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SEPARATION OF LIQUID MIXTURES BY PERVAPORATION

A review of pervaporation and vapour permeation – membrane separation techniques used to separate liquid mixtures, is presented. The separation of a given mixture is caused by the differences in sorption and diffusion of its components in the nonporous liophilic membrane. Pervaporation, vapour permeation and chosen related processes were characterized. Examples of polymers for membranes preparation as well as model theories and performance parameters of pervaporation were described. In the last part of the paper, the industrial applications of pervaporation and vapour permeation were presented.

1. INTRODUCTION

Most industrial scale separation processes are based on energy-consuming methods such as distillation, evaporation, and freeze crystallization. For instance, 30% of the energy used in all chemical plants and petroleum refineries was consumed in distillation systems. Membrane separations offer significant advantages over the existing separation processes.

Membranes separate mixtures by discriminating the components on the basis of their physical or chemical attributes such as molecular size, charge or solubility. Due to their ability to pass water and to retain salts, membranes are used to produce over half of the world's desalinated potable water. Membranes can also separate oxygen and nitrogen from air as well as hazardous organics from contaminated water.

Current membrane separation technologies can offer energy savings, low-cost modular construction, high selectivity of separated materials, and processing of temperature-sensitive products. Synthetic membranes are providing enhanced separation capabilities in the case of gases, liquids, metals, and microbes. Six major membrane processes: microfiltration, ultrafiltration, reverse osmosis, electrodialysis, gas separation and pervaporation are applied in such areas as water purification, chemical and food processing, drug delivery, bioseparations, and medical treatment.

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The need for the membrane separation technology increases as environmental requirements tighten, water circuits close, the recycling of wastes increases and the purity requirements for foodstuff and pharmaceuticals increase. In fact, membrane separation applications are possible almost anywhere in liquid or gas processing. As a result, the world market for synthetic membranes could expand exceeding \$3,500,000,000 in the next decade.

Present paper deals with pervaporation and vapour permeation – two particularly useful and relatively new membrane separation processes.

2. PERVAPORATION FUNDAMENTALS

2.1. DEFINITION OF THE PERVAPORATION PROCESS

Pervaporation was discovered by Kober (USA) in 1917, accidentally, just as the discovery of osmosis by Nollet. Kober mentioned the phenomenon called 'pervaporation' in a publication describing experiments with water selective collodion containers [1].

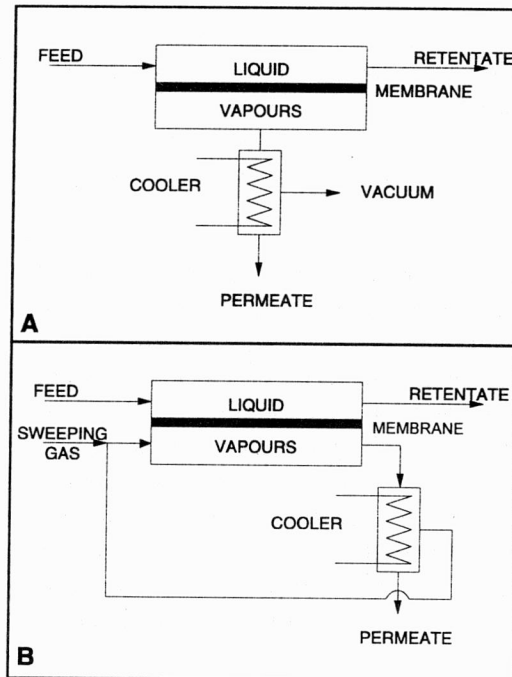


Fig. 1. Scheme of pervaporation process:
A – vacuum pervaporation, B – sweeping gas pervaporation

Today, pervaporation is recognized as a separation process in which a binary or multicomponent liquid mixture is separated by partial vaporization through a dense nonporous membrane. During pervaporation, the feed mixture is circulated in contact with one side of the membrane, whereas the permeate is removed in a vapour state from the opposite side into a vacuum (Fig. 1A) or sweeping gas (Fig. 1B) and then condenses. Pervaporation is a unique kind of membrane separation, involving the liquid–vapour phase change to achieve the separation [2, 3].

The driving force of the mass transfer of permeants from the feed side to the permeate side of the membrane is a gradient of chemical potential, which is established by applying a difference in partial pressures of the permeants through the membrane. The difference in partial pressures can be created either by reducing the total pressure on the permeate side of the membrane by using vacuum pump system or by sweeping an inert gas on the permeate side of the membrane [2, 3].

2.2. PERFORMANCE PARAMETERS OF PERVAPORATION MEMBRANES

The performance of a given membrane in pervaporation is estimated in terms of its selectivity and the permeate flux. The assessment is based on the mass transfer of the preferentially permeating species, regardless of whether the permeate or the retentate is the target product of the pervaporation process.

The pervaporation selectivity of a given membrane can be estimated by using the following two dimensionless parameters [2–5]:

separation factor α^{PV}

$$\alpha^{\text{PV}} = \frac{Y_A / Y_B}{X_A / X_B} = \frac{Y_A / (1 - Y_A)}{X_A / (1 - X_A)}, \quad (1)$$

and enrichment factor β^{PV}

$$\beta^{\text{PV}} = \frac{Y_A}{X_A}, \quad (2)$$

where: X_A – weight fraction of preferentially permeating species in the feed liquid phase, Y_A – weight fraction of preferentially permeating species in the permeate vapour phase;

$$X_A + X_B = 1, \quad (3)$$

$$Y_A + Y_B = 1. \quad (4)$$

The McCabe–Thiele diagram, employed usually for the analysis of liquid–vapour equilibrium, can also be used to evaluate pervaporation selectivity. Figure 2 compares the distillation and pervaporation of water–ethanol binary mixture through hydrophilic polyvinyl alcohol membrane. It is seen that pervaporation with highly hydro-

philic membrane favours the transport of the higher boiling water. The high efficiency of pervaporation occurs also near the azeotropic composition of the water-ethanol

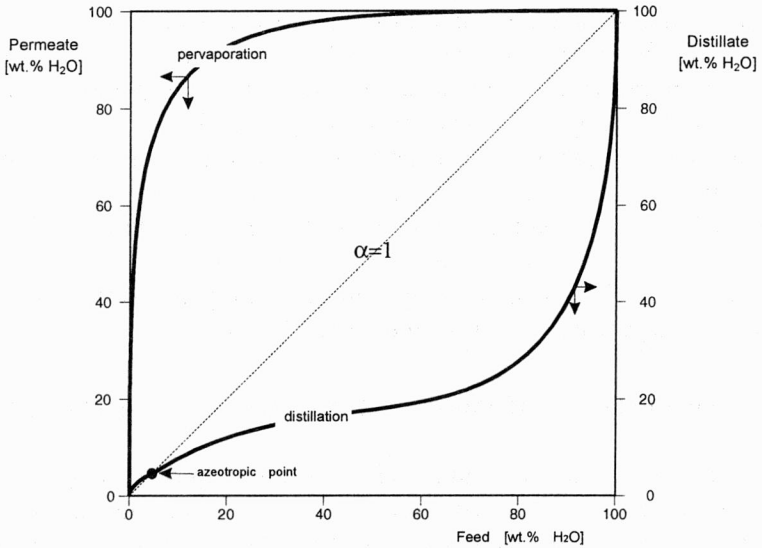


Fig. 2. McCabe-Thiele separation diagram.
Comparison of pervaporation selectivity with distillation selectivity.
System: water-ethanol. Membrane: PVA composite hydrophilic membrane

system. The diagonal line in Fig. 2 represents azeotropic compositions, for which separation does not take place (compositions of the product and the feed mixture are the same, i.e. $\alpha = 1$).

