CHAPTER II
BACKGROUND AND LITERATURE REVIEW

2.1 Background

Membranes have been known for more than 100 years, but the membrane technology has gained its importance in a broad range of applications since 1960s. Generally, membranes are viewed as semipermeable barriers that have the ability to control the permeation of species in contact with them. In separation application, this key property is manipulated with the aim to allow only desirable species of feed mixture to permeate at higher rate than another or other species (McCabe et al., 1993).

The potential to save large amount of energy is the outstanding advantage of membrane process compared to other separation processes. Industrial applications of membrane separation processes include reverse osmosis, dialysis, electrodialysis, microfiltration, ultrafiltration, pervaporation, and gas separation. The principal types of membranes are categorized depending upon their structures. Isotropic microporous membrane has a rigid highly voided structure with randomly distributed, interconnect pores. Nonporous dense membrane is uniform film through which permeants are transported by diffusion under the driving force such as pressure and concentration. Electrically charged membrane or ion exchange membrane is most commonly microporous of which the pore walls carrying fixed positively or negatively charged ions. Asymmetric membrane consists of extremely thin film layer supported by a thicker porous dense substucture. Other types of membranes include ceramic membranes, metal membranes, and liquid membranes (Rousseau 1987; Grant 1991).

During 1950s and 1960s, palladium and palladium alloy membranes were installed in a commercial plant to separate hydrogen from refinery off-

gas. This invention led to the great development of membrane gas separation processes in the 1980s, and the rapid expansion and simultaneously substantial growth until 1990s. However, membrane-based gas separation is still the developing technology and in the area of considerable research interests which is expected to increase over the next few years (Kesting and Frotzsche, 1993).

In gas separation, a mixed gas feed at an elevated pressure is passed across the surface of a membrane that is selectively permeable to one component of the feed. The pressure difference between the pressurized feed gas and the lower pressure penetrant is the driving force of separation operation. Both porous and dense membrane can be utilized as permselective layers. Mechanisms for gas permeation through porous membranes depend on the size of pores of the membranes. Gases traverse a membrane by bulk or convective flow in the membrane of which the pore diameter is large compared to the molecular diameter. Such a flow is not permselective and, therefore, no separation between components of the feed occurs. If the pores are of the order of molecular size for at least some of the components in feed mixture, the mixture of components will be restricted, resulting in an enhanced separation. Molecules of size larger than the pores will be prevented from diffusing through the pores. This phenomenon is referred to as sieving mechanism (Grant, 1991).

Although porous membranes are a topic of research interest, most commercial gas separation membranes are dense types in which gases are transported by solution diffusion mechanism. The solution diffusion mechanism is driven by a difference in thermodynamic activity existing between the feed and the downstream boundary of a membrane. This mechanism of gas permeation involves the sorption of gas onto membrane and diffusion of gas through membrane. Gases dissolve into membrane at the feed boundary. Gas diffusion through membrane occurs as a result of concentration difference between feed and downstream boundary of membrane. Finally

permeate gas dissociates or evaporates from the downstream boundary (Rousseau, 1987).

2.2 Theory

Thomas Graham, who performed the first recorded experiments on the transport of gases and polymeric membranes in 1829, proposed the so-called solution diffusion model (Kesting and Frotzsche, 1993).

Under the driving force of a pressure difference across a membrane, penetrant molecules dissolve in the upstream (or high pressure) face of membrane, diffuse across membrane, and desorb from the downstream (or low pressure) face of the membrane. Diffusion is the rate-controlling step in penetrant permeation (Freeman, 1999).

It is well known that the transport process through a pore-free polymeric medium can be described by Fick's first law of diffusion (Yamamoto et al., 1990; Wijmans and Baker, 1995; Koros and Kamaruddin, 1997). The flux of A, J_A, resulting from diffusion transport, is

$$J_A = -D_A \left(\frac{dC_A}{dx} \right) \tag{2.1}$$

where D_A is the diffusion coefficient or diffusivity and C_A (cm^3 (STP)/cm^3) is the concentration of A inside the membrane.

