CHAPTER II
BACKGROUND AND LITERATURE REVIEW

2.1 BACKGROUND

2.1.1 Membrane Technology

In a membrane separation process, a feed consisting of a mixture of two or more components is partially separated by means of a semipermeable barrier (the membrane) through which one or more species move faster than another or other species (Clark and Castellano, 1993). The most general membrane process is shown in Figure 2.1 where the feed mixture is separated into a retentate (that part of the feed that does not pass through the membrane) and a permeate (that part of the feed that does pass through the membrane).

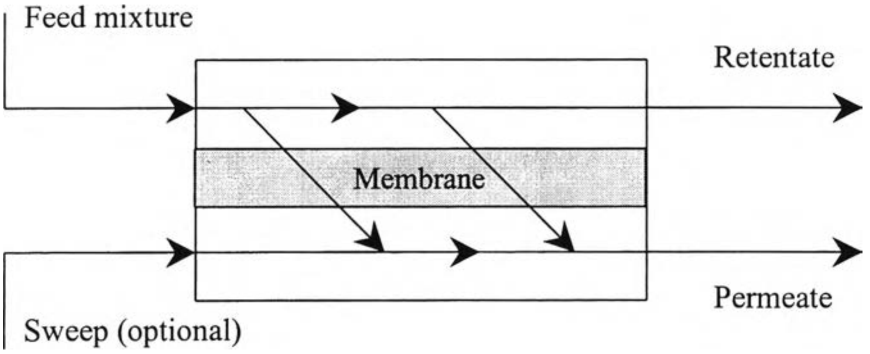


Figure 2.1 General membrane process.

The feed, retentate, and permeate are usually liquid or gas. The barrier is most often a thin, nonporous polymeric film, but may also be porous polymer, ceramic, or metal material, or even a liquid or gas. The barrier must not dissolve, disintegrate, or break. The optional sweep is a liquid or gas, used to help remove the permeate.

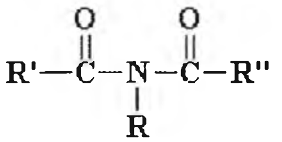
In membrane separations: (1) the two product are usually miscible, (2) the separating agent is a semipermeable barrier, and (3) a sharp separation is often difficult to achieve. Thus, membrane separation differs in two or three respects from the more common separation operations of adsorption, stripping, distillation, and liquid-liquid extraction (Clark and Castellano, 1993).

Although membranes as separating agents have been known for more than 100 years, large-scale applications have only appeared in past 60 years (Lonsdale, 1982). For example, in the mid-1960s, reverse osmosis with cellulose acetate was first used to desalinize seawater to produce potable water. Commercialization of alcohol dehydration by pervaporation began in 1980s. The replacement of the more common separation operations with membrane separation has the potential to save large amount of energy. This replacement requires the product of high mass-transfer flux, defect-free, long-life membranes on a large scale and the fabrication of the membrane into compact, economical modules of high surface area per unit volume.

Membrane separation is an emerging unit operation. Important progress is still being made in the development of efficient membrane materials and the packaging thereof for the processes. Applications covering wider ranges of temperature and types of membrane materials are being found. Already, membrane separation processes have found a wide range of applications in such diverse industries as the beverage, chemical, dairy, electronic, environmental, food, medical, paper, petrochemical, petroleum, pharmaceutical, and textile industries. Often, compared to other separation equipment, membrane separators are more compact, less capital intensive, and more easily operated, controlled, and maintained. Desirable attributes of a membrane are good permeability, high selectivity, chemical and mechanical compatibility with processing environment, stability, freedom from fouling, and reasonable useful life, amenability to fabrication and packaging, and ability to withstand large pressure difference across the membrane thickness.

Almost all industrial membrane processes are made from natural or synthetic polymers. Natural polymers include wool, rubber, and cellulose. A wide variety of synthetic polymers has been developed and commercialized since 1930. Polyimides are a very interesting group of incredibly strong and astonishingly heat and chemical resistant polymers. Their strength and heat and chemical resistance are so great that these materials often replace glass and metals, such as steel, in many demanding industrial applications. Polyimides are even used in many everyday applications such as struts and chassis in some cars as well as some parts under-the-hood because they can withstand the intense heat and corrosive lubricants, fuels, and coolants cars require. They are also used in the construction of many appliances as well as microwave cookware and food packaging because of their thermal stability, resistance to oils, greases, fats, and their transparency to microwave radiation (Brust, 1996).

