CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Introduction of pervaporation

Over the past five years, membrane pervaporation has gained acceptance by the chemical industry as an effective process tool for separation and recovery of liquid mixtures. It is currently best identified with dehydration of liquid hydrocarbons to yield high purify organics, most notably ethanol, isopropanol, and ethylene glycol. Due to its favorable economics, efficiency, and simplicity, it can be easily integrated into distillation and rectification process and, depending on the specific process, even replace them. Presently considerable data are available on industrial-scale processes utilizing pervaporation to evaluate its performance.

2.2 Background of pervaporation [8,9]

The historical development of pervaporation technology can be trackeed by the number of U.S. patents issued each year that relate to pervaporation, as illustrated in Figure 2.1. Prior to 1960, only a handful of patents had been issued on pervaporation , but beginning in 1960 a series of patents were issued to Binning, Lee and others at American Oil Company (Amoco) in Taxas covering the use of pervaporation membranes for dehydration of a ternary azeotrope of isopropanol-ethanol-water mixture from the overhead of a distillation column. Membrane technology was not sufficiently advanced to make this application practical at that time, and American Oil abandoned the program after a few years.

The capacity for separating aqueous-organic and organic-organic mixtures was demonstrated by 1965, but commercial development did not proceed, primarily due to the lack of market need. Traditional separation technologies including distillation, extraction, and adsorption were deemed sufficient. Further, the membranes then being utilized lacked the high selectivity and permeability necessary to make pervaporation economically attractive. There was much greater interest in the other membrane processes being developed, reverse osmosis and ultrafiltration, in particular.

The energy crisis in the 1970s refocused interest in separation technologies that possed a high potential for energy savings. Pervaporation was aggressively pursued, primarily in Europe, because of its demonstrated ability to dewater aqueous mixtures for fuel utilization. The low level of interest was maintained in the process at Monsanto, Exxon and Standard Oil, principally with the hope of separating organic mixtures such as styrene/ethyl benzene. Further, better membrane materials were being developed in the analogous technologies of reverse osmosis and gas permeation, therefore, the potential for economically attractive separations by pervaporation was greatly enhanced.

In the 1980s, GFT (West Germany) commercialized an economical pervaporation process for dehydration of ethanol and production a high purity of ethanol that rivaled azeotropic distillation. Following pilot trials in Europe, the first industrial plants were built in Brazil and the Philippines for processes utilizing continuous fermentation of sugar can, bagasses, and sweet sorghum containing 5 to 7% ethanol, primary distillation to a mash containing 80 to 85% ethanol, with vacuum pervaporation to 96% ethanol.

In the 1990s, the Exxon group in particular devoted considerable resources to developing membranes able to separate close boiling aromatic/aliphatic refinery mixtures. Membranes with toluene/*n*-octane separation factors of up to 10 were obtained, and the process was taken to the pilot scale.

Currently pervaporation research and development is occurring on a worldwide basis. Japan and Europe account for 46 and 31 % of the citations, respectively, with the United States trailing with 15 %. Commercialization of pervaporation membranes and technology has expanded as well. Following the lead of GFT, Table 2.1 provides a current listing of seven companies now providing industrial-scale pervaporation systems worldwide.

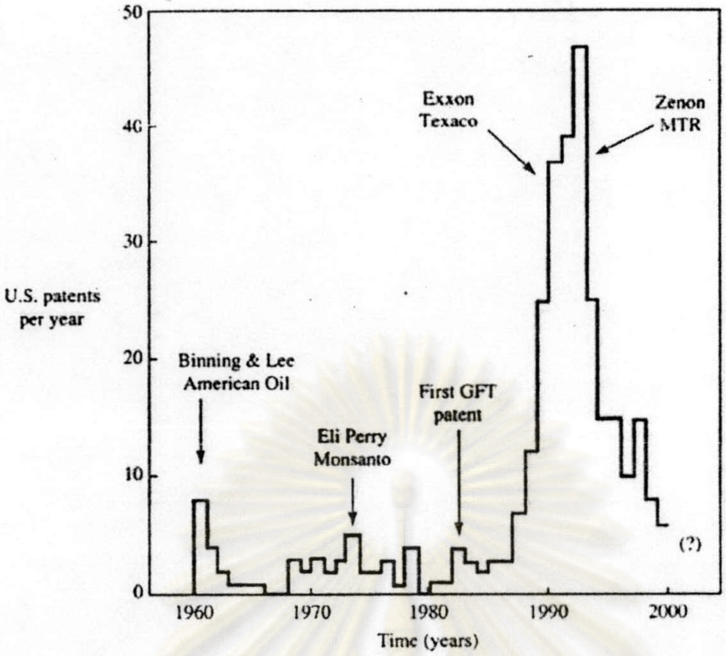


Figure 2.1 Pervaporation-related U.S. patents issued from 1960 to present. (Reproduced from [9].)

Table 2.1 Current commercial producers of pervaporation system [8]

Organization	Primary application	Module configuration	Membrane materials
GFT	Dehydration of liquid organics	Plate-and frame	Poly(vinyl alcohol) composites
MTR	Organic recovery from wastewaters	Spiral wound	Silicones
Lurgi	Dehydration of liquid organics	Plate-and frame	Poly(vinyl alcohol) composites
	Dehydration of vapors	Plate-and frame	Poly(vinyl alcohol) composites
Tokuyama Soda	Dehydration of isopropanol	Hollow-fiber	Chitosan
Kalsep	Dehydration of liquid organics	Tubular	Ion exchange composites
Hoechst Celanese	MeOH/MTBE	Spiral wound	Cellulose acetates
Mitsui	Dehydration of liquid organics	Plate-and frame	Poly(vinyl alcohol) composites

2.3 Pervaporation definition

The term pervaporation is a combination of the two words, permeation and evaporation. In pervaporation, the liquid mixture to be separated (feed) is placed in contact with one side of a membrane and the permeated product (permeate) is removed as a low pressure vapor from the other side as shown in Figure 2.2. The permeate vapor can be condensed and collected or released as desired. The chemical potential gradient across the membrane is the driving force for the mass transport. The driving force can be created by applying either a vacuum pump or an inert purge (normally air or steam) on the permeate side to maintain the permeate vapor pressure lower than the partial pressure of the feed side.