3. RELATED PROCESSES

There are several membrane processes which resemble to some extent pervaporation. To avoid misunderstandings, the following subsections give the general outlook for these techniques [3,6,7].

3.1. GAS SEPARATION

Separation of mixtures of gases is possible using either porous or nonporous membranes although quite different mechanisms of transport are involved (Fig. 3A, Table 1). Separation in porous membranes is through the differences in the Knudsen diffusion of the components in the pores which are of a size less than the mean free paths of the molecules. With porous membranes, generally low separations are obtained with most gas mixtures except those containing hydrogen or helium. Separation

of gases through nonporous membranes depends on the differences in permeabilities of the constituent gases.

3.2. VAPOUR PERMEATION

Vapour permeation is a membrane process for the separation of saturated mixed vapours, with no change of phase involved in its operation (Fig. 3B and Table 1). Thus, compared to pervaporation, the addition of heat equivalent to the enthalpy of vaporization is not required in the membrane unit. Operation in the vapour phase eliminates the effect of the concentration polarization prevalent in such liquid phase separations as pervaporation. Vapour permeation can be used to separate a vapour from either non-condensable gases or from a mixture of vapour compounds. Preferred membranes are nonporous and their materials are similar to those for pervaporation. Organophilic membranes such as polydimethylsiloxane (PDMS) are used to separate organic species from air and other gases. For the separation of mixed vapours a range of membrane materials is broad, depending upon the desired penetrant, e.g. polyvinyl alcohol (PVA) membranes are used to separate water from alcohols. Some examples of the application of vapour permeation will be presented in the subsequent part of this paper.

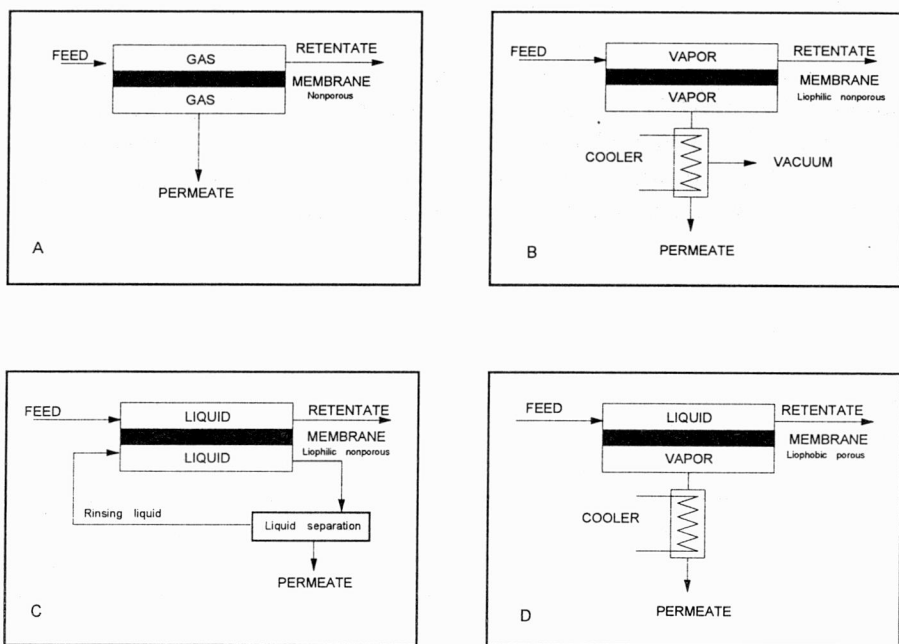


Fig. 3. Schematics of the chosen membrane processes. A – gas separation, B – vapour permeation, C – pertraction, D – membrane distillation

3.3. PERTRACTION

Pertraction may also be considered as a membrane separation technique displaying some similarity with pervaporation. During pertraction the permeate is evolved from the downstream surface of the membrane by circulating a suitable solvent which maintains low penetrant concentration in the downstream layer of the permselective barrier (Fig. 3C, Table 1). In contrast with pervaporation, pertraction does not involve any phase change of the permeate during its transport through the membrane. This technique has been proposed to separate the benzene/cyclohexane by preferential extraction of aromatic component into decalin through a membrane obtained from a blend of cellulose acetate and a phosphonated polymer.

3.4. MEMBRANE DISTILLATION

Membrane distillation denotes transfer of the solvent from the liquid phase to the vapour phase through the pores of non-wetted liophobic microporous membrane (Fig. 3D, Table 1). The membrane material is not wetted by the liquid feed preventing the liquid penetration and transport through the membrane. Separation occurs by the liquid–vapour phase transition at the pore inlet and vapour transport through the pore network of the membrane. The membrane exerts little influence on the separation of the liquid mixture, as the vapour–liquid equilibrium is not disturbed. The driving force of membrane distillation is the temperature gradient between feed and permeate side of the membrane. The typical membrane materials are polypropylene, polytetrafluoroethylene (PTFE) with submicron pore sizes, which have penetration pressure of several bar. Potential applications of membrane distillation are in the following areas: water purification and demineralization of sea water, brackish water and waste water, concentration of aqueous salt solution and acid.

Table 1

Overwiev of pervaporation and related process

Membrane process	Feed phase/ permeate phase	Driving force (gradient)	Membrane	Main applications
Pervaporation	liquid/vapour	chemical potential	dense, liophilic	separation of liquid mixtures
Gas separation	gas/gas	hydrostatic pressure	porous or dense	separation of gaseous mixtures
Vapour permeation	vapour/vapour	chemical potential	dense, liophilic	separation of vapour mixtures or vapours from gases
Pertraction	liquid/liquid	concentration	dense, liophilic	separation of organic solutions
Membrane distillation	liquid/vapour	vapour pressure	porous, liophobic	ultrapure water, concentration of solutions

4. TRANSPORT MODELS OF THE PERVAPORATION PROCESS

In pervaporation, nonporous membranes are used and transport of the components proceeds by the solution-diffusion mechanism. Selectivity is obtained because of the differences in solubility or diffusivity. The interactions of liquid with the polymeric membrane can become very strong, resulting in a high swelling. Qualitatively, pervaporation can be described as a process which proceeds by the following successive steps [5, 7-9]

1. Preferential sorption into the membrane at the feed side.
2. Diffusion of the liquid components through the membrane.
3. Phase transition from liquid to vapour phase.
4. Diffusion of vapours to the permeate side of the membrane.
5. Desorption into a vacuum or sweeping gas at the permeate side.

