

## Chapter 3

### Theory

Pervaporation is a separation process in which a liquid mixture is concentrate on one side of the membrane. The driving force in the membrane is achieved by lowering the activity of the permeating components at the permeate side. At the permeate side, components are evaporated as a result of the partial pressure on the permeate side being lowered than saturation vapor pressure, and collected downstream. The driving force is controlled by applying the vacuum. An alternative, at least in principle is to use an inert carrier such as water vapor on air, lowering the partial pressure of the permeation component. Figure 3.1 shows the principle of the process.

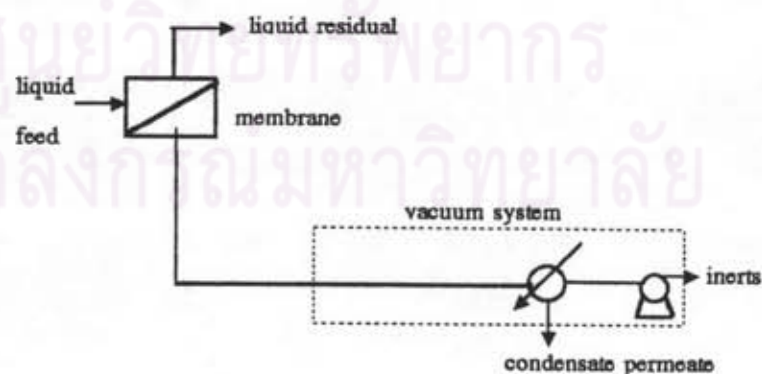


Figure 3.1 The pervaporation process.[6]



### 3.1 Model descriptions.[16]

There are two ways to rationalized the observed separation effects in the pervaporation process.

#### 3.1.1 Solution -Diffusion Model

According to the solution-diffusion model, membrane permeability is a function of solubility and diffusivity of the permeants in the polymer phase under the driving force of a chemical potential gradient. The driving force in the pervaporation process is the partial pressure gradient between the liquid feed and the permeate vapor pressure.

This model have 3 processes of the pervaporation process.

##### 1.Sorption Process

The sorption of component by a membrane is base on the affinity of chemical substance for each other. The sorption can be described by a distribution coefficient( $S_i$ ).[10]

$$S_i = \frac{c_m}{c_s} \quad (3.1)$$

where  $S_i$  is the distribution coefficient of "i" component,  $c_m$  is the concentration of "i" component in membrane phase and  $c_s$  is the concentration of "i" component in liquid-membrane interface.

The sorption of liquid in glassy polymer can be described by Florry-Huggins isotherm at low concentration.[6]

$$S_i = \gamma_{ii} \exp(-1+X) \quad (3.2)$$

where  $X$  is the liquid-membrane interaction parameter and  $\gamma_{ii}$  is the activity coefficient of "i" component in liquid-membrane interface.

The sorption of liquid or gas in elastomeric polymer can be described by Henry's isotherm. [16]

$$S_i = \gamma_{im}^{\infty} / \gamma_{ii}^{\infty} \quad (3.3)$$

where  $\gamma_{im}^m$  is the activity coefficient of "i" component in membrane at low concentration of liquid and  $\gamma_u^m$  is the activity coefficient of "i" component in liquid-membrane interface at low concentration of liquid.

The distribution coefficient depends on interaction between molecules of solute and molecules of membrane. Some studies indicate that the slow sorption process may be the basis of the phenomena in some pervaporation experiment.

## 2. Diffusion Process

The description of mass transfer in the membrane can be described by Fick's law.

$$J_i = -D_i \frac{dc_{im}}{dl} \quad (3.4)$$

where  $J_i$  is a flux of "i" component,  $D_i$  is the diffusivity of "i" component and  $\frac{dc_{im}}{dl}$  is the concentration gradient along the membrane thickness.

This diffusivity depends on the concentration which can be shown by equation 3.5.

$$D_i = D_{i,0} \exp(bc) \quad (3.5)$$

where  $b$  is the swelling parameter, and  $D_{i,0}$  is the diffusivity of  $i$  without swelling effect.

