



**SYNTHESIS OF SILICA CERAMIC MEMBRANE VIA
SOL-GEL DIP-COATING METHOD FOR REMOVAL OF
CARBON DIOXIDE (CO₂) FROM BIOGAS**

BY

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**A thesis submitted in fulfilment of the requirement for the
degree of Master of Science (Materials Engineering)**

**Kulliyyah of Engineering
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ABSTRACT

Biogas energy conversion is a new technique that has been developed for effective and proper utilization of renewable energy. The carbon dioxide (CO₂) has to be removed in order to increase the energy conversion. The silica ceramic membranes were fabricated via sol-gel dip-coating method. The silica sol was prepared using mixture of water, tetraethyl orthosilicate (TEOS), ethanol and nitric acid. Various process method are used such as amount of acid, water:TEOS molar ratio, number of dipping and calcination temperature. The ceramic substrate was dipped into the prepared silica sol. After the dipping step, the samples were dried for 24 hours at room temperature and then heat treated via calcination process. For XRD analysis, all fabricated silica ceramic membranes shows the existence of silica. The FTIR analysis showed the major peaks for all fabricated membranes occurs in the same area of absorption band, with the range of 1070 to 1080 cm⁻¹, are corresponds to the existence of Si-O-Si bond. After silica particles was deposited onto the substrates, the surface of the membranes shows the appearance of fine particle aggregates, which is proved to be the agglomeration of silica particles via FESEM analysis. The pore size of the raw ceramic substrate is around 0.5 to 0.6 μm. The pore size of fabricated silica ceramic membranes was reduced to around 4 to 25 nm, which analyzed using TEM and BET analysis. Weight and thickness of fabricated silica ceramic membranes were increasing with increasing of the value of water:TEOS molar ratio, amount of acid, and numbers of dipping. However, when silica ceramic membranes were heat treated at the different calcination temperature, the weight and thickness were decreased as the temperature increased. From the permeability test, the silica ceramic membrane able to permeate only a small amount of CO₂, which is around 1%. In summary, silica ceramic membranes are successfully fabricated and pore size of the membranes has been reduced. Besides, the fabricated silica ceramic membranes demonstrate the potential in the removal of CO₂ from the biogas despite having a small permeation percentage.

خلاصة البحث

طاقة الغاز الحيوي (Biogas Energy) تُعد تقنية جديدة تم تطويرها لفعاليتها في استخدام الطاقة المتجددة. يتوجب علينا إزالة ثاني أكسيد الكربون (CO_2) لزيادة نسبة تحوّل الطاقة. تم صناعة غشاء سيليكات السيراميك (silica ceramic) عن طريق تقنية الغمس في محلول الهلام. تم تحضير محلول السيليكات بخلط كُلي من الماء، وتيترا إيثيل أورثو سيليكات (tetraethyl orthosilicate)، وإثانول وحمض النيتروجين. تم استخدام أساليب مختلفة للعملية ككمية الحمض، والنسبة المولية للماء/التيترا إيثيل أورثو سيليكات (TEOS) وعدد مرّات الغمس وتكليس الحرارة. تم غمس ركيزة السيراميك في محلول السيليكات المجهّز. بعد خطوة الغمس، تم تخفيف العينات لمدة 24 ساعة في درجة حرارة الغرفة، ثمّ تمّ تسخينها بتطبيق عملية التكليس. فيما يخص تحليل تشتت الأشعة السينية (XRD)، أظهرت أغشية سيليكات السيراميك وجود السيليكات. كما أظهرت تحليلات التصوير الطيفي بالأشعة تحت الحمراء (FTIR) نقاط ذروة عالية لجميع الأغشية الصناعية والتي وقعت في نفس مساحة شريط الامتصاص حوالي 1070 إلى 1080 cm^{-1} ، وهذا يُشير إلى وجود رابطة $Si-O-Si$. بعد إدخال جسيمات السيليكات في الركائز، أظهر سطح الغشاء تجمّعات لجسيمات دقيقة وقد أثبت المجهر الإلكتروني الماسح ذو الإصدار الحقلية (FESEM) أنه تكثّل لجسيمات السيليكات. بلغ حجم مسام داعم خام السيراميك حوالي 0.5 إلى 0.6 ميكرومتر. تم تصغير حجم غشاء سيليكات السيراميك الصناعي باستخدام تقنيات المجهر الإلكتروني النافذ (TEM) و برانر إيميت تيلر (BET) إلى أن وصلت إلى نسبة 4-25 نانومتر. ازداد وزن وسمك غشاء سيليكات السيراميك الصناعي مع زيادة النسبة المولية للماء/التيترا إيثيل أورثو سيليكات (TEOS) و كمية الحمض وعدد مرّات الغمس. ومع ذلك، فعند تسخين غشاء سيليكات السيراميك في درجات حرارة تكليس مختلفة فإننا نلاحظ أن الوزن والسمك قد تضاعفا مع ارتفاع درجة الحرارة. أما بالنسبة لاختبار النفاذية، فقد أظهر أن غشاء سيليكات السيراميك استطاع اختراق كمية ضئيلة فقط من ثاني أكسيد الكربون والتي تبلغ نسبة 1%. وباختصار، فإنه تم صناعة غشاء سيليكات السيراميك بنجاح كما تم تصغير حجم مسام الأغشية. بجانب ذلك، فإن أغشية سيليكات السيراميك الصناعية تتمتع بقدرتها على إزالة ثاني أكسيد الكربون من الغاز الحيوي على الرغم من أن نسبة نفوذيتها ضئيلة.

