DEVELOPMENT OF HYBRID MEMBRANE (POLYSULFONE AND ZEOLITES) FOR GAS SEPARATION APPLICATION

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ABSTRACT

Objectives of this research are developing and fabricate hybrid membrane (polysulfone and zeolites) for gas application, in a way to increase the selectivity and permeability. To achieve this characteristics polymer, zeolites and coupling agent were used as material to produce this hybrid membrane. In the experiment, the membrane prepared at different zeolites and chloroform loading. The solution was stirred at 24 hours to get a homogenous solution. New coupling agent (a mix of formaldehyde and carboxylic acid) was used. After casting process, the membrane was tested by permeation cell to study the permeability and selectivity of the produced membrane. Several gases were used to test this membrane such as O_2, N_2, CH_4 and CO_2. The result was compared to original membrane which means the membrane not mix with zeolites. The permeability and selectivity values for 40% zeolites loading for gas CO_2 and CO_2/CH_4 were 995 X 10^{-6} and 0.889. Results for O_2 and O_2/N_2 were 732 X 10^{-6} and 0.660. For zeolites loading 12%, permeability and selectivity values for gas CO_2 and CO_2/CH_4 were 595 X 10^{-6} and 0539. For O_2 and O_2/N_2, the values were 947 X 10^{-6} and 1.008. Result obtained was not at the standard values due to incompatibility of new coupling agent used, and the pair of zeolites-polymer. To produce hybrid membrane, the parameter studied, the zeolites and polymer pair and the use appropriate of coupling agent are very important.

ABSTRAK

Tujuan dari kajian ini adalah memperluaskan dan membuat membran hibrid (polisulfon dan zeolite) untuk aplikasi gas, dengan tujuan untuk meningkatkan selektiviti dan ketelapan. Untuk mencapai objektif ini ciri-ciri polimer, zeolite dan bahan penghubung digunakan untuk menghasilkan membran hibrid. Dalam kajian ini, membran dibuat pada kandungan zeolite dan klorofom yang berbeza. Larutan membran adalah di kacau selama 24 jam untuk mendapatkan larutan yang sebati. Bahan penghubung baru (campuran formaldehyde dan asid karboksilik) digunakan. Membran diuji oleh permeasi sel untuk mengetahui ketelapan dan selektiviti dari membran yang dihasilkan. Beberapa gas digunakan untuk menguji membran ini seperti O_2, N_2, CH_4 dan CO_2. Hasilnya dibandingkan dengan membran asal di mana membran tidak bercampur dengan zeolite. Nilai-nilai ketelapan dan selektiviti pada kandungan zeolite sebanyak 40% yang diuji menggunakan gas CO_2 dan CO_2/CH_4 adalah 995 X 10^{-6} dan 0,889. Keputusan untuk O_2 dan O_2/N_2 adalah 732 X 10^{-6} dan 0,660. Untuk kandungan zeolite 12%, nilai ketelapan dan selektiviti untuk gas CO_2 dan CO_2/CH_4 adalah 595 X 10^{-6} dan 0539. Untuk gas O_2 dan O_2/N_2, nilai-nilai itu 947 X 10^{-6} dan 1,008. Data yang diperolehi tidak menepati piawai sebenar kerana bahan penghubung baru yang digunakan, tidak sesuai dan pasangan zeolite-polimer juga tidak sesuai. Untuk menghasilkan membran hibrid, perkara yang diteliti, pasangan zeolite dan polimer dan penggunaan bahan penghubung yang tepat.

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CHAPTER 1

INTRODUCTION

1.1 Background Study

Natural gas is a gas which is containing several gases like acid gases. Acid gases need to remove because it will give effect like corrosion to the pipeline, low the quality that gas. Acid gas also can make the gas not environmental friendly and dangerous for user.

They are several methods to remove acid gases from natural gas (a) processes based on chemical solvents (b) processes based on physical solvents (c) acid gas removal by adsorption (d) acid gas removal by gas permeation.

