

DEVELOPMENT OF SUPERHYDROPHOBIC CERAMIC HOLLOW FIBRE
MEMBRANES FROM MALAYSIAN KAOLIN FOR EFFICIENT CARBON
DIOXIDE CAPTURE IN MEMBRANE CONTACTOR

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A thesis submitted in fulfilment of the
requirements for the award of the degree of
Doctor of Philosophy (Gas Engineering)

Faculty of Chemical and Energy Engineering
Universiti Teknologi Malaysia

SEPTEMBER 2017

I would like to dedicate this thesis to my beloved mother, wife, and sisters for their endless support and encouragement.

ACKNOWLEDGEMENT

In preparing this thesis, I was in contact with many people, researchers, and academicians. They have contributed towards my understanding and thoughts. In particular, I wish to express my sincere appreciation to my main thesis supervisor, Assoc. Prof. Dr Mohd Hafiz Dzarfan Othman, for encouragement, guidance, critics, and friendship. Without his continued support and interest, this thesis would not have been the same as presented here. My sincere appreciation also extends to my co-supervisor Prof. Dr Ahmad Fauzi Ismail who has been the most energetic and great inspiration to me in my research and gave me the inspiration to keep on the right direction during my research. I have learned from him not only how to perform and interpret experiments but also how to think and move the project forward. His exceptional insights into engineering have immensely helped me to enrich my knowledge. I would also like to thank my external supervisor, Associate Prof. Dr Zawati Harun from UTHM, for the patient guidance, encouragement, and advice he has provided throughout my time as his student. I have been extremely lucky to have a supervisor who cared so much about my work, and who responded to my questions and queries so promptly. My sincere appreciation also extends to all my colleagues and others who have provided assistance on various occasions. Their views and tips are useful indeed. Unfortunately, it is not possible to list all of them in this limited space. In addition, I want to extend my thanks to all Advanced Membrane Technology Research Centre (AMTEC) members for their friendship, invaluable assistance and giving me invaluable advice during throughout this period. Finally, yet importantly, I would like to express utmost appreciation to my lovely and kind wife for their love, support, and encouragements throughout my life.

ABSTRACT

This study initiated the development of clean technology in carbon dioxide (CO₂) capture using ceramic membrane inspired by gas–liquid contacting system. The main objective in this study is to prepare inexpensive, high performance and superhydrophobic ceramic hollow fibre membranes for effective CO₂ separation. Malaysian kaolin was used as the primary material for the membrane preparation. A range of additives were used in this work including alumina of different particle sizes. The hollow fibre membranes were prepared via phase inversion-based extrusion and sintering techniques, followed by grafting with fluoroalkylsilane (FAS). The effect of the addition of alumina to the pure kaolin with monosized or multisized particles on the ceramic membrane gas permeation, mechanical strength, pore size, porosity, tortuosity, morphology, and contact angle were investigated. By varying the overall loadings and particles sizes of alumina addition, different morphologies of the membrane were obtained due to alumina with multiparticle sizes exerts a thermodynamic destabilisation effect within the kaolin, accelerating the onset of demixing rate between solvent and nonsolvent, thus reducing the time during bath immersion. All fabricated kaolin-alumina membranes with multisized particles possessed higher porosity, gas permeability, mechanical strength, than the membranes prepared from pure kaolin. Finger-like structure was obtained when the suspension containing multisized particles instead of of monosized particles due to the different particles promoted the exchange between the solvent and non-solvent. In addition, the small particles moved faster to the surface during phase inversion process than those of large, resulting, multisized particle in shorter inversion time, hence, fast precipitation. The superhydrophobic membrane was obtained when kaolin with or without alumina were used as membrane materials, since kaolin surface possessed a large number of O-H groups which can easily reacting with FAS during the grafting process. The successful grafting with FAS was evidenced by the increase in contact angle from nearly equal to zero degree before grafting to 140 degrees after the grafting process. The kaolin-alumina membrane was subsequently applied in membrane contactor for CO₂ absorption. The CO₂ absorption flux as high as 0.18 mol m⁻² s⁻¹ was achieved at the liquid flow rate of 100 ml min⁻¹ which was far above the fluxes of some commercial and in-house made polymeric and ceramic membranes. In conclusion, the modified kaolin-alumina hollow fibre membrane with the superhydrophobic surface, high permeability, and absorption flux is suitable for CO₂ post-combustion capture, due to its outstanding chemical and thermal stabilities.