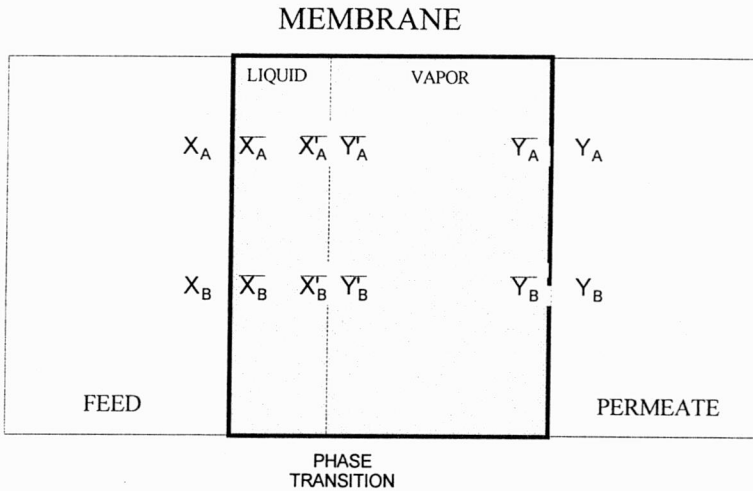


Fig. 4. Qualitative model of the pervaporation separation

This 5-step model is presented schematically in Fig. 4 with the concentrations of permeating species A and B defined at each step. In this approach, it was assumed, as in the pore-flow model, that there is a boundary of liquid and vapour phases inside the membrane [5, 10, 11]. The transport of sorbed liquid within a membrane from feed side to phase transition point was assumed to be nonselective $\bar{X}_A = \bar{X}'_A$; $\bar{X}_B = \bar{X}'_B$ (Fig. 4). Moreover, it is generally accepted that desorption of vapours into the permeate side is a fast and nonselective step [3, 7], so the following relations are also valid:

$$\bar{Y}_A = Y_A, \quad (5)$$

$$\bar{Y}_B = Y_B. \quad (6)$$

According to Eq. (1) and the above 5-step model, one can derive equations for the separation factor of each step in pervaporation process [5]:

$$\alpha^S = \frac{\bar{X}_A / (1 - \bar{X}_A)}{X_A / (1 - X_A)}, \quad (7)$$

$$\alpha^{DL} = \frac{\bar{X}'_A / (1 - \bar{X}'_A)}{\bar{X}_A / (1 - \bar{X}_A)} = 1, \quad (8)$$

$$\alpha^{EV} = \frac{\bar{Y}'_A / (1 - \bar{Y}'_A)}{X'_A / (1 - X'_A)}, \quad (9)$$

$$\alpha^{DV} = \frac{\bar{Y}_A / (1 - \bar{Y}_A)}{X'_A / (1 - X'_A)}, \quad (10)$$

$$\alpha^{DES} = \frac{Y_A / (1 - Y_A)}{\bar{Y}_A / (1 - \bar{Y}_A)} = 1. \quad (11)$$

Combining Eq. (1) with Eqs. (7)–(11) one gets the following expression for the components of the separation selectivity in pervaporation process:

$$\alpha^{PV} = \alpha^S \alpha^{DL} \alpha^{EV} \alpha^{DV} \alpha^{DES}. \quad (12)$$

According to this equation the overall separation factor in pervaporation depends both on the properties of the membrane (sorption, diffusion and desorption) represented by α^M and thermodynamic properties of penetrating mixture (evaporation) represented by α^{EV} :

$$\alpha^{PV} = \alpha^M \alpha^{EV} \quad (13)$$

with

$$\alpha^M = \alpha^S \alpha^{DL} \alpha^{DV} \alpha^{DES}. \quad (14)$$

The above equation can be rearranged taking into account Eqs. (8) and (11):

$$\alpha^M = \alpha^S \alpha^D, \quad (15)$$

where, for the sake of simplicity of notation, the vapours diffusion separation factor α^{DV} is replaced by α^D :

$$\alpha^D \equiv \alpha^{DV}. \quad (16)$$

The aspects of pervaporation that are amenable to modelling are numerous, and up-to-date models that can determine its performance a priori for a given separation

have not been developed successfully. Transport of a single component through a homogeneous, nonporous membrane, where either side of the membrane can be assumed at thermodynamic equilibrium, can be well-described [7, 12]. When binary mixtures are considered the mass transport is complicated by the permeant-permeant and permeant-membrane interactions. Diffusivities are generally dependent on all of the permeants' concentration, and this is especially true when the membrane has a strong affinity for the permeating species [13, 14]. Many approximate models have been developed with varying levels of empiricism, but they are generally only applicable to specific situations that coincide with the model assumptions [8, 10-19].

Nowadays there are several different theoretical approaches which were applied in the description of the separation and transport phenomena observed in pervaporation:

- the pore-flow model [10, 11, 15];
- the solution-diffusion model [2, 13, 19];
- the thermodynamics of irreversible processes [13, 14, 16];
- Stefan-Maxwell equation [17];
- the Michaelis-Menten approach [18].

5. MEMBRANES AND MEMBRANE MODULES

The composition and morphology of the membranes are the key factors in effective use of pervaporation technology. The choice of the membrane is strongly dependent on the type of its application [20-22]. Depending on the mixtures to be separated and their compositions, three different kinds of pervaporation processes can be distinguished: i) dehydration of organic liquids, ii) removal of organics from water streams, and iii) separation of two organic solvents. Another question about the liquid mixture is which of the components should be separated from the mixture and whether this component is water or an organic liquid. Generally, the component with the smallest weight fraction in the mixture should preferentially be transported through the membrane.

For the removal of water from water/organic liquid mixtures, hydrophilic polymers have to be chosen. The hydrophilicity is caused by groups present in the polymer chain that are able to interact with water molecules. The examples of hydrophilic polymers are as follows: ionic polymers, poly(vinyl alcohol) PVA, poly(acrylonitrile) PAN, poly(vinyl pyrrolidone) PVPD. For the removal of an organic liquid from water/organic mixture, hydrophobic polymers are the most suitable as membrane materials. These polymers possess no groups that show affinity for water. Examples of such polymers are: poly(dimethylsiloxane) PDMS, poly(ethylene) PE, poly(propylene) PP, poly(vinylidene fluoride) PVFD, poly(tetrafluoroethylene) PTFE.

For the mixture of two organic liquids, three kinds of mixtures can be distinguished: polar/apolar, polar/polar and apolar/apolar mixtures. For the removal of the polar component from polar/apolar mixture, polymers with polar groups should be chosen and for the removal of the apolar component, completely apolar polymers are

favourable. The polar/polar and apolar/apolar mixtures are very difficult to separate, especially when the two components have similar molecular sizes. In principle, all kinds of polymers can be used for these systems, the separation has to take place on the basis of differences in molecular size and shape, since no specific interaction of one of the two components can take place.