The popular method used in processes based on chemical solvents such as amine scrubbing and potassium carbonate scrubbing. Amines act by chemical affinity due to their basic character. Monoetanolamine (MEA), diethanolamine (DEA), diglycoamine (DGA), diisopropanolamine (DIPA) and methyldiethanolamine (MDEA) are used to sweeten natural gas (A.Rojey, C.Jaffret *et al*, 1997).

Another method is acid gas removal by adsorption. Adsorption is appropriate when very high gas purity is required. The use of molecular sieve helps to achieve simultaneous water and acid gas removal down to very low water contents such as 0.1 ppm volume (Thomas and Clark, 1967).

These several methods need higher cost. So to get the effective way to remove acid gas and nitrogen from natural gas, we will develop the hybrid membrane technology which the cost low than all the methods used before.

Membrane processes have also been considered for natural gas denitrogenation. The challenge, not yet overcome, is to develop membranes with the required nitrogen/methane separation characteristics. Either glassy polymers, which are usually nitrogen-permeable, or rubbery polymers, which are usually methane-permeable, could be used. Obtaining suitable nitrogen-permeable membranes does not seem feasible (Lokhandwala *et al,* 1993).

Acid gas removal will perform by use of development of (polysulfone and zeolites) hybrid membrane. Advance of research will give high permeability and selectivity towards acid gas removal. Polysufone is a high performance engineering thermoplastic which resists degradation. It is an amorphous and hydrophobic polymer. Due to of polysulfone membrane usage in removing acid gases, it is one of the challenge to produce a high quality hybrid membrane (polysulfone and zeolites) that fulfill the necessities of selectivity and high permeated flux en route for a better implication in separating acid gas from natural gas.

Thus, this study sums up the growth and development of hybrid membrane (polysulfone and zeolites) used in separation for gases that would be comparison in the experiment.

1.2 Problem Statement

Natural gas contains other gas components such as carbon dioxide (CO_2), hydrogen sulfide (H_2S), and also nitrogen (N_2) that would give the affect to the pipeline such as corrosion, reducing the hydrocarbon content, and the quality of the natural gas. Membrane technology one of the ways used in removal acid gas. So this research is about to introduce new development of the hybrid membrane.

1.3 Objective of Study

The objective of this study is to develop and characterize hybrid membrane (polysulfone and zeolites) for gas separation application.

1.4 Scope of Study

In order to achieve the objectives, several scopes of study have been outline:

a) To prepare hybrid membrane (polysulfone and zeolites) for the usage of the permeating several gases
b) Gas permeation test using CO_2, N_2, O_2 and CH_4
c) To study permeability and selectivity at different loading of zeolites

CHAPTER 2

LITERATURE REVIEW

2.1 Membrane Definition

A selective barrier between two phases the term ‘selective’ being inherent to a membrane or membrane process (Murder, 1996). The origin of the world ‘membrane’ is from the Latin word ‘membrana’ which means skin of body. Membrane can be defined as a flexible enclosing or separating tissue forming a plane or film and separating two environment (usually in a plant or animal). It is also known as a mechanical, thin, flat flexible part that can deform or vibrate when excited by an external force (Rundell, 2003).

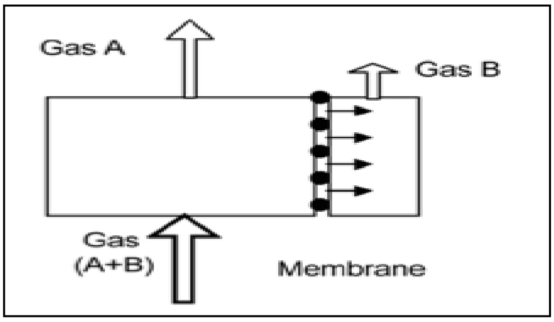

Figure 2.1:The mechanism for membrane separation.(Geodome, 2007)

2.2 The Concept of Membrane Process

Separation membrane processes a rather new, consider as technically important separation process 25 years ago. Today start used in a wide range of applications and still growing. Membrane processes such like microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), and gas separation. Separation is achieved because the membrane has the ability to transport one component from the feed mixture more readily than any other components or one component. The performance or efficiency of a given membrane is determined by two parameters: its selectivity and the flow through the membrane (Murder, 1996).

