CHAPTER II
LITERATURE SURVEY

2.1 VOCs and the Approach to Collect VOCs

In natural-gas processing, the by-products of volatile organic compounds (VOCs) such as C_4H_{10}, C_5H_{12} are obtained and have to be separated in the purification process, as shown in Figure 2.1. The mass volume of the mixtures of various gases combining with the complicated purification and collection processes makes VOCs never been considered for any value. The elimination is normally done by discharging into the atmosphere which increases the air pollution. Recently, many attempts have been made on the recovery of VOCs not only because VOCs are the potential petrochemical material but also for the environmental issues. Membrane separation process becomes of interest for VOCs owing to the simple process and cost performance (Baker *et al.*, 1994).

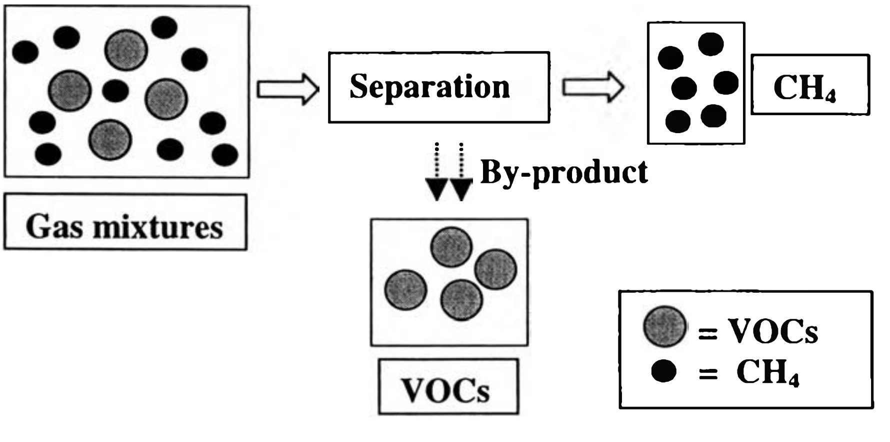

Figure 2.1 Schematic diagram of natural-gas processing.

2.2 Gas Separation Membrane

Generally, gas separation process can be defined as a simple movement of gas molecules through a membrane via permeation as shown in Figure 2.2.

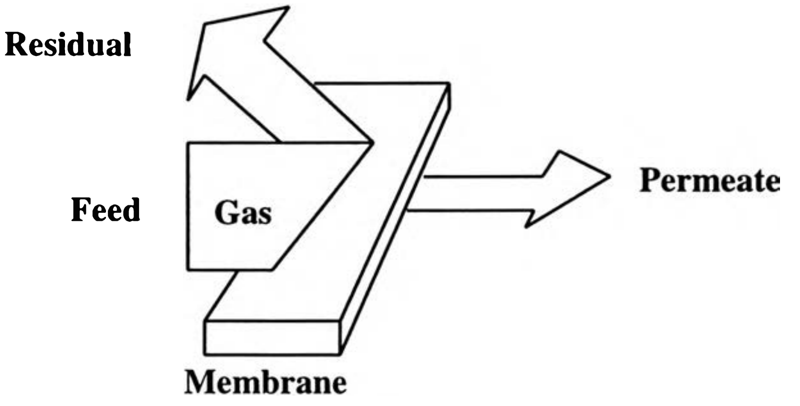

Figure 2.2 Concept of gas separation membrane.

The permeation of a gas through isotropic membrane is determined by permeability coefficient (P) which consists of two parameters, diffusion(D) and solubility(S), with a relation of,

$$P = D \bullet S \quad (2.1)$$

In practice, the gas for membrane separation is a mixtures of gases. The efficiency of membrane for gas separation can be expressed in terms of the selectivity(α) or the ratio of the permeability coefficient belonging to each gas, as show in the following equation.

$$\alpha_{A/B} = P_A/P_B = (D_A/D_B) \bullet (S_A/S_B) \quad (2.2)$$

Where, D_A/D_B is diffusion selectivity

S_A/S_B is solubility selectivity

2.3 Diffusion and Solubility Selectivity Process

Generally, gas permeation through the membrane is based on the diffusion and the solubility process. In the diffusion process, small penetrants permeate through the polymer matrix while the large size molecules remaine in the feeding reservoir, which is called size-sieving mechanism(Freeman *et al.*, 1997). Poly(vinyl chloride)(PVC), polysulfone(PSF) and cellulose acetate are reported as the membrane for separating gas mixtures by size-sieving mechanism (Roberson *et al.*, 1991).

Recently, solubility selectivity membrane has been considered as an alternative type of membrane. Comparing to the conventional size-sieving mechanism, the effective permeation depends on the interaction of the substrates with the polymer matrix of the membrane.