Recently, ceramic membranes and membranes prepared from conducting polymers have also been used as the selective barriers in pervaporation [23–26].

Table 2

Flux and selectivity of ethanol/water mixture for different homogeneous membranes.
Feed: 90 wt.% ethanol. Temperature: 70 °C. Membrane thickness: $\approx 50 \mu\text{m}$ [6]

Polymer	Flux [$\text{kg m}^{-2} \text{h}^{-1}$]	α (Eq. (1))
Polyacrylonitrile	0.03	12500
Polyacrylamide	0.42	2200
Polyvinyl alcohol	0.38	140
Ployether sulfone	0.72	52
Polyhydrazide	1.65	19

For a given mixture a large variety in membrane performance can be observed with various polymers. Table 2 gives the selectivity and fluxes of various homogeneous membranes for ethanol–water mixtures. It is seen that the selectivity can range from extremely high to very low. The choice of material is mainly based on structural parameters that determine preferential sorption. For dehydration, where the small

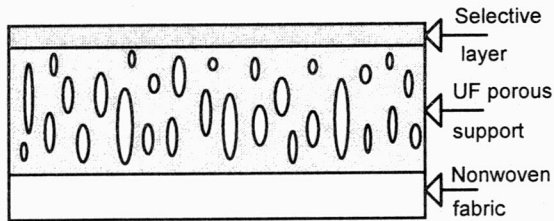


Fig. 5. Morphology of the pervaporation composite membrane

molar volume favours the preferential sorption of water, the materials selected have to show a higher affinity for water than for the other component. For instance, the commercial dehydration membrane PERVAP 1000 (SULZER Chemtech) is a composite membrane with a PAN sublayer and a thin crosslinked PVA skin as a selective layer. Both PVA and PAN show a much higher affinity for water than for ethanol.

When a highly selective material has been selected the membrane performance can be optimized further by reducing the effective membrane thickness. It is the best to

use a thin film of the discriminating layer deposited on a highly porous support structure. This means that either asymmetric or composite membranes have to be developed with a dense top layer and an open porous sublayer. The requirements for the sublayer are such that the resistance for vapour transport must be negligible compared to the resistance of the top layer. Therefore optimization of the sublayer is very important. It might be even worthwhile to develop a three-layer membrane consisting of a very porous sublayer rather than a nonselective intermediate layer and the dense top layer (Fig. 5) [21].

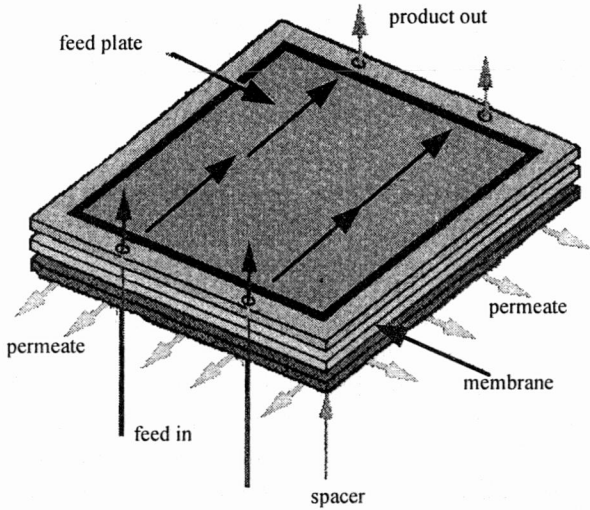


Fig. 6. Scheme of a plate-and-frame module

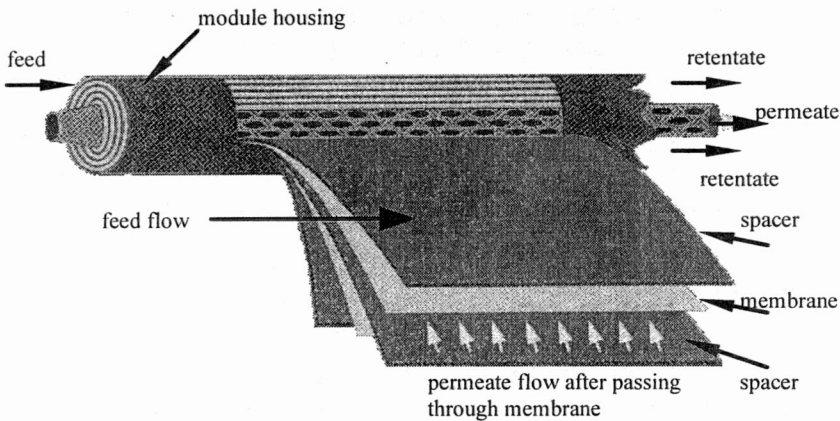


Fig. 7. Scheme of a spiral-wound module

Overview of companies offering PV units

Company	Types of available modules	Membranes	Applications
SULZER Chemtech (Germany)	plate and frame spiral wound	composite hydrophilic, organophilic, zeolite filled with organophilic material	separation of water-organic, organic-organic mixtures, removal of VOCs from air streams
MTR (USA)	spiral wound	polymeric, organophilic	removal of VOCs from water and air streams
GKSS (Germany)	spiral wound, envelope type flat sheet (GS module)	polymeric, organophilic	removal of VOCs from water and air streams
PERVATECH (the Netherlands)	tubular	ceramic, hydrophilic	dehydration of organic solvents

The composite membranes can be produced either in a flat configuration or in a tubular configuration. The main module designs are the plate-and-frame system (Fig. 6) and the spiral-wound system (Fig. 7) that are based on the flat membranes and the tubular, capillary and hollow fiber modules that are based on the tubular membrane configuration. All these types of modules are commercially available today. Market leader is SULZER Chemtech (former GFT Company) with over 100 pervaporation plants installed worldwide, but some new companies try to enter the market, too (Table 3).

6. PRACTICAL APPLICATION OF PERVAPORATION AND VAPOUR PERMEATION

The first major research effort to commercialize pervaporation was made by Binning in the late 1950s. Binning reported the utilization of membrane pervaporation for dehydration of a ternary azeotrope of isopropanol-ethanol-water from the top of a distillation column. This work was followed by several others presenting the separation of *n*-heptane and isooctane, the separation of benzene-methanol azeotrope or separation of pyridine-water azeotrope. Figure 8 presents the scheme of the hybrid distillation-pervaporation process proposed by Binning for the separation of water-pyridine mixture [27, 28]. The capacity of pervaporation for separating liquid mixtures was demonstrated by 1965 but the commercial development did not proceed mainly due to the lack of a market need. Traditional separation technologies including distillation, extraction or adsorption were sufficient. Moreover, the membranes being

utilized then lacked the high selectivity and permeability necessary to make pervaporation economically attractive. Only the energy crisis in the 1970s refocused interest on separation technologies that possessed a high potential for energy savings. In the mid-1970s, GFT (West Germany) commercialized an economical pervaporation process for dehydrating ethanol that rivalled azeotropic distillation [29, 30]. Following pilot trials in Europe, the first industrial plants were built in Brazil and the Philippines for the processes utilizing continuous fermentation of sugar cane and sweet sorghum containing 5–7% of ethanol, primary distillation to a mash containing 80–85% of ethanol followed by vacuum pervaporation to 96 wt.%. In the late 1970s and early 1980s, other integrated distillation/pervaporation plants were built in Europe and Asia. Most of them were of moderate capacity, with typically 1000–50000 l/day of ethanol recovered. As the cost of the permselective membrane module was reduced and the selectivity increased, ethanol purity increased (99.85 wt.% was easily attainable) and the integrated process gained industrial acceptance.