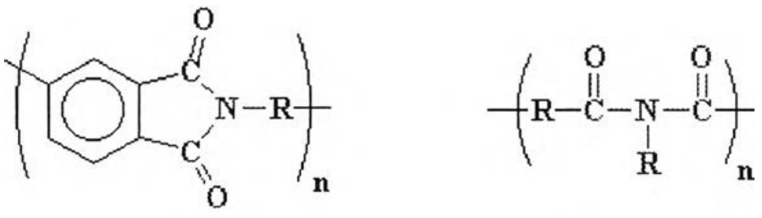
Polyimide is a polymer that contains an imide group. An imide is a group in a molecule that has a general structure as in Figure 2.2.



$$R'-\overset{\overset{O}{\|}}{C}-\underset{\underset{R}{|}}{N}-\overset{\overset{O}{\|}}{C}-R''$$

Figure 2.2 Imide molecule.

Polyimides usually take one of two forms. The first is a linear structure where the atoms of the imide group are part of a linear chain. The second of these structures is a heterocyclic structure where the imide group is part of a cyclic unit in the polymer chain as in Figure 2.3.



(a) (b)

Figure 2.3 (a) aromatic heterocyclic polyimide (b) linear polyimide.

Aromatic heterocyclic polyimides (Figure 2.3a) are typical of most commercial polyimides, such as Ultem from G.E. and Dupont's Kapton. Ultem 1000 is an example of polyimide. It is a thermoplastic polyetherimide high heat polymer designed by General Electric for injection molding processing. Through the development of new extrusion technology, Ultem 1000 combines excellent machinability and provides a cost saving benefit in high heat applications (continuous use to 340°F).

So, these polymers have such incredible mechanical and thermal properties that they are used in place of metals and glass in many high performance applications in the electronics, automotive, and even the aerospace industries. These properties come from strong intermolecular forces between the polymer chains (Brust, 1996).

2.1.2 Mixed Matrix Membrane (MMM)

One of the most exciting and significant unit operations introduced in recent years is the use of membranes to separate gaseous mixtures. However, commercialization of this technique has been limited by low permeabilities and selectivities and by low mechanical and chemical resistance of membranes to operating conditions. Nowadays, the applications of new structural modifications to different polymer chemistries have shown great advances. One of the emerging membrane morphology with a future potential is a MMM. A so-called "mixed matrix" comprised of molecular sieving domains dispersed in an appropriate continuous matrix. Silicalite is an example of the molecular sieve that is commonly used in MMM studies. Polymer matrix selection determines minimum membrane performance while molecular sieve addition can improve membrane selectivity in the absence of defects. Intrinsically, the matrix polymer selected must provide industrially acceptable performance (Zimmerman and Koros, 1998).

2.1.3 Extraction

In liquid-liquid extraction, a liquid feed of two or more components to be separated is contacted with a second liquid phase, called the extractant. The solute is transferred from the liquid, often termed as feed solution to the extractant. The feed solution and the extractant are essentially immiscible. When the feed solution is brought in contact with the extractant, the solute tends to distribute itself between the two phases depending on the solubility of the solute between two liquids (Anderson *et al.*, 1998).

In conventional liquid-liquid extraction processes, the feed solution and the extractant are intimately mixed to promote the distribution of solute between the two. However, in certain cases this intimate mixing leads to either formation of emulsion which is difficult to break or stable dispersions of extractant in the feed solution which takes long time to separate. But for the membrane extraction process, the membrane serves as the partition between the feed solution and the extractant (Lee *et al.*, 1976). So, there is no emulsion-formation problem in this system.

In the MMM extraction process, a membrane is the barrier between the feed solution and the extractant. The solute is first adsorbed into the pore of the adsorbent and then under the thermodynamic activity gradient, the solute diffuses by molecular diffusion and pressure gradient across the membrane and finally desorbed by the extractant.

The selectivity which is expressed by the separation factor α is shown in Equation (2.1), can be calculated by analyzing the permeate and retentate composition with gas chromatography.

$$\alpha_{A/R} = (Y_A/Y_R) / (X_A/X_R) \qquad (2.1)$$

In Equation (2.1), Y represents the permeate and X is the retentate concentration (%wt). R is the reference component.

