UPGRADING LOW QUALITY NATURAL GAS WITH CO_2 SELECTIVE POLYMERS MEMBRANE

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"I hereby declare that I have read this thesis and in my opinion
this thesis is sufficient in terms of scope and quality for the award of
Bachelor of Chemical Engineering (Gas Technology)"

Signature : ....

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I declare that this thesis entitled "*Upgrading Low Quality Natural Gas with CO_2 Selective Polymers Membrane"* is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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To my beloved father and mother, Mr Mior Zahidi and Madam Amnah

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IN THE NAME OF ALLAH THE MOST GRACIOUS AND THE MOST MERCIFUL

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ABSTRACT

The aim of this research is to determine the most suitable polymer membrane between polyvinylidene fluoride (PVDF), Polyacrylonitrile (PAN) and hybrid polymer membrane of polysulfone (PSU) and polyethersulfone (PES) for separating CO_2 from crude natural gas. These polymers are mixed with suitable solvent in order to create polymeric solution. Flat sheet membranes were developed from this polymeric solution using standard method. Flat sheet membranes are then introduced to the separation process using permeability unit to study permeability and selectivity of each membrane. The test was carried out by using three gas inlet volumetric flow rate, 0.1, 0.2 and 0.3 L/min at 0.5, 1.0 and 1.5 Bar. The test gas used was CO_2 and CH_4 gas, both have purity over 99%. Standard soap bubble method was used to determine permeate gas flow rate. Results shows, PVDF membrane are determined as the suitable membrane for the separation process because PVDF membrane has low CO_2 selectivity and high permeability of CH_4 compare to the other polymers membrane. It is also discovered that by increasing gas inlet flow rate, permeability of the gas also increase and selectivity is inversely proportional to permeability. In order to improve in the next study, other parameter such as coating the membranes need to be considered as well.

ABSTRAK

Kajian ini dijalankan adalah untuk mengenal pasti membran polimer yang bersesuaian di antara polyvinylidene fluoride (PVDF), Polyacrylonitrile (PAN) dan membran polimer hibrid, polysulfone (PSU) dan polyethersulfone (PES). Polimer ini dibancuh dengan pelarut dan membrane nipis yang dihasilkan kemudiannya diuji untuk proses pemisahan gas dengan melakukan ujian kebolehtelapan dan pemilihan menggunakan unit ketelapan. Ujian dijalankan menggunakan tiga kadar aliran masuk iaitu 0.1, 0.2 dan 0.3 L/min pada tekanan 0.5, 1.0 dan 1.5 Bar. Ujian ini menggunakan gas CO_2 dan CH_4 sebagai gas ujian. Kaedah 'standard soap bubble' digunakn bagi mengetahui kadar aliran gas yang terlepas dari membrane. Dari hasil ujian dijalankan, terbukti bahawa membran polimer PVDF adalah polimer yang paling sesuai untuk prosess pemisahan CO_2 daripada gas asli, dimana membran PVDF mempuyai nilai rendah untuk pemilihan CO_2 dan kebolehtelapan yang tinggi bagi CH_4 berbeanding dengan membran polimer yang lain . Terbukti juga bahawa, dengan menaikkan kadar aliran masuk gas, kebolehtelapan gas juga meningkat dan pemilihan berkadar songsang dengan kebolehtelapan gas. Pada masa hadapan, untuk meningkatkan kualiti kajian beberapa parameter perlu di kaji seperti menkaji kebolehtelapan dan pemilihan membran yang telah di salut oleh agen salut bahan kimia.

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LIST OF ABBREVIATIONS

NG	-	Natural Gas
NGV	-	Natural Gas Vehicle
ppm	-	parts per millions
CH_4	-	Methane
CO_2	-	Carbon Dioxide
PVDF	-	Polyvinylidene fluoride
PAN	-	Polyacrylonitrile
PSU	-	Polysulfone
PES	-	Polyethersulfone
RO	-	Reverse Osmosis
NF	-	Nanofiltration
UF	-	Ultrafiltration
MF	-	Microfiltration
PV	-	Pervaporation
GP	-	Gas Separation
TIPS	-	Thermal Induced Phase Separation

