CHAPTER III

PERVAPORATION SEPARATION PROCESS

Pervaporation is a membrane-based process for separating miscible liquids. Here the absorption of one of the components of the liquid by the membrane, diffusion of this component across the membrane and evaporation, as permeate vapour, into the partial vacuum applied to the underside of the membrane.

Pervaporation, in its simplest form, is an energy efficient combination of membrane permeation and evaporation. It's considered an attractive alternative to other separation methods for a variety of processes. For example, with the low temperatures and pressures involved in pervaporation, it often has cost and performance advantages for the separation of constant-boiling azeotropes. Pervaporation is also used for the dehydration of organic solvents and the removal of organics from aqueous streams. Additionally, pervaporation has emerged as a good choice for separation heat sensitive products.

Pervaporation involves the separation of two or more components across a membrane by differing rates of diffusion through a thin polymer and an evaporative phase change comparable to a simple flash step. A concentrate and vapor pressure gradient is used to allow one component to preferentially permeate across the membrane. A vacuum applied to the permeate side is coupled with the immediate condensation of the permeated vapors. Pervaporation is typically suited to separating

a minor component of a liquid mixture, thus high selectivity through the membrane is essential. Figure 3.1 shows the pervaporation process.

Pervaporation can used for dehydration of solvents and other volatile organics, organic/organic separations such as ethanol or methanol removal, and wastewater purification.
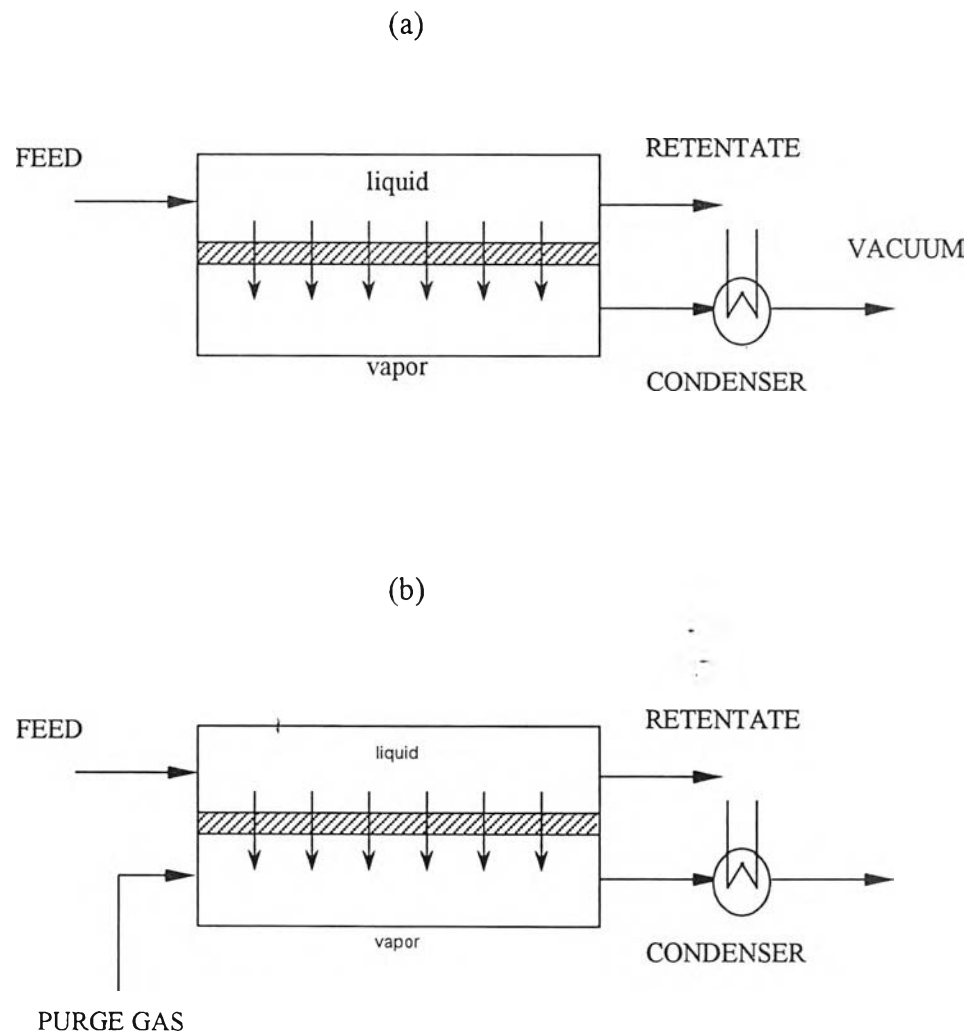
(a)