2.3 Class of Membrane

Membrane can classified according to few points, 1st classification by nature which is biological or synthetic membranes. The synthetic membrane has two types which is organic and inorganic. Another classifying is morphology and structure. Structures divide into two, symmetric and asymmetric (Murder, 1996).

2.3.1 Asymmetric membrane

Asymmetric membrane has very dense top layer skin (0.1-0.5µm) supported by a porous sub layer (50-150µm). This membrane combines the high selectivity of a dense membrane with the high permeation rate of a very thin membrane (Murder, 1996).

2.4 Type of Polymer Membranes

2.4.1 Porous Membrane

This membrane applied in microfiltration and ultrafiltration. the processing requirements, fouling tendency and chemical and thermal stability of the membrane is used to determine the choice of material.

Microfiltration usually has thickness (0.1-10µm) and ultrafiltration usually has thickness (2-100µm). Selectivity mainly determined by the dimensions of the pore but the choice of material affects phenomena such as adsorption and chemical stability under condition of actual application and membrane cleaning. This implies that the requirements for the polymeric material are not primarily determined by the flux and selectivity but also by the chemical and thermal properties of the material.

Membranes of this class induce separation by discriminating between particle sizes, such membrane are used in microfiltration and ultrafiltration. High selectivity can then be obtained when the solute size or particle size is large relative to the pore size in the membrane (Murder, 1996).

2.4.2 Nonporous membrane

Nonporous membranes are used in gas and vapour separation and pervaporation. For these processes either composite or asymmetric membranes are used. In this type of membrane the performance (permeability and selectivity) is determined by the intrinsic properties of the material. The choice of material is determined by the type of applications, and the polymer type can range from an elastomer to a glassy material.

Membranes from this class are capable of separating molecules of approximately the same size from each other. Separation takes place through differences in solubility and/or differences in diffusivity. This means that the intrinsic properties of the polymeric material determine the extent of selectivity and permeability. Such membranes used in pervaporation, vapour permeation, gas separation and dialysis (Murder, 1996). Figure 2.2 shown picture of non-porous membrane:

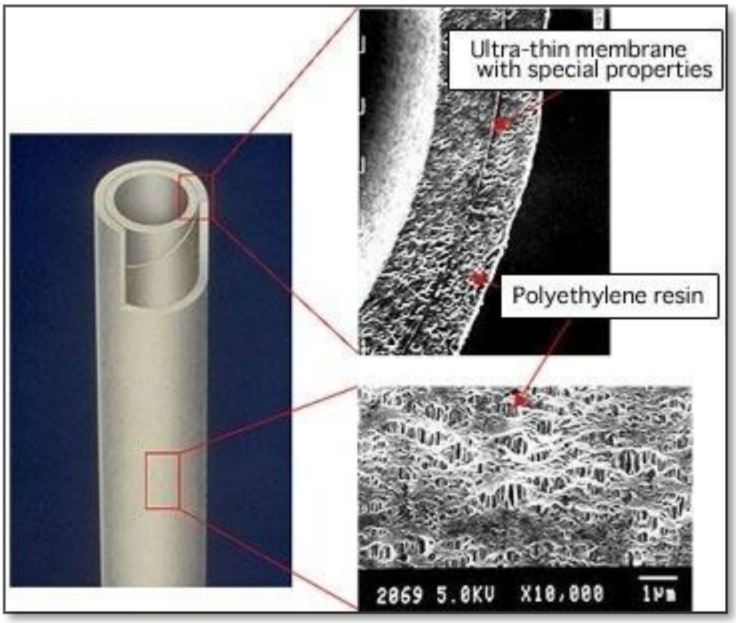

Figure 2.2: Picture of nonporous membrane (Mutsibishi Rayan Eng. Co. Ltd)

2.5 Membrane Modules

Membrane module can be defined as housing of membrane in a suitable device. There are 4 major types of module normally used in membrane separation processes which are plate and frame, spiral wound, tubular and also hollow fibre.