APPROVAL PAGE

I certify that I have supervised and read this study and that in my opinion, it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a thesis for the degree of Master of Science (Materials Engineering).

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DECLARATION

I hereby declare that this thesis is the result of my own investigations, except where otherwise stated. I also declare that it has not been previously or concurrently submitted as a whole for any other degrees at IIUM or other institutions.

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Signature:

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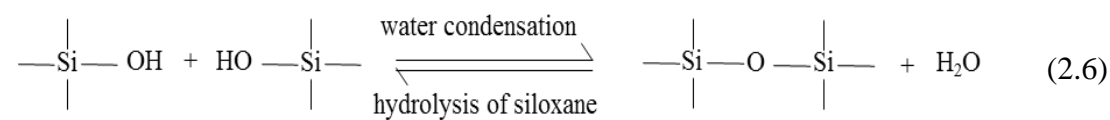
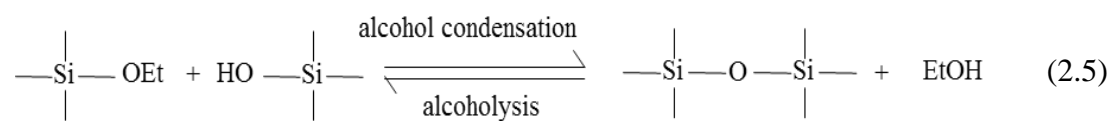
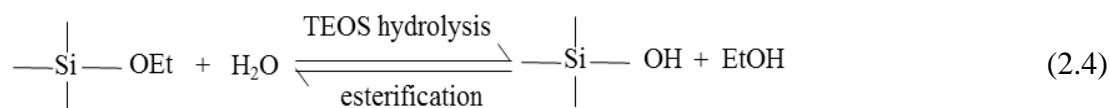
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LIST OF EQUATION



LIST OF ABBREVIATIONS

AD	Anaerobic Digestion
BET	Brunauer-Emmet-Teller
BJH	Barret-Joyner-Halenda
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transfer Infrared Spectroscopy
GHG	Green House Gas
H ₂ O	Water
HRTEM	High Resolution Transmission Microscopy
ICDD	International Centre of Diffraction Data
MMM	Mixed matrix membrane
SAD	Selected Area Diffraction
TEM	Transmission Electron Microscopy
TEOS	Tetraethyl orthosilicate
XRD	X-Ray Diffraction

LIST OF SYMBOLS

%	Percentage
°	Degree
°C	Degree Celcius
Å	Amstrong
α	Alpha
μm	Micron / micrometer
mm	Millimeter
θ	Theta
<	Less than
nm	Nanometer

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND OF THE STUDY

Biogas is a renewable energy source similar to wind and solar energies. Biogas is a carbon neutral fuel formed from anaerobic digestion (AD) which is one of the most competent techniques to store energy (Chen et al., 2015). Biogas is considered as renewable fuel since it is produced from organic waste. Frequently, biogas is transformed into electrical energy by gas engines with an efficiency of around 40%. Upgrading of biogas to natural gas quality increase the efficiency of energy conversion to levels near 100%, which can be performed through various methods. Upgraded biogas, which called biomethane, can be applied as vehicle fuel or injected into the gas grid. Vehicle fuel from biomethane is the purest possible fuels, because it barely contains any carbon dioxide emissions and very small amount of local pollutants (Lems et al., 2008).

