassy polymers and dispersed mesoporous silica spheres for gas separation. **Journal of Membrane Science**. 368(1-2): 100-109.

BIOGRAPHY

Mr. Wittawat Laiphaditthagron was born on 19th June 1993 in Ubon Ratchathani, Thailand. In 2011, he studied in Environmental Engineering, Ubon Ratchathani, Thailand. He received his Bachelor's degree of engineer (Environmental Engineering) in 2015.

In November 2015, he got a scholarship for Master program from Assoc. Prof. Dr. Apichat Boontawan, Suranaree University of Technology, Thailand. He studied in field of Bioprocessing engineering at School of Biotechnology, Institute of Agricultural Technology, Suranaree University of Technology from November 2015 to August 2018 with thesis entitled "Preparation of Zeolitic Immidazolate Framework-8 (ZIF-8) Membrane for Quality Upgrading of Biogas". His topic "Preparation of Zeolitic Immidazolate Framework-8 (ZIF-8) Membrane for Quality Upgrading of Biogas" was accepted to be published in 2018 International Conference on Advances in Bioenergy and Clean Energy (ICBCE 2018).