2.5.1 Plate and Frame Membrane Modules

Flat membranes were mainly used in experiments to characterize the permeability of the membrane. The modules were easy to fabricate, used and the areas of the membranes are well defined. In some cases modules were stacked together like a multilayer sandwich or plate-and-frame filter press. (Geankoplis, 2003)

2.5.2 Spiral Wound Membrane Module

A spiral module having a length and a radius and a circular cross section, having reduced flow resistance, comprising; an envelope sandwich having a width equal to the length of the membrane module and comprising a layer of membrane and where in the envelope sandwich is wrapped increasing the radius of the radius of the membrane module and a structural assembly located between each wrap of the envelope sandwich to provide an open path for each feed chamber throughout the length of membrane. (Herron, 2005)

2.5.3 Tubular Membrane Module

An ultra-filtration and reverse osmosis module comprising a tubular casing having a plurality of tubular membrane assemblies spaced therein by spacing plates, in stepped end portions of the casing bore, and held therein by sealing plates clamped to flanges on the ends of the casing. The tubular membrane assemblies are sealed around bores in the spacing plates and boxes in the sealing plates by “O”-rings and are held against collapse by sleeves in the ends of the tubular membrane assemblies (Thayer *et al*, 1984).

2.5.4 Hollow-fibre Membrane Module

The membranes were in the shape of very small mall diameter hollow fibres. The inside diameter of the fibres is in the range of 100-500μm and the outside 200-1000μm, with the length up to 3-5m. The module resembles a shell and tube heat exchanger. Thousands of fine tubes were bound together at each end into a tube sheet that was surrounded by a metal shell having a diameter if 0.1-0.2m, so that the membrane area per unit volume is up to 10 000m^2/m^3, as is Figure 2.3 (Geankoplis, 2003).

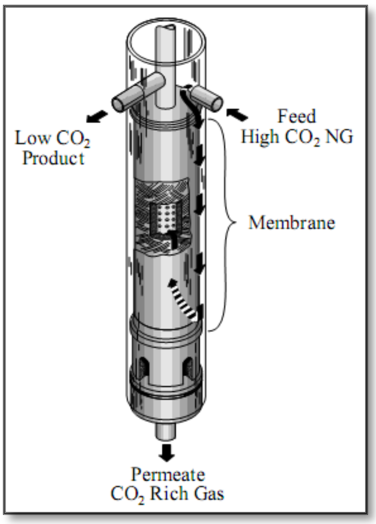

Figure 2.3: Hollow Fibre Membrane Module (Dortmundt *et al*, 1999).

2.6 Advantages of Mixed Matrix Membranes

2.6.1 Structure of Membranes

The hybrid membranes further comprises an organic/ceramic support structure which is based on ceramic-coated polymer fibers and which is thin and flexible, so that the hybrid membrane is likewise flexible. The choices of the modules and housings, therefore, the hybrid membranes involve virtually no restrictions whatsoever compared with pure polymer membranes. The pronounced flexibility of the hybrid membrane of the invention, it withstands mechanical loads very much better than hybrid membranes based on inorganic supports. The hybrid membranes have the advantages, moreover, that they are extremely favourable than metal or glass nonwovens or woven of these materials. In contrast to glass fibers, moreover, the polymer fibers are much less brittle, thereby likewise greatly simplifying the handling of the starting material and so making it more favorable.

Having a selective separating layer and comprising a permeable composite and polymeric material, has the distinctive features that the selective separating layer is formed by the polymeric material and the composite is based on a permeable support which comprises polymer fibers and on which and/or in which there inorganic components. (Hennige, 2005)

2.6.2 Performance of Membranes

The hybrid membrane can have selectivity and/or permeability that are significantly higher than the pure polymer membranes for separation. Addition of a small weight percent of molecular of molecular sieves to the polymeric matrix, therefore, increases the overall separation efficeincy significantly. Molecular sieves improve the performance of the mix matrices membrane by including selective holes/pores with a size that permits a gas. In order to obtain the desired gas separation in the mix matrices membrane, it is preffered that steady-state permeability of the faster permeating gas component in the molecular sieves be at least equal to that of faster permeating gas in the original polymer mix matrices membrane (Liu, 2009)

2.6.3 Environmentally Friendly

Membrane systems do not involve the periodic removal and handling of spent solvents or adsorbents. Permeate gases can be flared, used as fuel, or reinjected into the well. Items that do need disposal, such as spent membrane elements, can be incinerated (Dortmundt *et al*, 1999).

2.7 Type of Gas Separation Membranes

2.7.1 Polymeric Membrane

Polymeric membranes have a range of applications due to their filtration capabilities, including on micro and nano scales. This is further assisted by the physical structure/shape providing a large surface area relative to the volume of material.

Perhaps the most prominent application is in the Proton Exchange Membrane Fuel Cells which help convert chemical energy into electrical energy without the process of combustion. This technology is expected to overhaul the way in which vehicles are powered and/or fuelled (Raptra, 2005).

2.7.2 Metal Membrane

Dense metal membranes are a well-developed technology for the production of high-purity hydrogen. The physical mechanism of hydrogen transport across metal films—dissociation of molecular hydrogen, diffusion of interstitial atomic hydrogen, and subsequent recombinative desorption of molecular hydrogen—means that metal membranes can have extremely high selectivities for hydrogen transport relative to other gases. We describe current experimental and theoretical trends in the development of metal alloy membranes for hydrogen purification in practical, chemically robust processes (Sholl and Ma, 2006).

2.7.3 Ceramic and Zeolite Membrane

Ceramic and zeolite based membranes have begun to be used for commercial separations. These membranes are all multilayer composite structures formed by coating a thin selective ceramic or zeolite layer onto a microporous ceramic support. Extraordinarily high selectivities have been reported for these membranes, and their ceramic nature allows high temperatures, so fluxes are high. These advantages are however, offset by the costs of the membrane modules (Baker, 2004).

2.8 Phase Inversion Membranes

2.8.1 Precipitation by Solvent Evaporation

The simplest technique for preparing phase inversion membranes is precipitation by solvent evaporation. In this method a polymer dissolved in a solvent and the polymer solution is cast on a suitable support, for example a glass plate or another kind of support, which may be porous (e.g. polyester) or nonporous (metal, glass or polymer such as polymethylmethacrylate or Teflon).

The solvent is allowed to evaporate in an inert (e.g. nitrogen) atmosphere, in order to exclude water vapour, allowing a dense homogenous membrane to be obtained. Instead of casting it is also possible to deposit the polymer solution on a substrate by dip coating or by spraying followed by evaporation.

2.8.2 Precipitation from the Vapour Phase

This method was used as early as 1918 by Zsigmondy. A cast film, consisting of a polymer and a solvent, is placed in a vapour atmosphere where the vapour phase consists of a non solvent saturated with the same solvent. The high solvent concentration in the vapour phase prevents the evaporation of solvent from the cast film. Membrane formation occurs because of the penetration (diffusion) of non solvent into the cast film.

This lead to a porous membrane without top layer. With immersion precipitation an evaporation step in air is sometimes introduced and if the solvent is miscible with water precipitation from the vapour will start at this stage. An evaporation stage is often introduced in the case of hollow fiber preparation by immersion precipitation (wet-dry spinning) exchange between the solvent and non solvent from the vapour phase leading to precipitation (Murder, 1996).