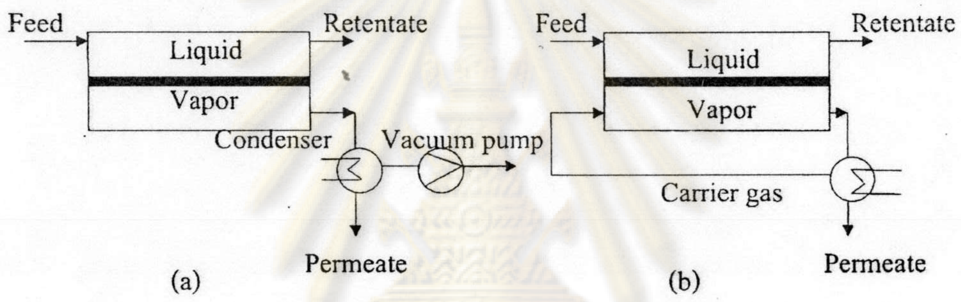


Figure 2.2 Schematic diagram of pervaporation processes.
(a) vacuum pervaporation (b) purge gas pervaporation

Vacuum pervaporation, which is customarily referred to as the standard pervaporation, is the most widely utilized mode of operation, while inert purge pervaporation is normally of interest if the permeate can be discharged without condensation.

2.4 Economic comparison by different techniques

An example of costs for ethanol dehydration system is given in Table 2.2. The poly(vinyl alcohol), PVA, membrane is used in this application to increase ethanol concentration from 99.4 to 99.9 volume % [10].

Table 2.2 Comparison of the dehydration costs of ethanol by different techniques [10]

utilities	pervaporation ($\$$ ton^{-1})	entrainer distillation ($\$$ ton^{-1})	molecular sieve adsorption ($\$$ ton^{-1})
vapor	12.80	120.00	80.00
electricity	17.60	8.00	5.20
cooling water	4.00	15.00	10.00
entrainer	-	9.60	-
replacement of membranes and molecular sieves	30.60	-	50.00
total costs	64.00	152.60	145.20

2.5 Applications of pervaporation

The applications of pervaporation can be classified into three catagories:

(i) removal of water in organic solvents

Removal of water from liquid-organic mixtures now accounts for the largest segment of new industrial pervaporation plants. PVA is one type of the materials which are used for this application. In 1999, Nam, S. Y., et al. [11] studied the pervaporation of a isopropanol-water mixture using carboxymethylated PVA composite membrane. Separation of a 2-methoxyethanol/water mixture by PVA composite membrane was reported by Neto, J. M., et al. in 2000 [12].

(ii) removal of organic compounds from aqueous solutions

In 1998, Kaseno, et al. [13] used the polypropylene, PP, membrane to increase the rate of ethanol removal in ethanol fermentation and to reduce the amount of waste water discharged during long term fermentation. The pervaporation module was coupled to the conventional feed batch fermentation system. Moreover, PP membrane was used for treating methyl *tert*-butyl ether (MTBE) contaminated in water by Keller, A. A., et al. in 2001 [14].

(iii) separation of organic mixtures

The separation of a methanol-toluene mixture by pervaporation using cellulose acetate membrane was investigated by Bhat, A. A., et al. in 2000 [15]. In 2001, Gonzalez, B. G., et al. [16] studied pervaporation using PVA composite membrane for the separation of a methanol-methyl *tert* butyl ether (MTBE) mixture. These membranes were shown to give high affinity toward methanol.

2.6 Economic analysis of integrated fermentation/pervaporation system

Industrial application of pervaporation for alcohol i.e. ethanol, recovery from fermentation broths is dependent on several factors. Membranes with acceptable performance characteristics and low susceptibility to fouling must be developed. Condensation of the permeate (under vacuum), while it may be relatively efficient on a heat transfer basis, would require a refrigeration system for condenser cooling water, creating additional costs over conventional cooling water. However, the economics of such a system should be judged by comparing complete processes; i.e., because of the higher ethanol productivities, a continuous fermentation/pervaporation system would require much less fermentor volume (compared to a conventional batch process), a significant savings in capital costs. In addition, distillation capital and energy costs would be lower because of a more highly concentrated feed. The balance of these savings against the cost of membrane system and refrigeration system would largely determine the economics of pervaporation for ethanol recovery from fermentation broths.

In Figures 2.3 and 2.4 show the batch fermentation and continuous fermentation-pervaporation processes, respectively [17]. A module of a hydrophobic membrane made of a poly(dimethylsiloxane), PDMS, layer on a polysulfone support was used for the pervaporation process [18]. From the level of 7.1 wt % ethanol in the fermentor, a concentrated ethanol product of 42 wt % was obtained. Pervaporation flux and selectivity were found to be 0.15 kg m^{-2} h^{-1} and 10.3, respectively.

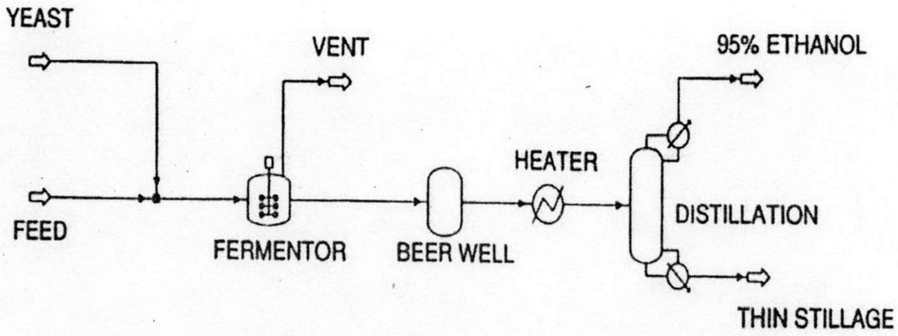


Figure 2.3 Schematic for fermentation and distillation sections of batch fermentation process. (Reproduced from [17].)

