Removal Carbon Dioxide from Natural Gas Stream by using Ceramic Membrane

by

Muhd Rusydi b Abd Malek

Dissertation submitted in partial fulfillment of

the requirement for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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January 2009

CERTIFICATION OF ORIGINALITY

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

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MUHD RUSYDI B ABD MALEK

ABSTRACT

Porous Silica membrane in particular has some advantages which are high stability in thermal, mechanical and chemical. The pores size of the silica membrane is desirably controlled using sol gel method. Because of this advantage, it's suitable for gas separation at high temperature where membrane separation is highly desired from the view point of energy conservation in many chemical processes and also suitable for separating gas mixture through molecular sieving mechanism.

This research project consists of two experiments; Preparation of α-Alumina Substrate and Preparation of Silica Membrane using sol gel method. For the first experiment the goal is to achieve 25 – 30% porosity of the substrate. There are two parameter that will be manipulated; addition of starch and sawdust into substrate. The results show addition of these two parameters will increase the porosity of the substrate which the maximum porosity is 22%.

For the second experiment, nitric acid is used as a catalyst for silica sol preparation because of its low branched cluster that will result a narrower pore size. This experiment is divided into 3 part based on its dipping time; 1 hour, 2 hour and 3 hours. The results show the maximum separation factor of CO_2/CH_4; for 1 hour dipping time, the separation factor is 1.194, 2 hours (1.240) and for 3 hours (1.370).

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CHAPTER 1

INTRODUCTION

1.1 Background

Removing carbon dioxide is the most demanding application in a gas treating. Removing carbon dioxide from other gases present in natural gas, flue or synthesis gas, in conjunction with a suitable means of storing in the carbon dioxide could allow the utilization of abundant fossil fuel reserves with significantly decrease emissions of carbon dioxide to the atmosphere. Carbon dioxide which falls into the category of acid gases is commonly found in natural gas. Why must we need to remove carbon dioxide? It is because combination carbon dioxide with water can makes highly corrosive and rapidly detroys in pipelines and equipment. It is also can reduce heating value of natural gas stream and waste pipeline capacity. In LNG plants, carbon dioxide need to be remove to prevent frezzing low temperature chillers. The presence of carbon dioxide, hydrogen sulphide and free water can cause severe corrosion problems in oil and gas pipelines. Internal corrosion in wells and pipelines is influenced by temperature, CO_2 and H_2S content, water chemistry, flow velocity, oil or water wetting and composition and surface condition of the steel. A small change in one of these parameters can change the corrosion rate considerably, due to changes in the properties of the thin layer of corrosion products that accumulates on the steel surface.

Nowadays there are so many technologies available for removing carbon dioxide such as cryogenic process, adsorption process (pressure swing adsorption, PSA and thermal swing adsorption, TSA) and also membranes. Membrane separation of carbon dioxide from other gas is an active field, but the best membranes today are likely too energy intensive and expansive to be implemented on large scale [1]. Gas separation in membranes is driven by a pressure difference on either side of membrane. Decreasing the required pressure difference by increasing the permeability of the membrane would reduce energy costs and required membrane area.

1.2 Problem Statement

Currently there is several methods use for removing carbon dioxide from natural gas, flue gas or synthesis gas. The methods are adsorption, absorption, hybrid solution and also membrane technology. Practically in industry use amine adsorption as an absorbent for removing carbon dioxide which is categorized under acidic gas group. However, the cost of acid gases removal by using the mixed amines system is highly expensive. Besides, the disposal of waste amine to Kualiti Alam also required a lot of money to pay for it. One way to reduce the cost of amine is by replacing amine adsorption with other method which is more economical and easy to optimize. In this research project, one method has been chose as case study to replace amine adsorption and this method is called membrane technology. Membrane technology is known as an effectively method for gas separation. Membrane technology has two mechanisms available for gas separation; Knudsen Diffusion and Molecular Sieving (Physical Separation) [2].

1.3 Objectives and scope of study

The objectives of this research project are:

- To prepare porous silica layer on a porous alumina substrate by using sol gel method.
- To study the permeability of carbon dioxide and methane on synthesis silica membrane.

The scopes of study for this research project are:

- To do literature review of membrane separation technique – CO_2/CH_4 gas stream.
- To apply appropriate methodology in conducting the experiment to produce good results and findings – Temperature and Pressure.

CHAPTER 2

LITERATURE REVIEW / THEORY

2.1 Principle of Membrane

According to Warren L. McCabe (2005), many processes for separation of gaseous or liquid mixtures use semi permeable membranes that allow one or more constituents of the mixture to pass through more readily than others. A membrane is defined as a thin layer of material which separates two phases and controls the movement of solutes across it in a specific manner. It also can be define as a selective barrier that permits the separation of certain species in a fluid by combination of sieving and sorption diffusion mechanism. Systems that membrane can work are:

- Liquid-solid
- Liquid-liquid
- Solid- gas
- Gas-gas

2.1.1 Membrane Structure - Selective Layer

Membrane can be classified into three; porous membranes classify according to size particles or molecules, non-porous membranes classify according to chemical affinities between components and membrane materials and also carrier membrane classify according to carrier transport [24].

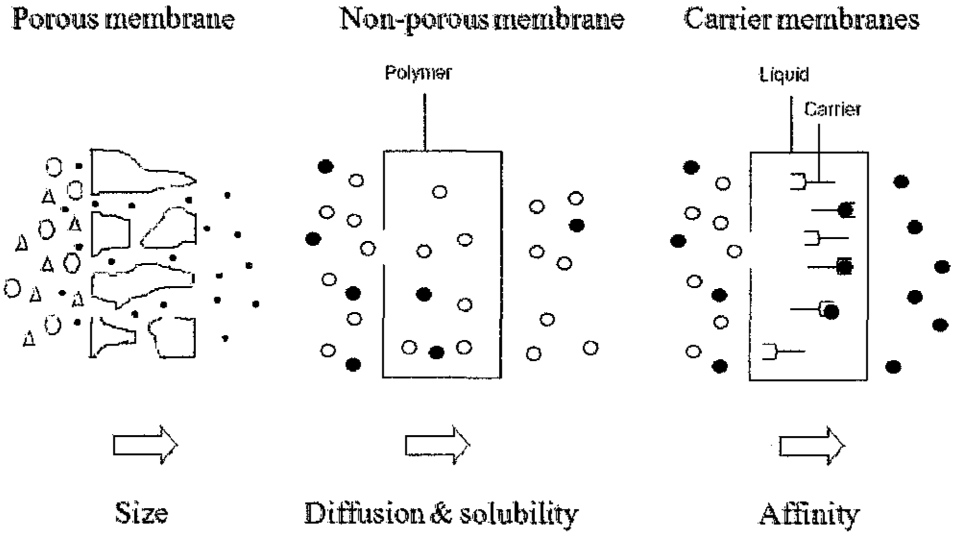


Figure 2.1: Membrane Structure

In porous membranes the selectivity is mainly decided due to the size of the pores. These types of membranes are used in microfiltration and in ultrafiltration. As stated by Hartmut Bruschk (1995) a gradient in hydraulic pressure acts as the driving force. Small molecules of the solvent of a solution, usually water, can pass through the pores, whereas particles or large molecules are retained.

The non-porous membranes are normally used in gas separation and pervaporation. In these membranes the molecules first dissolves into the membrane and then diffuse through it. The separation is based on how well different compounds dissolve and diffuse through the membrane. Some molecules diffuse fast and others diffuse slowly. Example of non-porous membrane is polymeric membrane such as polysulfone and polycarbonate.

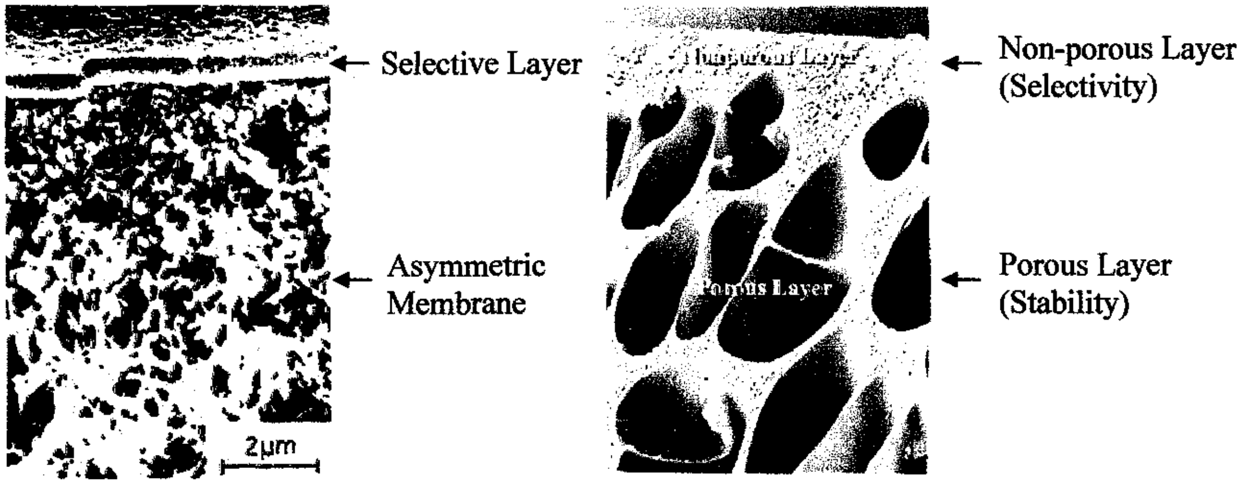
In the carrier transport membranes a specific carrier molecule facilitates the transport of a specific molecule though the membrane. This kind of transport occurs for example in the lipid bilayer of a cell. The carrier mediated transport is very selective and can be used to remove components like gases, liquids and ionic or non-ionic components.

2.1.2 Typical Membrane Structure for Gas Separation

Membrane materials are usually made as thin as possible to increase the permeability, which is the ability of a chemical to pass through a material. This makes the membrane very fragile.

To overcome this problem the membranes are made with an asymmetric structure where the thin selective nonporous layer is grafted on a thicker porous layer of the same material [25]. This porous layer provides the stability and allows a free flow of the compounds that permeate through the selective layer. The disadvantage of this membrane structure is that as they are made of only one type of material, which is normally very expensive. This problem is solved by making a composite membrane. This consists of a thin selective layer made from one type of polymer, which is on top of another asymmetric membrane composed of another polymer.

These types of composite membranes are being used in most of the newer advanced CO_2 removal membranes as the selective layer can be adjusted without increasing the membrane cost too much.