(b)

Figure 3.1 Schematic diagram of the pervaporation process. (a) Vacuum pervaporation, (b) purge gas pervaporation

Characteristics of the pervaporation process include:

1. Low energy consumption

2. No entrainer required, no contamination

3. Permeate must be volatile at operating conditions

4. Functions independent of vapor/liquid equilibrium

3.1 Pervaporation for Separation

Liquid transport in pervaporation is described by various solution-diffusion models. The steps included are the sorption of the permeate at the interface of the solution feed and the membrane, diffusion across the membrane due to concentration gradients (rate determining steps), and finally desorption into a vapor phase at the permeate side of the membrane. The first two steps are primarily responsible for the permselectivity. Therefore, the liquid transport in pervaporation membranes can be described by the solution-diffusion-mechanism (see Figure 3.2). As material passes through the membrane a "swelling" effect makes the membrane more permeable, but less selective, until a point of unacceptable selectivity is reached and the membrane must be regenerated.

The other driving force for separation is the difference in partial pressures across the membrane. By reducing the pressure on the permeate side of the membrane, a driving force is created. Another method of inducing a partial pressure gradient is to sweep an inert gas over the permeate side of the membrane. These methods are described as vacuum and sweep gas pervaporation respectively.

3.1.2 Classification of liquid mixtures separation by pervaporation method

The separation of liquid mixtures by using pervaporation method can be classified into three fields:

1) Solvent dehydration,

2) Separation of dissolved organics from water,

3) Separation of organic mixtures.

3.1.2.1 Solvent dehydration

Most of the early solvent dehydration systems were installed for ethanol dehydration. This is a particularly favorable application for pervaporation because ethanol forms an azeotrope with water at 95 percent and a 99.5 percent pure product is needed. Essentially all pervaporation dehydration systems installed to date have been equipped with poly(vinyl alcohol) membrane. Because an ethanol/water azeotrope forms at 95% ethanol, the concentration of ethanol from fermentation feeds to high degrees of purity requires rectification with a benzene entrainer, some kind of molecular-sieve drying process, or a liquid-liquid extraction process. All these processes are expensive. However, the availability of extremely water-selective pervaporation membranes allows pervaporation systems to produce almost pure ethanol (>99.9 percent ethanol from a 90 percent ethanol feed). Reliable capital and operation cost comparisons between pervaporation and distillation are not available.

Pervaporation is less capital and energy-intensive than distillation or adsorption processes for small plants treating less than 5000 L/h of feed solution. However, because of the modular nature of the process, the costs of pervaporation are not as sensitive to economies of scale as are the costs of distillation and adsorption processes. Distillation costs, however, scale at a rete proportional to 0.6 to 0.7 times the power consumption. Thus, distillation remains the most economical process for large plants.

More recently pervaporation has been applied to dehydration of other solvents, particularly isopropanol used as a cleaning solvent. Dehydration of other solvents, including glycols, acetone, and methylene chloride, has been considered. A final interesting application of dehydration membranes is to shift the equilibrium of chemical reactions. For example, esterification reactions are usually performed in batch reactors, and the degree of conversion is limited by buildup of water in the reactor. By continuously removing the water, the equilibrium reaction can be forced to the right. In principle, almost complete conversion can be achieved.