Assuming that thermodynamic equilibrium exists at the two fluid-membrane interfaces, the concentrations in Fick's law can be related to the membrane face by Henry's law, which is linear relation that is most conveniently written for membrane application.

From Henry's law :

$$C_A = p_A * S_A \tag{2.2}$$

Using equation 2.2 (McCabe *et al.*, 1993) to replace the concentration gradient for a pressure pressure gradient gives

$$J_A = \frac{D_A S_A (p_{A0} - p_{AI})}{l} \tag{2.3}$$

$$\frac{J_A \times l}{p_{A0} - p_{AI}} = D_A \times S_A \tag{2.4}$$

The product $D_A S_A$ is the flux per unit pressure gradient, which is called the permeability coefficient, q_A , and is often expressed in Barrers, where

$$1 \text{ Barrers} = 10^{-10} \text{ cm}^3 \text{ (STP)} - \text{cm} / \text{cm}^2\text{-sec-cmHg}$$

Since the actual thickness of membrane is not always known or specified for commercial membranes, the term 'Permeability' , P_A , defined as the thickness and pressure normalized flux, is more convenient to use (McCabe *et al.*, 1993).

$$J_A = \frac{q_A (p_{A0} - p_{AI})}{l} \tag{2.5}$$

Therefore, the permeability depends on both diffusivity of the gas component in the membrane and the solubility of that component in the membrane (Rousseau, 1987; Grant, 1991).

The selectivity of a membrane for a penetrant A relative to penetrant B is characterized by an "ideal separation factor", which is defined by

$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{D_A S_A}{D_B S_B} \tag{2.6}$$

where D_A/D_B is called mobility selectivity and S_A/S_B is called solubility selectivity (Grant, 1991; Kamaruddin and Koros , 1997).

The mobility selectivity is a measure of the relative ease with which components perform diffusive jumps while solubility selectivity is a measure of the relative condensiblity of the components and affinity of the polymer to the components. Using the mobility and solubility aspects of the components to explain permeation properties of membrane systems has been instrumental in bringing about better understanding of transport in polymeric materials (Baker *et al.*, 1998.).

2.3 Literature Review

2.3.1 Polymeric Gas Separation Membrane

Gas separation membranes have greatly evolved during 1980's when the membrane field was thought to be matured. Ito and Hwang (1989) examined various polymer membranes for the permeation of propylene and propane. The polysulfone and silicone rubber membranes were appeared to show the high selectivities of 3.5 and 1.2, respectively for the propylene/propane systems.

Pellegrine and Kang (1995) measured CO_2 and CH_4 gas permeation through polyperfluorosulfonate ionomer (PSFI) that was sovated with water, methanol, ethanol, and 1-propanol. The increased permeablity of CO_2 when the membrane was swollen by the solvent in the sequence ethanol > methanol > water implied the effect of polar solvents. The higher permeability of CH_4 compared to the values measured from the dry PSFI film was observed. They suggested that the solvents penetrated into polymer phase and increased the permeability, which was resulted from the increase in diffusivity.

Hayashi *et al.* (1996) attempted to shift the trade-off relationship of the BPDA – pp'ODA polyimide membrane by carbonization at optimized temperature. The carbonized membranes showed much improvement in selectivity. The selectivity was increased further when the carbonized membrane was modified by chemical vapor deposition with propylene as carbon source. The repetition of carbonization served to increase the membrane performance. They also studied the temperature dependence on selectivity of these membranes. Both C_3H_6/C_3H_8 and C_2H_4/C_2H_6 systems showed that permeances decreased and selecitivity increased as decreasing temperature.