(a) (b)

Figure 2.2: (a) Composite Membrane Structure (b) Asymmetric Membrane Structure

2.2 Material Selection of the Membrane

In principle all types of materials can be used as membranes. However, the selection of a type of material is dependent on the cost, on the separation task, the desired structure of the membrane and the operating conditions under which it has to perform. Membrane materials are normally divided into biological, and synthetic. A biological membrane or bio membrane is an enclosing or separating *amphipathic* layer that acts as a barrier within or around a cell. It is almost invariably, a lipid bilayer, composed of a double layer of lipid molecules and proteins that may constitute close to 50% of membrane content. [26] Example for biological membrane is cell membrane and mucous membrane. Synthetic membrane also known as artificial membrane is a syntheticly created membrane which is usually intended for separation purpose in laboratory or in industry. Synthetic membranes have been successfully used for small and large scale industrial processes. It can be produced from organic materials such as polymers and liquids as well as inorganic materials. The most of commercially utilized synthetic membrane in separation industry are made of polymeric structure.

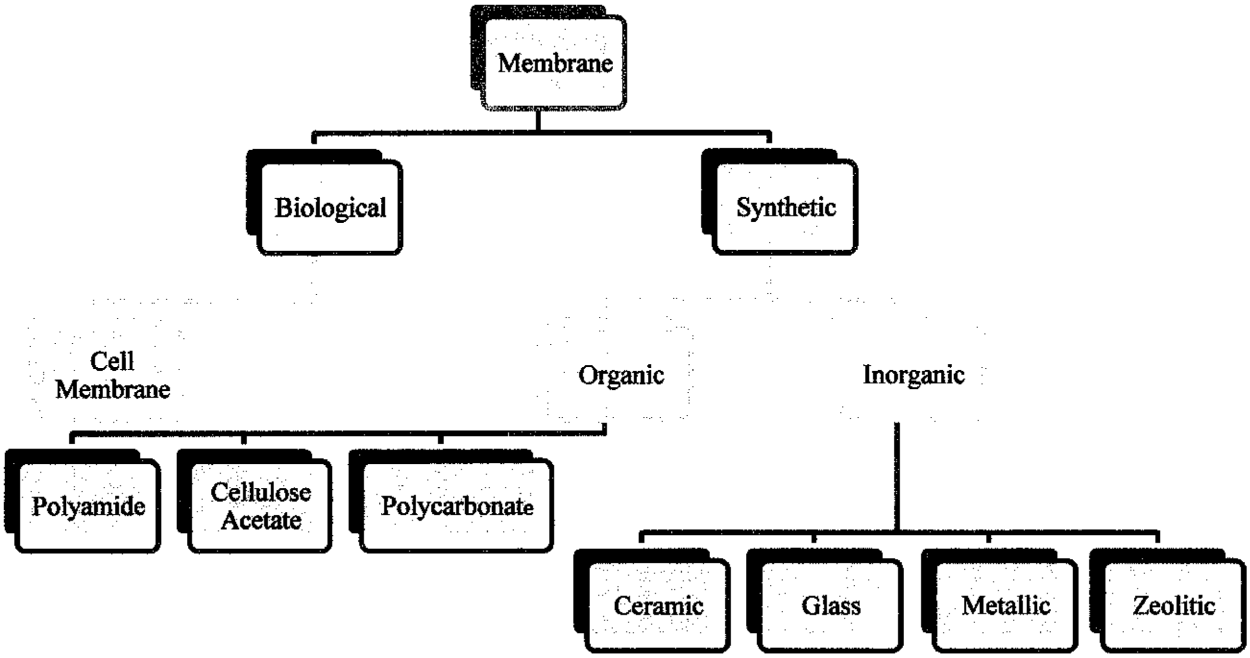


Figure 2.3: Type of Membrane

2.2.1 Organic Membrane

The most commonly used membrane materials. There are a large number of polymer materials available. Some of the advantages of polymers are flexibility, permeability and ability to be formed into a variety structures. On the other hand, polymers are generally not thermally stable, which can be a problem for many separation tasks. The polymer morphology and mobility determine the gas permeability and selectivity. **Figure 2.4** shows an asymmetric hollow fiber membrane. A thin layer of functional cardo polyimide material supported by a porous structure allows high permeability.

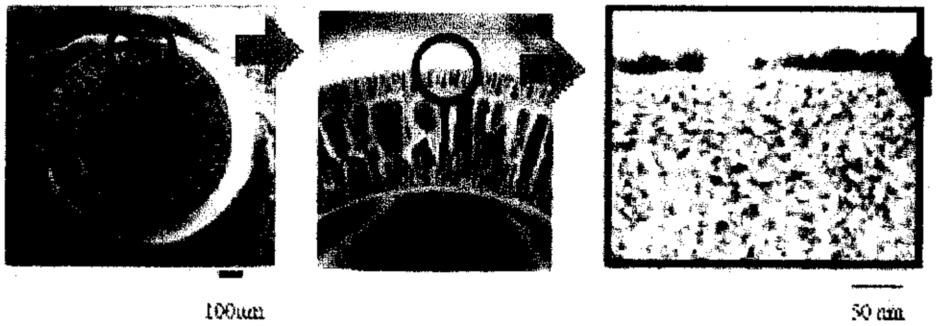


Figure 2.4: Cardo polyimide hollow fiber membrane with a thin, functional outer layer

2.2.2 Inorganic Membrane

Inorganic membranes are versatile. They can operate at elevated temperatures, with metal membranes stable at temperatures ranging from 500-800° C and with many ceramic membranes usable at over 1000° C. They are also much more resistant to chemical attack. Because of the wide variety of materials that may be used in the fabrication of our inorganic membranes, resistance to corrosive liquids and gases, even at elevated temperatures, can be realized. Inorganic membranes compete with organic membranes for commercial use. In many of the harsh operational environments listed above, organic membranes will not perform well, or will not survive at all. For these environments, only inorganic membranes offer needed solutions.

In this project the focus is only for inorganic membrane because of its physical properties and become demand for time being.

2.3 Separation Technique

There are three mechanisms that available for gas separation at high temperature which is Knudsen diffusion, Molecular Sieving and Solution Diffusion. Molecular Sieving is quite attractive use for gas separation but requires porous membrane less than several angstroms.

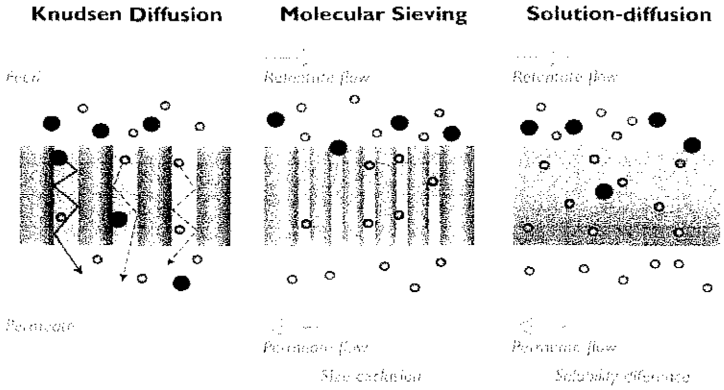


Figure 2.5: Mechanism of Membrane

2.3.1 Knudsen Diffusion

Knudsen mode of gas transport is important when the mean free path of the gas molecules is much greater than the pore size of the membrane [3]. I such situation the collisions of the molecules with the pore wall are more frequent than the collisions among molecules. This mechanism is often predominant in macroporous and mesoporous membrane [4] and described by Knudsen Equation for diffusive flow of molecules in a capillary tube in this regime:

$$J_k = -D_k \frac{dC}{dz} \tag{2.1a}$$

or

$$J_k = -\frac{D_k}{RT}\left(\frac{dp}{dz}\right) \tag{2.1b}$$

Where D_k is the Knudsen diffusion coefficient

J_k is Knudsen diffusive flow

It is dependent on the mean molecular speed, u and pore radius, r_p and is given by:

$$D_k = \frac{2}{3} u r_p \tag{2.2}$$

An expression for the mean molecular speed can be obtained from the kinetic theory of gas [5,6]:

$$u = \sqrt{\frac{8RT}{\pi M}} \tag{2.3}$$

where R and T are the gas constant and temperature respectively and M is the molecular weight of the gaseous species, in $g.mol^{-1}$. Substituting equation (2.2) and (2.3) into equation (2.1b) and then integrating, the permeation rate based on the Knudsen diffusion mechanism can be obtained for a single capillary tube:

$$n_k = \left(\frac{32\pi}{9MRT} \right)^{1/2} r_p^3 \frac{p_h - p_h}{l} \tag{2.4}$$

where n_k is the permeation rate define as:

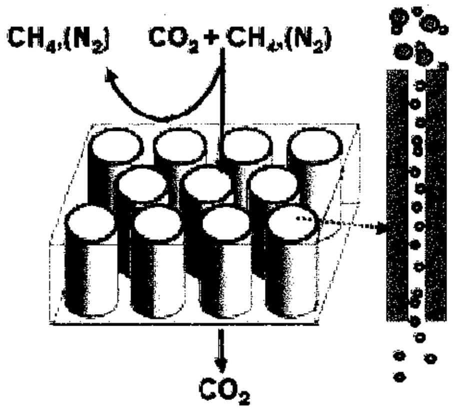
$$n_k = \pi r_p^2 J_k \tag{2.5}$$

In this research project, molecular sieving (physical separation) technique will be use a membrane mechanism. Molecular sieving mechanism mean the separation will occurs based on kinetic diameter of each atom or molecule where the atom or molecule will pass through (permeate) the porous membrane if its kinetic diameter size is less than pore size of the membrane. The table below show kinetic diameter of molecules [1]

Table 2.1: Kinetic Diameter of molecule in Angstrom

Molecule	Diameter, Angstrom
CH_4	3.8
CO_2	3.3
N_2	3.6
H_2O	2.7
H_2S	3.6

The figure below show how separation occurs based on size of molecule. In this case separation is in between nitrogen and carbon dioxide in flue gas. Both gases will release in the membrane and the result show carbon dioxide gas will permeate through membrane. The question is what type of membrane that will be use for this situation that have a pore size in between of size nitrogen and carbon dioxide so that nitrogen gas is trapped at membrane and carbon dioxide can permeate.



N_2 – 3.6 Angstrom

CO_2 – 3.3 Angstrom

CH_4 – 3.8 Angstrom

Figure 2.6: Porous inorganic membranes act as molecular sieves

2.4 Silica Membrane for Gas Separation

Microporous silica (SiO_2) membranes are representative of amorphous membranes. The first successful silica membranes for gas separation with good quality and high flux were prepared in 1989 using a sol gel method [7] where SiO_2, polymer sols were firstly prepared by acid catalysed hydrolysis of tetraethoxysilane (TEOS) in alcoholic solution. The acid catalyst reduces hydrolysis but enhances polycondensation rates during the sol preparation process resulting in a polymeric sol containing silica particles of fractal structure. Then the porous support is dipped in the SiO_2 gel solutions for some time followed by wiping to remove excess gel. Finally the deposited silica film is washed with distilled water, dried at 100-200^{0}C and calcined at around 450^{0}C. Such processes of dipping and heating are repeated several times so as to control the membrane thickness and compactness as well.