3.1.2.2 Separation of dissolved organics from water

A number of applications exist for pervaporation to remove or recover volatile organic compounds from water. If the aqueous stream is very dilute, pollution control is the principal economic driving force. However, if the stream contains more than 1 to 2 percent VOC, recovery for eventual reuse can enhance the process economics.

Several types of membrane have been used to separate VOCs from water. Usually the membranes are made from rubbery polymers such as silicone rubber, polybutadiene, natural rubber, and polyamide-polyether copolymers. Rubbery pervaporation membranes are remarkably effective at separating hydrophobic organic solutes from dilute aqueous solutions. The concentration of VOCs such as toluene or trichloroethylene (TCE) in the condensed permeate is typically more than 1000 times that in the feed solution.

3.1.2.3 Separation of organic mixtures

The third application area for pervaporation is the separation of organic/organic mixtures. The competitive technology is generally distillation, a well-established and familiar technology. However, a number of azeotropic and close-boiling organic mixtures cannot be efficiently separated by distillation; pervaporation can be used to separate these mixtures. It would be unusual for a pervaporation process to perform an entire organic/organic separation. Rather, pervaporation will be most efficient when combined with distillation in a hybrid process. The two main applications of pervaporation-distillation in hybrid processes are likely to be in breaking azeotrope and in removing a single-component, high-purity side stream from a multicomponent distillation separation.

The principal problem hindering the development of commercial systems for organic/organic separations is the lack of membranes and modules able to withstand long-term exposure to organic compounds at the elevated temperatures required for pervaporation.

The performance of the pervaporation process depends not only upon the physicochemical properties of the polymeric materials and the structure of membrane but also upon the operating conditions, e.g. temperature, downstream pressure and composition of mixture. The followings summarize the effects of various factors on the performance of the pervaporation process.

- **Physico-chemical properties**

The permeation of solvents through a non-porous membrane 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.

- **Operating temperature**

The variation of permeation rate follows from the operating temperature can be correlated with the Arrhenius' equation.

$$Jp = Jo \exp(-Ep/RgT) \qquad (3.1)$$

Where Jp is the permeation rate, Jo is the pre-exponential factor, Ep is the apparent activation energy of permeation, and Rg and T are the gas constant and temperature, respectively.

- **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 depends on the structure of polymer network. The lower affinity

to the membrane can penetrate into the swollen system, and contribute to better swelling.

- *Feed concentration*

According to Fick's law, the permeation is proportional to the activity gradient across the membrane. Since the feed concentration directly affects the membrane activity, the increased feed concentration increased the driving force and the permeation flux through the membrane.

- *Downstream pressure*

Pervaporation process controls downstream pressure by pumping the permeate from downstream interface in the vapor form to provide the driving force. The decreased vapor pressure in downstream compartment is equivalent to and increased driving force for component transportation.

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.

3.2 Membrane

A membrane is a permeable or semi-permeable phase, polymer, inorganic or metal, which restricts the motion of certain species. This membrane, or barrier, controls the relative rates of transport of various species through itself and thus, as with all separations gives one product depleted in certain components and a second

product concentrated in these components. The performance of a membrane is defined in terms of two simple factors, flux and retention or selectivity. Flux or permeation rate is the volumetric (mass or molar) flowrate of fluid passing through the membrane per unit area of membrane per unit time. Selectivity is a measure of the relative permeation rates of different components through the membrane. Retention is the fraction of solute in the feed retained by the membrane. Ideally a membrane with a high selectivity or retention and with a high flux or permeability is required, although typically attempts to maximize one factor are compromised by a reduction in the other.
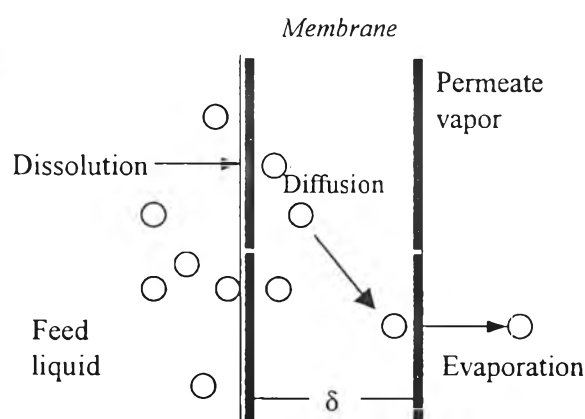
Figure 3.2 Schematic representation of the pervaporation transport mechanism: solution-diffusion model.

3.2.1 Membrane characteristics

Synthetic membranes are thin, solid-phase barriers that allow preferential passage of certain substances under the influence of a driving force. Both the

chemical and the physical nature of the membrane material control membrane separation. Membrane separation occurs because of differences in size, shape, chemical properties, or electrical charge of the substances to be separated. Microporous membranes control separation by size, shape and charge discrimination, whereas nonporous membranes depend on sorption and diffusion.

Three general categories of inorganic membranes are ceramics, metals and glass. Because they are so rigid, ceramic microfilters accommodate fluxes five to ten times greater than those of asymmetric polymeric membranes. They can be backwashed frequently without damaging the membrane skin layer. Ceramic membranes are highly resistant to cleaning chemicals and can be sterilized repeatedly by high pressurized steam. Their life span is up to ten years compared to the typical life spans for polymer membranes, which are about one year for hydrophobic membranes and up to four years for fluoropolymers. Ceramic membranes are brittle and are more expensive than polymeric membranes.

3.2.2 Membranes for pervaporation process

The membranes used in pervaporation processes are classified according to the nature of the separation being performed. *Hydrophilic membranes* are used to remove water from organic solutions. These types of membranes are typical made of polymers with glass transition temperatures above room temperatures. Polyvinyl alcohol is an example of a hydrophilic membrane material. *Organophilic membranes* are used to recover organics from solutions. These membranes are typically made up of elastomer materials (polymers with glass transition temperatures below room temperature). The

flexible nature of these polymers make them ideal for allowing organic to pass through. Examples include nitrile, butadiene rubber, and styrene butadiene rubber.

Pervaporation membranes are typically composites. The first layer is a porous, polymeric support coated with a second polymer, the "active" or "permselective" layer, which is engineered to preferentially absorb the chemical species of interest. The membranes' separation characteristics can be further refined by varying the thickness of the permselective layer. For example, asymmetric composite hydrophilic membranes such as composite PVA-PS (Poly(vinyl alcohol)-Polysulfone) are used for pervaporation. Pervaporation separation plants contain between ten and one hundred m^2 of membrane area, which must be packaged efficiently and economically into units called membrane modules. Flat-sheet and spiral-wound modules are commonly used. Silicon rubber membranes are also used in pervaporation. Spiral wound configuration offers a high membrane surface area per module and allows for relatively high feed flow rates which is common for pervaporation. Silicone rubber pervaporation modules are remarkably effective at separating organic solutes from dilute aqueous solutions. Spiral wound modules are available in 2, 4 and 8 inch diameters to accommodate a variety of feed flow requirements and to allow for economical system design. The choice membrane depends on the feed solution. The most efficient application of any membrane is to permeate the minor component of a mixture.

Membranes are used for various separations; the separation of mixtures of gases and vapors, miscible liquids (organic mixtures and aqueous/organic mixtures) and solid/liquid and liquid/liquid dispersions and dissolved solids and solutes from liquids. The main uses of membrane separations in industry are in:

- The filtration of micron and submicron size particulates from liquid and gases (Microfiltration),

- The removal of macromolecules and colloids from liquids containing ionic species (Ultrafiltration),

- The separation of mixtures of miscible liquids (Pervaporation),

- The selective separation of mixtures of gases and vapor and gas mixtures (Gas Permeation and Vapor Permeation),

- The selective transport of only ionic species (Electrodialysis),

- The virtual complete removal of all material, suspended and dissolved, from water or other solvents (Reverse Osmosis).

3.3 Pervaporative Membrane Reactor

A pervaporative membrane reactor is one of the membrane reactors for yield-enhancement of equilibrium-limited reactions. The concept was firstly proposed by Jenning and Binnings in 1960. While a reaction takes place in liquid phase, a by-product (usually water) is removed through a polymeric membrane in the permeate stream. The downstream pressure is kept below the vapor pressure of permeating species. The downstream side is evacuated by a vacuum pump or at least using an inert purge gas as illustrated in Figure 3.3

Pervaporative membrane reactors are expected to provide a promising alternative due to the following considerations: (1) pervaporation is a rate-controlled

separation process, and the separation efficiency is not limited by relative volatility as in distillation, (2) in pervaporation only a fraction of feed that is permeated by membrane undergoes the liquid-to vapor-phase change, and thus energy consumption is generally low as compared to distillation, (3) with an appropriate membrane, pervaporation can be operated at a temperature that matches the optimal temperature for reaction.
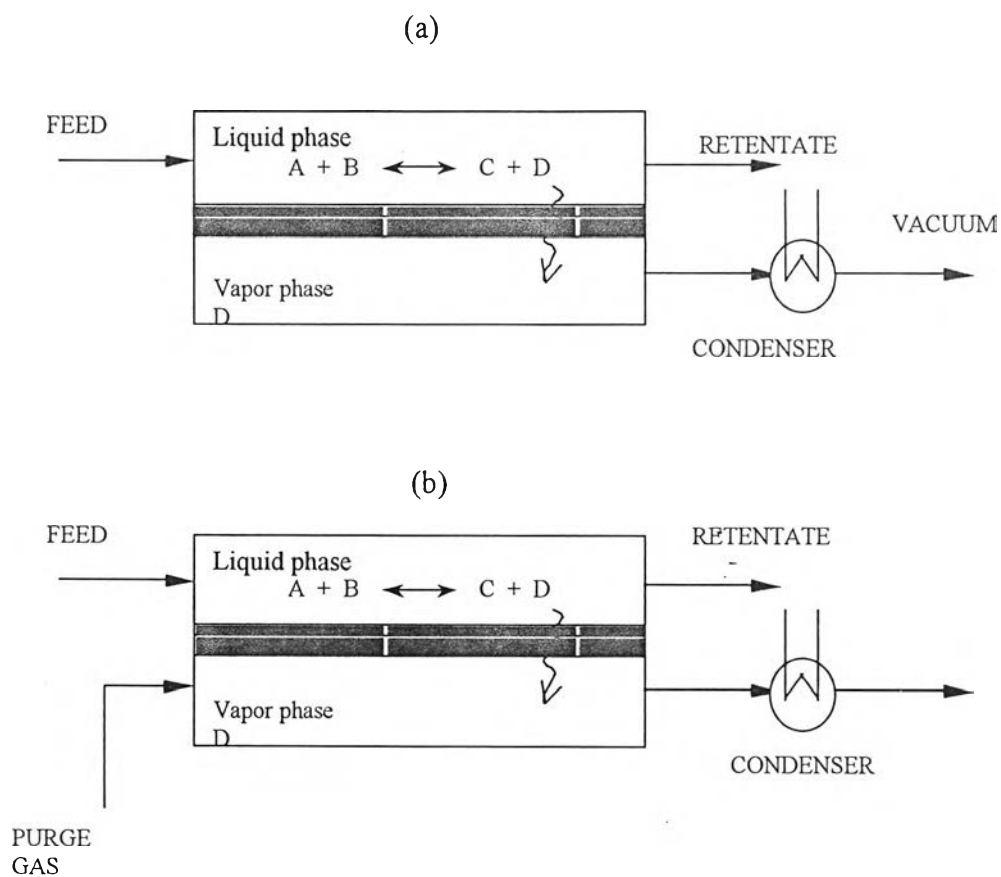
(a)

(b)