LIST OF SYMBOLS

^0C	-	temperature unit, degree celcius
atm	-	pressure unit, atmosphere
g/mol	-	molar mass
g/L	-	density
kg/m^3	-	density
K	-	temperature unit, Kelvin
kPa	-	pressure unit, kilopascal
mL	-	volume, millilitre
p/l	-	permeability coefficient
Q_i	-	inlet volumetric flow rate
Q	-	permeate volumetric flow rate
α	-	selectivity
L/min	-	volumetric flow rate unit
Bar	-	pressure unit, Bar
A	-	area
cm	-	length, centimetre
cm^2	-	area unit, centimetre square
t	-	time,second

CHAPTER 1

INTRODUCTION

1.1 Research Background

Natural gas (NG) is a mixture of combustible hydrocarbon gas and is considered as a fossil fuel in gas phase. It is a colourless, shapeless and odourless gas. Natural gas is formed primarily of methane, but also includes ethane, propane, butane as well as impurities such as carbon dioxide, nitrogen, helium, hydrogen sulphide and water. Natural gas is formed underground by decomposition process of an organic material in plant and animal. Natural gas usually found in oil field (associated) or in the natural gas own reservoir (non-associated).[10][14][15]

Once natural gas brought from underground, the natural gas is refined to remove impurities such as carbon dioxide, nitrogen, helium, hydrogen sulphide, water, sand, and other compounds. Other hydrocarbons are removed and sold separately, including ethane, propane and butane. Impurities like hydrogen sulphide can be refine of which can produce sulphur, which is then also sold separately to needed customers. After refining, the clean natural gas is transmitted through a network of pipelines and from these pipelines natural gas is delivered to its consumers.[10]

Today, natural gas are widely use not just only in industrial. Natural gas is a major source in power generation industry, which is use to generate electricity though the use of gas and steam turbines. Natural gas is also used to produce hydrogen, and a major feedstock for the production of ammonia via the Haber

process which is use in fertilizer production. For commercially use, natural gas that have been convert to natural gas vehicle (NGV) provide an alternative fuel to automobiles. As for residential usage, natural gas is use for purpose as cooking, clothes dryers, heater and many more.[10]

Compare to all type of fossil fuels like coal, petroleum, natural gas is the most environmental friendly fossil fuel. Because of natural gas are clean burning and the expanding of gas industry worldwide, demand for natural gas is increasing by each year. Natural gas brought from well or underground reservoir are low quality crude natural gas, which must go through a separation process for upgrading by removing impurities such as carbon dioxide and hydrogen sulphide that can cause problems to the pipelines and the appliances or equipments. The most widely use method for gas separation is by membrane separation process, and polymers is the most widely membrane materials at the moment.[10]

1.2 Problem Statement

Natural gas is a vital component of the world's supply energy. It is one of the cleanest, safest, and most useful of all energy resources. Despite of its importance, over 30 percent of the current natural gas production is in the form of low-quality natural gas that contains significant amount of carbon dioxide and hydrogen sulphide. With this situation, upgrading low quality crude natural gas attracts an increasing interest due to the growth in demand in recent years. Carbon dioxide and hydrogen sulphide gas must be removed to increase the quality of natural gas because it is acidic that would cause corrosion to the equipments and pipelines also may reduce heating value of natural gas beside of being greenhouse gas.[14][15]

Membrane separation process can reduce the concentration of carbon dioxide and hydrogen sulphide in natural gas to meet pipelines and demand specifications. For an example, according to United State pipelines specifications, natural gas must contain not more than two mol% carbon dioxide and four ppm of hydrogen

sulphide.[14][15] Polymer is the best materials for membrane, as polymer is more chemically stable compare to others and relatively low cost of manufacturing. Three polymers with different properties have been selected for this research involve removing carbon dioxide, which are polyvinylidene fluoride (PVDF), Polyacrylonitrile (PAN) and hybrid polymer membrane of polysulfone (PSU) and polyethersulfone (PES). Between these three polymer membranes, comparison will be done as to ensure which polymer membrane more suitable for this gas separation process.

1.3 Objectives

As described in the research background and problem statement section, the objective of this research is to develop and prepare polymer membranes from polyvinylidene fluoride (PVDF), Polyacrylonitrile (PAN) and hybrid of polysulfone (PSU) and polyethersulfone (PES) for separating carbon dioxide from natural gas and also to determine the best polymer membrane for this separation process.