2.4.1 Sol Gel Process

The advantage of the sol gel technique is that the pore size of the membrane can be desirably controlled, especially for small pores. As shown in **Figure 2.7**, there are two (2) main routes through which the sol gel membrane is prepared [28]

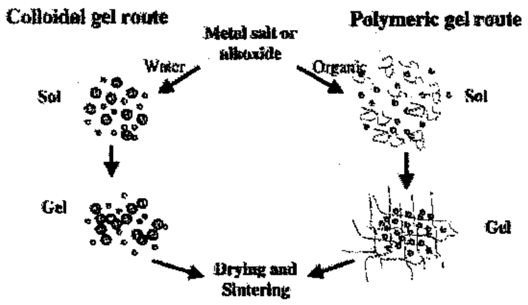


Figure 2.7: Sol Gel Method

1. The colloidal in which a metal salt is mixed with water to form a sol. The sol is coated on a membrane support, where it forms a colloidal gel.
2. The polymer route in which metal-organic precursors are mixed with organic solvent to form a sol, which is the coated on a membrane support, where it forms a polymer gel.

Colloidal sol is the colloidal solution of dense oxide particles such as Al_2O_3, SiO_2, TiO_2 or ZrO_2. As the pore sizes of these membranes are in the ultrafiltration range, they have been used in separation of colloidal particles and large molecular weight solutes or have been used as membrane support where smaller pore size membrane can be further developed.

For gas separation based on molecular sieving effects, the membrane with pore sizes less than 1nm must be employed. In this case the membrane can be prepared through the polymer sol route using the alumina membrane prepared from the above colloidal sol as a support.

It should be noted that in the polymer sol route the pore size of the membrane prepared is determined by the degree of branching of the inorganic polymer as shown in **Figure 2.8**. As can be seen a low degree of branching would result in a narrower pore system. Polymeric sols of SiO_2 with low branched cluster have been prepared using acidic hydrolysis with the corresponding Si alkoxides [8]. These sol gel membranes show high selectivities in gas separation [9].

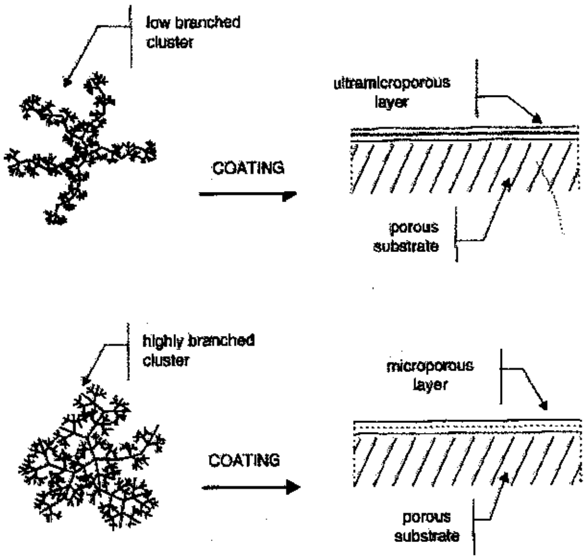


Figure 2.8: Influence of the branching of the polymer sol on the porosity; low branch cluster form narrower pore system than highly branched cluster.

2.5 Silica Membrane for Gas Separation

2.5.1 Separation of inorganic/organic gas mixtures by porous silica membranes [10]

The sol–gel procedures were applied to fabricate porous silica membranes coated on cylindrical porous α-alumina tubes by the hot coating methods. The pore diameters of the silica membranes were determined by the gas permeation methods to be less than 0.4 nm. The active layer thickness was about 1 μm, giving a large hydrogen permeance of around 3×10^{-5} m3 m^{-2} s^{-1} kPa^{-1} (1.3×10^{-6} mol m^{-2} s^{-1} Pa^{-1}) at 300°C. The permeance of H_2 and He were slightly dependent on temperature, while the observed CO_2 permeance showed a large temperature dependency. As the CO_2 permeance increases at a lower temperature, CO_2 removal from organic gas mixtures can be preferably performed at a lower temperature near the room temperature. An example of observed CO_2 permeance at 35°C was approximately 2×10^{-5} m3 m^{-2} s^{-1} kPa^{-1} (0.9×10^{-6} mol m^{-2} s^{-1} Pa^{-1}). **The permeance ratio of CO_2/CH_4 was around 80–110 at 35–50°C and the ratio became smaller at higher temperature.** The porous silica membranes fabricated in this work were quite stable when used in dry conditions.

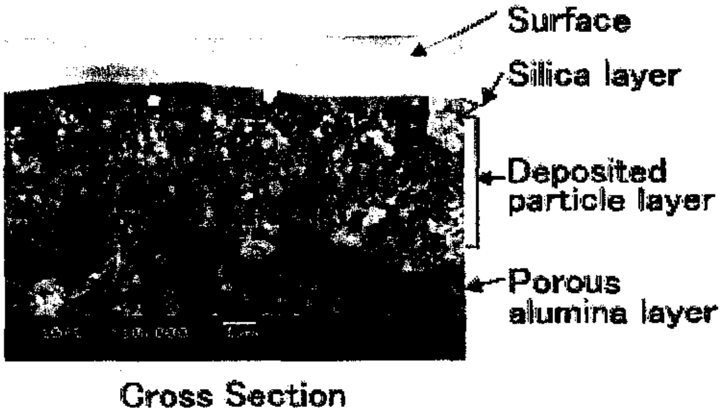


Figure 2.9: A SEM photo of cross-section of silica membrane fabricated.

2.5.2 Effect of additive of particle size on extruded porous Alumina[11]

The effect of additives and particle size on the porosity and pore size of sintered alumina (Al_2O_3) was studied in this research. Carboxymethyl Cellulose (CMC), Polyvinyl Alcohol (PVA) and Polyethylene Glycol (PEG) were used as additives by varying each of them for the content of 1.5, 3 and 6% by Al_2O_3 weight. The Al_2O_3 particle sizes were varied at 0.7 μm, 5 μm, the mixture of 0.7 μm (50 wt%) and 5 μm (50 wt%) and the mixture of 5 μm (50 wt%) and 58 μm (50 wt%). The mixture was then extruded, dried and sintered at 1300° C - 1500° C. The sintered samples were measured porosity and pore size. It was found that the amount water in raw material was a very important factor for body forming. The appropriate amount of water was 25%-30%. Particle size is the most important factor affecting porosity and pore size, sample prepared from the mixture of 5 μm (50 wt%), 58 μm (50 wt%) Al_2O_3, and CMC (6% by Al_2O_3 weight) resulted in the biggest pore size of 2.7 μm and60% porosity. The type and amount of additive affected the porosity of sintered Al_2O_3. Sample prepared from CMC resulted in higher porosity compared to sample prepared from PVA and PEG at the same amount.

2.5.3 Effects of starch addition on characteristics of porous ceramic membrane substrates[12]

As shown in **Figure 2.10**, the maximum pore size and mean pore size of substrates were clearly influenced by the corn starch addition. There was a significant increase in the maximum pore size and mean pore size with 15 wt% of corn starch addition. According to the preceding reports, the packing alumina particles in the green specimen would be disrupted by the larger starch particles. The disruption by each starch granule, including the wall effect and the contact effect, is limited to the first layer of alumina particles. When the starch content in the green specimen is low (e.g., less than 10 wt%), the isolated shells derived from the wall effect between alumina particles are in the majority within the microstructure of sintered specimen.

Presumably, this phenomenon will result in the nominal pore size close to the tubular ceramic substrate without starch addition. Meanwhile, a fewer interconnection between the isolated shells will result in a gradual increase on maximum pore size. However, as the starch content increase (e.g., more than 10 wt%), a greater number and degree of contacts among the individual shells will result in a larger nominal pore size and maximum pore size.

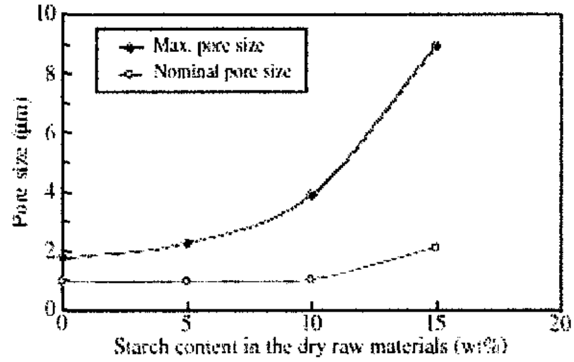


Figure 2.10: Effects of starch addition on maximum pores size and mean pore size of tubular ceramic substrate