Figure 3.3 Schematic of a typical pervaporative membrane reactor (a) using vacuum pump, (b) using purge gas
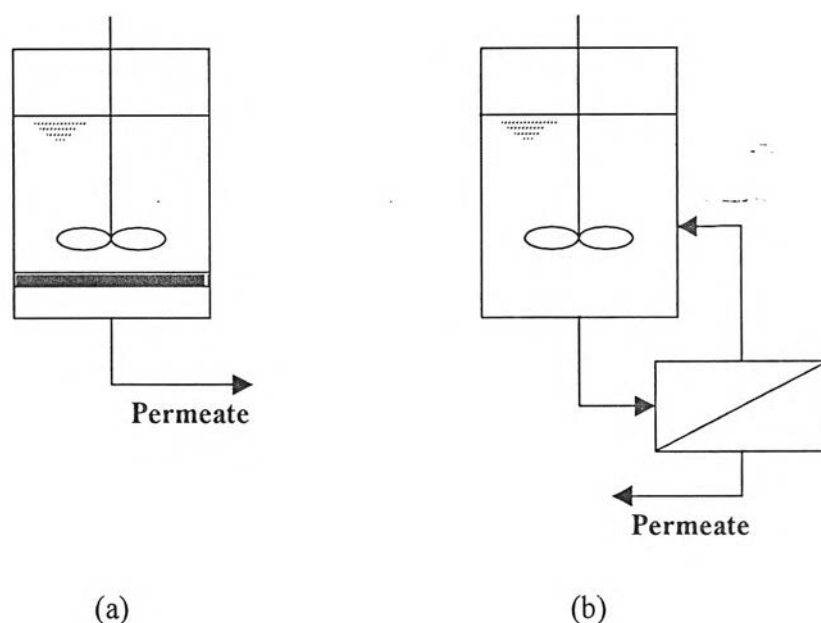
(a)   (b)

Figure 3.4 Configuration of a pervaporation reactor with an internal pervaporation unit (a) and with an external pervaporation unit (b)

The most common reaction system studied for the application of pervaporative membrane reactor is an esterification reaction between an alcohol and an acid in the presence of a highly acidic catalyst:

$$R_1COOH + R_2OH \longleftrightarrow R_1COOR_2 + H_2O \qquad (3.2)$$

The esterification represents an important class of chemical reactions. As esterification is equilibrium reaction (3.2), high yields can be obtained by adding an excess of one reactant or by constant removal of the produced water from the reaction mixture in order to shift the reaction to the product side.

Application of pervaporation processes to selectively separate water from the reacting mixture forms an interesting alternative to conventional distillation,

especially in the case of azeotrope formation and low boiling reactants. Both polymer and ceramic membranes are applied in pervaporation-based reactors, for which Figure 3.4 shows the two basic configurations.

The influence of four different operating parameters on the conversion are evaluated, which can be divided into three group:

- Factors, which influence directly the esterification reaction (the catalyst concentration and initial molar ratio),

- Factors, which influence the pervaporation kinetics directly (the ratio of membrane area to reactor volume),

- Factors, which influence simultaneously the esterification as well as the pervaporation kinetics (the temperature).

For a rapid conversion of lab-scale results into an economically viable reaction-pervaporation system, an optimum value can be determined for each parameter. Based on experimental results as well as a model describing the kinetics of the system, it has been found that the temperature has the strongest influence on the performance of the system as it affects both the kinetics of esterification and of pervaporation. The rate of reaction increases with temperature according to Arrhenius law, whereas an increased temperature accelerates the pervaporation also. Consequently, the water content fluctuates much faster at a higher temperature. The second important parameter is the initial molar ratio. It has to be noted that a deviation in the initial molar ratio from the stoichiometric value requires a rather expensive separation step to recovery the unreacted component afterwards. The third factor is the ratio of membrane area to reaction volume, at least in the case of a batch reactor.

For continuous operation, the flowrate should be considered as the determining factor for the contact time of the mixture with the membrane and subsequently the permeation flux. The catalyst concentration exhibits the weakest influence on the pervaporation-esterification system. The reaction rate increases linearly with the catalyst concentration.