Typically, biogas contains 55-60% of methane, CH_4 , and 38-40% of carbon dioxide, CO_2 (Chen et al., 2015). CO_2 plays a crucial role in global warming, where it is one of the most essential contemporary environmental issues. So, it is necessary to search for technology or method to minimize the emission of CO_2 into the atmosphere (Meisen & Shuai, 1997). Aside from CO_2 , CH_4 also responsible for climate change, or global warming. Moreover, CH_4 is a powerful greenhouse gas, which is 35 times more powerful than CO_2 as global warming potential. The only practicable way to reduce the volume of waste gases without restraining oil production is to increase electrical power generation efficiency and reduce flaring by exploiting the opportunities of gas conversion (Abedini & Nezhadmoghadam, 2010).

The existence of CO₂ and other acidic gases dilute the calorific value of biogas, which make the gas streams become acidic and corrosive. This reduces the potentials of gas compression and the transport within the transportation systems. Pipeline specifications for natural gas usually require CO₂ concentrations below 2% (Othman et al., 2009). One major phase to treat the various gas streams is to eliminate acid gas such as CO₂, H₂S and SO₂ before it is compressed and delivered. The separation of CO₂ from CH₄ is important in many industrial processes such as natural gas sweetening (for example, CO₂ removal from high pressure CH₄ in natural gas wells), biogas upgrading, oil recovery enhancement and landfill gas purification (Yang et al., 2008). Besides, highly concentrated CO₂ can also be generated from such separation process rather than direct release into the atmosphere which causing the mitigation of greenhouse gas emissions. The pure or highly concentrated CO₂ captured is pumped and stored deep underground, which help in treating the greenhouse gas emissions (Yang et al., 2008; Figueroa et al., 2008). Hence, economic and effective methods for the removal of CO₂ from CH₄ have attracted great interest (Zhang et al., 2013). Currently, there are three categories of gas separation that have been exploited, which are sorbents/solvents, cryogenic distillation and membrane separation as illustrated is Figure 1.1. Membrane separation methods have several benefits over other CO₂ separation technologies. For example, it required very simple process equipment, relatively easy to operate and control, compact, clear process and easy to scale up (Songolzadeh et al., 2014).

Gas separation via membrane technology lets one component to pass through faster than the others in a gas stream. There are many types of membranes, such as polymeric membranes, porous inorganic membranes, palladium membranes and

zeolites. Membranes usually unable to attain separation at high degree, so multiple stages and/or recycle of one of the streams is required. This resulting in increasing in complexity, cost and energy consumption. Some membranes with different characteristics might be essential for the separation of high-purity CO₂. Development of solvent assisted membranes is currently being established in order to combine the greatest features of membranes and solvent scrubbing. A lot of improvement is necessary before membranes could be applied on a large scale to capture in power stations.