2.1.4 Pervaporation

Pervaporation processes are membrane-based separations of liquid mixtures. Thereby a transfer of mass from a liquid phase to the vaporous phase through a polymeric membrane is performed (Schleiffelder and Staudt-Bickel, 2001). The liquid mixture is fed at the pressure that is usually ambient or elevated high enough to maintain a liquid phase. The other side pressure is maintained at or below the dew point of the permeate, making it vapor. The low pressure is maintained by use of vacuum pumping and/or carrier gases. Vaporization may occur near the downstream face of the membrane. The separation mechanism of pervaporation is a solution-diffusion mechanism, in which the permeate rate is a function of solubility and diffusivity. Concentration differences across the membrane provide the driving for transport, and the transport process across the membrane is divide into three step: (1) sorption into the membrane at the upstream side, (2) Diffusion through the membrane, and (3) desorption into a vapor phase at the downstream side. The pervaporation process is illustrated in the schematic diagrams presented in Figure 2.4. The final step is then the condensation of the permeate. This condensation usually occurs outside of the separator.

Presently, the most promising application for pervaporation membranes are in the separations of isomeric and azeotropic systems, especially if the boiling characteristics of the components are nearly identical such as the dehydration of ethanol. The selectivity that is expressed by the separation factor α is shown in Equation (2.2), can be calculated by analyzing the permeate and retentate composition with gas chromatography.

$$\alpha_{A/R} = (Y_A/Y_R) / (X_A/X_R) \tag{2.2}$$

In Equation (2.2), Y represents the downstream and X is the upstream concentration (%wt). R is the reference component.

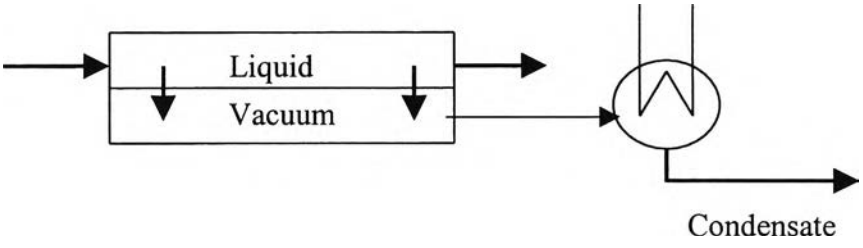


Figure 2.4 Schematic diagrams of pervaporation.

2.1.5 Theory of Solution-diffusion for Liquid Mixtures in Membrane

In a membrane process, a feed consisting of a mixture of two or more components is partially separated by means of a semipermeable barrier (the membrane) through which one or more species move faster than another or other species. The feed mixture is separated into a retentate (that part of the feed that does not pass through the membrane) and a permeate (that part of the feed that does pass through the membrane). The barrier is most often a thin, nonporous polymeric film, but may also be porous polymer, ceramic, or metal materials (Clark and Castellano, 1993).

Figure 2.5 shows typical solute concentration profiles for liquid mixtures with nonporous membranes. Include in this diagram is the drop in concentration across the membrane and, also, possible drops due to resistances tin the fluid boundary layers of film on either side of the membrane.

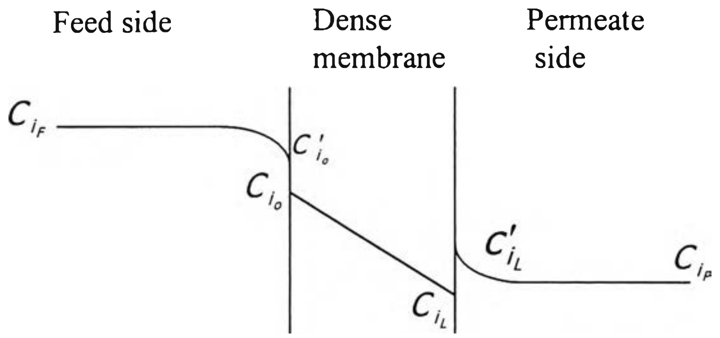


Figure 2.5 Concentration profiles for solute transport through membranes, liquid mixture with a nonporous membrane.

For nonporous membranes, solute concentration C_{i_o} is that in the feed liquid just adjacent to the upstream membrane surface, whereas C_{i_o} is that in the membrane just adjacent to the upstream membrane surface. In general, C_{i_o} is considerably smaller than C_{i_o}, but the two are relateed by a thermodynamic equilibrium partition coefficient K_i defined by Equation (2.3)

$$K_{i_o} = C_{i_o}/C_{i_o} \tag{2.3}$$

Similary, at the other face:

$$K_{i_L} = C_{i_L}/C_{i_L} \tag{2.4}$$

Fick's law applied to the nonporous membrane of Figure 2.5 is:

$$N_i = \frac{D_i}{I_m}(C_{i_o} - C_{i_L}) \tag{2.5}$$

where *Di* is the diffusivity of the solute in the membrane. If Equations (2.3) and (2.4) are combined with Equation (2.5), and the partition coefficient is assumed to be independent of concentration, such that $K_{i_o} = K_{i_L} = K_i$, we obtain for the flux

$$N_i = \frac{K_i D_i}{I_m}(C_{i_o} - C_{i_L}) \tag{2.6}$$

If the mass-transfer resistances in two flued boundary layers or films are negligible:

$$N_i = \frac{K_i D_i}{I_m}(C_{i_F} - C_{i_P}) \tag{2.7}$$

In Equations (2.6) and (2.7), K_iD_i is the permeability, P_{M_i} , for the solution-diffusion model, where K_i accounts for the solubility of the solute in the membrane and *Di* account for diffusion through the membrane.