ABSTRAK

Kajian ini menjadi permulaan pembangunan teknologi bersih dalam penangkapan karbon dioksida (CO_2) menggunakan membran seramik berdasarkan sistem sesentuh gas-cecair. Objektif utama kajian ini adalah untuk menyediakan membran seramik berongga yang murah, berprestasi tinggi dan super hidrofobia untuk pemisahan CO_2 yang berkesan. Kaolin Malaysia telah digunakan sebagai bahan utama dalam penyediaan membran. Pelbagai bahan tambahan telah digunakan dalam kajian ini termasuklah alumina dengan saiz zarah yang berbeza. Membran gentian berongga telah disediakan melalui teknik penyemperitan dan pensinteran berasaskan-penyongsangan fasa, diikuti dengan cantuman dengan fluoroalkilsilana (FAS). Kesan penambahan alumina dengan saiz mono atau saiz campuran terhadap kadar kebolehtelapan gas, kekuatan mekanikal, saiz liang, keliangan, keliukan, morfologi, dan sudut sentuh membran seramik telah dikaji. Dengan memvariasikan jumlah campuran keseluruhan dan penambahan alumina bersaiz multipartikel, morfologi yang berlainan daripada membran diperoleh kerana alumina dengan saiz multipartikel menghasilkan kesan ketidakstabilan termodinamik dalam kaolin, mempercepatkan permulaan kadar pertukaran antara pelarut dan bukan pelarut, dengan itu mengurangkan tempoh rendaman. Semua membran kaolin-alumina yang dihasilkan dengan campuran pelbagai saiz memiliki keliangan, kebolehtelapan gas, kekuatan mekanikal dan sudut sentuh yang lebih tinggi daripada membran yang dihasilkan dengan kaolin tulen. Struktur seperti jejari telah diperoleh apabila ampaiian mengandungi campuran pelbagai saiz berbanding ampaiian yang bersaiz mono kerana zarah yang berbeza telah menggalakkan proses pertukaran antara pelarut dan bukan pelarut. Di samping itu, zarah kecil bergerak lebih pantas ke permukaan semasa proses penyongsangan fasa berbanding zarah yang besar, hasilnya, masa rendaman yang lebih singkat, maka, proses pemendakan juga cepat. Membran super hidrofobia telah diperoleh apabila kaolin bersama atau tanpa alumina digunakan sebagai bahan membran, kerana permukaan kaolin mempunyai sejumlah besar kumpulan O-H yang mudah bertindak balas dengan FAS semasa proses cantuman. Kejayaan cantuman dengan FAS terbukti dengan peningkatan dalam sudut sentuhan daripada hampir sama dengan sifar darjah sebelum cantuman kepada 140 darjah selepas proses cantuman. Membran kaolin-alumina kemudiannya digunakan dalam penyentuh bermembran untuk penyerapan CO_2 . Fluks penyerapan CO_2 setinggi $0.18 \text{ mol m}^{-2}\text{s}^{-1}$ telah dicapai pada kadar aliran cecair 100 ml min^{-1} yang jauh lebih tinggi daripada fluks beberapa membran komersil dan membran polimer dan seramik yang lain. Kesimpulannya, membran gentian berongga kaolin-alumina yang telah diubah suai dengan permukaan super hidrofobia, kebolehtelapan tinggi, dan fluks penyerapan sangat sesuai untuk penangkapan CO_2 selepas pembakaran, disebabkan oleh kestabilan kimia dan haba yang sangat baik.