The considerable research efforts to develop new polymers for gas separation membranes presuppposed the eventual need for composite membranes in which these new materials would serve as the ultrathin film barrier layers that can increase the flux of penetrant. Yamasaki *et al.* (1997) prepared asymetric membranes from polysulfone/N,N-dimethyl acetamide solutions by the phase inversion technique. The oxygen permeance was inversely proportional to the immersion time. This resulted from the increased skin layer thickness as increasing immersion time. Beuscher and Goodings (1999) commercialized a flat sheet and a hollow fiber composite membrane for volatile organic compounds after their investigation in the permeation properties of silicone rubber coated composite membranes. Other four polymeric materials made from poly(phenylene oxide), polysulfone, ethylcellulose and cellulose acetate were studied by Sridhar and Khan (1999) for the separation of propylene from propane. Their results of high permeabilties and reasonably good selectivities made ethylcellulose to be the most promising for commercial application. Polyimides based on 4,4'–(hexafluoroisopropylidene) diphthalic anhydride (6FDA) was another very promising material for membrane-based separation of olefin/paraffin mixtures. Bickel and Koros (2000) obtained the ideal ethylene/ethane separation factor ranged between 3.3 and 4.4 and the ideal propylene/propane separation factor ranged between 10 and 16 at a feed pressure of 3.8 atm and 308 K.

2.3.2 Facilitated Transport Membranes

The liquid media can be incorporated in the membrane matrix by wetting a microporous polymeric membrane. This results in a liquid filled membrane which can be utilized as a medium for gas separation. Meldon *et al.* (1985) measured carbon dioxide and oxygen permeabilities to study facilitated transport in immobilized liquid films comprised of mixutes of polyethylene glycol (PEG) and alkanolamines. The CO_2 permeability of PEG was found to be 500 Barrers and CO_2/O_2 selectivity was 5. For the membranes containing alkanolamines they found that the apparent CO_2 attained a minimal value that varied with amine concentration. It was due to elevated CO_2 concentrations, the amine is fully converted to carbamate species throughout liquid films. They suggested that reduced CO_2 partial pressure in the sweep gases promote a carbamate concentration gradient across the imobilized liquid films.

Saha and Chakma (1995) studied CO_2 separation from a mixture of CO_2/C_2H_6 through membranes containing immobilized solutions of diethanolamine (DEA) and PEG. The counter-current mode of operation was found to produce a higher flux. They suggested that in the counter-current mode an increase in the sweep gas flow rate resulted in the lowering of down stream partial pressure and consequently enhanced the mass transfer rate. The permeation rate of CO_2 in DEA/PEG membranes was higher than the value measured in PEG membranes. They concluded that the enhancement of CO_2 separation constituted to the addition of DEA in membrane matrix.

Li *et al.* (1998) investigated the effect of PEG molecular weight in the range of 200-20000 on gas permeabilities and selectivities in a series of miscible cellulose acetate (CA) blend membranes. PEG2000 appeared to be the most promising for the improved of the permeability of CO_2 and CO_2/N_2 selectivity of blend membranes. The improvement of the permeability coefficients resulted from the increased CO_2 diffusivity coefficient, though

their results from the sorption experiments revealed the decreased CO_2 solubilty coefficient. They claimed the characterization of the membranes that showed the occurrence of microphase separation and the densified intersegmental chain packing to confirm the decrease in CO_2 solubility coefficient.

Metal ion can be manipulated in facilitated transport of olefins. Yang and Hsuise (1998) studied swollen complex membrane made of linear low density polyethylene and compared with the corresponding membranes based on silicone rubber (SR) and poly[1-(trimethylsilyl)-1-propyne]. The polymeric matrix was first grafted with acrylic acid (AA) and then incorporated with silver ions (Ag^+) in glycerol solution for forming the swollen complex membrane. Various metal ions and swollen liquids were compared. The results for isobutene/isobutane separation showed that the selectivity of the complex membrane incorporated with Ag^+ ion was higher than those incorporated with Cu^+ and Cu^{2+} ions. Glycerol was found to be promising swelling agent compared to ethylene glycol or 1,2-propanediol. They concluded that glycerol in these membranes functioned as a plasticizer. Moreover the silver nitrate was solvated by glycerol and led to the high selectivity for olefin.