2.2 LITERATURE REVIEW

Kulprathipanja *et al.* (1988) studied the separation of a monosaccharide from an aqueous solution comprising monosaccharide and polysaccharide. The MMM's were prepared by the dispersion of CaY, silicalite or activated carbon in cellulose acetate (CA) membranes. Used in the experiments was an aqueous solution comprising 20 to 30 wt% of dry solids of which 75.4 wt% was monosaccharide, 3.6 wt% disaccharide, 0.3 wt% trisaccharide , and 20.7 wt% tetra and higher saccharides. The mixture was charged to one face of the membrane at a rate of 200 ml/min and the temperature was 60° C. The pressure drop across the membrane was 6.8 atm. For comparison purpose, a plain CA membrane was also prepared and used in the test cell. Between the CaY/CA MMM and plain CA membrane, it was found that the CaY/CA MMM gives higher flux of monosaccharide and can maintain that high flux over an extended period than the plain membrane. For CaY, silicalite, or activated carbon/CA MMM tested, the higher the flux, the higher purity of monosaccharide reduction obtained regardless of the membrane material used.

Sartori *et al.* (1990) studied the separation of aromatics/saturates separation by polyester membranes. A film of polyethylene terphthalate was used in the pervaporation apparatus for separation of 50 wt% toluene and 50 wt% iso-octane. It was found that at 170° C, the toluene/iso-octane separation factor was 23, and the normalized flux was 108 kgμmm^{-2}/day. At 200°C, the separation factor was 18 and the normalized flux was 190 kgμmm^{-2}/day. In addition, a film of PETG (polyethylene terephthalate/cyclohexane-dimethanol terephathalate) was used in the pervaporation apparatus for the same feed mixtures. It was shown that the selectivity of this membrane was 50 and the permeability was 300 kgμmm^{-2}/day at 100°C. The selectivity decreased with increasing the temperature. At 150°C, this membrane still had a good selectivity, 12, and the permeability was 1300 kgμmm^{-2}/day.

Satori *et al.* (1992) studied the separation of aromatics and non-aromatics mixtures using polysulfone membrane. In a pervaporation experiment, the feed contained 20 wt% isooctane, 10 wt% toluene, 30 wt% n-octane and 40 wt% p-xylene. The membrane showed that the selectivity of toluene/n-octane was 11 and a normalized flux was 100 kgμM/M^2/D at 210° C. For the feed of 50 wt% toluene and 50 wt% n-octane, the separation factors of toluene/n-octane were 9.3, 6.5, and 4.6 at 150, 175, and 200° C, respectively. Normalized flux of were 283, 624, and 1170 kgμM/M^2/D at 150,175, and 200° C, respectively.

Pure gas separation and sorption experiments were carried out for ethylene, ethane, propylene, and propane by Staudt-Bickel and Koros (2000). 6FDA-based polyimide membranes were used to find the ideal ethylene/ethane and ideal propylene/propane selectivities. Ideal selectivity was obtained from the pure-component feed, at 3.8 atm feed pressure and 308 K. For all polyimides investigated, a preferred permeability of olefins compared to paraffins was found. The best selectivity as well as permeability of olefin/paraffin was achieved with the 6FDA-6FpDA polyimide membrane. The differences in the solubility for olefin and paraffin were very small. In other words, the preferred permeation of olefins compared to paraffins is due to their preferential diffusion, which is based on the smaller and flat shape of olefins. 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. In the 50:50 olefin/paraffin mixed gas permeation experiments, up to 20% and 50% lower in the ethylene/ethane separation and selectivity for the propylene/propane separation compared to the ideal selectivity were obtained.