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LIST OF ABBREVIATIONS

CAP	-	Cellulose acetate phthalate
CMS	-	Carbon molecular sieves
DMF	-	Dimethylformamide
DMSO	-	Dimethyl sulfoxide
LiCl	-	Lithium chloride
NF	-	Nano filtration
NMP	-	N-methyl-2-pyrrolidone
PEI	-	Polyethyleneimine
PES	-	Polyether sulfone
PTFE	-	Polytetrafluorethylene
PSf	-	Polysulfone
PVDF	-	Polyvinylidene fluoride
PVP	-	Polyvinylpyrrolidone
SEM	-	Scanning Electron Microscope
XRD	-	X-ray Diffraction

LIST OF SYMBOLS

A	-	Contact area (m ²)
A_i	-	Inner surface of the hollow fibre membranes (m ²)
C_l	-	Solute gas concentration in liquid (mol m ⁻³)
$C_{l,i}$	-	Liquid phase CO ₂ concentrations in the inlet of the membrane modules
$C_{l,o}$	-	Liquid phase CO ₂ concentrations in the outlet of the membrane modules
C_g	-	Solute concentration in gas (mol m ⁻³)
ΔC_L^{Av}	-	Logarithmic mean of the difference in the concentration of Solute gas in liquid phase (mol m ⁻³)
d_p	-	Pore diameter (m)
d_i	-	Inner diameter of hollow fiber (m)
d_o	-	Outer diameter of hollow fiber (m)
d_{lm}	-	Log mean diameter (m)
Gz	-	Graetz number, dimensionless
H	-	Henry's constant
J_{av}	-	Average absorption flux (mol m ² s ⁻¹)
J_{CO_2}	-	CO ₂ stripping flux (mol m ² s ⁻¹)
K_{OL}	-	Overall mass transfer coefficient (m s ⁻¹)
K_L	-	Liquid side mass transfer coefficient (m s ⁻¹)
K_g	-	Gas side mass transfer coefficient (m s ⁻¹)
K_m	-	Membrane mass transfer coefficient (m s ⁻¹)
L	-	Hollow fiber membrane length (m)

L_p	-	Effective pore length (m)
M	-	Molecular weight (g mol^{-1})
m	-	Distribution factor
p	-	Pressure (Pa)
\bar{p}	-	Mean pressure (Pa)
\bar{P}	-	Total gas permeance (mol m^{-2})
P_p	-	Gas permeance by Poiseuille flow regime ($\text{mol m}^{-2}\text{Pa}^{-1} \text{s}^{-1}$)
P_K	-	Gas permeance by Knudsen flow regime ($\text{mol m}^{-2}\text{Pa}^{-1} \text{s}^{-1}$)
Q_L	-	Liquid flow rate (ml s^{-1})
r_p	-	Pore radius (m)
$r_{p,m}$	-	Mean pore radius (m)
R	-	Universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)
Sh	-	Sherwood number, dimensionless
T	-	Temperature (K)
V_l	-	Liquid velocity in lumen side (m s^{-1})
ζ	-	Surface porosity
θ	-	Contact angle of liquid and surface
μ	-	Gas viscosity (Pa.s)
η	-	CO_2 stripping efficiency (%)

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CHAPTER 1

INTRODUCTION

1.1 Research Background

It is no secret that one of the most serious problems facing the world in the third millennium is global warming, in which CO₂ is primarily responsible for human-induced climate change as shown in Figure 1.1. There has been a steady increase in the volume of gas emissions over the last decades caused by the population growth and the frequent use of fossil fuels as the main source of energy, and this lead to the increase in the concentration of CO₂ in the atmosphere from 275 to 387 ppm (Merkel *et al.*, 2010; Nakajima *et al.*, 2016). In addition, it is estimated that the average global surface temperature shall increase an additional $1.1 \pm 0.62^{\circ}\text{C}$ during the 21st century if the emission of greenhouse gases are not governed (Dai, 2016; Pachauri, 2008). Hence, the mitigation of CO₂ content in gas streams and its emission to the atmosphere seem unavoidable. There are numerous developed technologies for the removal of CO₂ that absorption of CO₂ by means of direct contact between gas and liquid through packed columns is widely established.

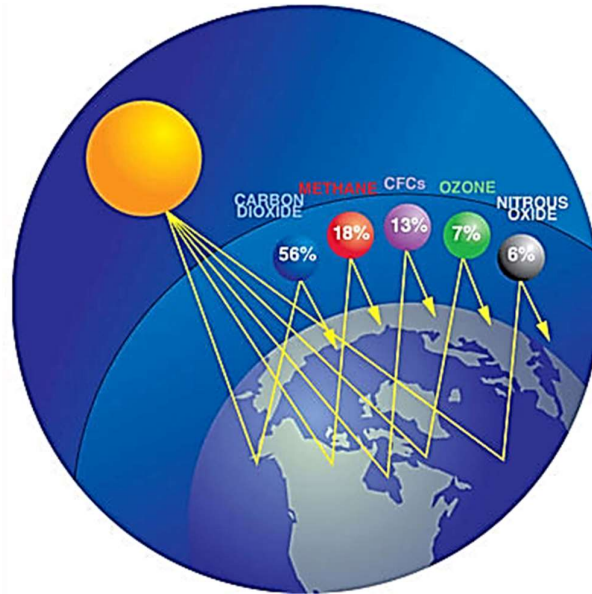


Figure 1.1 Greenhouse gases (Ramaswamy et al., 2001)

Gas separation membranes are likely to play a key role in the CO₂ capture system owing to their light weight, operational flexibility, compactness, less energy consumption and their ability to minimise overall environmental impacts (Ismail *et al.*, 2015a). Significant attention has been paid by engineering communities to acquire a new technology that would lead us to the goal of technological sustainability. Among others, membrane contactor is one of the promising technology seen as reliable for substituting conventional system. Its unique characteristics such as high interfacial area per unit volume, small size, easy to scale up and down, and independent control of gas and liquid flowrates make the membrane contactors as a superior option compared to conventional methods (Rezaei *et al.*, 2014a).

The capture of CO₂ from gas streams by a membrane contactor process has been the attention of researchers since the 1980s. Qi and Cussler (1980) introduced microporous membrane contactor in the application of CO₂ capture, subsequently many investigations to improve the idea (Qi and Cussler, 1985a, 1985b). Ultimately, researchers have considered several factors such as membrane materials, absorption solutions, modules and operating conditions to improve the performance of CO₂ capture. Yu *et al.* (2015) had successfully developed a superhydrophobic ceramic

membrane for CO₂ absorption after coating the surface of the alumina tube with a (ZrO₂) layer. Lee *et al.* (2015) modified the surface of alumina hollow fibre membrane by fluoroalkyl silane (FAS) for CO₂ capture using H₂O as low-cost absorbent at room temperature. Moreover, Wei and Li (2009) developed pre-treatment by alkaline to the YSZ membrane before grafting to get robust hydrophobic membrane.

Overall, membrane contactors for gas absorption have proven to be an attractive, effective and competitive alternative for conventional gas absorption devices since they combine both membrane separation (compactness) and conventional absorption (high selectivity).

1.2 Problem Statement

Porous asymmetric hollow fibre membranes in gas-liquid membrane contactors process are indisputably favourable for CO₂ capture. Though this technology is confirmed to have several advantages over conventional absorption devices, the presence of membranes introduces supplementary resistance to the overall mass transfer process. The phenomenon becomes of serious concern when the liquid absorbent is penetrated to the pores of the membrane which render the stability of the process due to the wetting issue. The essential requirements of membrane contactor include high porosity and hydrophobicity that allow easy diffusion of the gas into the liquid and prevent liquid from penetrating into pores (Aroon *et al.*, 2010). Since the membrane materials play the most crucial role in governing the gas transport through the membrane, there is a need to wisely select the membrane materials to fulfil the requirement of the gas/liquid contacting processes. Currently, most of the commercially available hollow fibre membranes are made from polymeric materials such as, but not limited to polyvinylidene fluoride (PVDF), polypropylene (PP), polysulfone, polyethylene (PE) and polyimide (Rezaei *et al.*, 2014a). Porous polymeric membranes applied in membrane gas absorption process appear to undergo wetting especially during the long-term operation which significantly reduces the performance (Rezaei *et al.*, 2014b). Moreover, there are reports that the currently available

polymeric membranes are often encountered with significant morphological and properties changes during a long-time contact with the absorbent (Li, 2007). For example, it was found that the performance of polymeric membrane contactors completely stopped after a couple weeks of operation due to the membrane wetting (Dindore *et al.*, 2004a). Therefore, there is a need to find an alternative to the polymeric materials. A promising example that could exhibit superior structural, chemical and thermal stabilities over polymeric membrane is the ceramic membrane.

Ceramic hollow fibre membranes have been recently used for membrane contactor applications after some modification (Abdulhameed *et al.*, 2016; Faiz *et al.*, 2013; Koonaphapdeelert *et al.*, 2009; Yu *et al.*, 2015). Ceramic membrane is hydrophilic in nature owing to the O-H group on the membrane surface (Koonaphapdeelert and Li, 2007). Hence in order to make the membrane surface hydrophobic, the chemical modification needs to be applied. Many literatures reviews have reported on the grafting of different FAS on the surface of alumina, titania, zirconia and silica (Lee *et al.*, 2015; Wei and Li, 2009). Unfortunately, these materials are expensive and/ or need high sintering temperature, which have adverse impacts on membrane cost. In addition, there is a trade-off between the hydrophobicity and the sintering temperature of the membrane. Koonaphapdeelert and Li (2007) found that when sintering temperature increased, the contact angle of alumina hollow fibre decreased due to the number of (OH-) group on the surface have effected by increasing the sintering temperature and as a result, it is no longer enough (OH-) group could react with FAS. Therefore, new materials recently have been proposed to lower the ceramic membrane cost and make it more affordable. Thus, to lower the cost, recent investigation on the preparation of ceramic membrane is to focus toward the utilization of inexpensive raw materials, such as fly ash (Fang *et al.*, 2011), apatite powder (Fang *et al.*, 2011; Masmoudi *et al.*, 2007), dolomite (Saffaj *et al.*, 2006), natural raw clay and kaolin (Boudaira *et al.*, 2009; Saffaj *et al.*, 2005).

The unique features of kaolin clay ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), such as good availability, effectiveness, low melting point. and ease of processing (Han *et al.*, 2011; Johnson and Arshad, 2014), makes this material an attractive option. However, the fabrication of kaolin membrane by the phase inversion technique has been rarely reported. One of

the reasons may be the low density of kaolin. The kaolin powder has a density of 2.4 g/cm³ compared to 3.95 and 4.23 g/cm³ for alumina and titania, respectively. The density of kaolin is able to create difficulty in preparing dope with higher loading especially when exceed more than 50%wt. It is worth noting, that the optimal ceramic content in the dope is 50-60 wt.% (Li, 2007) in order to fabricate well-structured membranes with small pore sizes and a narrow pore size distribution. To overcome this problem, alumina particles of various sizes were added to reach the desired total ceramic powder loading. Alumina is suitable as an additive due to its compatibility with kaolin during the sintering process. The sintering reaction may also take place between kaolin and alumina to produce the mullite. The formation of kaolin-alumina ceramic material is also beneficial since it can be produced from relatively low-cost materials and at lower sintering temperatures than pure alumina.

Therefore, ceramic membrane preparing from low-cost material would be beneficial due to it combines the advantages of each phase may be an easy and effective material for utilising in gas sweetening process. At present, and to the best of our knowledge, no study has been reported on the application of ceramic hollow fiber membrane prepared from low cost material in membrane contactor for the removal of CO₂. It is indicated that the addition of alumina with multiparticle sizes can play a role in modifying the properties of kaolin membranes. Meanwhile, the selection of ceramic materials should be based on fulfilling the requirements of the absorption process.

1.3 Objectives of the Study

Based on the above-mentioned problem statements, the main goal of this thesis is to develop high performance ceramic membrane contactor from inexpensive, abundantly available kaolin material for carbon dioxide capture. The specific objectives are to:

- i. fabricate ceramic hollow fiber membranes from local kaolin at different composition and manipulate their structures by blending alumina particles into spinning solution.
- ii. investigate the effects of kaolin/polymer binder ratio and sintering temperature on the resultant ceramic membrane properties.
- iii. investigate the effects of alumina particles loading and size on the resultant kaolin membrane properties.
- iv. evaluate the performance of the modified ceramic membranes for CO₂ absorption.