2.3.3 Mixed Matrix Membranes

Since 1980's, the mixed matrix membranes or multicomponent membranes have been suggested to improve the conventional gas separation membranes in achieving higher permselectivity with at least equivalent productivity. Henis and Tripodi (1980) disclosed multicomponent membranes having desirable permeation rates and desirable selectivity of separation. The multicomponent membranes according to this invention were prepared by coating a thin dense semi-permeable material onto the top of porous support layer. It appeared that the improvement in the permeation rate was attributed to the decrease in the thickness of dense selective layer. The less dense region in such a membrane provide sufficient structural support to prevent the rupture of the membrane under the operating pressure.

The multicomponent membranes fabricated from the combination of a porous support and a coating layer that combines different materials with their own excellent properties were proposed by Riley and Grabowsky (1981). By utilizing various semi-permeable membranes forming prepolymer as the thin component of the gas membrane, the various gas separations can be affected because the various polymers that form a thin posses varying permeabilities with regard to specific gases. One of their examples, with the same cellulose acetate- cellulose nitrate support, multicomponent membrane having dimethyl silicone as selective dense layer provided higher O_2 transport rate when compared to the membrane with dense layer formed from nylon-6.

Okita (1985) developed the membrane having highly permselective and superior strength and heat resistant for application in concentrating oxygen from the air, separating hydrogen from petroleum gas, etc. Their membranes comprised of a heat resistant porous layer and a thin layer of a tertiary carbon or tertiary organic silicon-containing compound, the layer being polymerized by means of plasma.

Another membrane for the oxygen enrichment of air was disclosed by Cabasso and Lundy (1986). They prepared membranes by in situ crosslinking of aminoorganofunctional polysiloxane directly coated on the polysulfone support. The characteristics sought in this membrane were good permselectiviy for oxygen, reasonably high flux and adaptability to hollow fiber technology.

Kulpratipanja and Kulkrani (1986, 1988) manipulated the glycol plasticizer to separate polar gases from non polar gases. The multicomponent membrane composed of polyethylene glycol (PEG) emulsified silicone rubber as the first selective polymer and porous polysulfone support as the second polymer. The results showed that the selectivities of silicone rubber/PEG on polysulfone were higher than the values obtained from the silicone rubber alone on polysulfone. The increase in selectivities was attributed to the much higher permeation of polar gases through PEG that resulted from the solubility of polar gases in PEG. The efficiency of multicomponent membranes depend upon the amount of PEG introduced in silicone rubber phase.

Kulpratipanja and Neuzil (1992) disclosed a multicomponent membrane whixh is a solid particulate adsorbent distributed in an organic polymer. They mixed the silicalite with solvent and then mixed with cellulose acetate to prepare the multicomponent membrane. It was surprisingly found that silicate, due to its adsorptive affinity to CO_2, which was incorporated in cellulose acetate altered the selectivity of CO_2/H_2 mixtures whereas the plain cellulose acetate is selective to H_2.

Another separation of polar gases from non polar gases was studied by Serivalsatit (1999). She compared the membranes prepared from silicone rubber on various types of commercial porous support The selectivities of polar gases were improved when compared to the porous support alone, though the selectivities were comparable among the various porous supports. The results implied that the coated silicone rubber did not have interaction with the porous supports. It was concluded that the selectivity of multicomponent membrane was mainly controlled by the thin selective surface layer of silicone rubber.

Sukapintha (2000) studied the separation of olefin from paraffin through mixed matrix membranes containing PEG and various types of zeolites as incorporating materials. PEG was shown to enhance the ethylene selectivity which agreed with the previous literature. Another attempt to increase the olefin selectivity was done by the manipulation of Ag^+ ion facilitation. Ag-X, Ag-LZ, and Ag-A were used as source of olefin carrier. The ethylene selectivities of membranes incorporated with the three zeolites were not improved.