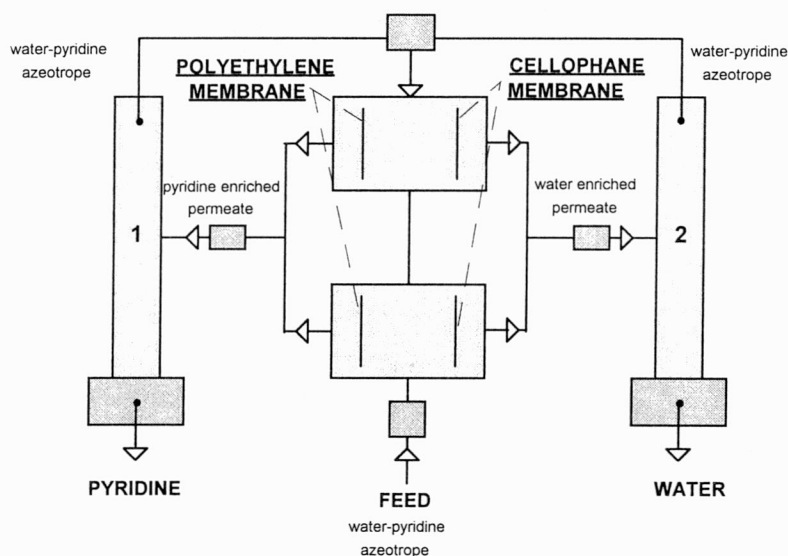


Fig. 8. Scheme of the distillation-pervaporation process for the dehydration of water-pyridine azeotrope (according to Binning) [27]

In general, pervaporation will especially be used in those cases where a small quantity has to be removed from a large quantity. The overview of the practical applications of pervaporation, classified into three different areas, is presented in Table 4.

A typical pervaporation plant includes usually several membrane modules connected in series and separated by reheaters (Fig. 9) [6, 29, 31]. This multistage operation is required because latent heat of evaporation of permeate is drawn from sensible heat of feed liquid. This feed liquid is therefore cooled down, and the permeate flux through the membrane decreases. The reheating of feed optimizes membrane flux and therefore reduces mem-

Practical applications of pervaporation

Application	Details
Separation of water from organic/aqueous mixtures	separation and/or dehydration of water-organic azeotropes (water-ethanol, water-isopropanol, water-pyridine) dehydration of organic solvents shifting of the reaction equilibrium (e.g. esterification)
Removal of volatile compounds from aqueous and gas streams	removal of chlorinated hydrocarbons separation of organics from the fermentation broth separation of aroma compounds wine and beer dealcoholization removal of VOCs from air
Separation of organic/organic mixtures	separation of azeotropes (e.g. ethanol-cyclohexane, methanol-MTBE, ethanol-ETBE) separation of isomers (e.g. xylenes)

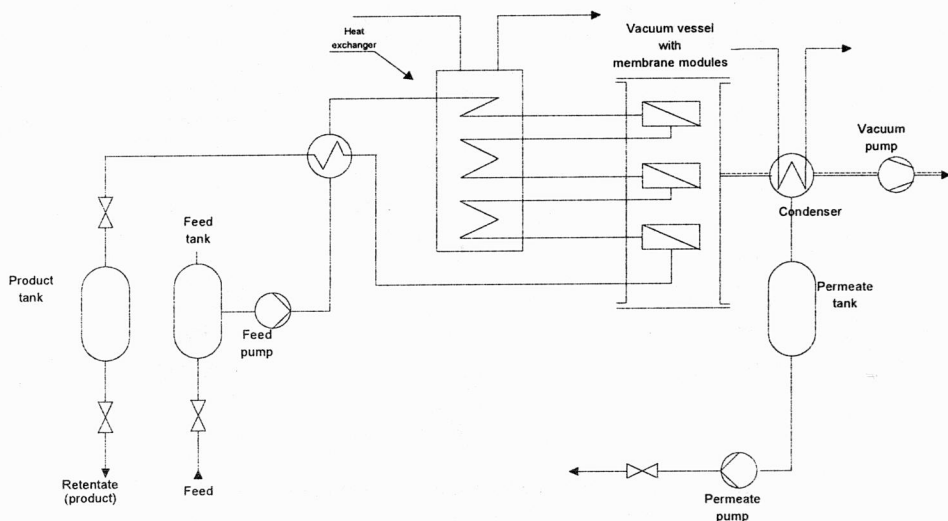


Fig. 9. Scheme of a pervaporation plant

brane area. The membrane modules are placed inside a vacuum vessel where permeate is collected. A condenser using chilled brine condenses permeate and a vacuum pump maintains the required vacuum level in the system by removing non-condensable gases. Commercial applications are using plate and frame or spiral-wound modules in stainless steel, with solvent-compatible gaskets. This is due to the harsh environment, the concentrated solvents at high temperature on one side and the vacuum on the other side.

6.1. DEHYDRATION OF ORGANIC SOLVENTS BY PERVAPORATION [6, 29–35]

Solvent dehydration is the most common application of pervaporation. As membrane processes are not governed by thermodynamic equilibrium and selectivities are determined by the differences in sorption and transport rates of components through the membrane, mixtures of components with close boiling points and azeotropic mixtures can effectively be separated. Pervaporation is generally economic with water contents of approximately 10 wt.% and less, with final product water content from hundreds of ppm to 10 ppm attainable. To get considerably lower water contents, significantly greater installed membrane area and possibly greater reduced pressure on the permeate side are required. Table 5 gives a list of organics currently dehydrated by pervaporation.

Table 5

Organic solvents dehydrated by pervaporation (other than ethanol)

Solvent	Water content		Solvent	Water content	
	Feed (wt.%)	Product (ppm)		Feed (wt.%)	Product (ppm)
Isobutanol	8.4	135	Ethanol/MeOH	2.9	780
<i>n</i> -Butanol	5.4	800	Ethanol/benzene	14.1	320
<i>t</i> -Butanol	10.4	581	Allyl alcohol	4.85	620
THF	0.4	220	Ethanol/IPA	0.6	610
Xylene	0.1	140	MEK	3.8	220
Methanol	7.1	1650	Methylene chloride	0.20	140
Methanol/IPA	0.21	300	Ethylene dichloride	0.22	10
Caprolactam	10.3	671	Chloroethene	0.0617	12

As it was mentioned, dehydration of ethanol by pervaporation was the first industrial scale application proposed by GFT in 1980s. Today, more than 40 industrial pervaporation plants built by Sulzer Chemtech Membrantech (former GFT) are in the operation worldwide. They are used for the dehydration of different solvents and/or solvent mixtures.