1.4 Scope of the Study

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

- i. Selection of alumina particles with three different sizes average size of 1 μm , 0.05 μm , and 0.02 μm for preparing kaolin-alumina membranes
- ii. Preparation of ceramic suspensions with various ratio of kaolin to polyethersulfone (PESf) binder (5:1, 7:1 and 9:1)
- iii. Fabrication of hollow fibre membranes by dry/wet spinning technique at air gap 4.5 cm
- iv. Undergoing the precursor to the heat treatment that is called sintering process. The sintering temperature would be varied from 1200 to 1500°C.
- v. Modification of the surface of sintered hollow fibre membrane from hydrophilic to hydrophobic by immersing the membrane into 0.01 mol/L FAS solution in hexane at room temperature
- vi. Investigation of the effect of the ceramic loading, sintering temperature and alumina particles addition on the resultant membrane properties

- vii. Studying membrane morphology and structure using various techniques including scanning electron microscopy (SEM), X-ray diffraction (XRD), gas permeation, three-point bending test, critical water entry pressure, water contact angle and mass transfer resistance.
- viii. Testing CO₂ absorption performance of fabricated membranes via membrane contactor using water and pure CO₂ as absorbent and solute gas respectively.

1.5 Organisation of the Thesis

This thesis consists of seven chapters, which describes the fabrication of ceramic membranes for CO₂ absorption through gas-liquid membrane contactors. Chapter 1 outlines a brief introduction on the membrane contactor for the capture of CO₂ and background of the research. It is followed by the problem statement, which identifies the research direction. Based on the problem statement defined, the objective and scope of the study are explained in detail.

Chapter 2 describes a general overview of the methods of CO₂ capture. Brief information about the advantages of membrane CO₂ capture in comparison with the other removal processes is provided. After that, the challenges faced by CO₂ absorption membranes and the proposed prevention methods are also presented. Then, comprehensive study about the combination of ceramic as novel materials and applicable ceramic materials for membrane gas-liquid contacting application are provided. The methodologies for the fabrication of ceramic hollow fibre membranes and related characterizations in membrane absorption processes are described in detail in Chapter 3.

In Chapter 4, fabrication of pure kaolin hollow fibre membranes via dry/wet phase inversion process. The effects of polymer binder ratio in the kaolin spinning dopes on the phase inversion process, structure, and performance of the membranes are also discussed. The prepared kaolin was characterised in terms of gas permeability

and mechanical strength. Furthermore, the effects of sintering temperature and on the structure of the kaolin hollow fibre were studied intensively.

Alumina particles with mono and multiparticle sizes addition in the kaolin spinning dopes are used and the results are discussed in Chapter 5. The purpose of this chapter is to improve hydrophobicity on the membrane surface and observe the effect of addition alumina with two different particle sizes (mono-particle, graded particles) to the kaolin on structure and pore size.

Chapter 6 presents the performance of prepared membrane was investigated by the absorption of CO₂ in distilled water in a contactor system and the results were compared with commercial and in-house made membranes.

Finally, the general conclusions are drawn from this research and some recommendations for the future research are provided in Chapter 7.

1.6 Significant of Research

The development of ceramic membrane has gained much attention nowadays due to its characteristics that provide high chemical resistivity, temperature stability and mechanical strength that able to sustain harsh and extreme condition. However, preparation of ceramic membrane often connected to complex preparing routes i.e involve with multistep or complex treatment and modification and high-cost production material (expensive ceramic material i.e. alumina, silica, titania, etc.) has limited their applications. The development of ceramic membrane with regard to the above problem from inexpensive material i.e kaolin will offer an initial idea to trim back the ceramic membrane production cost.

The selection of phase inversion technique which provides better approach information of asymmetric membrane structure which in turn lead to reduce the

multistep in membrane layering structure and as a result give better structure. In this work, two parameters based on the result of addition alumina with mono or multiparticle size to the kaolin and overall loading were selected to be studied as its count as simple parameters that able to be controlled easily and can raise significantly the membrane performance.

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