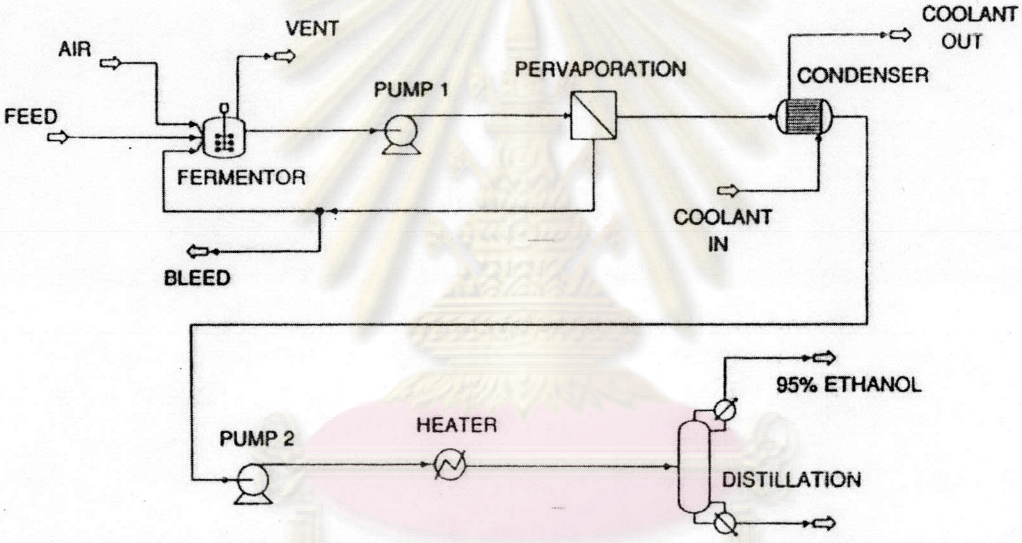


Figure 2.4 Schematic for fermentation and distillation sections of continuous fermentation-pervaporation process. (Reproduced from [17].)

The cost comparison between the base case (batch fermentation case) and the fermentation-pervaporation case is presented in Table 2.2. Capital costs are annualized based upon a 9-year life.

Table 2.3 Ethanol production costs: fermentation-pervaporation case and batch fermentation case [17]

	Fermentation	Pervaporation	Distillation and dehydration	Refrigeration	Total annual $	Unit costs $/Gal
Fermentation/pervaporation costs						
Cap cost — Total	$4, 797, 900	$19, 847, 600	$7, 410, 600	$8, 579, 900	$40, 636, 000	$0.813
Cap cost — Annualized [based on 9-year life]	$533, 000	$2, 205, 000	$823, 000	$953, 000	$4, 515, 000	$0.090
Utilities						
Steam	$0	$0	$1, 582, 200	$505, 700	$2, 087, 900	$0.042
Cooling water	$159, 400	$0	$156, 400	$140, 500	$456, 300	$0.009
Electric power	$18, 600	$35, 800	$18, 200	$37, 600	$110, 200	$0.002
Membrane replacement		$898, 400			$898, 400	$0.018
Annual utilities	$178, 000	$934, 000	$1, 757, 000	$684, 000	$3, 553, 000	$0.071
Plant labor	$126, 000	$523, 000	$195, 000	$226, 000	$1, 070, 000	$0.021
Supplies	$119, 900	$496, 300	$185, 300	$214, 500	$1, 016, 000	$0.020
General works	$48, 000	$198, 300	$74, 300	$85, 700	$406, 000	$0.008
Total annual cost	$1, 004, 900	$4, 356, 600	$3, 304, 300	$2, 163, 200	$10, 560, 000	$0.211
Batch fermentation costs						
Capital costs						
Cap cost — Total	$19, 175, 314	$0	$13, 565, 679		$32, 740, 993	$0.655
Cap cost — Annualized [based on 9-year life]	$2, 131, 000	$0	$1, 507, 000		$3, 638, 000	$0.073
Utilities						
Steam	$0	$0	$2, 323, 000	$0	$2, 323, 000	$0.046
Cooling water	$160, 500	$0	$298, 900	$0	$459, 400	$0.009
Electric power	$146, 000	$0	$59, 600	$0	$205, 600	$0.004
Membrane replacement						
Annual utilities	$307, 000	$0	$2, 682, 000	$0	$2, 988, 000	$0.600
Plant labor	$766, 000	$0	$541, 000	$0	$1, 307, 000	$0.026
Supplies	$479, 700	$0	$339, 300	$0	$819, 000	$0.016
General works	$192, 000	$0	$135, 000	$0	$327, 000	$0.007
Total annual cost	$3, 875, 700	$0	$5, 204, 300	$0	$9, 079, 000	$0.182

Analysis of the costs revealed major differences between the two processes. Fermentor capital costs for the fermentation-pervaporation case were only 25% that for the base case because of the 12-fold reduction in required volume. In the distillation and dehydration area, total annual costs were 61.5% lower for the fermentation-pervaporation case with the saving spilt between capital costs (42.4%) and utility costs (57.6%). However, with additional costs for the pervaporation membrane modules and the refrigeration system not common to the base case (0.182 $ gallon^{-1}), the costs for the fermentation-pervaporation case (0.211 $ gallon^{-1}) are slightly higher. Therefore, the improvements in either flux or selectivity could make the pervaporation case cost competitive.

2.7 Mass transport in membrane

According to the solution-diffusion model, pervaporation consist of three consecutive steps as shown in Figure 2.5:

(i) sorption of the permeate from the feed liquid to the membrane

(ii) diffusion of the permeate in the membrane

(iii) desorption of permeate to the vapor phase on the downstream side of the membrane

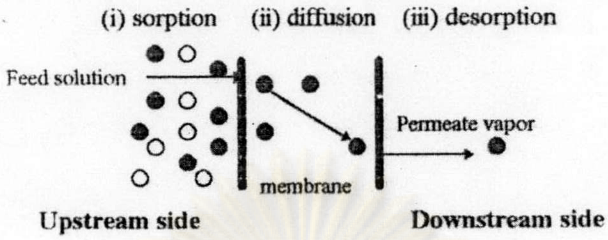


Figure 2.5 Schematic representation of the pervaporation transport mechanism: solution-diffusion model.

Sorption and diffustion in the polymer are the important steps in transport of diffusing component. The desorption step is not normally considered the controlling resistance.

Membrane permeability is a function of solubility and diffusivity of the permeates in the polymer phase under the driving force of a chemical potential gradient. The driving force is the partial pressure gradient between the liquid feed and the permeate vapor. The chemical potential is expressed as the equation

$$\mu_i = \mu_i^o + RT\ln a_i \tag{2.1}$$

where μ_i^o is the standard chemical potential, μ_i the chemical potential, a_i the activity of component *i*, *R* the ideal gas constant, and *T* the temperature.

Relating the activity a_i of a component to its partial vapor pressure in a liquid mixture p_i leads to

$$a_i = p_i/p_i^o \tag{2.2}$$

where a_i is the activity of component *i*, p_i^o the saturated vapor pressure of component *i*, and p_i the partial vapor pressure of component *i*.