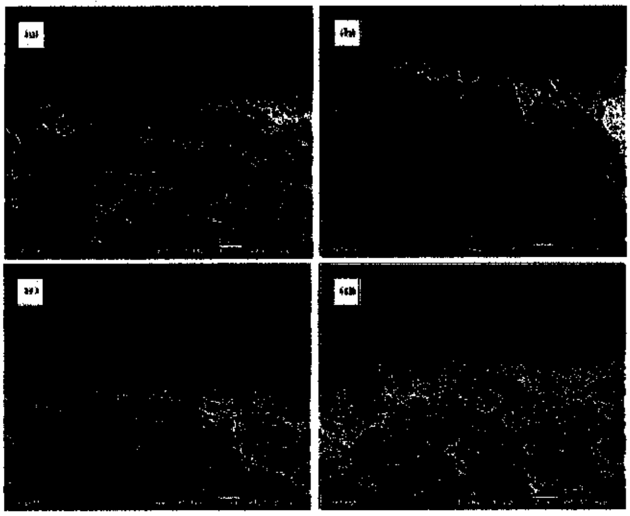
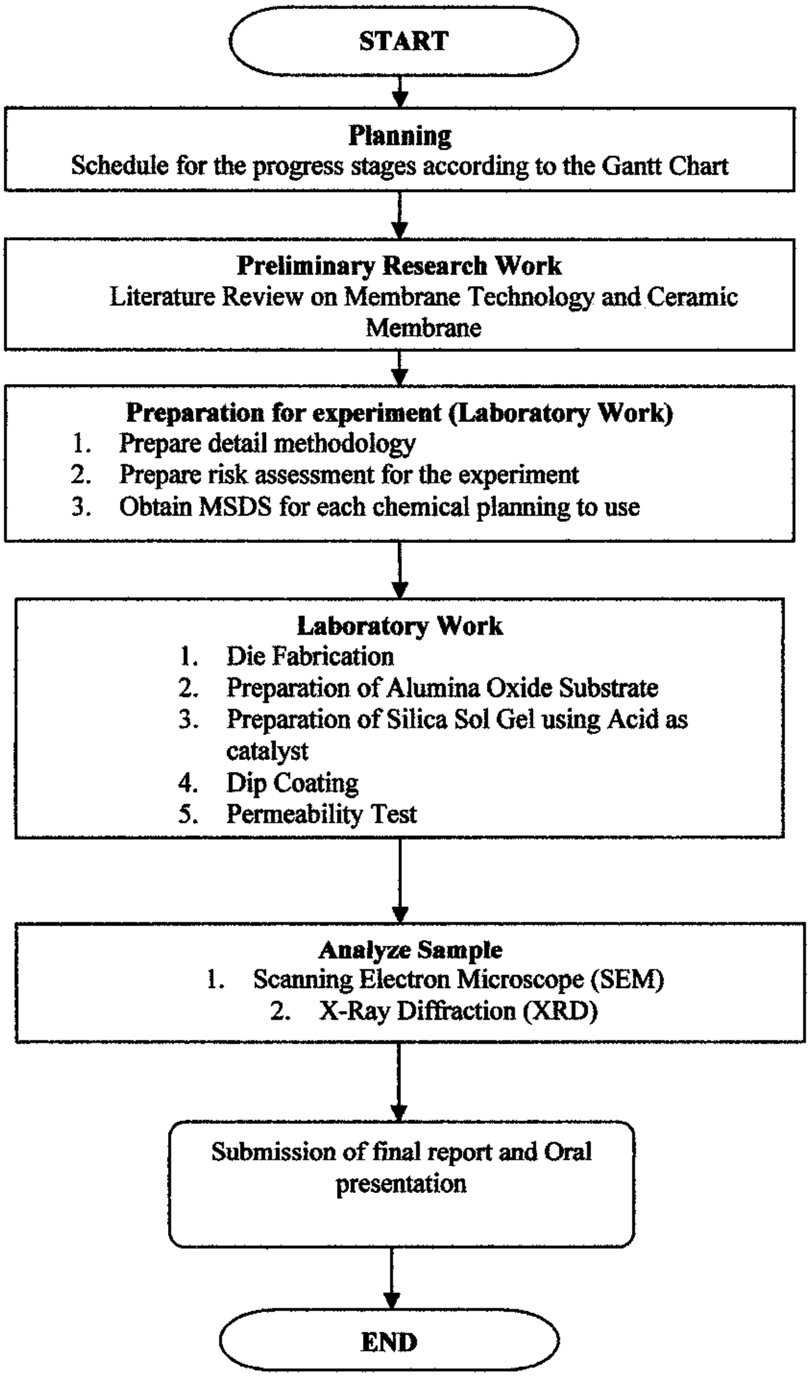


Figure 2.11: SEM image of the cross sections of the sintered tubular ceramic substrates with: (a) 0 wt% of starch; (b) 5 wt% of starch; (c) 10 wt% of starch; (d) 15 wt% of starch addition.

CHAPTER 3

METHODOLOGY & PROJECT WORK



3.1 Experimental Scope

For this Final Year Research Project, there are two main parts of the experiment that will conduct. The first part is preparation of α-Alumina Oxide Substrate followed by preparation of silica sol gel using acid as catalyst and dip coating method. The second part is permeability test followed by characterization of membrane by using Scanning Electron Microscopic (SEM) and X-Ray Diffraction (XRD).

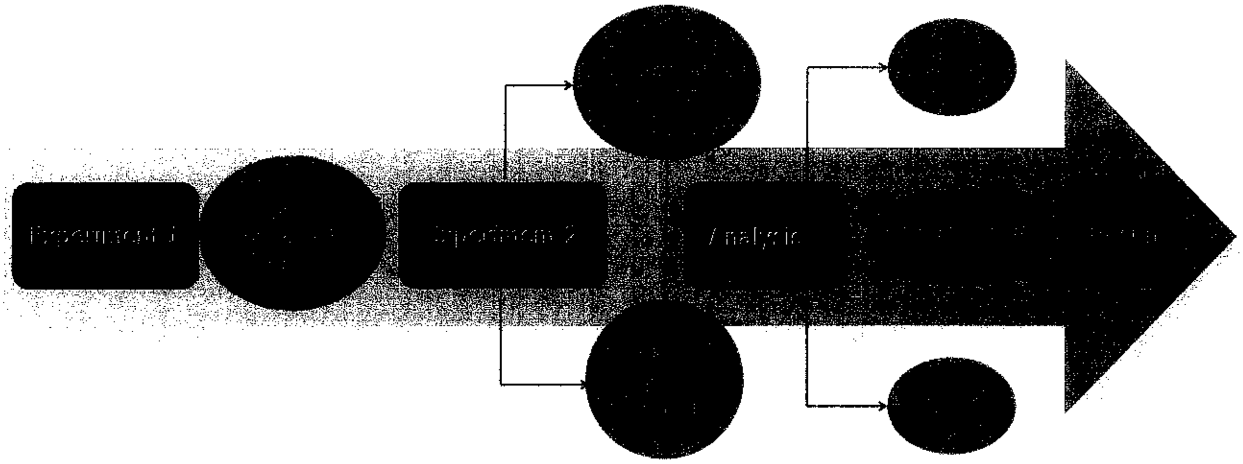


Figure 3.1: Methodology of the Experiments

3.2 Experiment Tools and Chemicals

The tools required for this project are:

- Die
- Hand Pressing
- Furnace (minimum temperature is 1400 ^{0}C) and Oven
- Permeability Test

The chemicals required for this project are:

- Alumina Oxide (Al_2O_3)
- Starch
- Nitric Acid (HNO_3)
- Tetra-ortho-silicate (TEOS)
- Ethanol (C_2H_5OH)

3.2.1 Die and Hand Pressing

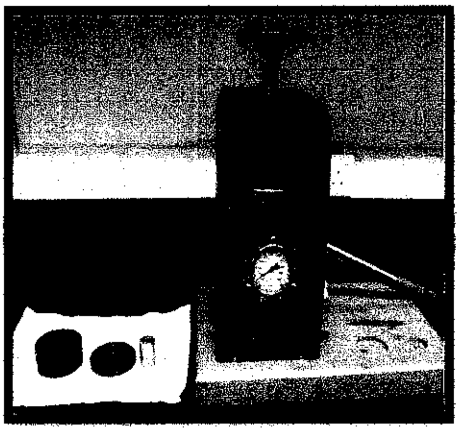


Figure 3.2: Die and Hand Pressing

Die is fabricated at R&R Tools Ipoh with inner diameters are 2.54 cm (1 inch) and 5 cm based on the diameter of permeability test. There are using manual hand pressing and the maximum press is 12 tonne.

3.2.2 Permeability Test Equipment

Gas permeation measurements were performed using pure CO_2 and pure CH_4 in Membrane Fabrication Unit (MFU) laboratory. The permeation experiment always begins with methane and ended with carbon dioxide. Feed side pressure was varied from 1 bar to 3 bar. The equipment set-up as illustrated in **Figure 3.8** was used to carry out the gas permeation measurement. The set-up consists of a feed gas tank, a pressure gauge of inlet gas, a dead-end membrane cell and a bubble soap flow meter. Membranes were located in the dead end membrane cell or module. This type of module allows the feed gas to flow into the membrane perpendicularly to the membrane position.

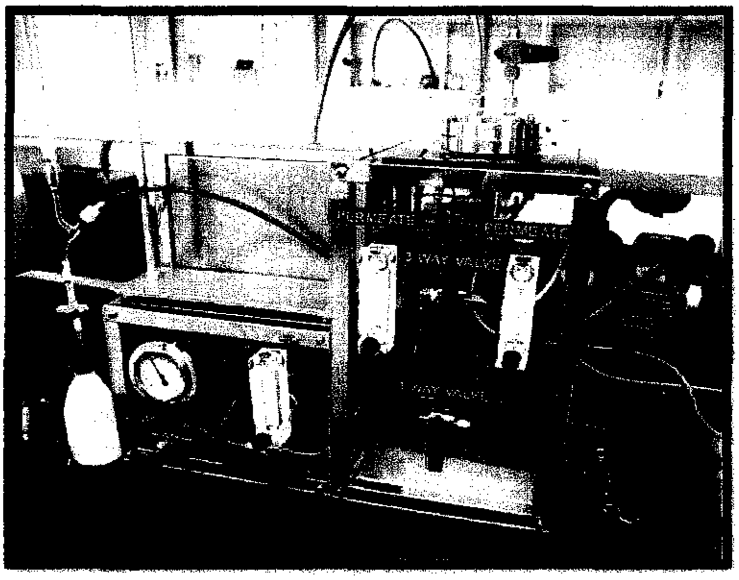


Figure 3.3: Permeability Test

3.3 Experimental Procedure

3.3.1 Preparation of α-Alumina Oxide Substrate

i) Experiment 1:

An experiment had been done for the preparation of α-Alumina Oxide substrate. The materials that use for the substrate are aluminum oxide, starch and distilled water. Starch is use as a binder replacing Polyvincyl alcohol (PVA), Carboxymethyl Cellulose (CMC) and Polyethylene Glycol (PEG) that is not available in lab.

Methodology:

1. 100 mL beaker was filled with distilled water and boiled it.
2. 15 gram of starch is adding into beaker with boiled water.
3. 5 gram of aluminum oxide was prepared on the glass plate
4. The dropper is used to mix solution of starch with alumina oxide and the no of starch drop is 5
5. Pour the powder solution into a die and press using hand pressing.
6. Step 4 and 5 will repeated with different no of starch drop; 15 and 25
7. Then disc of alumina was heated at temperature 1500^{0}C in the furnace for 3 hours.

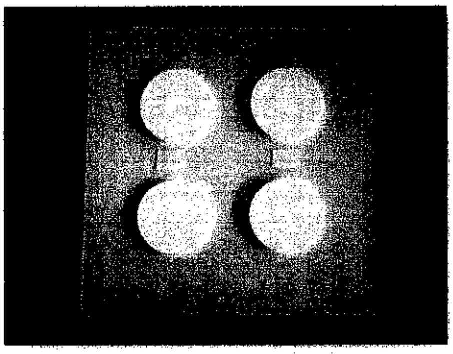


Figure 3.4: Alumina Oxide Substrate (disc)

ii) Experiment 2:

In this experiment sawdust is used to increase the percentage of porosity. Sawdust will burn after heating and it will make substrate more pores. The weights of alumina oxide also increase to 10 grams because of the diameter die is change from 2.54 cm to 5 cm.