2.8.3 Precipitation by Controlled Evaporation

Precipitation by controlled evaporation was already used in the early years of this century. In this case the polymer is dissolved in a mixture of solvent and non solvent (the mixture act as solvent for the polymer). Since the solvent is more volatile than the non solvent, the composition shifts during evaporation to a higher non solvent and polymer content. This leads eventually to the polymer precipitation leading to the formation of a skinned membrane (Murder, 1996).

2.8.4 Thermal Precipitation

A solution of polymer in a mixed or single solvent is cooled to enable phase separation to occur. Evaporation of the solvent often allows the formation of a skinned membrane. This method is frequently used to prepare microfiltration membranes (Murder, 1996).

2.8.5 Immersion Precipitation

Most commercially available membranes are prepared by immersion precipitation. A polymer solution (polymer + solvent) is cast on a suitable support and immersed in a coagulation bath containing a non solvent. Precipitation occurs because of the exchange of solvent and non solvent. The membrane structure ultimately obtained result from a combination of mass transfer and phase separation. All phase inversion processes are based on the same thermodynamic principles will be described (Murder, 1996).

2.9 Preparation Technique for Immersion Precipitation

Most of the membranes in use today are phase inversion membranes obtained by immersion precipitation. Phase inversion membranes can be prepared from a wide variety of polymers. The only requirement is that only the polymer must be soluble in solvent or solvent mixture. In general the choice of polymer does not limit the preparation technique.

The various techniques will be described very schematically here, so that their characteristics maybe understood. Pre-treatment and post-treatment will not be considered because that are very specific and depend on the polymer used and on the type of application. Basically the membranes can be prepared in two configurations: flat or tubular (Murder, 1996).

2.9.1 Flat membranes

Flat membranes are used in plate-and-frame and spiral-wound systems where as tubular membrane are used in hollow fiber, capillary and tubular system. The same flat membranes can be used for both flat membrane configuration (plate-and-frame and spiral wound). The preparation of flat membranes or a semi-technical or technical scale is shown in Figure 2.4, next page:

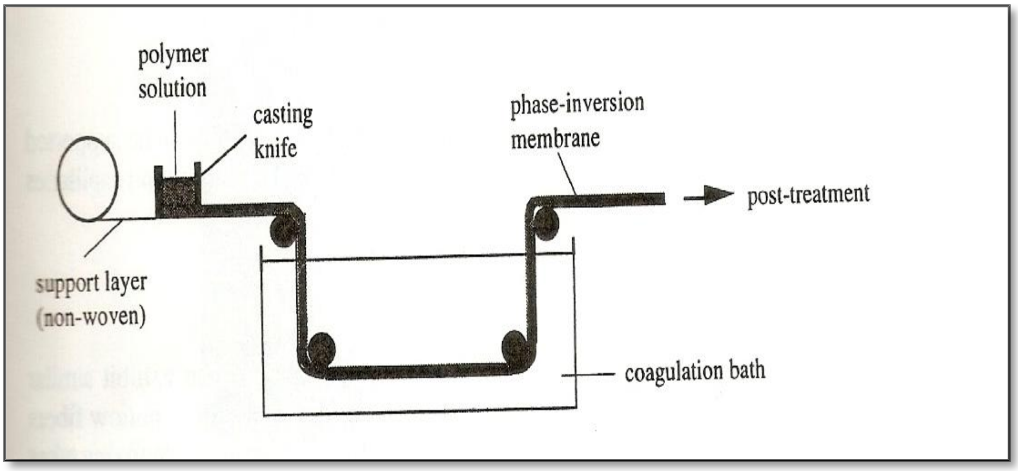

Figure 2.4: schematic of preparation flat membrane (Murder, 1996)

The polymer is dissolved in a suitable solvent or solvent mixture (which may include additives). The viscosity of the solution depends on the molecular weight of polymer, its concentration, the kind of solvent (mixture) and the various additives. In figure 2.6 the polymer solution (often referred to as casting solution) is cast directly upon a supporting layer, for example non-woven polyester, by means of a casting knife. The casting thickness can vary roughly from 50-500μm. The cast film is then immersed in a non solvent bath where change occurs between the solvent and non solvent and eventually the polymers precipitate. Water is often used (and from an environmental point of view also preferred) as a non solvent but organic solvent (e.g. methanol) can be used as well. Since the solvent/non solvent pair is a very important parameter in obtaining the desired structure the non solvent cannot be chosen.

Other preparation parameters are: polymer concentration, evaporation time, humidity, temperature and the composition of the casting solution (e.g. additives). These parameters are mainly determining the ultimate membrane performance (flux and selectivity) and hence for its application. The membrane obtained after precipitation can be used directly or past a treatment (e.g. heat treatment) can be applied. Free flat membrane can be obtained by casting the polymer solution upon a metal or polymer belt. After coagulation (and thorough washing) the free flat-sheet can be collected (Murder, 1996).

2.10 Polysulfone Membrane

Polysulfone is a high performance engineering thermoplastic which results degradation. Is an amorphous and hydrophobic polymer. Good gas permeability and selectivity values, low cost, excellent thermal, chemical and mechanical properties and has a widespread use as a commercial polymer.

2.11 Natural Gas

Natural gas is a subcategory of petroleum that is naturally occurring, complex mixture of hydrocarbons, with a minor amount of inorganic compounds (Ghalambor, 2005).

2.11.1 Acid Gases Removal

Hydrogen sulfide and carbon dioxide are the main acid gases which have to be removed from natural gas. As already indicated, removal of hydrogen sulfide (natural gas sweetening) must normally be much more thorough than that of carbon dioxide. The specifications on acid gas contents are imposed by safety requirements (very high toxicity of hydrogen sulfide), transport requirements (need to avoid corrosion and crystallization in the case of liquefaction), and distribution specifications (commercial gas) (Rojey, 1997).

Besides the acid gas, nitrogen also small quantities in most natural gas deposits at a level less than 2%. Nitrogen does not have a major influence on the gas properties, but sometimes some gases contain 10% and higher, so need to remove. Nitrogen is difficult to remove. The conventional method is by liquefaction where all of the other components are condensed, and the methane and nitrogen separated by distillation. Nitrogen need to remove because it lowers the BTU value of the gas and makes it unsalable to most pipelines. Natural gas will accept if nitrogen less than specified amount of nitrogen (Seddon, 2006).

Acid gas removal is a very important industrial operation which has been described in many works. The main processed are used are based on absorption, and the selectivity of the solvent with respect to acid gases based on an affinity of the chemical or physical type. Adsorption is also used for intensive purification. Gas permeation has a substantial potential in this process. There are the process with used in acid gas removal:

a) Process based on chemical solvents
b) Processes based on physical solvent
c) Acid gas removal by adsorption
d) Acid gas fractionation
e) Sweetening of liquid fractions
f) Conversion of hydrogen sulfide to sulfur
g) Acid gas removal by gas permeation

2.12 Zeolites

2.12.1 Definition of Zeolites

Zeolites are microporous crystalline aluminosilicate, composed of TO_4 tetrahedra (T = Si, Al) with O atoms connecting neighboring tetrahedral. For a completely siliceous structure, combination of TO_4 (T = Si) units in his fashion leads to silica framework, the +3 charge on the Al makes the framework negatively charged, and requires the presence of extraframework cations (inorganic and organic cations can satisfy this requirement) within the structure to keep the overall framework neutral. The zeolite composition can be best described as having three components:

$M^{m+}_{n/m}$	•	$[Si_{1-n}Al_nO_2]$	•	nH_2O
Extraframework		framework		sorbed phase