For multicomponent mixtures, the component activity is represented by

$$a_i = \gamma_i x_i \tag{2.3}$$

where γ_i is the activity coefficient of component *i*, and X_i the mole fraction of component *i* in feed.

The unique feature of pervaporation is the swelling state of the membrane, ranging from fully swollen at the feed side to virtually dry at the permeate side. Under these conditions, solubility refers to permeate concentration at the feed side of the membrane, and is approximated by liquid phase equilibrium sorption. Permeate concentration at the permeate side of the membrane is governed by sorption from the vapor phase, and is correspondingly low. Diffusivity, following the swelling gradient, is concentration dependent.

2.8 Membrane performance

The performance of pervaporation, as with any separation process, is assessed in terms of flux and selectivity. Assessment is based upon the mass transfer of the preferentially permeating species, irrespective of whether the depleted retentate or the enriched permeate is the target product of the process.

1. Total flux or permeation rate (*J*)

Total flux relates to the product rate to the membrane area required to achieve the separation. This term is defined as

$$J = W_{i,P}/A.t \tag{2.4}$$

Where $W_{i,P}$ is the weight of component *i* in permeate (kg), *A* the membrane area (m^2), and *t* the time (h).

2. Selectivity

The degree of separation which can be obtained with any particular separation process is indicated by the selection factor. Since the object of a separation device is to produce products of differing compositions, it is logical to define the selection factor in terms of product compositions. The selection factor between component *i* and *j*, α_{ij}, is defined as

$$\alpha_{ij} = (y_i/y_j)/(x_i/x_j) \qquad (2.5)$$

where x_i and y_i are the weight fractions of component *i* in feed and in permeate, respectively. x_j and y_j are the weight fractions of component *j* in feed and in permeate, respectively.

An effective separation is accomplished to the extent that the selection factor is significantly different from unity. If $\alpha_{ij} = 1$, no separation of components *i* and *j* has been accomplishd. If $\alpha_{ij} > 1$, component *i* tends to concentrate in product more than component *j* does, and component *j* tends to concentrate in feed more than component *i* does. On the other hand, if $\alpha_{ij} < 1$, component *j* tends to concentrate preferentially in product and component *i* tends to concentrate preferentially in feed. By convention, components *i* and *j* are generally selected so that α_{ij}, defined by Equation (2.5), is greater than unity.

Usually there is a trade-off between these two factors: i.e. when one factor increases, the other decreases. As both of them are important factors in the separation process, a pervaporation separation index (PSI) can be defined as a measure of the separation ability of a membrane

$$\mathrm{PSI} = J.(\alpha_{ij} - 1) \qquad (2.6)$$

2.9 Membrane modules

Industrial membrane plants often require hundreds to thousands of square meters of membrane to perform the separation required on a useful scale. Before a membrane separation can be used industrially, therefore, methods of economically and efficiently packaging large areas of membrane are required. These packages are called "membrane modules". The following membrane modules are largely used for industrial applications.

1. Plate-and-frame modules

Plate-and-frame modules were one of the earliest types of membrane system as shown in Figure 2.6. Membrane, feed spacers, and product spacers are layered together between two end plates. The feed mixture is forced across the surface of the membrane. A portion passes through the membrane, enters the permeate channel, and makes its way to a central permeate collection manifold.

Plate-and-frame units have been developed for some small-scale applications; but these units are expensive compared to the alternatives, and leaks through the gaskets required for each plate are a serious problem. Plate-and-frame modules are now only used in electrodialysis and pervaporation systems and in a limited number of reverse osmosis and ultrafiltration applications with highly fouling feeds.

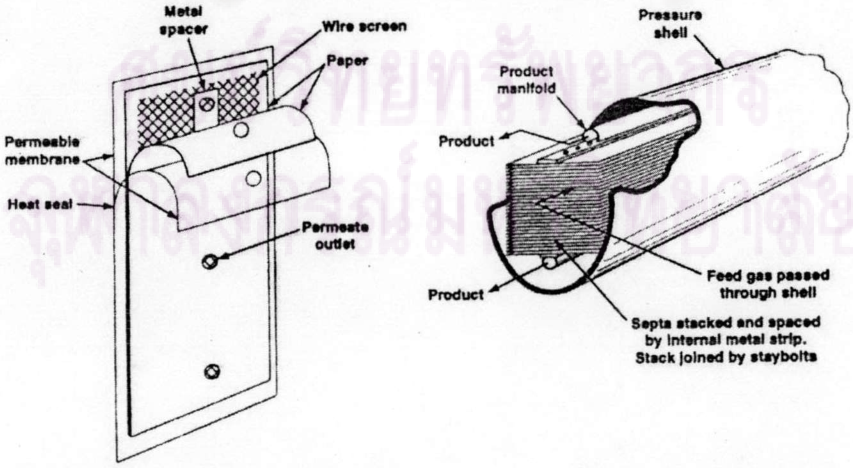


Figure 2.6 Schematic of a plate-and-frame module. (Reproduced from [19].)

2. Tubular modules

Tubular modules are now generally limited to ultrafiltration applications, for which the benefit of resistance to membrane fouling due to good fluid hydrodynamics outweighs the high cost. Typically, the tubes consist on a porous paper or fiberglass support with the membrane formed on the inside of the tubes, as shown in Figure 2.7.

In a typical tubular membrane system, a large number of tubes are manifolded in series. The permeate is removed from each tube and sent to a permeate collection header.

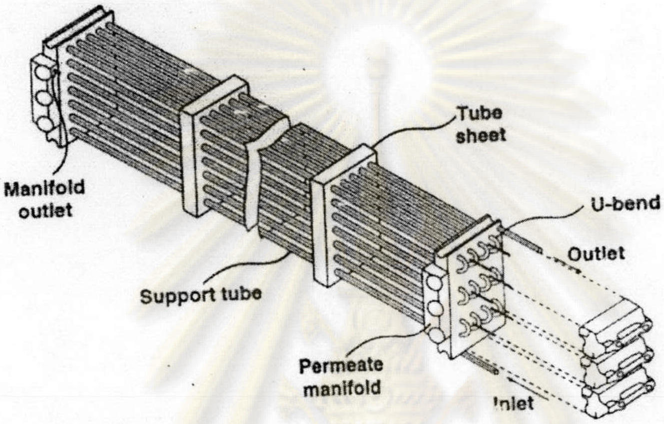
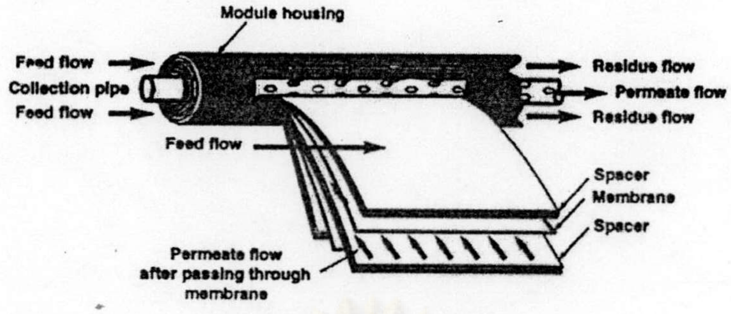