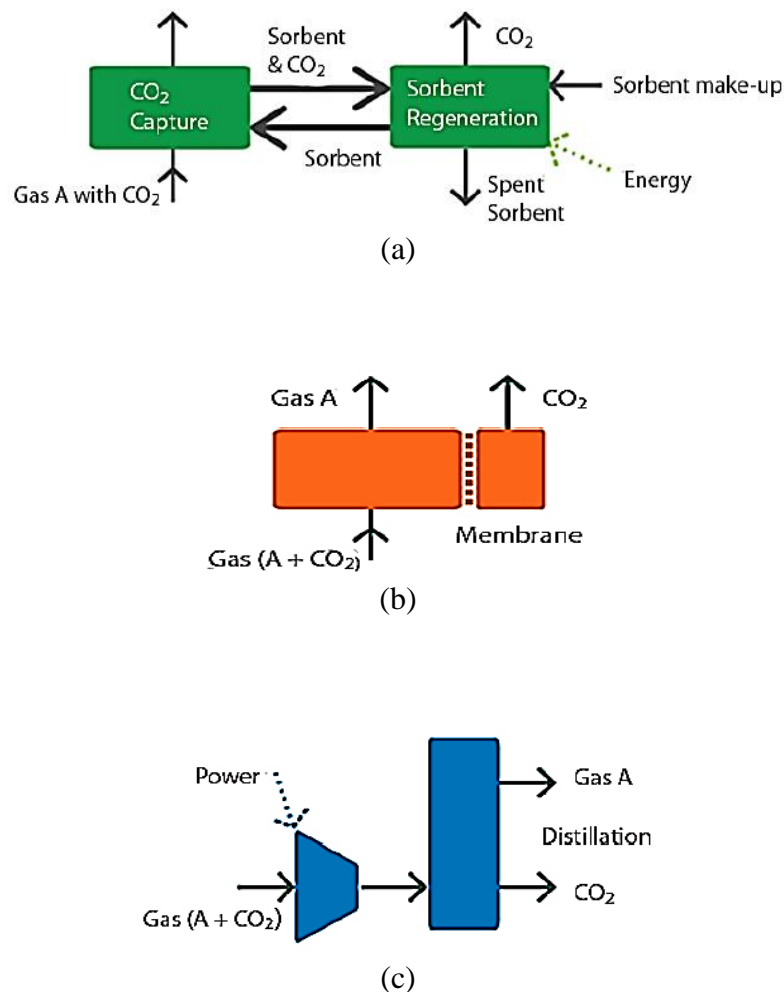


Figure 1.1 Schematic representation of three basic types of gas separation; (a) separation with sorbents/solvents, (b) separation with membranes and (c) separation by cryogenic distillation (<https://www.co2captureproject.org>)

There are various types of membranes that are available for separation of CO₂ from CH₄. Based on the materials used, membranes can be categorized into three major groups, which are polymeric, inorganic and mixed matrix membranes (Vrbová & Ciahotny, 2017). Inorganic membranes are convenient for separation of CO₂ under severe condition such as at high temperature and pressure, where organic based membrane are not functional. Inorganic membranes can be categorized into porous and non-porous types. Porous membranes are characterized by high permeabilities and low selectivities (Ismail et al., 2015). Carbon-based membranes for gas separations are normally fabricated via the pyrolysis of thermosetting polymers. Carbon membranes are highly selective because of the molecular dimensions of pores. Alumina use in the gas separation mainly as support, where the structural properties, and chemical and hydrothermal stabilities beyond 1000 °C, which make it very desirable. A few studies have been made to modify alumina membranes in order to facilitate CO₂ surface diffusion with limited success. Compared to alumina, which have a tendency undergo phase transition at relatively low temperature, or carbon, which can exhibit extensive pore size changes in oxidizing environments, silica shows extraordinary chemical, thermal, and structural stability in both reducing and oxidizing environments (Li, 2007; Yang et al., 2008).

Therefore, in this work, silica ceramic membranes are developed via sol-gel dip-coating method, in order to overcome the aforementioned weaknesses. The difficulties of CO₂ separation from CH₄ have been addressed through the design of a novel silica ceramic membrane separation to improve the ideal separation factor and diffusion characteristics. The aims of this study are that the fabrication silica ceramic membrane via sol-gel dip-coating technique reduce the pore size of the membranes to

nanometer scale without pinholes or crack, and provide good gas permeability for the removal of CO₂ in biogas.

1.2 STATEMENT OF THE PROBLEM

Environmental concerns because of the pollutant emission which caused by the combustion of fossil fuels have assumed as worldwide proportion. The use of fossil fuels for electricity generation contributes to several environmental issues all over the world (Olajire, 2010). Hence, there is essential for development of a sustainable and renewable energy sources in order to live up to the increasing in energy demand. In the long term perspective, it has become an obligation to think for renewable energy sources. Novel methods are being established for effective and proper consumption of renewable energy. Removal of CO₂ is necessary to increase the calorific value of biogas (Kalambe et al., 2012). Some techniques already exist for separation of CO₂, such as cryogenic distillation, absorption and adsorption. However, these method encountered some drawbacks. For example, absorption of CO₂ through amine based solvent remains the leading method in large scale industrial process but costly (Nwogu et al., 2015). A membrane technique for separation of CH₄ and CO₂ is employed in order to enhance the performance of biogas plant. The membrane gas separation process intentions is to upgrade the biogas in order to substitute natural gas, by using low pressure and distributing the substitute natural gas in the natural gas network. A stream rich in CO₂ is the by-product of the membrane gas separation methods, where it could be liquefied to generate very pure, industrial CO₂ (Norrdahl & du Preez, 2007; Kalambe et al., 2012). The residual biogas components that are left after liquefaction, which include CH₄, are recycled into the membrane gas separation

process, thus reducing the biogas loss. Both CO₂ and CH₄ gases have extraordinary industrial value. Biomethane has been utilized as a vehicle fuel substitute, and also can be used in electricity generation. CO₂ can be used as a greenhouse gas and in supercritical fluid application, carbonated drinks and ice making industries (Baker, 2006; Kalambe et al., 2012). Therefore, the development of membrane separation systems for CO₂ from CH₄ requires energy-saving, low operating pressure and cost as well high chemical resistance performance.

Five decades ago, membrane technique was applied for natural gas processing and desalination purposes (Lu et al., 2007; Adewole et al., 2013; Kajama et al. 2016). The separation of gas mixtures is a mutual and important unit operation in chemical industries, especially for natural gas processing plants. Since 1979, polymeric membranes have been commercially used for separation of acid gases such as CO₂ and H₂S from natural gas (Othman, Mukhtar, & Ahmad, 2004). Polymeric membranes exhibit several benefits, such as cheap, good quality control, simple production and high stability when operating at high pressure condition (Lu et al., 2007; Vrbová & Ciahotny, 2017). However, polymeric membranes efficiency decreased with time due to compaction, chemical degradation, fouling, and thermal instability. Due to restricted thermal stability and susceptibility to abrasion and chemical attack, polymeric membranes have found application in separation methods where hot reactive gases are encountered. This leads to a change of interest toward inorganic membranes (Abedini & Nezhadmoghadam, 2010). Ceramics and metals are examples of inorganic membrane materials that are still in research stages. In the past years, the well-organized preparation of ceramic membranes have received considerable attention because the occurrence of pinhole defects on the membranes could reduce the selectivity and integrity of the subsequence skin layer (Zhu et al., 2011). Hence, it

is very important to take these factors into account throughout the fabrication of membranes in order to avoid any existence of the defects to transfer into the separation layer (Kajama et al., 2014).

Current ceramic membranes are not appropriate for most gas separation applications. This is because their pore sizes are at least one order of-magnitude bigger than the gas molecular size. Hence, the ceramic membrane needs to be fabricated with silica, as silica could generate uniform, mono-dispersed pore size. Besides, silica also responsible for its large surface area and high pore volume. Therefore, silica is a promising contestant for the ceramic membrane that is likely allows high separation efficiency and selectivity. As for this reason, an approach has been employed in order to fabricate ceramic membranes or porous ceramic support with silica. Thus, the selection of silica ceramic membranes is regarded as promising candidates for removal CO₂ applications is proposed. There are a fundamental physical and chemical properties involved in the deposition of colloidal silica dispersions (sols) on porous supports for precise pore size and porosity control.

In this respect, preparation of novel silica ceramic membrane via sol dip-coating method is introduced since this method is known to have a high surface area and porosity as well homogenous pore size and as well to attain a defect-free nanoporous membrane. Fabricated silica ceramic membrane can be used effectively in order to remove CO₂ from the biogas system. This is because silica ceramic membrane is a highly permeable membrane material, it is possible to effectively remove CO₂ from biogas even at relatively low feed pressures. Besides, when pore walls of membrane supports were chemically modified using silica, it have the ability to attracts CO₂ toward to the wall of the membranes (Kajama et al., 2016), which increase the potential of CO₂ permeation even when the pore size is not small enough.