The diffusivity of  $i$  without swelling effect depends on temperature. The relation between diffusivity without swelling effect, and temperature can be described by

$$D_{i,0} = D_{i,00} \exp(-E_p/RT) \quad (3.6)$$

where  $D_{i,00}$  is the preexponential factor,  $E_p$  is the apparent activation energy,  $R$  is the gas constant, and  $T$  is temperature.

### 3. Desorption Process or Evaporation Process

This process is fast compared to the diffusion process. Partial pressure for each component can be shown by

$$p_i = \gamma_i P = \gamma_{im}^{\infty} x_{im} P_i^{\circ} \quad (3.7)$$

where  $p_i$  is the partial pressure of "i" component,  $P$  is permeate pressure,  $P_i^{\circ}$  is the vapor pressure of "i" component,  $\gamma_i$  is the mole fraction in liquid of "i" component,  $x_{im}$  is the mole fraction of "i" component in membrane phase and  $\gamma_{im}^{\infty}$  is the activation coefficient.

From the solution-diffusion model, multicomponent can be described by Fig 3.2

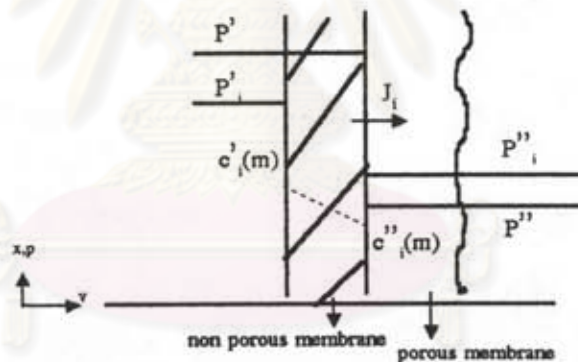


Figure 3.2 Concentration and pressure distribution in membrane

Fick's law for "i" component

$$J_i = -D_i \frac{dc_{im}}{dl} \quad (3.4)$$

This equation can be integrated along the membrane thickness.

$$J_i = D_i \frac{(c'_i(m) - c''_i(m))}{l} \quad (3.8)$$

Applying the Henry's law,

$$J = Dk \frac{(p'_i - p''_i)}{l} \quad (3.9)$$

$$J_i = P_i \frac{(p_i' - p_i'')}{l} \quad (3.10)$$

where,  $P_i = D_i k_i =$  permeability

For "j" component,

$$J_j = P_j \frac{(p_j' - p_j'')}{l} \quad (3.11)$$

### 3.1.2 Thermodynamic Accounting Approach.

Thermodynamic accounting divides the pervaporation process into two identifiable steps which in effect make up the process. The approach is visualized by a Thompson's diagram (Figure 3.2), in which the contribution of membrane selectivity to the overall separation effect is represented as change of composition of vapor on lowering the total permeate pressure below the equilibrium vapor pressure.

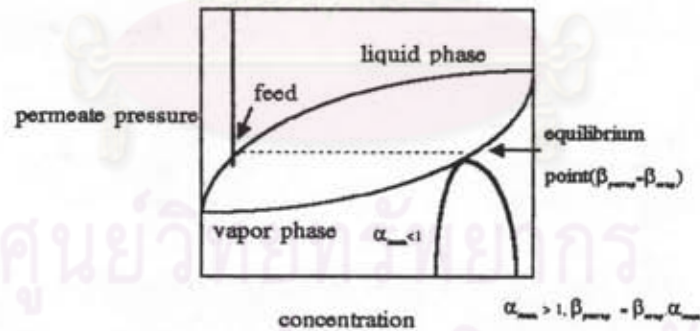


Figure 3.2 Thompson's diagram.[16]

The selectivity for each stage can be shown by [17]

$$\beta_{\text{pervap}} = \beta_{\text{evap}} \cdot \beta_{\text{mem}} \quad (3.12)$$

where;

$$\beta_{\text{pervap}} = \frac{p_i''/p_i''}{c_i'/c_i'} \quad (3.13)$$

$$\beta_{\text{evap}} = \frac{p_i'/p_i'}{c_i'/c_i'} \quad (3.14)$$

$$\beta_{\text{mem}} = \frac{p_i''/p_i''}{p_i'/p_i'} \quad (3.15)$$

From above equation, vapor pressures of feed components directly affect the separation factor.