For the membrane-based separation of p-/o-xylene mixtures, pervaporation properties of several crosslinked and non-crosslinked 6FDA (4,4′-(hexafluoro-isopropylidene)-diphthalic anhydride))-based copolyimide membranes have been investigated by Schleiffelder and Staudt-Bickel (2001). The copolyimide was synthesized by polycondensation of 6FDA with different diamino monomers such as 4MPD (2,3,5,6-tetramethyl-1,4-phenylene-diamine), 6FpDA (4,4′-(hexafluoro-isopropylidene)-dianiline)) and DABA (3,5-diaminobenzoic acid). Among the monomers, DABA is the only monomer containing a crosslinkable carboxylic acid group. By variation of the diamino monomer ratio, different crosslinkable copolyimides were synthesized. It has been found that crosslinkable carboxylic acid containing copolyimides are stable towards p-/o-xylene mixtures at 60°C. The normalized flux through the different membranes strongly depends on the polymer backbone structure, but it is also influenced by the crosslinking agent. For p-/o-xylene mixtures, normalized fluxes between 0.04 kg μ mm^{-2} h^{-1} and 25 kg μ mm^{-2} h^{-1} were reached with separation factors between 1.15 and 1.47.

Chan *et al.* (2002) studied the separation C_2 and C_3 hydrocarbon in poly (1,5-naphthalene-2,2′-bis(3,4-phtahalic) hexafluoropropane) diimide (6FDA-1,5-NDA) dense membranes at 35°C under 5 atm. It was found that 6FDA-1,5-NDA polyimide was more permeable to C_2H_4 and C_3H_6 than C_2H_6 and C_3H_8. The membrane permeabilities were 0.15, 0.87, 0.023 and 0.24 Barrer with respect to pure ethane, ethylene, propane and propylene, respectively. The 6FDA-1,5-NDA dense membranes displayed an ideal selectivity of 5.8 and 10 with respect to the separations of C_2H_4/C_2H_6 and C_3H_6/C_3H_8. The separation factors for these olefins/paraffins were controlled by the diffusivity selectivity. The feed pressure effect was also investigated. It showed that pure C_2H_4 and C_2H_6 permeability coefficients decreased smoothly with increasing the feed pressure, but a different observation was found for C_3H_6 and C_3H_8 permeability coefficients. The permeability coefficient first decreased with pressure, then increased when the feed pressure was further increased. So, C_3 hydrocarbons showed strong plasticisation effects, especially above 5 atm. But the effects were not obtained for C_2 hydrocarbon gases at pressure up to 16 atm.

Netke and Pangarkar (2002) studied the membrane-solvent extraction using a non-porous elastomeric membrane to extract naphthenic acids (NA) from hydrocarbon fractions into aqueous sodium hydroxide (NaOH). Kerosene containing dissolved NA was the organic phase whereas aqueous sodium hydroxide made up the aqueous phase. The apparatus emplolyed two glass vessel of 300 cm^3, which were connected by a bridge in which the membrane was located. Experiments were conducted over a wide range of NA concentration (1000 ppm to 3500 ppm), NaOH concentration (0.1 kg mole/m^3 to 2 kg mole/m^3) and speeds of agitation in the two vessels. Various elastomeric membranes were considered. Natural rubber, ethylene-propylene rubber and polyethylene membrane were attacked by kerosene, while crystalline polyethylene yielded very low rates of permeation. Finally, a silicone rubber membrane (RTV-2 comprising of VP 7660 A and 7660 B; poly dimethyl siloxane, PDMS) was found to afford relatively high sorption of the organic phase and also yielded the highest permeation rate. Liquid phases mass transfer resistance was negligible above speeds of agitation 6 rev/sec in both phases and NaOH concentration above 1 kg mole/m^3. For this case, the intrinsic permeability of the silicone rubber membrane was found to be 4.5 x 10^{-7} m^2/hr.

Yoshino *et al.* (2003) studied the gas permeation properties of asymmetric hollow fiber membrane of copolyimide prepared from equimolar portion of 2,2-bis (3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) and 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA) with 3,7-diamino-2,8(6)-dimethyldibenzothiophene sulfone (DDBT). For single-component light gases, olefins and paraffins as well as for mixed components of C_3H_6/C_3H_8 and C_4H_8/C_4H_{10}, the gas permeance decreased singnificantly with aging time and level off after about 10 months of aging. The silicone rubber coating enhanced the selectivity for C_3H_6/C_3H_8 and C_4H_8/C_4H_{10} especially at low temperature. The permeances of C_3H_6/C_3H_8 and C_4H_8/C_4H_{10} are 3.6 and 7.4 GPU, respectively. The separation factors of C_3H_6/C_3H_8 and C_4H_8/C_4H_{10} were 15 and 69, respectively, at 373K, 1 atm, and 50/50 mol% feed.