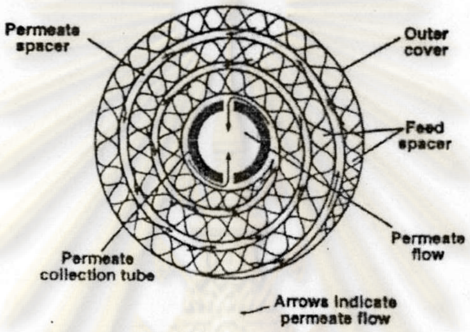
Figure 2.7 Schematic of a tubular module. (Reproduced from [19].)

3. Spiral-wound modules

Spiral-wound modules were used in a number of early artificial kidney, but were fully developed for industrial membrane separations as reverse osmosis. The design shown in Figure 2.8 is the simplest, consisting of a membrane envelope of spacers and membrane wound around a perforated central collection tube; the module is placed inside a tubular pressure vessel. Feed passes axially down the module across the membrane envelope. A portion of the feed permeates into the membrane envelope, where it spirals toward the center and exits through the collection tube.



Spiral-Wound Module



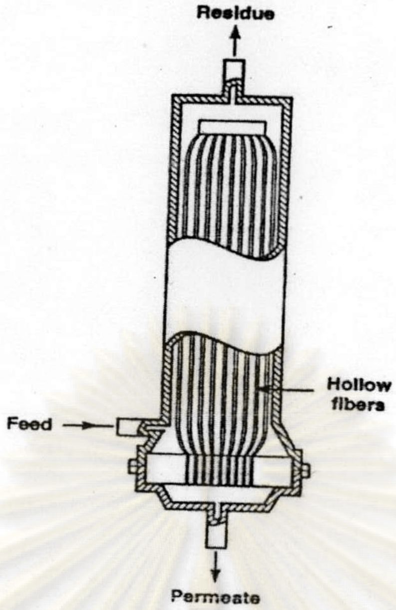
Spiral-Wound Module Cross Section

Figure 2.8 Schematic of spiral-wound module. (Reproduced from [19].)

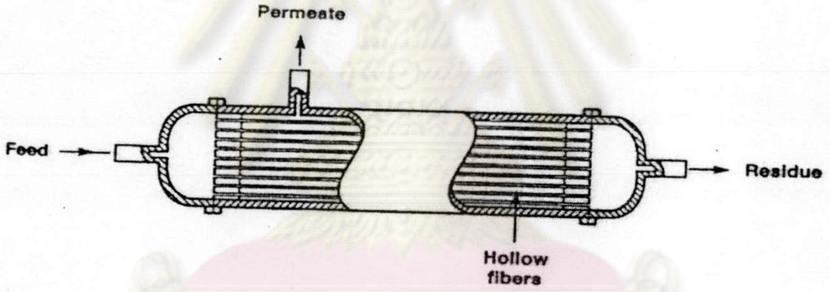
4. Hollow-fiber modules

Hollow-fiber membrane modules are formed in two basic geometries. The first is the shell-side feed design, illustrated in Figure 2.9a (hollow fine fiber). This system is pressurized from the shell side; permeate passes through the fiber wall and exits through the open fiber ends. The second type of hollow-fiber module is the bore-side feed type, illustrated in Figure 2.9b (capillary fiber). The fibers in this type of unit are open at both ends, and the feed fluid is circulated through the bore of the fibers.

The greatest single advantage of hollow-fiber modules is the ability to pack a very large membrane area into a single module.



(a) Shell-side feed



(b) Bore-side feed

Figure 2.9 Schematic of two types of hollow-fiber modules. (Reproduced from [19].)

2.10 Concentration polarization

The performance of pervaporation is usually assessed from the flux and selectivity that are affected by the transport mechanism which are dependent upon the operating conditions. The resistance to solute transport in pervaporation process may consist of liquid boundary layer resistance due to concentration polarization (CP) on the feed side.

CP is a common phenomenon in membrane processes since membrane separation is based on the difference in the permeation rates of different permeating components. Since, retention of the slow permeating component on the membrane surface, the concentration of the fast permeating component on the membrane surface is lower than that in the bulk phase, while the opposite is true for the slow component. As a resulting the flux and separation behaviors of the system correspond to a substantially higher feed concentration than is measured in the bulk stream. This is shown schematically in Figure 2.10. Where X_i and $X_{i,M}$ are the mole fractions of component i in the feed and on the membrane surface, respectively. Y_i is the mole fraction of component i in the permeate. J_i and J_j are the fluxes of component i and j, respectively. δ is the thickness of the concentration boundary layer.

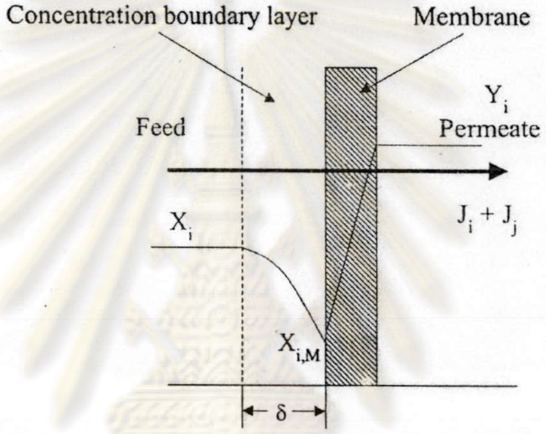


Figure 2.10 Schematic diagram of the boundary layer effect : concentration polarization. (Adapted from [5].)