$$\alpha_{\text{mem}} = \frac{P_i}{P_j} \quad (3.16)$$

The equalization ratio of flux and ratio of vapor pressure and the Fick's law leads to the relation between membrane selectivity and separation factor.

$$\frac{J_i}{J_j} = \frac{P_i(p_i' - p_i'')}{P_j(p_i' - p_i'')} \quad (3.17)$$

$$\frac{J_i}{J_j} = \frac{p_i''}{p_i''} \quad (3.18)$$

$$\frac{p_i''}{p_i''} = \alpha_{\text{mem}} \frac{(p_i' - p_i'')}{(p_i' - p_i'')} \quad (3.19)$$

$$\beta_{\text{mem}} = \alpha_{\text{mem}} \frac{(p_i' - p_i'') p_i'}{(p_i' - p_i'') p_i'} \quad (3.20)$$

The above equation can be considered in two ways.

1. Permeate pressure equal to apparent vapour pressure in feed.

$$p''/p' \rightarrow 1$$

$$p_i''/p_i' \rightarrow 1$$

$$p_i''/p_i' \rightarrow 1$$

thus;

$$\beta_{\text{mem}} = 1 \quad (3.21)$$

$$\beta_{\text{pervep}} = \beta_{\text{evap}} \quad (3.22)$$

2. Permeate pressure is vacuum.

$$p''/p' \rightarrow 0$$

$$\beta_{\text{pervep}} = \beta_{\text{evap}} \cdot \alpha_{\text{mem}} \quad (3.23)$$

### 3.2 The influence of operating parameters on the performance of pervaporation process. [16]

Pervaporation is a membrane process whose performance is extremely sensitive to the operating conditions. Parameters such as temperature, downstream pressure, and composition of mixture in contact with the membrane affect directly or indirectly the flux and selectivity of the process via a change in the physico-chemical properties of the membrane material. As a consequence, the way in which membrane are packed into compact modular might be a great important.

#### 3.2.1 Physico-chemical properties.

The permeation of solvents through a non-porous film usually can be described in terms of sorption and molecular diffusion. The extent of sorption (also called swelling) as well as the sorption selectivity are therefore determined by chemical nature of polymer and that of the solvents.[18] The thermodynamic equation enabling the calculations of these porperties are rather complex and inculde such thermodynamic parameters.

The extent of sorption is a result of equilibrium between the chemical tendency of mixing and the elasticity of polymer which tend to limit the swelling.

$$D_i = D_{i,0} \exp(k_{ji}c_i + k_{ij}c_j) \quad (3.24)$$

$$D_j = D_{j,0} \exp(k_{ji}c_i + k_{ij}c_j) \quad (3.25)$$

Where  $k_{ji}$  represents the plasticizing effect of the "j" solvent on the diffusivity of the "i" component. The zero permeant diffusivities  $D_{i,0}$  and  $D_{j,0}$  are function of structure of polymer as well as the size, and shape of molecules.  $D_i$  and  $D_j$  are diffusivity of "i" and "j" component, respectively.

From the above equations, diffusivity is a function of chemical properties of the solvent, concentration of solvent and structure of polymer.

The selectivity comes from the relative of transport of the two species through the membrane, the difference in diffusive transport, and from both phenomena depending on the physico-chemical properties of the system.[19]

### 3.2.2 Feed composition.

A change in feed composition directly affects the sorption phenomena at the liquid-membrane interface. The sorption selectivity depends obviously on the power of interaction between components. The extent of swelling as well as the sorption selectivity depend on the structure of polymer network. The lower affinity to the membrane can penetrate into the swollen system, and contribute to better swelling.

### 3.2.3 Feed concentration.

Activity of solvent is a function of the change of feed concentration. Concentration of less adsorp components are low diffusion and flux. This result can be shown by Fick's law (equation 3.4). Feed concentration are affected by membrane activity. From this reason, situation membrane can increase permeate diffusion and flux by rising feed concentrations.