2.4 Membrane for VOCs Separation

In practical process, separation of VOCs from gas mixtures can be considered either in terms of the molecule size or the specific interaction property. The separation based on the molecule size can be achieved quantitatively via diffusion selectivity membrane. In this case, the supercritical gas components of N_2, O_2, CO_2, H_2O permeate through the membrane and the VOCs can be obtained (Freeman *et al.*, 1997). However, the efficiency of the process depends on the large area of the membrane and the recompression of VOCs after separation (Freeman *et al.*, 1997) (Figure 2.3).

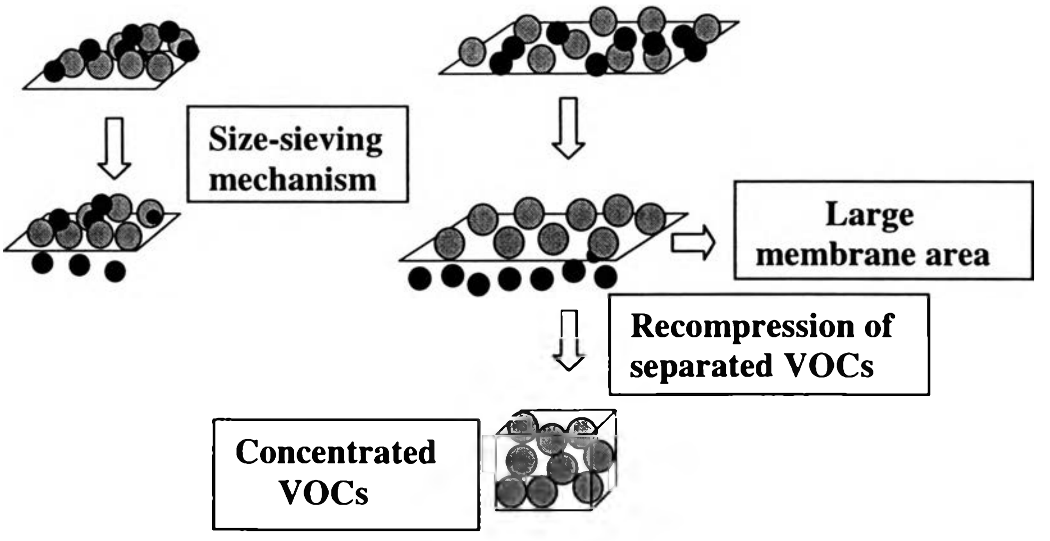

Figure 2.3 Schematic diagram of VOCs separation using diffusion selectivity.

In order to overcome the limitation of diffusion selectivity process, the solubility selectivity process is proposed as a high efficiency one. With the enhancement of the interaction between VOCs and the membrane matrix as the concept of 'like dissolve like', the VOCs component will be the preferred component covering on the membrane. Following by the pressure adjustment, the permeation of VOCs in high volume will be obtained. As a result, the separation of VOCs large molecules from small supercritical gases is successful (Pinnau *et al.*, 1996) (Figure 2.4).

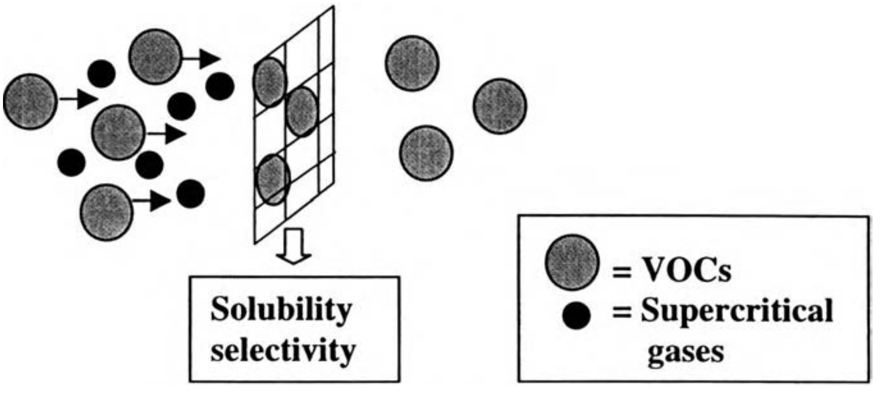

Figure 2.4 Schematic diagram of VOCs separation using solubility selectivity.

Historically, the gas separation by using solubility-selective polymer membrane has been proposed by Amerogen (Amerogen, 1964). The rubbery *cis*-polyisoprene was shown to allow the permeation of the larger hydrocarbons (propane, n-butane) rather than the smaller supercritical gases such as oxygen and nitrogen.

Pixton (Pixton *et al.*, 1994) proposed that polydimethylsiloxane (PDMS), a rubbery polymer with ultra-high free volume, is more permeable to propane than methane because propane has higher solubility in the membrane than methane while the diffusion of both gases are the same. It was concluded that in order to promote the high permeability of large size molecules, polymer membrane requires specific properties of not only a flexible backbone but also high free volume. Here, the rubbery property will retard diffusion of gas molecules and increase the solubility of the large size molecules in membrane matrix at the same time.

Recently, a unique concept of applying glassy polymer with ultra high free volume and specific functional group as a VOCs sensor was proposed by Pinnau *et al.* Poly(1-trimethylsilyl-1-propyne)(PTMSP), a superglassy polymer (T_g>250°C) with ultra-high free volume, exhibits higher permeability to volatile organic compounds than supercritical gases (Pinnau *et al.*, 1996).

2.5 Poly(vinyl alcohol) as a VOCs Gas Separation Membrane

In order to prepare a new membrane material for VOCs separation, the material requires a stable matrix with a high free volume as a glassy polymer. Moreover, the ease of modification is also important to obtain the specific functional group as a VOCs sensing group attached onto the polymer chain. Recently, trimethylsilyl group ($-Si(CH_3)_3$) was reported to be a VOCs sensing group (Pinnau *et al.*, 1996). For these requirements, poly (vinyl alcohol), a simple glassy polymer which contains the hydroxyl group for further modification, shows a potential to be a membrane material.

2.5.1 Poly(vinyl alcohol)

Poly(vinyl alcohol), a polymer obtained from poly(vinyl acetate), is a versatile material and widely used in the industries such as packaging of detergent and starting material for the synthesis of vinylon. The structure of poly(vinyl alcohol) is shown in Figure 2.5.

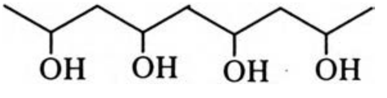

Figure 2.5 Chemical structure of poly(vinyl alcohol).

A unique property of poly(vinyl alcohol) is its biodegradability owing to the oxidation by enzyme of secondary hydroxyl group to obtain poly (enol-ketone) (Figure 2.6) leading to the degradation of chemical bonds in the main chain.

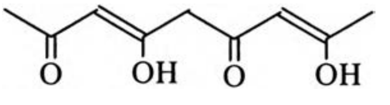

Figure 2.6 Chemical structure of poly(enol-ketone).

Poly(vinyl alcohol) is also known to be used as a membrane by crosslinking with dicarboxylic or dialdehyde. Recently, many reports dealt with the application of PVA material for example, the separation of alkali metal such as potassium ion and sodium ion (Uragami *et al.*, 1983), the separation of halogen ion (Yoshikawa *et al.*, 1984), and the separation of amino acid (Uragami *et al.*, 1993).

2.5.2 Chemical Modification of Poly(vinyl alcohol)

The modification of poly(vinyl alcohol) has received much attention in order to achieve the unique chemical properties. For example, Dumitriu (Dumitriu *et al.*, 1995) proposed the esterification of nalidixic acid on poly(vinyl alcohol) by using activator-catalyst(4-pirolidinopyridine) to apply as a drug retardation.

Recently, Moriman (Moriman *et al.*, 1997) proposed the partial silylation of poly(vinyl alcohol) with hexamethylenedisilazane in liquid ammonia as a solvent. The product showed interesting properties different from poly(vinyl alcohol) such as dissolvation in nonpolar solvent (tetrahydrofuran and chloroform) and low glass transition temperature.

Chemical modification of PVA with functional groups leads to an interesting application of PVA. For example, Gieminez *et al.* reported the partial esterification of poly(vinyl alcohol) with aromatic acid chlorides while the residual hydroxyl groups were reacted with hexamethylene diisocyanate to obtain tridimensional network (Gieminez *et al.*, 1996).

The reaction with acrylic and methacrylic acid with 2-vinyl-4,4-dimethyl-azlactone makes PVA a water-soluble polymer with pendant (methyl)acrylate and acrylamide groups. The material can be formed as a transparent network to apply as a contact len with good mechanical properties even with the low crosslink percentage and high water content (Pharisa *et al.*, 1997).

2.5.3 Molecular Design for PVA as a Solubility Selectivity Membrane Material

In the present work, gas separation by the solubility-selective polymer was studied. The poly(viny alcohol) glassy polymer is modified by coupling with silane coupling agent having trimethylsilyl group which is a VOCs sensing group. The molecular design will achieve a material with an increasing of the solubility between VOCs and membrane.