Ethanol from the fermentation broth is typically 8–12 %, which after several stages of distillation allowing its rectification and purification is produced as a near-azeotropic mixture. Anhydrous ethanol for chemical and fuel use is obtained typically by azeotropic distillation with cyclohexane or by adsorption on molecular sieves. Azeotropic distillation is relatively expensive method and, in addition, there is some concern on environmental and health grounds over the use of the dehydrating agents.

Pervaporation or vapour permeation is considered to be an appropriate and competitive replacement for azeotropic distillation and adsorption on molecular sieves (Fig. 10, Tab. 6).

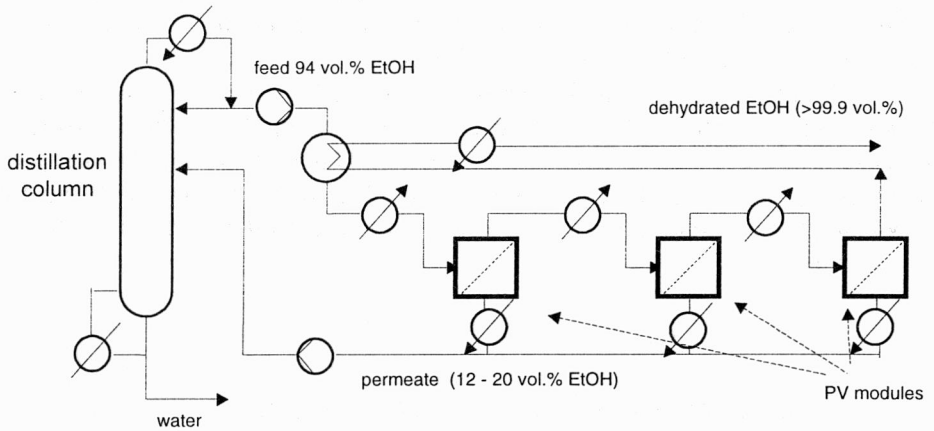


Fig. 10. Scheme of the dehydration of ethanol by distillation-pervaporation hybrid process

Table 6

Comparison of the dehydration costs of ethanol from 99.4 vol.% to 99.9 vol.% by different techniques

Utilities	Vapour permeation [DM/t]	Pervaporation [DM/t]	Entrainer distillation [DM/t]	Molecular sieves adsorption [DM/t]
Vapour	–	6.40	60.00	40.00
Electricity	20.00	8.80	4.00	2.60
Cooling water	2.00	2.00	7.50	5.00
Entrainer	–	–	4.80	–
Replacement of membranes and molecular sieves	9.50	15.30	–	25.00
Total costs	31.50	32.50	76.30	72.60

In many practical applications, it may be more economical to use pervaporation or vapour permeation only to break the azeotrope and to concentrate the retentate further by the above-azeotropic distillation. The corresponding flow diagram of a such hybrid distillation-vapour permeation process for the isopropanol dehydration is shown in Fig. 11. In this hybrid process, the water is finally removed from the system at the top of the above-azeotropic distillation column by vapour permeation before condensa-

tion. This concept is especially advantageous when an extremely high final alcohol concentration with a very low residual water content (less than 50 ppm) without any traces of entrainers is required.

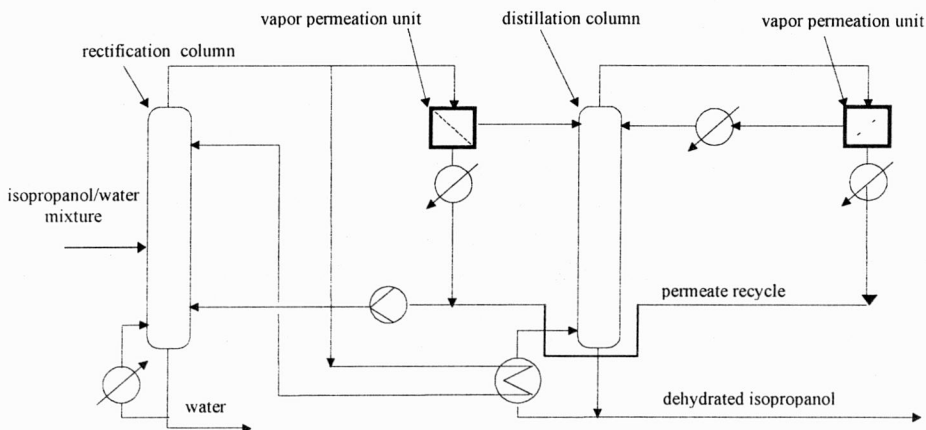


Fig. 11. Isopropanol dehydration by combined vapour permeation and above-azeotropic distillation

Flexibility with respect to part-load performance and changing product and feed concentrations is one of the advantages of pervaporation over other separation processes. A given pervaporation plant may be used to dehydrate a large number of different solvents. The change from one solvent to the other can be done quickly and without risk of mixing the solvents. For small feed streams the best flexibility is obtained with batch operation, where one single unit can dehydrate several solvents, with a wide range of water concentrations in feed and product, by changing only the batch time. This is specially useful in the production of fine chemicals and in the pharmaceutical industry, where solvents are used in campaigns and almost no single waste solvent is generated continuously. Table 7 presents the flexibility of the ethanol dehydration pervaporation plant with the membrane area of 480 m².

Table 7

Flexibility of the ethanol dehydration pervaporation plant

Feature	Figures			
Concentration				
Inlet	85.7%	93.9%	85.7%	93.9%
Outlet	99.8%	99.8%	99.95%	99.95%
Capacity	1,195 kg/h	1,500 kg/h	840 kg/h	970 kg/h
Utility requirements				
Steam	195 kg/h	110 kg/h	145 kg/h	83 kg/h
Power	85 kW	85 kW	85 kW	85 kW
Membrane: area – 480 m ² , height – 3,000 mm, length – 7,500 mm, width – 2,000 mm				

6.2. PERVAPORATION ENHANCEMENT OF THE CHEMICAL REACTION EFFICIENCY [6, 29, 36–39]

Another successful example of pervaporation is its application in the enhancement of the chemical reaction efficiency. There are many reactions of organics which produce water molecules as one of the product. Examples of such reactions are esterification or phenol–acetone condensation. These reactions often do not proceed with 100%-yield, reaching an equilibrium state. It can be shifted towards higher conversions by applying one reactant in excess and/or by selective removing products from the reaction mixture. In the case of esterification or condensation reaction, pervaporation can be applied to the continuous water removal. Figure 12 presents two possible solutions of a combined esterification-pervaporation process. Alcohol is used in a surplus and an alcohol/water mixture is evaporated out of the reaction vessel, condensed and water is separated in a pervaporation unit (Fig. 12A). Then alcohol is recycled to esterification reactor. Alternatively, water is continuously extracted in a side pervaporation loop from the mixture containing ester, acid and alcohol (Fig. 12B).