### 3.2.4 Temperature

When the temperature of the feed increase, the variation of permeation rate follows an Arrhenius-type law.

$$J_p = J_o \exp(E_p/RT) \quad (3.26)$$

where  $J_p$  is the permeation rate,  $J_o$  is the pre-exponential factor,  $E_p$  is the apparent activation energy of permeation, and  $R$  and  $T$  are the gas constant and temperature, respectively.





The value of apparent activation energy of permeation varies usually in the range 4-15 kcal/mole. The permeation rate may increase many times for each  $10^{\circ}\text{C}$  temperature increment.

The effect of temperature on membrane selectivity depends on the major phenomenon that govern the selectivity. A higher activation energy of diffusion of the component should lead to increase in selectivity with temperature.

In the pervaporation process, an increase in the feed temperature results usually in better productivity since the loss of selectivity.

#### 3.2.5 Downstream pressure

Pervaporation process use downstream pressure to provide the driving force by pumping the permeate from downstream interface in the vapor form. The decreased in the vapor pressure in downstream compartment is equivalent to an increase of driving force for component transportation. This behavior has been observed by R.A.Shelden et al.[20]

The effect of downstream pressure on selectivity is more difficult to explain. The values of partial vapor pressure, which directly control the transport of solvents, result from a dynamic equilibrium between the transport flux of the permeates and the pumping rate.

### 3.3 Pervaporation Membrane.[2]

Pervaporation membrane are polymeric solubility membranes in the peculiar state of anisotropic swelling, which is a consequence of the involved phase change. Pervaporation membranes are either solvent-selectivity membranes or water-selectivity membranes. Solvent-selectivity membrane is elastomeric polymer, which glass transition temperature is lower than conventional temperature and has small side group polymer

chain such as silicone rubber. Properties and molecular structure of silicone rubber are shown in Table 3.1 and Figure 3.4, respectively. Water-selectivity membrane is glassy polymer, which glass transition temperature is higher than conventional temperature such as polyacrylamide.

The choice of membrane materials is critical. The key to commercialization of pervaporation has been the development of asymmetric composition membrane, each layer of which fulfills a specific requirement.

Over the last 10 years, pervaporation membrane have been developed for high separation. For example, membrane for ethanol dehydration by pervaporation process utilized a supporting layer of nonwoven porous polyester for high flux and high selectivity.

Table 3.1 Properties of silicone rubber.[21]

Silicone Rubber	
Service Temperature	-100 to 315°c
Mechanical Properties	
ultimate tensile strength	100 to 1500 psi
ultimate elongation	over 1000%
practical hardness	25 to 75 (Shore A)
specific gravity	1.1 to 1.6
Electrical Properties	resistance, non-conducting ash and dielectric constant
Chemical Resistant	chemical, fuel and oil resistance
Thermal Properties	
thermal conductivity	1.5 to 4.1 Btu/h/ft <sup>2</sup> /in/°F
flame resistant	high
Permeability	high permeability to gas

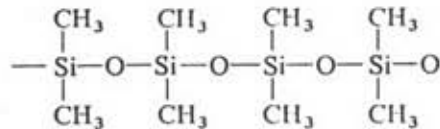


Figure 3.4 Molecular structure of silicone rubber.

### 3.4 Membrane module.

The cast membrane may be packed in modules in any of several geometry. Several membrane modules are design for many process. The geometry of module is determined primarily by economic aspects. The most common membrane modules are of the plate-and-frame system, the tube system, the spiral wound system, and the hollow fiber system. All modules have specific advatages, and disadvantages.

#### 3.4.1 The plate-and-frame system.

The membranes are installed similiary to a filter press as flat-sheet material. The advantage of this system is that it can easily be disassemble for membrane replacement or cleaning. However, the system requires a high initial investment.

#### 3.4.2 The tubular system.

The membrane is manufactured in the form of a tube with an inner diameter of 1-2 cm. supported by a rigid porous outer shell. The tubular system allows concentration polarization and membrane fouling to be easily controlled by appropriate flow on the membrane surface on the inner side. The low membrane surface per unit volume leads to high costs of the tubular system.

#### 3.4.3 The spiral wound system.

This system is also widely used. The membrane are place as a sandwich model on porous support, and then wound in spiral type configuration. Higher surface area per unit volume leads to low investment costs. However, concentration polarization may occur, especially when solutions with high solid contents are processed.