1.4 Scope of Study

In order to accomplish the set objectives, following scope of work has been drawn out;

i. Develop and prepare flat sheet membranes from PVDF, PAN and PSU-PES polymer for gas separation
ii. To study the permeability and selectivity for each membranes.
iii. Comparing data of membranes in term of permeability and selectivity

1.5 Rational and Significance

Demand for natural gas is increasing by each year. This is cause by the increasing numbers of application of natural gas in many sectors, primarily industrial sectors. Numbers of gas separation technologies have been developed in order to refine natural gas. Gas separation by membrane has been introduced decade ago and gas separation by membranes offer number of benefits over other gas separation technologies. Conventional technologies such as amine absorption to remove acid gases such as carbon dioxide from natural gas require a gas to liquid phase change in the gas mixture that is to be separated. The phase change adds significant energy cost to the separation cost, as now energy cost is rising. On the other hand, membrane gas separation does not require phase change. In addition, gas separation membrane units are smaller than others type of plants, like amine stripping plant and therefore have small footprints. A small footprint is important in environment such as offshore gas processing platforms. Also, the lack of mechanical complexit membrane is another advantage.

CHAPTER 2

LITERITURE REVIEW

2.1 Natural Gas (NG)

Natural gas is a gaseous fossil fuel consisting primarily of methane and generally considered as non-renewable fossil fuel. Natural gas is colourless, odourless, shapeless, lighter than the air, and non-toxic. Beside than methane, natural gas also consist other heavier hydrocarbon gas such as ethane, propane, butane which all of this hydrocarbon can be removed prior to the need of consumer, also consist impurities such CO_2, H_2S, N_2, He and water. Natural gas is brought from underground and is usually found in oil fields (associated) or isolated in natural gas fields (non-associated). Natural gas is often referred to as simply gas, especially when compared to other energy sources such as electricity. Before natural gas can be used as a fuel, it must undergo extensive processing to remove almost all materials other than methane. The by-products of that processing include ethane, propane, butanes, pentanes and higher molecular weight hydrocarbons, elemental sulphur, and sometimes helium and nitrogen.[19]

2.1.1 Formation of Natural Gas

Natural gas (NG) is a fossil fuel like oil and coal. Fossil fuels are essentially, the remains of plants and animals and microorganisms that lived millions and millions of years ago.

There are many different theories as to origins of fossil fuels. The most widely accepted theory says that fossil fuels are formed when organic matter such as the remains of a plant or animal is compressed under the earth, at very high pressure for a very long time. This is referred to as thermogenic methane. Similar to the formation of oil, thermogenic methane is formed from organic particles that are covered in mud and other sediment. Over time, more and more sediment and mud and other debris are piled on top of the organic matter. This sediment and debris puts a great deal of pressure on the organic matter, which compresses it. This compression, combined with high temperatures found deep underneath the earth's crust, break down the carbon bonds in the organic matter. The deeper under the earth's crust, the higher the temperature. At low temperatures, more oil is produced relative to natural gas. At higher temperatures, however, more natural gas is created, as opposed to oil. That is why natural gas is usually associated with oil in deposits that are 1 to 2 miles below the earth's crust. Deeper deposits, very far underground, usually contain primarily natural gas, and in many cases, pure methane.[10][19]

2.2 Composition of Natural Gas

As we know, natural gas is a combustible mixture of hydrocarbon gases. While natural gas is formed primarily of methane, it also includes other components such as ethane, propane, butane and some time even pentane. Table 2.1 shows the typical composition of natural gas before it is refined in U.S.A.[10]

Table 2.1: General composition of crude natural gas in U.S.A.[10]

Methane	CH_4	70~90%
Ethane	C_2H_6	0~20%
Propane	C_3H_8	
Butane	C_4H_{10}	
Carbon Dioxide	CO_2	0~8%
Oxygen	O_2	0~0.2%
Nitrogen	N_2	0~5%
Hydrogen sulphide	H_2S	0~5%
Rare gases	A, He, Ne, Xe	trace

Natural gas that contains hydrocarbons other than methane is called wet natural gas meanwhile, natural gas contain only of methane is called dry natural gas. Nitrogen, helium, carbon dioxide and hydrogen sulphide, water and odorants can also be present in natural gas even though in small amount. Natural gas also contains and is the primary market source of helium. Mercury is also present in small amounts in natural gas extracted from some fields. The exact composition of natural gas varies between gas fields that it been extracted from.[19]

2.2.1 Carbon Dioxide (CO_2)

Carbon dioxide is a chemical compound composed of two oxygen atoms covalently bonded to a single carbon atom. Exist as a gas at standard temperature and pressure and exist in the atmosphere. Carbon dioxide is a colourless, odourless and also a toxic gas when inhaled at concentrations much higher than usual atmospheric levels, it can produce a sour taste in the mouth and a stinging sensation