CP generally leads to a lower productivity and a lesser extent of separation. The boundary layer effect is often assumed to be insignificant for most of the current pervaporation membranes because the permeation fluxes are usually low. However, some researchers reported that the permeate fluxes were strongly affected by the operating conditions on the feed side. Feng , X. S., et al. [20] showed that the CP model was based on the film theory. The significance of CP was determined not only by the membrane permeability and hydrodynamic conditions but also by the membrane selectivity. CP in pervaporation should not always be overlooked even for membranes with moderated permeability. There has been a suggestion that CP may be more significant when the target component that preferential permeates through the membrane is present in the feed at lower concentration.

2.11 Selection of polymer membrane materials

Membrane selectivity is determined by sorption selectivity and diffusion selectivity. The suitable polymer materials for pervaporation process must exhibit higher affinity to one of the mixtures. The component that exhibits higher affinity sorbed by the polymer chain. The extent of sorption (also called swelling) as well as the sorption selectivity are therefore determined by the chemical nature of the polymer and that of the mixtures. Diffusion kinetics play a more important role for molecules with large differences in size mean smaller permeating molecules normally exhibit larger diffusivity.

Membranes in an aqueous environment have an attractive or repulsive response to water. The material composition of the membrane and its corresponding surface chemistry determine the interaction with water. This phenomena is termed hydrophilicity and hydrophobicity. These terms are usually expressed in terms of contact angle (θ) or a critical surface tension [21].

Hydrophilicity is a characteristic of materials exhibiting an affinity for water. Hydrophilic literally means "water-loving" and such materials readily adsorb water. The surface chemistry allows these materials to be wetted forming a water film or coating on their surface. Hydrophilic materials also posses a high surface tension value and have the ability to form "hydrogen-bonds" with water.

Also termed hydrophobicity, materials possessing this characteristic have the opposite response to water interaction compared to hydrophilic materials. Hydrophobic materials (water hating) have little or no tendency to adsorb water and water tends to "bead" on their surfaces (i.e., discrete droplets). Hydrophobic materials possess low surface tension values and lack active groups in their surface chemistry for formation of "hydrogen-bonds" with water.

The fundamental importance of surface tension comparison is that liquids having higher values will generally spread on materials which have high surface tension values. Such as water droplet (surface tension = 73 dyne cm^{-1}) will spread on PVA surface (surface tension = 37 dyne cm^{-1}) more than ethanol droplet (surface tension = 24 dyne cm^{-1}).

Membrane selection is critical in the commercial application of pervaporation, when used in the presence of organic compounds. For water permeation, hydrophilic membrane materials are preferred. On the other hand, for organics permeation, hydrophobic membrane materials are preferred. The separation of ethanol-water mixtures by pervaporation through silicone rubber membrane and PVA membrane was studied [22]. Results showed that the permeation behavior depends on ethanol composition, temperature, and type of membranes. The silicone rubber membrane (ethanol-selective membrane) gave high selectivity and ethanol flux, while the opposite trend was showed with using the PVA membrane (water-selective membrane). The pervaporation performances of volatile organic compounds (VOCs) from liquid mixtures were measured in two different types of polymers: PDMS, a hydrophobic rubbery polymer, and cellulose, a hydrophilic glassy polymer [23]. In case of cellulose membrane, the permeability was primarily determined by the diffusivities of permeates, i.e. smaller molecules permeate preferentially. On the other hand, the solubility behavior determined the permeability to a large extent in case of PDMS membrane. Therefore, the performance of a two-membrane column was demonstrated for the separation of water-ethanol and water-isopropanol azeotropic mixtures [24]. A combination of two different membrane columns, a column of silicone rubber for the concentration of alcohol from a solution of high water content and another for the dehydration of a low water content mixture using a cellulose acetate membrane, will lead to a more economic system than a column made of just one kind of membrane. The feed concentration of 20 mol % ethanol was firstly concentrated to 12.9 mol % ethanol by the silicone rubber column, and then it was finally concentrated to 79.1 mol % ethanol by the cellulose acetate column. For the isopropanol-water mixture, at feed concentration of 20 mol % isoprapanol was firstly concentrated to 11.5 mol % ethanol by the silicone rubber column, and then it was finally concentrated to 97.8 mol % ethanol by the cellulose acetate column.

The separation of aqueous-organic mixtures where the water molecules smaller than organic compounds is now considered. A hydrophilic membrane (water-selective membrane) favors both solubility and diffusivity for selective permeation of water, while an organophilic membrane (hydrophobic:organic-selective membrane) must have a large solubility to the organic compound inorder to permeate the organic compound preferentially because of the unfavorable diffusion selectivity. This may be the reason that many polymers are selective to water permeation, while only a few are selective to the permeation of organic compounds. It is well known that the water molecule is easily incorporated into the hydrophilic polymer membrane due to the strong affinity between the water molecule and the hydrophilic polymer, especially membranes made of polymers with very high hydrophilicity such as PVA and poly (acrylic acid), PAA. This generally leads to the excess swelling of the polymer making the polymer chain more flexible, and resulting in an increases permeability and a decreses membrane selectivity in pervaporation. Therefore, the modified hydrophilic membrane is developed to avoid this excessive swelling. Polymer crosslinking and blending are applied to modify the hydrophilic material. Such as the pervaporation of water-ethanol mixtures was performed with crosslinked PVA membranes [25]. The glutaraldehyde has been chosen as a crosslinking agent. In order to enhance the permselectivity of water through the crosslinked membrane, the surface of the crosslinked PVA membrane was hydrophilically modified by reacting with monochloroacetic acid. The permselectivity of water through the crosslinked and hydrophilically surface-modified PVA membrane was enhanced by a factor of nearly two compared to that through the crosslinked PVA membrane, while the total flux for the crosslinked and surface-modified membrane remained almost unchanged or even slightly increased. Thus, it was concluded that the surface modification technique appears to be very useful for the improvement of the pervaporation characteristics in dehydrating aqueous ethanol solution. However, this modified technology not only reduce the excessive swelling of hydrophilic membrane, but also reduced the water permeation rate due to the decrease in free volume of membrane. Moreover, it is difficult to choose an appropriate crosslinking agent.

To avoid any limits of hydrophilic membrane, hydrophobic membrane is considered as as easy way for pervaporation separation of aqueous-organic mixtures. Silicone rubber based PDMS is mainly used for this application [26, 27].

2.12 Hydration and swelling effect on hydrophobic membrane

The permeation behavior, particularly for an aqueous solution with a hydrophilic solute, is affected by the hydration of water to the solute. Generally, water molecules are always moving. The motion of water molecules in an aqueous solution containing a solute is affected by the water and solute interaction, and differ from water molecules in pure water. The water molecules adjacent to the solute become less mobile than in the pure water due to hydration. Hydrogen-bond formation of water molecules in an aqueous solution is thought to form clusters with an ice-like structure that is stabilized by the presence of a hydrophobic group of the membrane [28]. In the other word, in the presence of the hydrophobic polymer, it will shift the unassociated water molecules to larger clusters around the hydrophobic polymer due to repulsion by the exposure of hydrophobic chains to water. Therefore, as the polymer hydrophobicity increases, solute molecules can not disturb the structure of water cluster to decrease the polymer swelling in the aqueous solution [29]. The swelling behavior of crosslinked poly(dimethylsiloxane)-poly(methyl hydrogen siloxane) (PDMS-PMHS) in ethanol-water mixtures was studied [30]. The results showed that the swelling increased rapidly with the amount of ethanol in feed. The swelling of pure water was relatively low. This confirmed the low affinity for water of PDMS-PMHS membrane.

2.13 Effect of operating parameters on pervaporation performance [5,8]

The factors affecting flux and selectivity in pervaporation process are not only membrane material but also the operating parameters.

1. Feed concentration

Note that feed concentration refers to the concentration of the more permeable component in solution. According to solution-diffusion model, both sorption and diffusion of the components in the membrane characterize the membrane properties. A change in feed concentration directly affects the sorption phenomena at the liquid/membrane interface. The activity of the components of a mixture may vary more or less with the change in composition depending on the chemical nature of the mixture. But normally, feed concentration increases, sorption or concentration of the components in membrane tends to be increased. Since, the diffusion of the components is concentration dependence, the permeation rate increases with feed concentration. In addition, changes in concentration of the components in membrane affect coupling and membrane swelling which all play an important role in pervaporation process.

2. Downstream pressure

The downstream pressure is an important operating parameter, since the high vacuum is costly. In vacuum pervaporation, the downstream pressure is the total pressure of the vaporized permeate in contact with the membrane, ideally devoid of non-condensable gases. The downstream pressure is also directly related to the activity of components at the downstream side of the membrane. An increase in the vapor pressure in the downstream side leads to a decrease of a driving force for transport. The selectivity can increase or decrease with increasing downstream pressure, depending on the relative volatility of the permeating components.

3. Feed temperature

Temperature in pervaporation may mean the temperature of feed entering the process, or some representative temperature intermediate between feed (inlet) and retentate (outlet). Since the solubility and diffusivity of the feed mixture component in the polymeric membrane are generally dependent on the operating temperature, pervaporation characteristics in term of flux are also dependent on the temperature as follow (Arrhenius-type law)

$$J = A_{\mathrm{p}} \mathrm{e}^{-Ep/RT} \tag{2.7}$$

Where A_p is the pre-exponential constant parameter, and E_p the apparent activation energy of permeation.

The temperature dependence of flux is mainly governed by the temperature dependence of the diffusion coefficient, consequently and flux increases with temperature. The selectivity is not so strongly dependent on the temperature, in most case a small decrease of selectivity is found at increasing temperatures even it is known that the effect of temperature on membrane properties is a major phenomenon that governs the selectivity.

4. Feed flow rate

A change of feed flow rate affects concentration polarization in liquid boundary layer which is particular important if high fluxes through the membrane are combined with laminar regime. The mass transfer coefficient of component in liquid boundary layer increases with increasing feed flow rate and subsequently reduces concentration polarization.

2.14 Literature review

Firstly, previous work on pervaporation using hydrophilic membranes for methanol removal from methanol aqueous solutions was disscussed.

Wesslein, M., et al. [31] studied the pervaporation of binary mixtures containing water using PVA composite membrane. The flux and selectivity were measured at a temperature range of 25 to 75 °C. The pervaporation was not suitable for separation of the methanol-water mixtures with the PVA membrane, since the separation curve was found to be close to the straight line, indicating that there was almost no separation effect ($\alpha = 1$). In all cases it was found that pervaporation was a suitable method for extraction of water from organic solvents above weight fractions of 0.8 of the organic solvents.

Rhim, J. W., et al. [32, 33] prepared crosslinked PVA membranes with the low molecular weight of PAA as the crosslinking agent for pervaporation separation of methanol-water mixtures. The PVA/PAA ratios in the crosslinked membrane were 90/10, 85/15 and 80/20 by weight. The operating temperatures were set at 50, 60, and 70 °C, and the feed concentrations in the range of 70 to 95 wt % methanol. In all cases, the PVA/PAA ratio of 80/20 membrane showed the best results. Using the PVA/PAA of 80/20 membrane, the separation factors ($\alpha_{W/M}$) of 465 and 2650, and the permeation rates of 0.109 and 0.033 kg m^{-2} h^{-1} were obtained for feed concentrations of 90 and 95 wt % methanol, respectively, at 70 °C. Therefore, sulfur-succinic acid, SSA ,was used as the crosslinking agent for separation of alcohol-water mixtures. The separation performance of the methanol-water mixture was poor due to the existence of sulfonic acid, a hydrophilic group, in the crosslinking agent. However, this membrane was suitable for the separation of ethanol- and isopropanol-water mixtures.

Wang, X. P., et al. [34] prepared the three-layer structure composite membrane for alcohol dehydration such as methanol, ethanol and isopropanol. The top layer was a thin film of chitosan crosslinked with glutaraldehyde, and the support layer was made of microporous poly(acrylonitrile), PAN. The results indicated that the separation factor and the permeation rate of this composite membrane increased with an increase in the operating temperature. The water selectivity for the higher molecular weight alcohol-water mixtures was much higher than that for the methanol-water system, with nearly complete separation. Nevertheless, the permeation rate was the lowest for the ethanol-water system. Using 90 wt % methanol aqueous solution at 60 °C, the flux of 0.34 kg m^{-2} h and selectivity of 24 were obtained.

Doguparthy, S. P. [35] investigated the pervaporation of methanol-water and ethanol-water mixtures using photopolymerised composite membrane. This membrane gave a good selectivity to water in both methanol-water and ethanol-water mixtures. This suggested that good separation of methanol-water mixtures were possible with this composite membrane. As alcohol concentration in feed increased from 10 to 90 wt %, the total flux decreased from 0.244 to 0.056 kg m^{-2} h indicated that the permeation was a function of feed composition.

Yeom, C. K., et al. [36] studied the pervaporation of homologous series of alcohol aqueous mixtures through PVA membrane with glutaraldehyde. The experiments were carried out with feed having 70 to 97 wt % alcohol and at temperatures of 30 to 50 °C. In a high alcohol content above 90 wt %, the permeation rate increased in the order of the interaction strength between alcohol and water in feed. However, at a low alcohol content below 90 wt %, the tendency of the permeation rate was found to be the opposite, indicating that the interaction between permeant contituents plays an important role on the permeation and separation of the mixtures. The observations were discussed in term of changes in the interaction between the permeant/permeant or the permeant/membrane in varies feed compositions and feed temperatures.

Secondaly, the work on pervaporation using hydrophobic membranes for methanol removal from methanol aqueous solutions was summarized.

Hennepe, H. J. C., et al. [37] reported the pervaporation results of aqueous solutions of dilute alcohols such as methanol, ethanol and propanol, using silicalite-filled silicone rubber membranes. The experiments were performed at a feed composition of 5.5 wt % alcohol and a constant feed temperature of 22.5 °C. Both permeation fluxes and selectivities of those alcohols were found to be higher than those of silicone rubber membranes. The flux for the filled membranes increased with an increase in the silicalite content. At 60 wt % of silicalite-filled membrane, the best result was obtained. The selectivity for the higher molecular weight alcohol-water mixture mixtures was found to be higher than that for the methanol-water system, but the flux gave the opposite results. For the methanol-water mixture, the flux of 70.41 g m^{-2} h and selectivity of 13.0 were obtained. The results indicated that the flux increased with an increase in the temperature due to the high vapor pressure of the components of the feed resulting in an increase in driving force and leading to low selectivity of the membrane at high temperature.

Galindo, M. O., et al. [38] prepared the hydrophobic composite membranes with a crosslinked PDMS-PMHS selective layer for separation of volatile organic compounds (VOCs) from liquid mixtures by pervaporation. VOCs used in their experiment are methanol, ethanol, 1-buthanol, acetone and ethyl acetate. The experiments were performed at the feed composition of 5 volume % VOCs, the feed temperature of 40 °C, the feed flow rate of 4.8 l h^{-1} and the downstream pressure of 7 mmHg. A comparison of the performance of the two different PDMS-PMHS membranes studied showed that PV-2 (silicone coated of 0.0060 g cm^{-2}) had a very high selectivity but its flux was lower than that of PV-1 (silicone coated of 0.0048 g cm^{-2}). This is due to the fact that the silicone active layer of membrane PV-2 was thicker than that of membrane PV-1. For the methanol-water mixture, the total flux of 0.08 l m^{-2} h^{-1} and selectivity of 2.8 were obtained, using membrane PV-2.

Orme, C. J., et al. [39] studied the pervaporation of water-dye, alcohol-dye and water-alcohol mixtures, where the alcohols were methanol and isopropanol, using a polyphosphazene membrane. For the alcohol-water separations, the alcohol was the favored permeate in all cases with high fluxes observed for high concentrations of alcohol in feed, however, selection factors declined. In case of methanol-water mixtures, the fluxes were in excess of 2 kg m^{-2} h^{-1} with poor selection factor, at feed concentrations of higher than 70 wt % methanol. At lower concentrations of methanol, the fluxes dropped off in a near linear fashion. Correspondingly, the selection factor also increased in a near linear fashion.

Finally, the work on PTFE membrane used for separation of organic-water mixtures was disscused.

Calibo, R. L., et al. [40] tested the pervaporation for removal of 8 wt % ethanol in water, using a tubular PTFE module. The overall mass transfer coefficient (K_G) was more affected by the liquid feed flow rate than by the sweeping gas flow rate. At an average solution temperature range of 21 to 32 °C, no significant change in the K_G was determined. This phenomenon implied that the increment of the vaporization rate was mainly due to the change of vapor pressure, which was incorporated in the Henry's constant. Moreover, the membrane properties remained unaffected in the given temperature range, i.e. membrane swelling could not occurr.

Atichatpongkul, C., et al. [41] studied the effects of the temperature and concentration of feed on the pervaporation performance of ethanol-water mixture using the PTFE membrane. The permeate side pressure was kept constant at 5 mmHg The temperature of feed was controlled at 27.5, 30, or 40 °C, and the concentrations in the range of 6 to 30 wt % were used. At the constant temperature, the ethanol concentration in permeate and the flux increased with an increase in the concentration of ethanol in feed, but the separation factor decreased. At the constant concentration, the ethanol concentration in permeate and the flux increased with an increase in the feed temperature, but the separation factor decreased. From 27.5 to 40 °C, the flux was enhanced from 710.65 to 1155.65 kg m^{-2} h^{-1} but the separation selectivity decreased from 3.88 to 2.71 at a constant feed concentration of 6 wt % ethanol in water.

Bandini, S., et al. [42] presented the removal of different volatile organic compounds (VOCs) from aqueous streams through the PTFE membrane. The dilute binary aqueous mixtures used contained acetone, ethanol, isopropanol, ethyl acetate, methyl acetate and methyl *tert* butyl ether. The following conditions were used: the concentrations of 2 to 10 wt % VOCs, the temperatures of 25 to 35 °C, the flow rates of 0.05 to 3 l min^{-1}, and the downstream pressures of 10 to 70 mbar. The results showed that high VOCs compositions in the permeate and high fluxes were obtained at high compositions in the liquid feed. The effect of temperature appeared very interesting, at high temperatures, high fluxes and low VOCs compositions in the permeate were obtained. When the downstream pressures increased, the fluxes decreased and the VOCs compositions in the permeate increased. Both the organic and water fluxes significantly increased with an increase in the feed flow rate, especially in the range of low flow rate.

PTFE is chosen as membrane material in this study because of its exceptional characteristics suitable for pervaporation separation. It has low surface energy (surface tension = 18 dyne cm^{-1}), acts as water repellency (surface tension of water = 73 dyne cm^{-1}), possibly due to the potential factor governing preferential permeation of methanol (surface tension of methanol = 23 dyne cm^{-1}) when separating water and methanol. Moreover, it is highly stable at high temperature and resistant toward chemicals and solvents. The linear molecular structure of PTFE is shown in Figure 2.11.

$$-\!\!\left[\, CF_2\text{-}\ CF_2 \,\right]_n\!\!-$$

Figure 2.11 Schematic molecular structure of PTFE or Teflon.