#### 3.4.4 The hollow fiber system.

The capillary membrane are installed in rigid shell. This type of membrane have a large membrane area per unit volume. The hollow fiber membrane module with the feed solution on the inside have a good distribution of feed as well as of the permeate flow streams. This system requires low overall production costs. A disadvantage is the restricted pressure stability in case of high operating pressure in the fiber lumen. Therefore, the hollow fiber module with the feed flow on the inside is preferentially used in low pressure applications, such as pervaporation. Hollow fiber operating with the high pressure on the outside of fiber lumen have a much higher pressure stability, but also a higher pressure losses on permeate side, that might reduce the flux, and the separation characteristics.

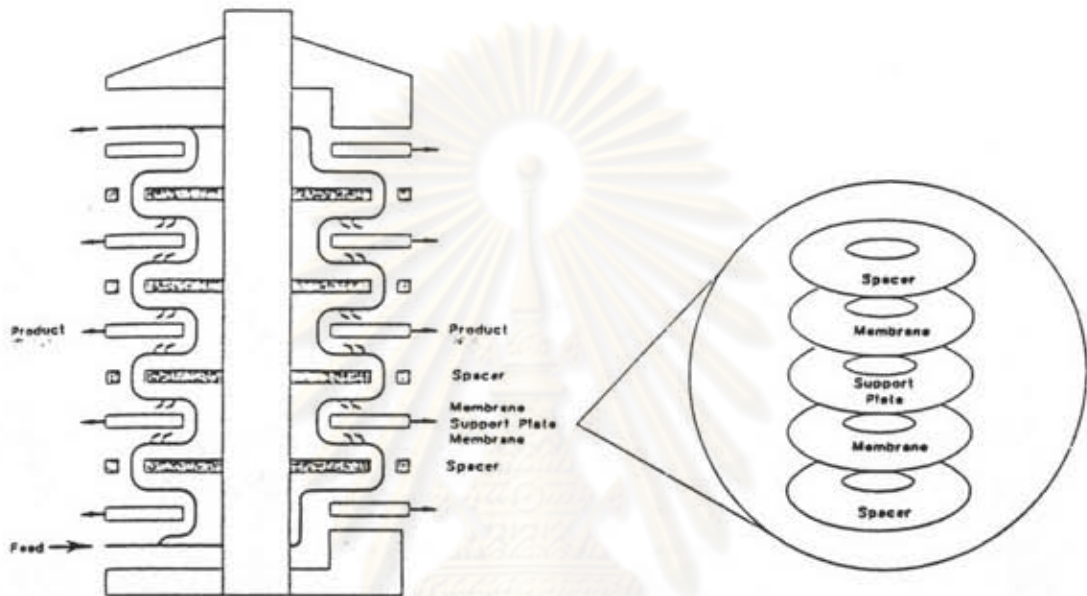


Figure 3.4 Plate and frame membrane module.[2]

จุฬาลงกรณ์มหาวิทยาลัย

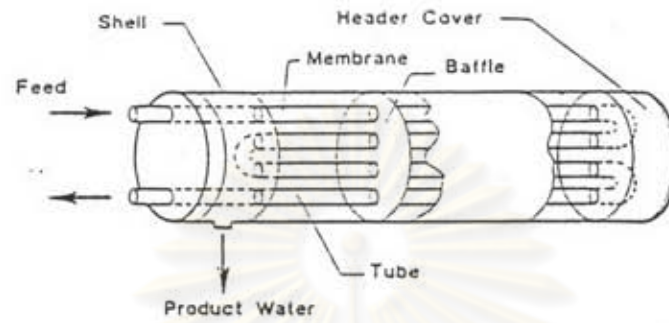


Figure 3.5 Tubular membrane module.[2]