Methodology:

1. 100 mL beaker was filled with distilled water and boiled it.
2. 15 gram of starch is adding into beaker with boiled water.
3. 10 gram of aluminum oxide was prepared on the glass plate
4. 10% of sawdust was mixed together with alumina oxide.
5. The dropper is used to mix solution of starch with alumina oxide and sawdust.
6. Pour the powder solution into a die and press using hand pressing.
7. Step 4 until step 6 was repeated with 20% of sawdust.
8. Then disc of alumina was heated at temperature 1500^{0}C in the furnace for 3 hours.

3.3.2 Determination porosity of Alumina Oxide Substrate

1. Readings of weight (gram) and diameter (cm) of alumina substrate on air.
2. Readings of weight of alumina substrate in water.
3. Readings of weight after the substrate was immersed in boiled water for 1 hour.

$$\%Porosity = \frac{Weight\ in\ Boiling\ Water\ for\, 1hr - Weight\ in\ air}{Weight\ in\ Boiling\ Water\ for\, 1hr - Weight\ in\ water} x100\%$$

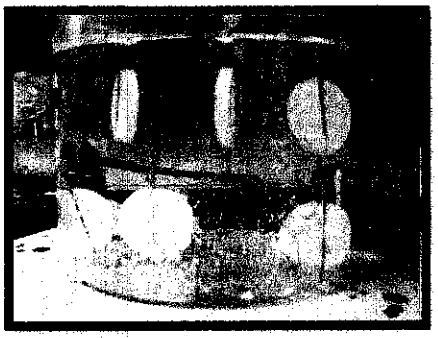


Figure 3.5: Porosity Calculation

3.3.3 Preparation of Silica Sol

1. The solution of silica sol was prepared by dissolving 10.63 mL TEOS , 53.15 Ethanol, 100 mL distilled water and 0.5 mL Nitric Acid as a catalyst
2. The solution was leave for 2 days before dip coating method.

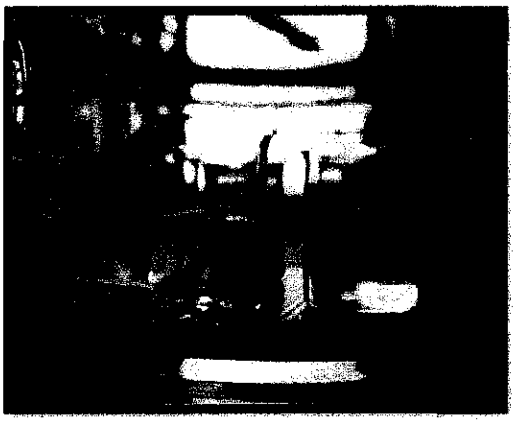


Figure 3.6: Silica Sol with Acid as Catalyst

3.3.4 Dip Coating Method

1. The substrate is fully immersed in silica sol for several times.
2. The substrate then dries in oven at 100 ^{0}C for 2 hours to remove water contain.
3. Final step is sintered the substrate in furnace at 500^{0}C for 4 hours.

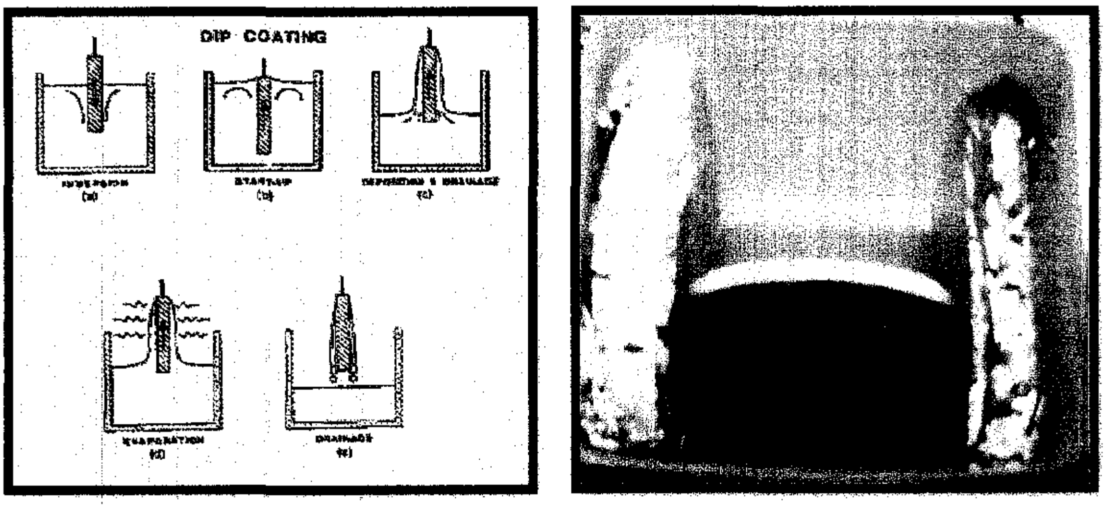


Figure 3.7: Dip Coating Method

3.3.5 Permeability Test

Before performing the experiment, the gas permeation test unit was evacuated to less than 0.1 bar by vacuum pump for 1 hour to remove all residual gases remaining in the equipment. The feed gas was supplied directly from the gas tank, which is equipped with a pressure regulator. The feed gas pressure was set up within range of test pressure and the permeate stream was assumed to be at atmospheric pressure. In this permeation experiment, time (t) required to reach certain volume of gas in the permeate stream was observed and recorded. In addition, the volume of gas in permeate stream was also measured using a bubble soap flow meter. The permeation of each gas through a membrane was measured twice at steady state condition.

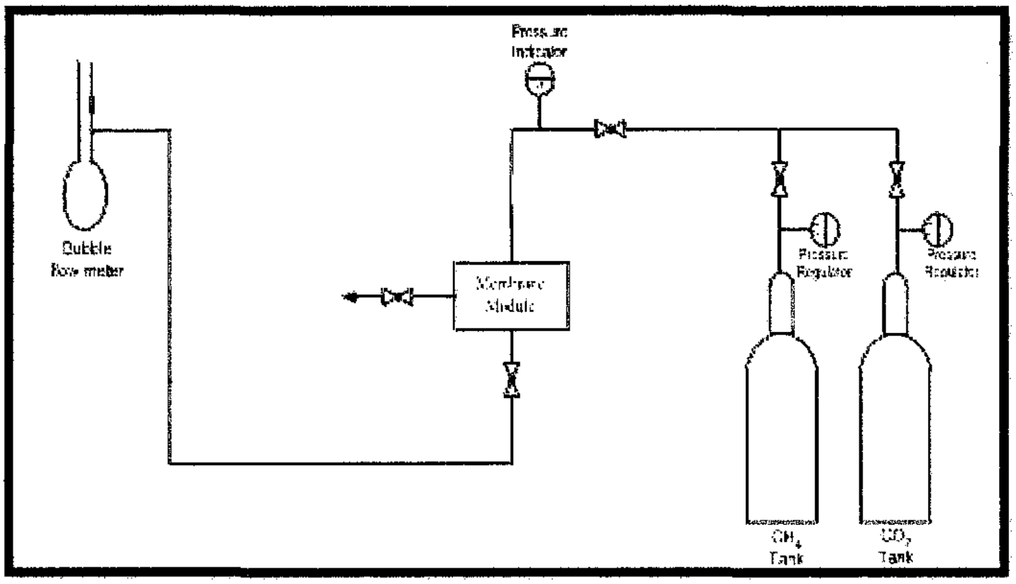


Figure 3.8: Schematic Diagram of Permeability Test

Gas Permeation

The method of gas permeation is very simple. It measures flow rates of a gas through a porous membrane at different operating pressures. Then the average pore size and effective surface porosity of the membrane can be obtained from measure data.

According to Tan et al. [13], total gas permeation rate through ceramics membrane can be written in a general flux equation in terms of **Poiseuille** flow **and Knudsen** flow in the porous medium as follow:

$$N_t = P_v A_p \frac{\Delta p}{L_p} + P_k A_p \frac{\Delta p}{L_p}$$

Where N_t = total permeation flow rate ($mol.s^{-1}$)

A_p = porous area on the membrane surface (m^2)

L_p = effective pore length (m)

P_v and P_k = permeability coefficient of gas transport according to Poiseuille flow&Knudsen flow mechanism ($mol.mm^{-2}.Pa^{-1}.s^{-1}$)

Δp = pressure difference across membrane (Pa)

As the effective pore length of the ceramic membranes is usually uknown value and cannot be determined using available methods, the total gas permeation rate through the membrane is usually expressed as:

$$N_t = \bar{P} A_t \Delta p$$

Where $\bar{P}$ is the gas permeance, in $mol.m^{-2}.Pa^{-1}.s^{-1}$ and A_t is total membrane permeation area in m^2

The CO_2/CH_4 ideal selectivity (unitless), α_{CO_2/CH_4}, of asymmetric membrane can be determined by dividing CO_2 permeance, over CH_4 permeance.

$$\alpha_{CO_2/CH_4} = \frac{\bar{P}_{CO_2}}{\bar{P}_{CH_4}}$$

3.4 Membrane Characterization

3.4.1 Scanning Electron Microscope (SEM)

Scanning electron microscopy was used to characterize the structure of surface and sub-layer of membrane. Images obtained from SEM shows detailed 3-dimensional at much higher magnifications than is possible with a light microscope. Magnification of images is created by electrons instead of light waves as in conventional light microscope, which uses a series of glass lenses to bend the light waves.

Membrane structure was determined by LEO SUPRA 50 VP FESEM. Samples were coated with gold using a sputter coater. After coating, membrane samples were observed using SEM with magnification range from 300 to 1500 X. Figure shows the SEM used in this research.

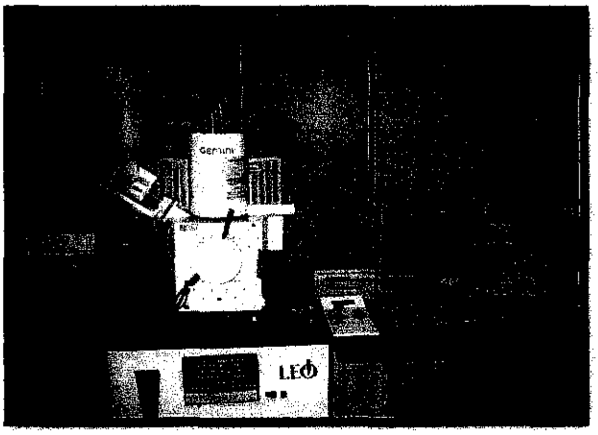


Figure 3.9 SEM for membrane structures observation.

CHAPTER 4

RESULT AND DISCUSSION

There are two parts of the experiment that had run for this Final Year Research Project. The first experiment is preparation of α-Alumina Oxide (Al_2O_3) substrate followed by determination of substrate porosity in percentage (%). The second experiment is preparation of silica sol gel using acid as a catalyst for dip coating method followed by permeability test for silica membrane with respect to the time different of dip coating. The time of dip coating for this experiment are 1 hour until 3 hours.

For the first experiment the objective is to achieve the target which is 25% to 30% of porosity. There are several parameters that will be manipulated to control the percentage of porosity. These parameters are addition of starch and also usage of sawdust to increase the porosity.

4.1 Preparation of α-Alumina Oxide Substrate

4.1.1 Effect on addition of starch

Table 4.1: Percentage of porosity with different amount of starch addition

Sample	Diameter (cm)	No. of starch drop	Weight in air (g)	Weight in water (g)	Weight in boiling water for 1hr (g)	Porosity (%)
1	2.4	5	4.937	1.333	5.427	11.96
2	2.4	15	4.909	1.363	5.406	12.29
3	2.4	25	4.902	1.340	5.426	12.8

From **Table 4.1,** the results shows when the content of starch is high, the porosity is increase. It can be see through the different percentage of porosity at different samples. Sample 3 show high porosity which is 12.8% which is slightly higher than sample 1 and 2 that content low starch. The result is basically same with the statement that ***Gordon and Chi Ming***[12] said.

4.1.2 Effect on addition of sawdust with starch on substrate

Table 4.2: Percentage of porosity with different weight of sawdust

Sample	Diameter (cm)	Sawdust (g)	Weight in air (g)	Weight in water (g)	Weight in boiling water for 1hr (g)	Porosity (%)
1	4.9	0.1	9.830	2.880	11.664	20.88
2	4.9	0.1	9.920	2.891	11.732	20.50
3	4.9	0.2	9.805	2.875	11.838	22.68
4	4.9	0.2	9.908	2.884	11.951	22.53

The results show the porosity of substrate is increasing using sawdust. It is because when the substrate is heated at 1500 ^{0}C, sawdust will burn and creates pores inside the substrate. It makes the substrate become more pores. As can see for sample 1 and 2 using 0.1 g of sawdust resulting 20.7% porosity compared to when using 0.2 g sawdust, its show high porosity, 22.5%.

4.2 Permeability Test

4.2.1 Dip Coating for 1 hour @ 500^{0}C

Table 4.3: Permeation Flux of CO_2 at different pressure

Pressure (Bar)	Q (cm3/s)	Qstp (cm3/s)	J (cm3[STP]/cm2.S)	Nt (mol/s)	***P***
1.500	12.500	11.568	0.589	0.00071310	0.00002421
2.000	13.889	12.853	0.654	0.00105956	0.00002697
2.500	16.129	14.926	0.760	0.00154247	0.00003141
3.000	18.315	16.949	0.863	0.00210815	0.00003578

Table 4.4: Permeation Flux of CH_4 at different pressure

Pressure (Bar)	Q (cm3/s)	Qstp (cm3/s)	J (cm3[STP]/cm2.S)	Nt (mol/s)	***P***
1.500	11.364	10.516	0.535	0.00064513	0.00002190
2.000	11.710	10.836	0.552	0.00088704	0.00002258
2.500	14.577	13.490	0.687	0.00138266	0.00002816
3.000	15.625	14.460	0.736	0.00178042	0.00003022

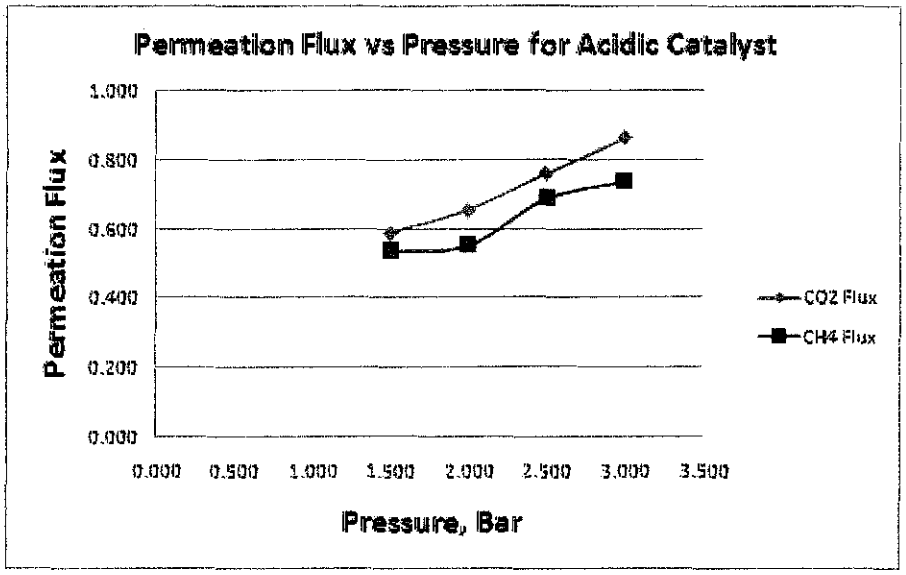


Figure 4.1: Permeation Flux vs. Pressure for CO_2 and CH_4

4.2.2 Dip Coating for 2 hours @ 500^0C

Table 4.5: Permeation Flux of CO_2 at different pressure

Pressure (Bar)	Q (cm3/s)	Qstp (cm3/s)	J (cm3[STP]/cm2.S)	Nt (mol/s)	*P*
1.500	10.000	9.254	0.471	0.00057048	0.00001936
2.000	10.417	9.640	0.491	0.00079467	0.00002023
2.500	10.870	10.059	0.512	0.00103949	0.00002117
3.000	11.364	10.516	0.535	0.00130801	0.00002220

Table 4.6: Permeation Flux of CH_4 at different pressure

Pressure (Bar)	Q (cm3/s)	Qstp (cm3/s)	J (cm3[STP]/cm2.S)	Nt (mol/s)	*P*
1.500	8.333	7.712	0.393	0.00047310	0.00001606
2.000	8.772	8.118	0.413	0.00066450	0.00001692
2.500	8.929	8.263	0.421	0.00084688	0.00001725
3.000	9.259	8.569	0.436	0.00105507	0.00001791

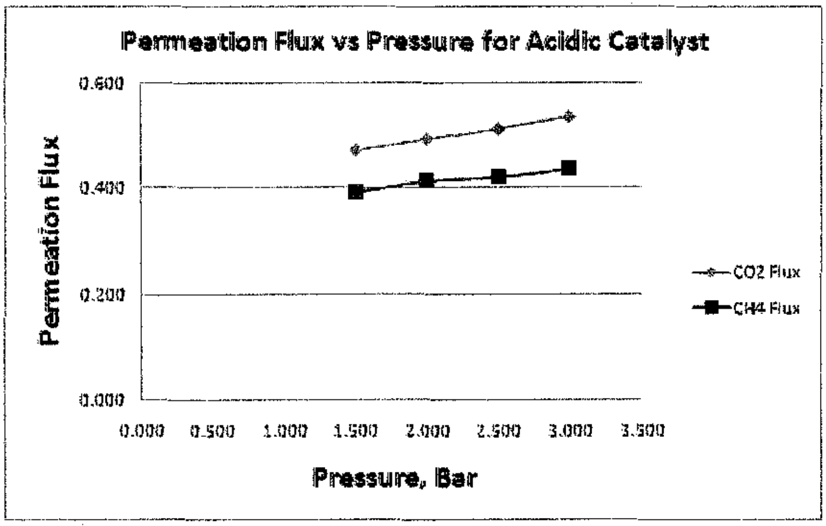


Figure 4.2: Permeation Flux vs. Pressure for CO_2 and CH_4

4.2.3 Dip Coating for 3 hours @ 500^{0}C

Table 4.7: Permeation Flux of CO_2 at different pressure

Pressure (Bar)	Q (cm3/s)	Qstp (cm3/s)	J (cm3[STP]/cm2.S)	Nt (mol/s)	***P***
1.500	9.091	8.413	0.428	0.00051862	0.00001760
2.000	9.434	8.730	0.445	0.00071970	0.00001832
2.500	10.000	9.254	0.471	0.00095633	0.00001948
3.000	10.417	9.640	0.491	0.00119901	0.00002035

Table 4.8: Permeation Flux of CO_2 at different pressure

Pressure (Bar)	Q (cm3/s)	Qstp (cm3/s)	J (cm3[STP]/cm2.S)	Nt (mol/s)	***P***
1.500	6.667	6.169	0.314	0.00037848	0.00001285
2.000	7.353	6.805	0.346	0.00055701	0.00001418
2.500	7.576	7.011	0.357	0.00071856	0.00001463
3.000	7.937	7.345	0.374	0.00090434	0.00001535

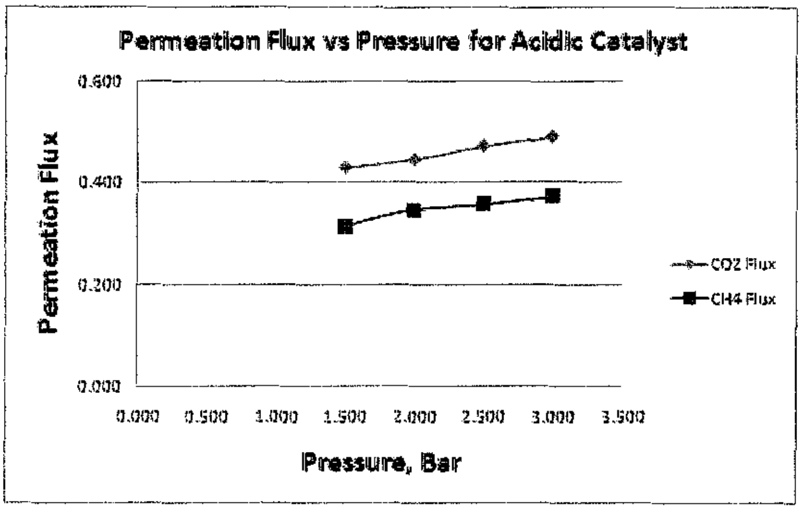


Figure 4.3: Permeation Flux vs. Pressure for CO_2 and CH_4

4.2.4 Separation Factor ($\alpha_{CO2}/\alpha_{CH4}$)

Table 4.9: Separation Factor of $\alpha_{CO2}/\alpha_{CH4}$

Pressure, bar	F_{α}	F_{α}	F_{α}
	1 hr	2 hr	3 hr
1.50	1.105	1.206	1.370
2.00	1.194	1.196	1.292
2.50	1.176	1.227	1.331
3.00	1.184	1.240	1.326

From **Table 4.9** shows the experimental separation factor, F_α of CO_2/CH_4 for different time of dipping, 1hour, 2 hours and 3 hours. For 1 hours dipping time, the maximum separation factor is 1.194. For 2 hours dipping time the maximum separation factor is 1.24 followed by 3 hours dipping time that give 1.37 separation factors. Compared to three different on dipping time, 3 hours dipping time give goods in separation factor and less permeance which are $2.035x10^{-5}$ $mol.cm^{-2}.bar^{-1}.s^{-1}$ for CO_2 and $1.535x10^{-5}$ $mol.cm^{-2}.bar^{-1}.s^{-1}$ for CH_4

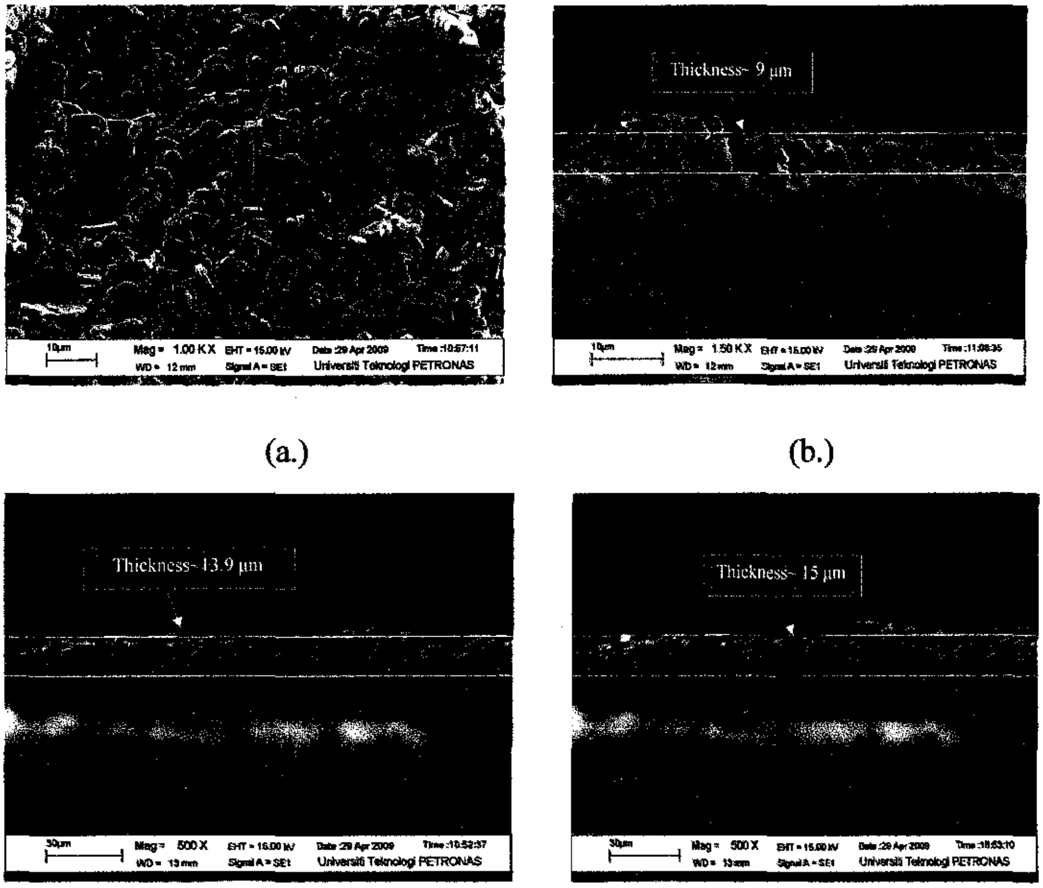
The ideal Knudsen separation factor is the ratio of square root of the molecular weight of CO_2 and CH_4 and the value is 1.66 [14]. In this experiment the maximum separation factor 1.37 is obtained at differential pressure 1.5 bar. Comparison between ideal Knudsen and experimental separation factor shows that the experimental separation factor is slightly lower than the ideal. This is because of microcracks produced on porous alumina substrate due to high pressure used and it cannot see through the naked eyes. This cause can be overcome by increasing the heating temperature during calcinations process so that the porous alumina substrate is more harden and strong.

Some modification needs to be done so that the separation factor of the membrane is higher than the ideal. First is on the dipping time of substrate in silica sol. The dipping time need to be increase so that the more particles of the silica is suspend on the surface of the substrate. In this case it's related to the concentration of the silica sol. If concentration of silica sol is high, the dipping time is less. The second improvement is using multilayer of the silica. The process is start with dipping followed by drying and then calcinations process. The step is repeated for several times so that the thickness of the silica layer is increase.

4.3 Scanning Electron Microscope (SEM) Analysis

Morphology of the membrane surface and cross sections can be visually examined using Scanning Electron Microscope (SEM). **Figure 4.4(a.)** show top view of silica layer on alumina substrate. It is same for all silica layers at different dipping time.

Figure 4.4 (b), (c.) and (d.) shows a cross sectional view at differential dipping time. For 1 hour dipping time, the thickness of silica layer is 9 µm, for 2 hour the thickness is 13.9 µm and for 3 hour the thickness is 15 µm. It is clearly show that when the dipping time is increase, the thickness also increases.



(a.) (b.)

(c.) (d.)

Figure 4.4: SEM diagram of (a.) Top view silica layer on alumina substrate (b.) Cross section view 1 hour dipping time (c.) Cross section view 2 hour dipping time (d.) Cross section view 3 hour dipping time

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Used of amine adsorption for removing of acidic components like CO_2 had gained widespread acceptance. However, the cost of acid gases removal by using the mixed amines system is highly expensive. Due to that, we need to replace the amine adsorption with the most economical method. From this research, it shown that membrane technology is the most economical method since it's easy to optimize and required less space to install.

In this research ceramic membrane is choosing as membrane due to its highly chemical, mechanical and thermal stability compared to polymeric membrane. The mechanism of the membrane is molecular sieve which mean separation of the gas is based on its kinetic diameter. This project is dividing into 2 experiments which are preparation of α-alumina substrate and preparation of silica membrane using sol gel method.

Using the silica sol gel method the pores size can be desirably controlled especially for small pores. For the first experiment it shows that when using the additive such as starch can increase the porosity of the substrates. For the second experiment which is preparation of the silica membrane, it shows the permeance flux of carbon dioxide ($3.578\text{x}10^{-4}$ cm^3 [STP]/cm^2.s) is slightly greater than permeance flux of methane gas ($3.022\text{x}10^{-4}$ cm^3 [STP]/cm^2.s). It is prove that separation is based on molecular size. The permselectivity of 3 hours dipping time result the highest selectivity which is 1.370 at pressure 1.5 bar.

As a conclusion, silica membrane is reasonable to be use as membrane for carbon dioxide removal since its pores size can be desirably controlled using sol gel method.

5.2 Recommendation

There are a few improvements to be recommended for the better experiment results in future research:

i. **Dipping Time of the membrane in Silica Sol**

   There are proving by Rudolph and Narayan K. Raman that the dipping time can control the pore size based on its separation factor. From their research, when the time of dipping is increase, the pores size decrease and cause highly selectivity of CO_2/CH_4. So the critical factors in dip coating are the viscosity of the particle suspension and the coating time or speed.

ii. **Using multilayer of silica thickness**

   In the multiple step process, after calcinations of the first layer, the complete cycle of dipping, drying and calcinations is repeated. This process can increase the thickness of the silica membrane layer.

iii. **Mixed gas needed to be use in the permeability test in order to get the real selectivity**

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APPENDIX

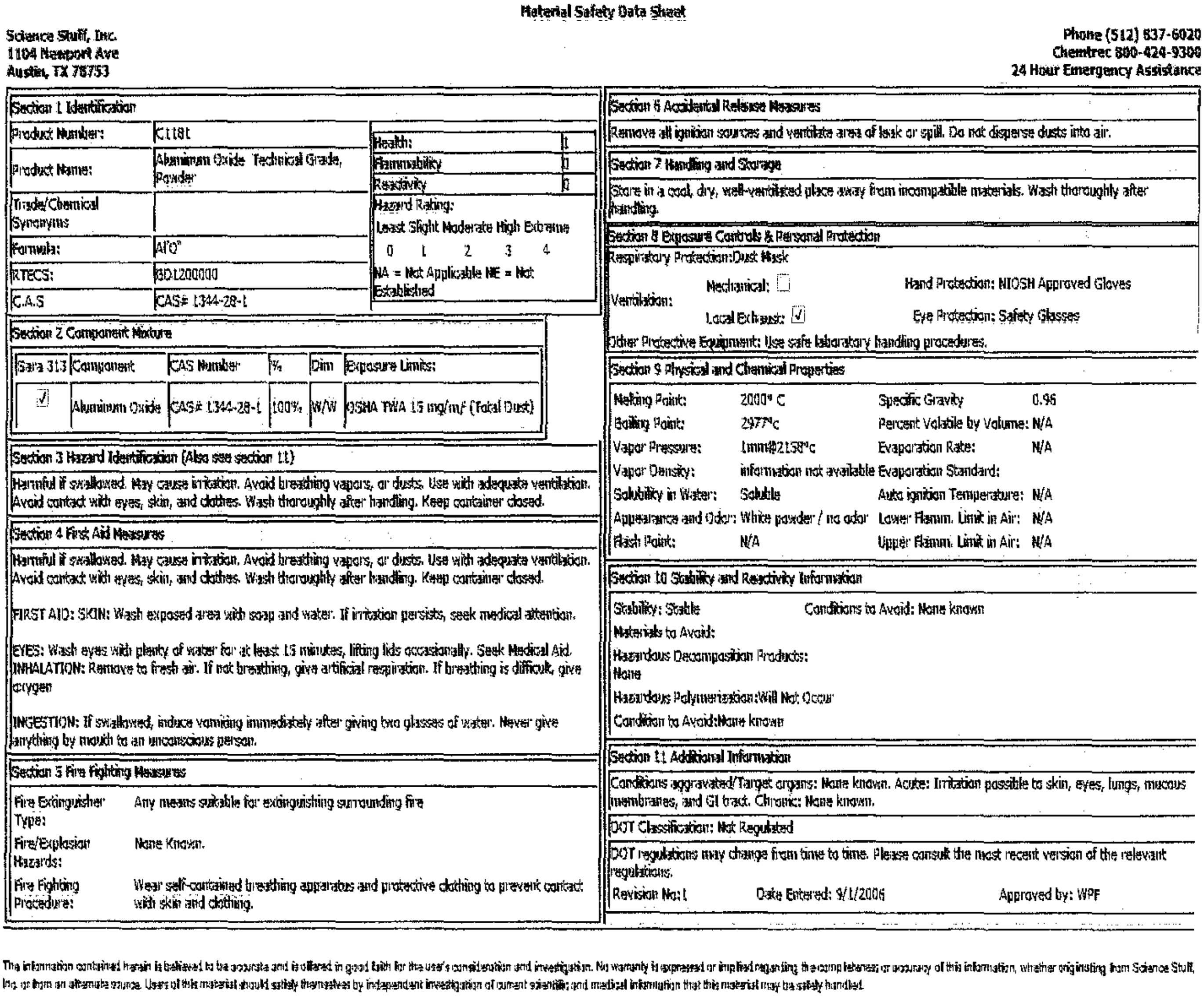
A.1 Sample Calculation for porosity calculation of α-Alumina Substrate

Sample	Weight (air)	Diameter	Weight (water)	Weight after immersed	Porosity %
1	4.937 g	2.4 cm	1.333 g	5.427 g	12
2	4.909 g	2.4 cm	1.363 g	5.406 g	12.3
3	4.902 g	2.4 cm	1.340 g	5.426 g	12.8

$$\%Porosity = \frac{Weight\ in\ Boiling\ Water\ for\, 1hr - Weight\ in\ air}{Weight\ in\ Boiling\ Water\ for\, 1hr - Weight\ in\ water} x100\%$$

$$Bulk\ Porosity = \frac{(5.427 - 4.937)}{(5.427 - 1.333)} x100\% = 12\%$$

A.2 Material Safety Data Sheet (MSDS) for Alumina Oxide



Material Safety Data Sheet

Science Stuff, Inc.
1104 Newport Ave
Austin, TX 78753

Phone (512) 837-6020
Chemtrec 800-424-9300
24 Hour Emergency Assistance

Section 1 Identification

Product Number:	C1181
Product Name:	Aluminum Oxide Technical Grade, Powder
Trade/Chemical Synonyms	
Formula:	$Al^{2}O^{3}$
RTECS:	BD1200000
C.A.S	CAS# 1344-28-1

Health:	1
Flammability	0
Readivity	0

Hazard Rating:
Least Slight Moderate High Extreme
0 1 2 3 4
NA = Not Applicable NE = Not Established

Section 2 Component Mixture

Sara 313	Component	CAS Number	%	Dim	Exposure Limits:
☑	Aluminum Oxide	CAS# 1344-28-1	100%	W/W	OSHA TWA 15 mg/m³ (Total Dust)

Section 3 Hazard Identification (Also see section 11)

Harmful if swallowed. May cause irritation. Avoid breathing vapors, or dusts. Use with adequate ventilation. Avoid contact with eyes, skin, and clothes. Wash thoroughly after handling. Keep container closed.

Section 4 First Aid Measures

Harmful if swallowed. May cause irritation. Avoid breathing vapors, or dusts. Use with adequate ventilation. Avoid contact with eyes, skin, and clothes. Wash thoroughly after handling. Keep container closed.

FIRST AID: SKIN: Wash exposed area with soap and water. If irritation persists, seek medical attention.

EYES: Wash eyes with plenty of water for at least 15 minutes, lifting lids occasionally. Seek Medical Aid.
INHALATION: Remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen

INGESTION: If swallowed, induce vomiting immediately after giving two glasses of water. Never give anything by mouth to an unconscious person.

Section 5 Fire Fighting Measures

Fire Extinguisher Type:	Any means suitable for extinguishing surrounding fire
Fire/Explosion Hazards:	None Known.
Fire Fighting Procedure:	Wear self-contained breathing apparatus and protective clothing to prevent contact with skin and clothing.

Section 6 Accidental Release Measures

Remove all ignition sources and ventilate area of leak or spill. Do not disperse dusts into air.

Section 7 Handling and Storage

Store in a cool, dry, well-ventilated place away from incompatible materials. Wash thoroughly after handling.

Section 8 Exposure Controls & Personal Protection

Respiratory Protection:Dust Mask

Ventilation: Mechanical: ☐ Local Exhaust: ☑

Hand Protection: NIOSH Approved Gloves

Eye Protection: Safety Glasses

Other Protective Equipment: Use safe laboratory handling procedures.

Section 9 Physical and Chemical Properties

Melting Point:	2000° C	Specific Gravity	0.96
Boiling Point:	2977°c	Percent Volatile by Volume:	N/A
Vapor Pressure:	1mm@2158°c	Evaporation Rate:	N/A
Vapor Density:	information not available	Evaporation Standard:	
Solubility in Water:	Soluble	Auto ignition Temperature:	N/A
Appearance and Odor:	White powder / no odor	Lower Flamm. Limit in Air:	N/A
Flash Point:	N/A	Upper Flamm. Limit in Air:	N/A

Section 10 Stability and Reactivity Information

Stability: Stable Conditions to Avoid: None known

Materials to Avoid:

Hazardous Decomposition Products:
None

Hazardous Polymerization:Will Not Occur

Condition to Avoid:None known

Section 11 Additional Information

Conditions aggravated/Target organs: None known. Acute: Irritation possible to skin, eyes, lungs, mucous membranes, and GI tract. Chronic: None known.

DOT Classification: Not Regulated

DOT regulations may change from time to time. Please consult the most recent version of the relevant regulations.

Revision No: 1 Date Entered: 9/1/2006 Approved by: WPF

A.3 Sample Calculation for Permeance Flux and Ideal Knudsen Diffusion

Acid-Cataylst

CO_2

Pressure (Bar)	volume (cm3)	time (s)	Q (cm3/s)	Qstp (cm3/s)	J (cm3[STP]/cm2.S)	Nt (cm3/s)	***P***
1.500	50.000	4.000	12.500	11.568	0.589	0.00071310	0.00002421
2.000	50.000	3.600	13.889	12.853	0.654	0.00105956	0.00002697
2.500	50.000	3.100	16.129	14.926	0.760	0.00154247	0.00003141
3.000	50.000	2.730	18.315	16.949	0.863	0.00210815	0.00003578

Acid-Cataylst

CH_4

Pressure (Bar)	volume (cm3)	time (s)	Q (cm3/s)	Qstp (cm3/s)	J (cm3[STP]/cm2.S)	Nt (cm3/s)	***P***
1.500	50.000	4.400	11.364	10.516	0.535	0.00064513	0.00002190
2.000	50.000	4.270	11.710	10.836	0.552	0.00088704	0.00002258
2.500	50.000	3.430	14.577	13.490	0.687	0.00138266	0.00002816
3.000	50.000	3.200	15.625	14.460	0.736	0.00178042	0.00003022

$$N_t = \bar{P} A_t \Delta p \text{ - - - - - - - - - - - - - - - } (1)$$

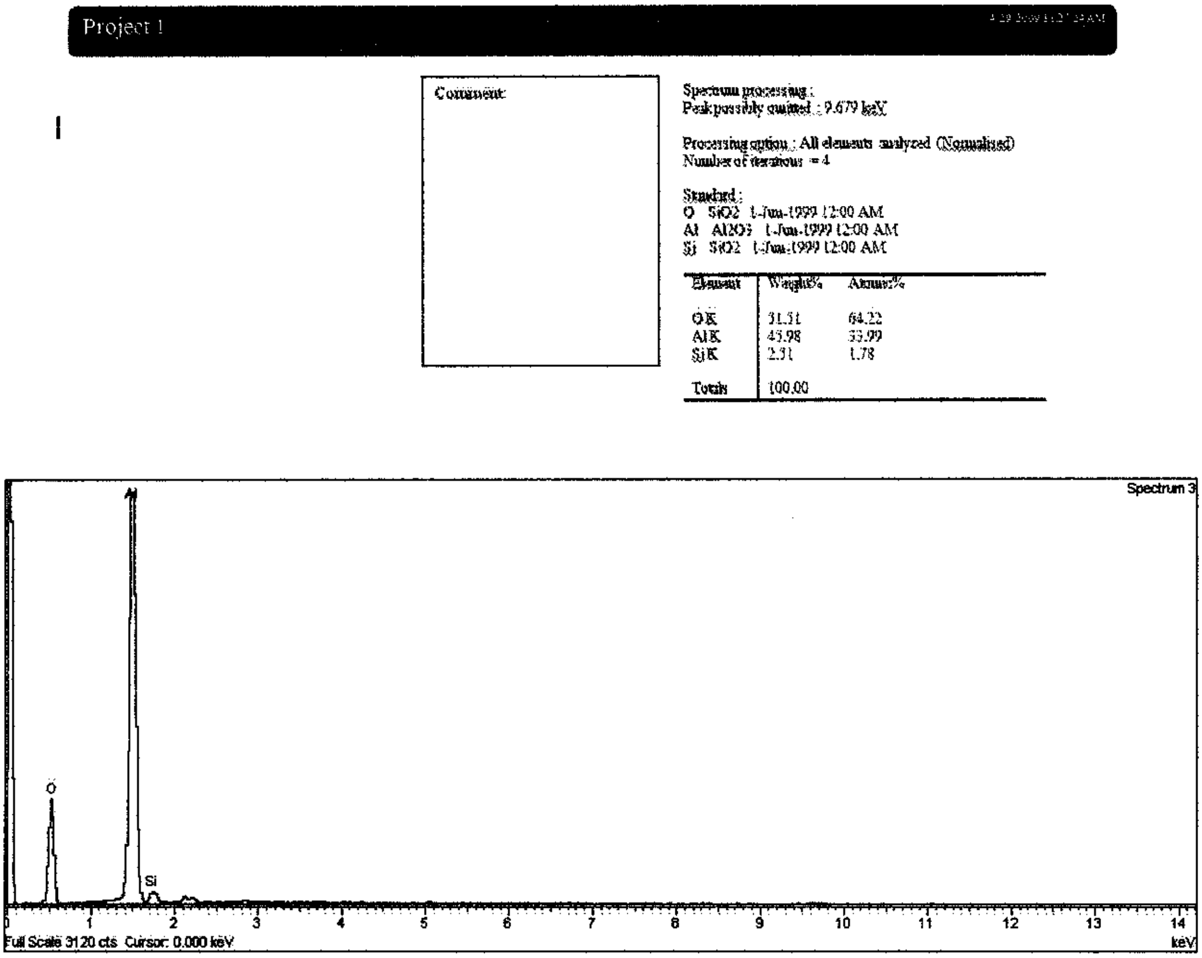
$$\bar{P} = \frac{N_t}{A_t \Delta p} \text{ - - - - - - - - - - - - - - - - - } (2)$$

Mr CO2 = 44.01

Mr CH4 = 16.04

Ideal Knudsen Separation Factor, $\alpha = \sqrt{\frac{MW_{co2}}{MW_{CH4}}} = 1.66$

A.4 Energy Disperse X-ray



Project 1

Comment:

Spectrum processing :
Peak possibly omitted : 9.679 keV

Processing option : All elements analyzed (Normalised)
Number of iterations = 4

Standard :
O SiO2 1-Jun-1999 12:00 AM
Al Al2O3 1-Jun-1999 12:00 AM
Si SiO2 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
O K	31.51	64.22
Al K	45.98	33.99
Si K	2.51	1.78
Totals	100.00	

A.5 X-Ray Diffraction