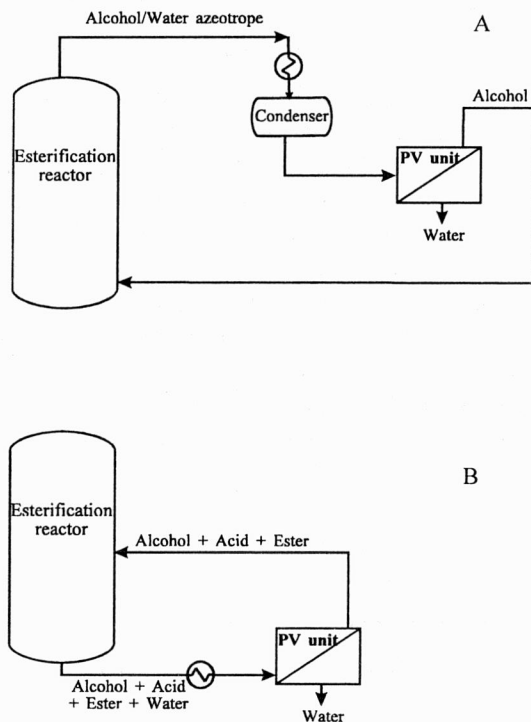


Fig. 12. Pervaporation enhanced synthesis of esters

The first industrial plant for the pervaporation enhanced ester synthesis was built in 1991 by GFT for BASF. Recently, the research on the shifting of the equilibrium of esterification reaction by pervaporation was undertaken also in Poland [39].

6.3. REMOVAL OF VOLATILE ORGANIC COMPOUNDS (VOCs) FROM WATER AND GAS STREAMS [6, 31, 40–46]

Contamination of groundwater with volatile organic compounds (VOCs) is a problem which has to be overcome both by industrial and government institutions. Examples of contaminants are petroleum hydrocarbons, methyl *t*-butyl ether, chlorinated hydrocarbons such as trichloroethylene and carbon tetrachloride. Many of VOCs are potential carcinogens. There is a need to develop separation systems that can remove organics from already contaminated sites and systems to prevent future contamination. There are several alternative methods which can be applied to the VOCs removal, including air stripping, carbon adsorption, biological treatment, steam stripping and incineration (Fig. 13). Membrane systems offer the potential to perform these types of separations. Pervaporation can be used in effectively removing VOCs from water, concentrating them for economical disposal or recycle/reuse using specially designed hydrophobic membranes. The membranes used for those purposes are rubbery polymers such as silicone rubber, polybutadiene, polyether copolymers, polydimethylsiloxane. The separation achieved is determined by the individual rates of permeation through the membrane and the relative volatility of the components of the feed mixture. Usually the VOCs permeate through a hydrophobic membrane by orders of magnitude faster than water, which results in higher VOCs' concentration (Table 8). Applying pervaporation it is possible to concentrate a 100 ppm VOC-solution to over 10% VOC solution (or suspension).

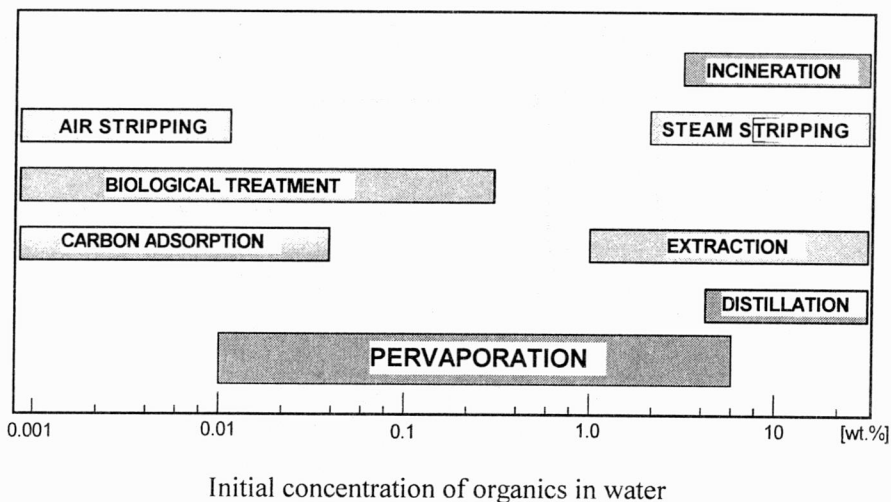


Fig. 13. Comparison of the separation methods for VOCs' removal from water

Pervaporation with organophilic membranes can be applied in the treatment of wash waters used to remove organics from solvent-laden air streams (Fig. 14). The dilute aqueous solution is treated by pervaporation to remove the solvent into the

permeate and to produce water, with a minor amount of solvent, in order to recycle to the air scrubbing unit.

Table 8

Typical pervaporation separation factors (α) for VOCs' removal from water

Separation factor α for VOC over water	Volatile organic compound (VOC)
200–1000	benzene, toluene, ethyl benzene, xylenes, TCE, chloroform, vinyl chloride, ethylene dichloride, methylene chloride, perfluorocarbons, hexane
20–200	ethyl acetate, propanols, butanols, MEK, acetone, aniline, amyl alcohol, methyl <i>t</i> -butyl ether
5–20	methanol, ethanol, phenol, acetaldehyde
1–5	acetic acid, ethylene glycol, DMF, DMAC

Nowadays, pervaporation with organophilic membranes can be used for solvent recovery, pollution abatement, concentration of organics (for disposal or incineration), recovery of aroma compounds and production of beverages with low content of alcohol.

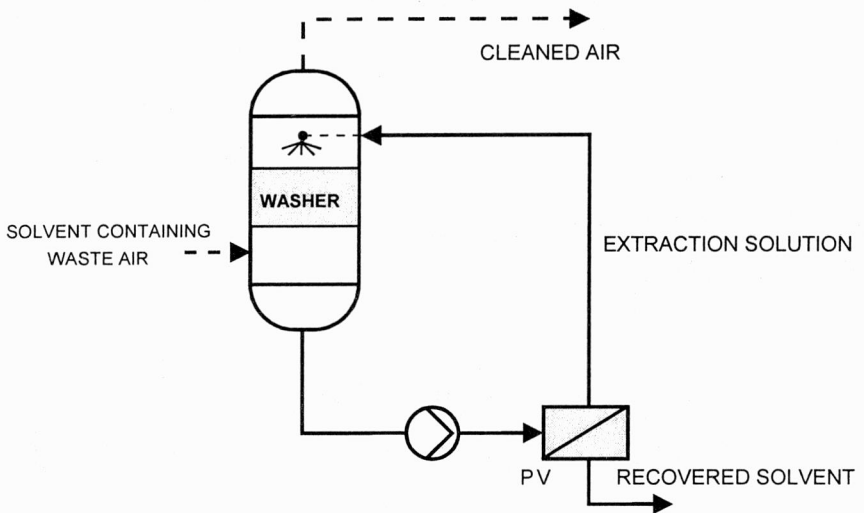


Fig. 14. Removal of solvents from waste air

Many industrial processes, which handle volatile solvents, produce air streams contaminated with organic vapours. These streams represent not only a serious pollution problem, but also a significant reuse and energy saving opportunities. Organic

contaminants in air and in other permanent gases can be recovered using vapour permeation through an appropriate membrane. Membranes are relatively impermeable to air and permanent gases and are usually made from rubbery polymers. Table 9 presents selectivities of chosen membranes in contact with vapours of organic solvents. The typical industrial applications of vapour recovery are off-gas treatment in gasoline tank farms, gasoline station vapour return, end of pipe solvent recovery in the chemical and pharmaceutical industry. Another interesting example of industrial application is VOCs recovery by compression-condensation and vapour permeation method, presented schematically in Fig. 15. This is a scheme of the process developed in ANWIL (Włocławek, Poland) which has been built by MTR (USA) for the recovery of monovinyl chloride (MVC). The gas stream from the synthesis line containing MVC and air is compressed and chilled to a temperature at which a substantial fraction of the condensable content of the stream liquefies. The non-condensed portion of vapour/air mixture is directed to the membrane unit equipped with organic permeable membranes. The membrane separates the gas into two streams: a permeate stream containing most of the remaining MVC and a MVC-depleted stream of air. The solvent-depleted air is vented from the system, whereas the permeate stream is recycled to the inlet of the compressor.

Table 9

Separation of organic solvents by vapour permeation
from air or N₂ if stated

Solvent	Membrane	Selectivity
Methanol	polyimide	221
	silicone	38
Ethanol	polyimide	297
Ethanol/N ₂	vycor glass	2-400
Acetone	PDMS	11-160
Acetone/N ₂	vycor glass	2-300
Hexane	polyimide	32
Benzene	polyimide	51
Toluene	polyimide	180
	PDMS	83
<i>p</i> -Xylene	polyimide	460
	PDMS	68
<i>m</i> -Xylene	polyimide	513
1,2-Dichloromethane	PDMS	142
Chloroform	polyimide	24
1,2-Dichloroethane	polyimide	52
	PDMS	103

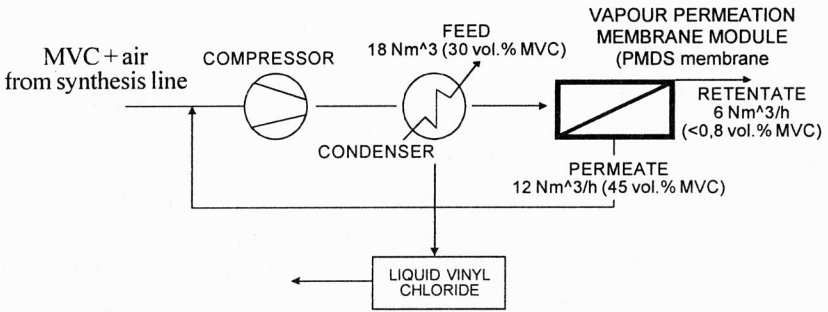


Fig. 15. Flow diagram of compression/condensation and membrane separation for MVC recovery

6.4. SEPARATION OF ORGANIC-ORGANIC LIQUID MIXTURES [6, 31, 47-49]

Separation of organic/organic mixtures represents the least developed and the largest potential commercial impact on pervaporation, but considerable membrane material and process development remains to be done. Here, unlike the cases of organic/water mixtures, no clear choice of membrane type presents itself. Membranes must be custom-designed for specific process objectives. There are several organic/organic mixtures which could be separated by pervaporation: aromatics/paraffins (benzene/hexane), branched hydrocarbons from *n*-paraffins (isooctane/hexane), olefins/paraffins (pentene/pentane), isomeric mixtures (xylenes), chlorinated hydrocarbons from hydrocarbons (chloroform from hexane), purification of dilute streams (isopropyl alcohol from heptane/hexane). The first industrial application of pervaporation to organic/organic separation was the separation of methanol from methyl *t*-butyl ether (MTBE) stream in the production of octane enhancer for fuel blends (Fig. 16). The success of this application is due to the high selectivity of the membranes for methanol over MTBE and in the ability to utilize MTBE/C₄ mixtures with some methanol remaining in the stream to the debutanizer column.

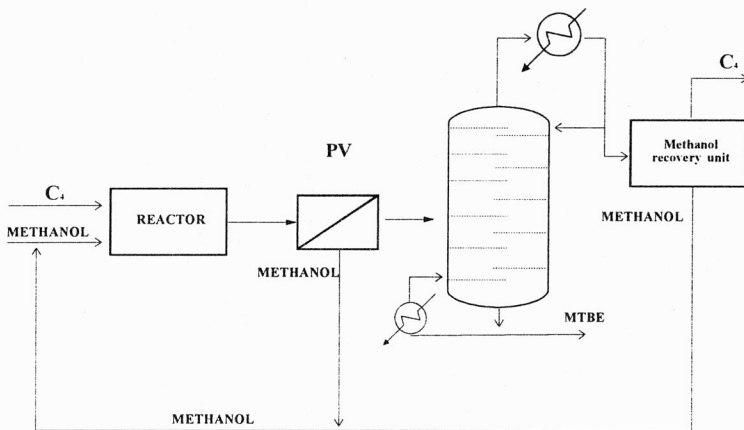


Fig. 16. Pervaporation enhanced MTBE production

7. CONCLUSIONS

After more than 25 years of worldwide intensive research, pervaporation has evolved from a novel research topic into a commercially viable process for certain applications. However, pervaporation must be regarded as a recent membrane process compared to other membrane processes like reverse osmosis, ultrafiltration, dialysis and even electrodialysis.

There are several practical advantages of pervaporation when compared with other conventional technologies: simple operation and control, reliable performance, high flexibility, unproblematic part-load operation, high product purity (no contamination by entrainer), no environmental pollution, high product yield, low energy consumption, compact design (low space requirements), short erection time and uncomplicated capacity enlargement.

Nowadays there are several areas of the techno-economical success of pervaporation:

- the separation of small amounts of water or highly polar organic components like methanol from complex organic aqueous and organic mixtures;
- the separation of traces of halogenated hydrocarbons or organic solvents from water;
- the removal of organic vapour from streams of permanent gases.

In all the above applications, the most successful processes require integration with existing conventional separation unit operations. Nevertheless, pervaporation has been identified as an area of vast potential for future research and commercial development. This is especially true for pervaporation in hollow-fiber configurations, an area which has not received attention commensurate with its potential for application.

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