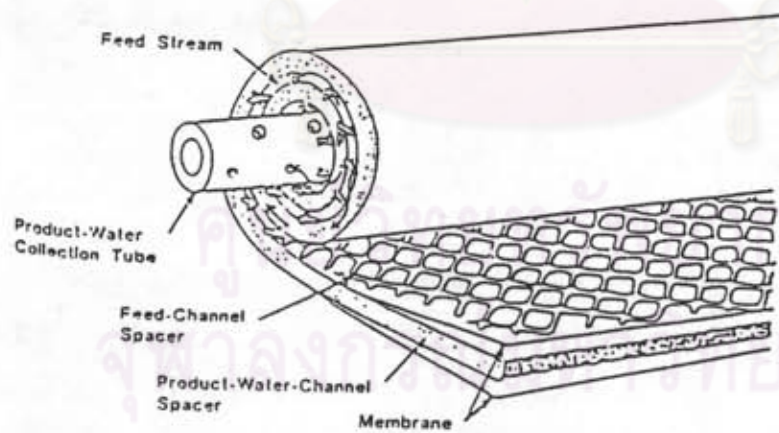
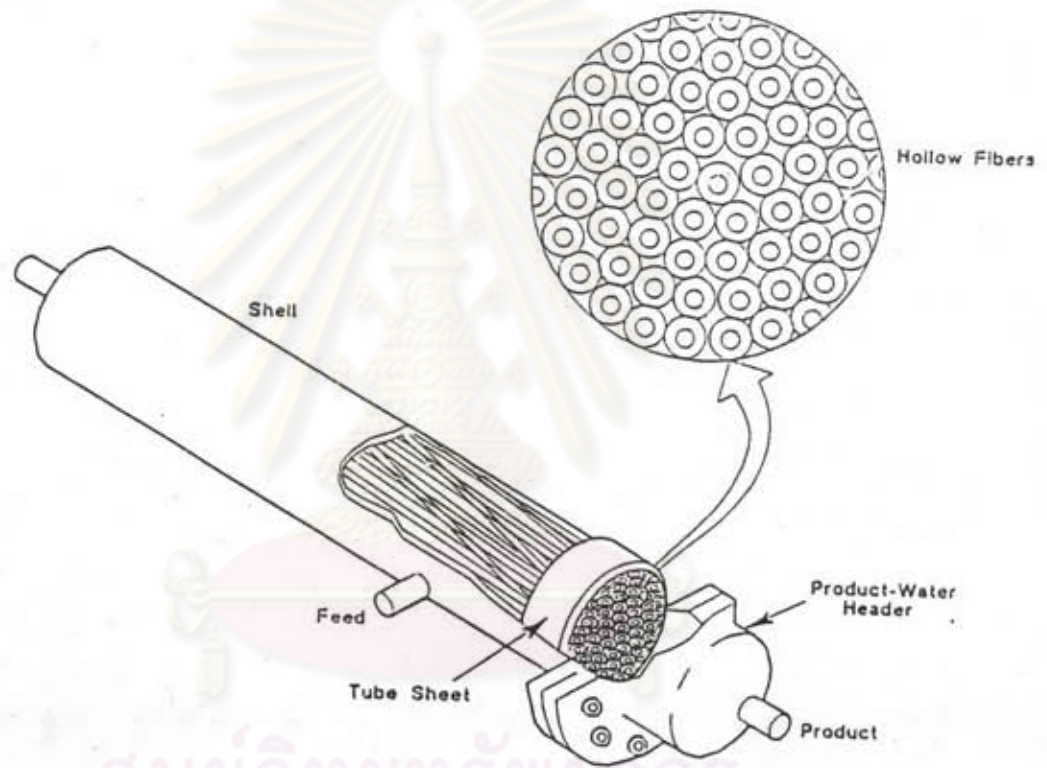


Figure3.6 Spiral wound membrane module.[2]



ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย  
Figure 3.7 Hollow fiber membrane module.[2]

### 3.5 Membrane Cleaning. [2]

The need of membrane cleaning is generally less than for analogous porous membrane. However, membranes do foul and must be treated. Membrane cleaning can be divided into 2 procedures as clean-in-place and off line. Most plants prefer the clean-in-place procedure. A typical cleaning cycle utilized one to three bed volumes of cleaning solvent at an elevated temperature such as isopropyl alcohol for dehydration membrane at 50-80°C. However, in organic permeating membrane, the system generally heat treated . Steam pressure is injected for 2-8 hour cycle during a cleaning cycle, and then deionized water is circulate to recondition the membrane to its former state.



ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย