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Application of Pervaporation and Vapor Permeation in Environmental Protection

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Abstract

A review concerning pervaporation and vapor permeation - membrane separation techniques used to separate liquid mixtures, is presented. Examples of polymers for membrane preparation as well as performance parameters of pervaporation and vapor permeation membranes are described. The second part of the paper presents applications of pervaporation and vapor permeation in environmental protection.

At the present, liquid product mixtures must fulfill high purity requirements as well as effluents; therefore, they have to be concentrated or reconditioned. In the process of product-integrated environmental protection, liquid substances should be separated specifically from the mainstream, either to save raw materials, to prevent or to minimize the disposal of effluents, or to recycle by-products. Such completely or partly soluble fluid mixtures can be separated with membrane methods. Pervaporation and vapor permeation as the most well-known membrane processes for the separation of liquid and vapor mixtures allow a variety of possible application areas:

i) dewatering of organic fluids like alcohols, ketones, ethers etc.;
ii) separation of mixtures from narrow boiling temperatures to constant (azeotrop) boiling temperatures;
iii) removal of organic pollutants from water and air streams;
iv) separation of fermentation products;
v) separation of organic-organic liquid mixtures.

Keywords: pervaporation, vapor permeation, polymers, membrane methods, environmental protection

Introduction

Most industrial scale separation processes are based on energy intensive methods such as distillation, evaporation, and freeze crystallization. Membrane separations offer significant advantages over existing separation processes. Current membrane separation technologies can offer energy savings, low-cost modular construction, high selectivity of separated materials, and processing of temperature-sensitive products [1-5]. Membranes separate mixtures by discriminating the components on the basis of physical or chemical attributes, such as molecular size, charge, or solubility [6]. By passing water and retaining salts, membranes are used to produce over half of the world's desalinized potable water. Membranes can also separate oxygen and nitrogen from air as well as hazardous organics from contaminated water in applications such as groundwater remediation.

The need for 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. Six major membrane processes (microfiltration, ultrafiltration, reverse osmosis, electrodialysis, gas separation and pervaporation) have found use in such application areas as water purification, chemical and food processing, drug delivery, bioseparations, and medical treatment [1-6].

This present paper reviews pervaporation and vapor permeation - two particularly useful and relatively new membrane separation processes.

Fundamentals

Definition of Pervaporation Process

Pervaporation is recognized as a separation process in which a binary or multicomponent liquid mixture is separated by partial vaporization through a dense non-porous membrane. During pervaporation, the feed mixture is in direct contact with one side of the liophilic membrane whereas the permeate is removed in a vapor state from the opposite side into a vacuum or sweeping gas (Fig. 1A, Tab. 1) and then condense. Pervaporation is unique among membrane separations, involving the liquid-vapor phase change to achieve the separation [7, 8].

The driving force for the mass transfer of permeants from the feed side to the permeate side of the membrane is a gradient in chemical potential, which is established by applying a difference in partial pressures of the permeants across 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 a vacuum pump system or by sweeping an inert gas on the permeate side of the membrane [7, 8].

Definition of Vapor Permeation

Vapor permeation is similar in principle to pervaporation. The only difference concerns the feed, which is a mixture of vapors or vapors and gases [9]. As in pervaporation, the permeate partial pressure is maintained by use of a vacuum or an inert sweep gas (Fig. IB, Tab. 1). There is no change of phase involved in its operation. Thus, compared to pervaporation, the addition of heat equivalent to the enthalpy of vaporization is not required in the membrane unit and there is no temperature drop along the membrane [10]. Operation in the vapor phase also eliminates the effect of the concentration polarization prevalent in liquid phase separations, such as pervaporation.

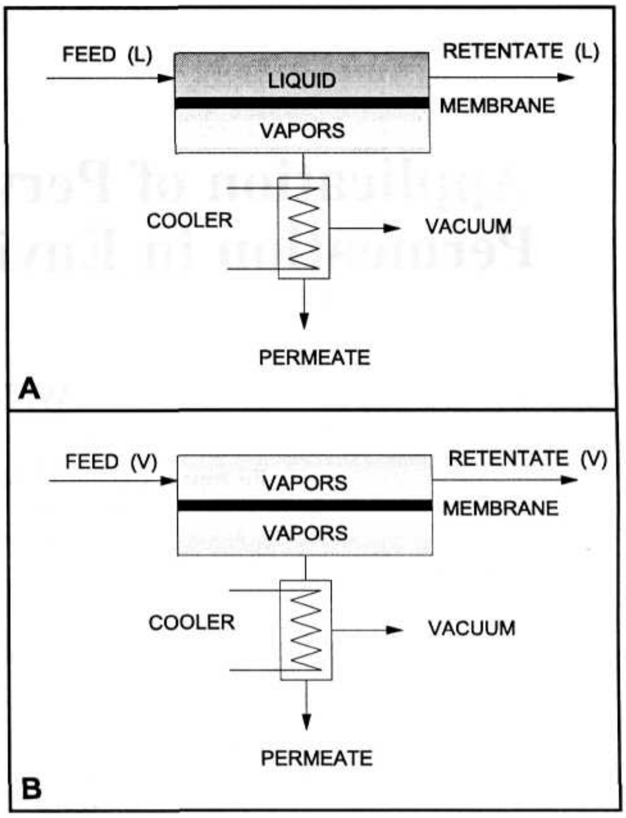


Fig. 1. Schema of pervaporation (A) and vapor permeation (B) processes.

Related Process

Table 1 presents the main characteristics of chosen membrane processes which resemble pervaporation or vapor permeation concerning either the membranes applied or type of application. To avoid any misunderstandings it is quite important to know both the differences and similarities of these processes [8, 11].

Table 1. Overview of chosen membrane separation processes.

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

Performance Parameters of Membranes

The performance of a given membrane in pervaporation or vapor permeation 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 [11].

The selectivity of a given membrane can be estimated by using the following two dimensionless parameters [11]:

- separation factor a

$$\alpha = \frac{Y_A / Y_B}{Y_A / X_B} = \frac{Y_A / (1 - Y_A)}{X_A / (1 - X_A)} \qquad (1)$$

– enrichment factor β

$$\beta = \frac{Y_A}{X_A} \qquad (2)$$

where:

X_A - weight fraction of preferentially permeating species in the feed phase,

Y_A - weight fraction of preferentially permeating species in the permeate phase, with $X_A + X_B = 1$ and $Y_A + Y_B = 1$.

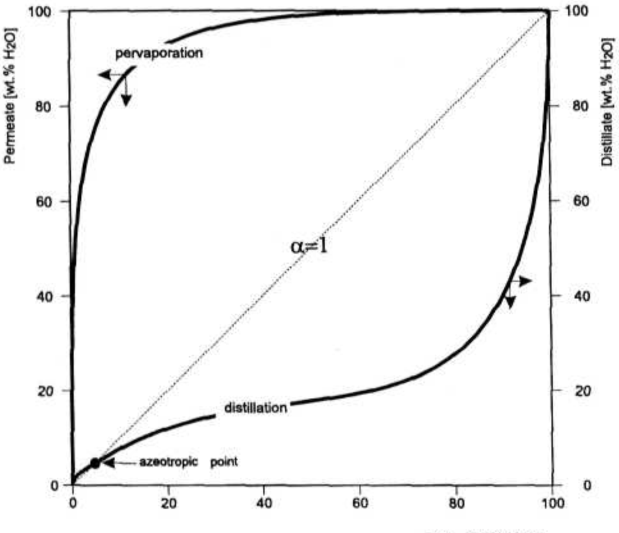


Fig. 2. McCabe-Thiele separation diagram. Comparison of pervaporation selectivity with distillation selectivity. System: water-ethanol. Membrane: PVA composite hydrophilic membrane.

Unfortunately, neither the separation factor nor the enrichment factor are constant. Both parameters are the strong function of the feed composition. Therefore, the McCabe-Thiele diagram, employed usually for the analysis of liquid-vapor equilibrium, is often used to the evaluation of pervaporation or vapor permeation selectivity. Fig. 2 compares the distillation and pervaporation through hydrophilic polyvinyl alcohol membrane of water-ethanol binary mixture. It is seen that pervaporation with highly hydrophilic membrane favors the transport of the higher boiling water. The high efficiency of pervaporation also occurs near the azeotropic composition of the water-ethanol 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. a = 1).

The permeate flux (J [kg m^{-2} h^{-1}]) shows also a strong dependency on the feed composition, permeate pressure and temperature of the process. Temperature dependence is of the Arrhenius type, usually with doubling of flux at temperature increase of 10-12 K.

Membranes and Membrane Modules

The composition and morphology of the membranes are a key to effective use of membrane technology. The choice of the membrane strongly depends on the type of application [12]. It is important which of the component 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 across the membrane.

Looking at the mixtures to be separated and their compositions, the following different kinds of pervaporation and vapor permeation processes can be distinguished [12-23]:

- Dehydration of organic liquids.

  For the removal of water from water/organic liquid or vapor 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. Examples of hydrophilic polymers are: ionic polymers, polyvinylalcohol (PVA), polyacrylonitryle (PAN), polyvinylpyrrolidone (PVPD).
- Removal of organics from water or air streams.

  For the removal of an organic liquid from water/organic or organic/air mixture hydrophobic polymers are the most suitable polymers as membrane materials. These polymers possess no groups that show affinity for water. Examples of such polymers are: polydimethylsiloxane (PDMS), polyethylene (PE), polypropylene (PP), polyvinylidenefluoride (PVFD), polytetrafluoroethylene (PTFE).
- Separation of two organic solvents.

  For the mixture of two organic liquids or vapors, again 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 favorable. 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 pre-

Table 2. Selective and transport properties of different types of pervaporation membranes.

Membrane material	Binary mixture A/B	Content of A component in feed [wt. %]	Temperature [°C]	Selectivity $\alpha_{A/B}$	Permeate flux [kg m^{-2} h^{-1}]	Ref.
Hydrophilic polymeric membranes						
polyvinyl acohol	water/ethanol	0.1-8	90-100	50-2000	0-2	[28]
polyamide-6	water/ethanol	30	80	2	1.15	[29]
polyamide-6	water/dioxane	50	35	45	0.04	[30]
polyamide-6/PAA	water/acetic acid	8.7	15	82	0.005	[31]
PESS Li+	water/isopropanol	11	25	40	0.087	[32]
PESS K+	water/isopropanol	11	25	60	0.026	[32]
Hydrophobic polymeric membranes						
polypropylene	acetone/water	45	116	3	0.1-1.2	[33]
silicone rubber	isopropanol/water	9-100	25	9-22	0.03-.11	[34]
silicone rubber	butanol/water	0-8	30	45-65	<0.035	[35]
PDMS	butyl acetate/water	0.7	50	370	0.55	[36]
PDMS	MTBE/water	2	50	280	1.2	[36]
PEBAX	aniline/water	5.5	80	198	1.8	[20]
Membranes made of conducting polymers						
polypyrrole	methanol/toluene	5	58	590	0.240	[26]
polypyrrole	methanol/isopropanol	10	58	2	0.004	[27]
Inorganic membranes						
zeolite NaA	ethanol/water	5	95	5100	3.35	[24]
zeolite NaY	methanol/MTBE	10	50	7600	0.32	[37]
PERVATECH®	water/acetic acid	5	75	150	2.5	[25]
PERVATECH®	water/isopropanol	1	100	250	4.0	[25]

pared from conducting polymers have also been used as the selective barriers in pervaporation [24-27]. Ceramic membranes combine high thermal and chemical stability with very high performance. Ceramic membranes can be used in a wide range of applications, including separation of mixtures at acid and alkaline conditions [25]. An overview of the performance parameters of different types of membranes is presented in Table 2.

For a given mixture a large variety in membrane performance can be observed with various polymers. Table 3 gives the selectivity and fluxes of various homogenous membranes for ethanol-water mixtures. It is seen that both the selectivity and flux can range from extremely high to very low.

Table 3. Flux and selectivity of ethanol/water mixture through different homogeneous membranes. Feed: 90 wt. % ethanol. Temperature: 70°C. Membrane thickness: = 50 µm [38],

Polymer	Flux [kg m^{-2} h^{-1}]	α (Eq. 1)
polyacrylonitrile	0.03	12500
polyacrylamide	0.42	2200
polyvinylalcohol	0.38	140
polyethersulfone	0.72	52
polyhydrazide	1.65	19

When a highly selective material is selected, membrane performance can be optimized further by reducing the effective membrane thickness. It is 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 toplayer and an open porous sublayer. The requirements for the sublayer are such that the resistance for permeate transport must be neglectable compared to the resistance of the toplayer. Therefore, optimization of the sublayer is very important [12]. It might even be worthwhile to develop a three layer membrane consisting of a very porous sublayer, than a nonselective intermediate layer and dense toplayer (Fig. 3) [12].

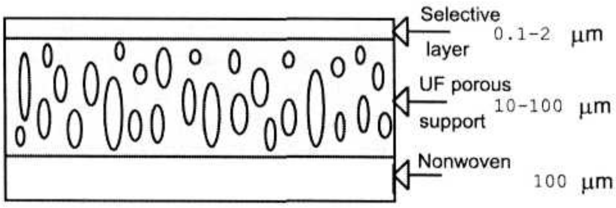


Fig. 3. Morphology of the pervaporation composite membrane.

Table 4. Commercial producers of pervaporation and vapor permeation systems.

Company	Types of modules available	Membranes	Applications
SULZER Chemtech Membrantechnik AG(Germany)	plate and frame spiral wound	composite hydrophilic, organophilic, zeolite filled organophilic	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

Table 5. Pervaporation and vapor permeation unit installations by Sulzer Chemtech Membrantechnik AG (Germany).

Application	Number of plants
Ethanol dehydration (500 – 150,000 l/d)	24
Isopropanol dehydration (5,000 – 15,000 l/d)	11
Dehydration of athylacetate (250 – 6,000 l/d)	3
Dehydration of ethers (2,000 – 6,000 l/d)	3
Dehydration of other organic solvents (250 – 15,000 l/d)	10
Multipurpose plants (pervaporation, vapor permeation, dehydration, organics extraction)	18
Pilot plants (1–4 m^2 surface of membrane area) installed to test the applicability of the technique to potential fractionation problems	41
Total number of plants	110

For dehydration, where the small molar volume favors the preferential sorption of water, materials have to be selected with a higher affinity for water than for the other component. For instance, the commercial dehydration membrane PERVAP 1000 (SULZER Chemtech Membrantechnik AG, Germany) 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.

The composite membranes can be produced either in a flat configuration or in a tubular configuration. Membranes have to be incorporated into modules in order to be used in the process. The main module designs are the plate-and-frame system and the spiral-wound system that are based on the flat membranes and the tubular, capillary and hollow fiber modules that are based on the tubular membrane configuration [39]. Fig. 4 shows a schema of the plate-and-frame module. Plates made of stainless steel form the feed channels and compartments, which are sealed to the membranes by gaskets. The membranes are supported by stainless steel perforated plates and spacers, which form the permeate channels. The latter ones are open to all sides, allowing for a fast and easy removal of the permeate. The arrangement assures a uniform, parallel flow of the feed mixture over all membranes in a module. The spiral wound modules (Fig. 5) are flat sheets arranged in parallel to form a narrow slit for fluid flow. In a typical construction two flat membrane sheets are placed together with active sides facing the feed spacer. Membranes are separated by the permeate spacer and glued together on 3 sides. The fourth

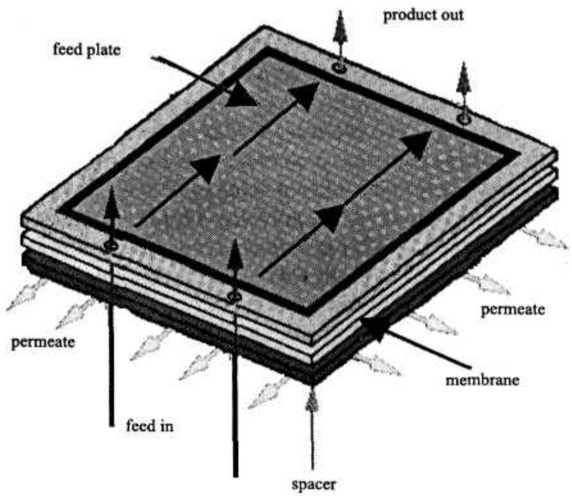


Fig. 4. Schema of a plate-and-frame module.

side is open and fixed around a perforated centre tube. The feed spacer is placed outside the membrane and forms the feed channel. The whole assembly is roled around the centre tube in a spiral and fitted inside the appropriate housing. Such configuration is compact and relatively inexpensive. Spiral wound modules are used mainly for organic extraction, with low organic concentration and lower temperatures.

Hollow fiber modules are made for a small scale but their applications are limited because of the concentration polarization inside the fibres. All type of modules are commercially available today from several companies (Table 4). The market leader is Sulzer Chemtech Membrantechnik AG (former GFT Company) with over 100 pervaporation plants installed worldwide (Table 5).

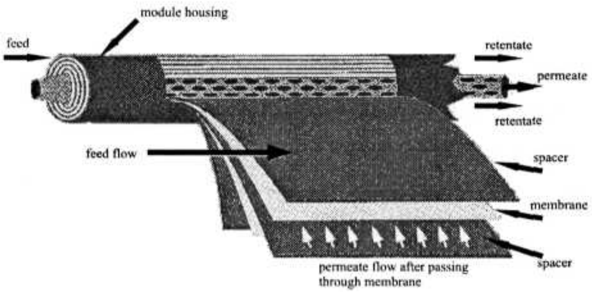


Fig. 5. Schema of a spiral-wound module.

Practical Applications of Pervaporation and Vapor Permeation

The first major research effort in commercializing pervaporation was undertaken 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 overhead of a distillation column. This work was followed by several others presenting the separation of n-heptane and iso-octane, the separation of benzene-methanol azeotrope or separation of pyridine-water azeotrope. Fig. 6 presents the schema of the hybrid distillation--pervaporation process proposed by Binning for the separation of water-pyridine mixture [40, 41]. The capacity of pervaporation for separating liquid mixtures was demonstrated by 1965, but commercial development did not proceed mainly due to lack of a market need. Traditional separation technologies including distillation, extraction or adsorption were sufficient. Moreover, the membranes then being utilized lacked the high selectivity and permeability necessary to make pervaporation economically attractive. Only the energy crisis in the 1970s refocused interest in separation technologies that possessed a high potential for energy savings. In the mid-1970s GFT Company (Germany) commercialized an economical pervaporation process for dehydrating ethanol that rivaled azeotropic distillation [42-44]. Following pilot trials in Europe, the first industrial plants were built in Brazil and the Philippines for processes utilizing continuous fermentation of sugar cane and sweet sorghum containing 5 to 7% ethanol, primary distillation to a mash containing 80 to 85% 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 1,000 to 50,000 I/day of ethanol recovered. As the cost of the permselective membrane module was reduced and selectivity increased, ethanol purity increased (99.85 wt.% was easily attainable) and the integrated process gained industrial acceptance [37].

Vapor permeation as a commercial process has been developed only recently [9, 11]. It is finding particular applications in the treatment of gaseous streams and in the recovery of solvents from solid-liquid mixtures [18, 19, 38, 45, 46].

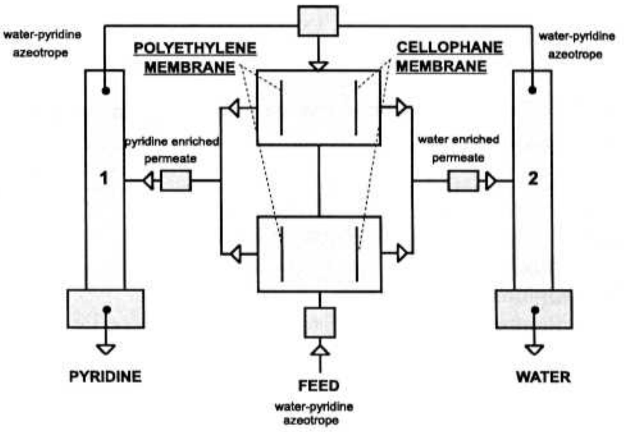


Fig. 6. Schema of the distillation-pervaporation process for the dehydration of water-pyridine azeotrope (according to Binning) [40].

An overview of the potential practical applications of pervaporation and vapor permeation (classified into three main areas) is presented in Table 6.

Table 6. Practical applications of pervaporation and vapor permeation [47],

separation of water from aqueous/ organic 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 organic compounds (VOCs) from aqueous and gas streams	removal of chlorinated hydrocarbons; separation of organics from the fermentation broth; separation of aroma compounds; wine and bear dealcoholization; removal of VOCs from air
separatrion of organic/organic mixtures	separation of azeotropes (e.g. ethanol-cyklohexane, methanol-MTBE, ethanol-ETBE); separation of isomers (e.g. xylenes).

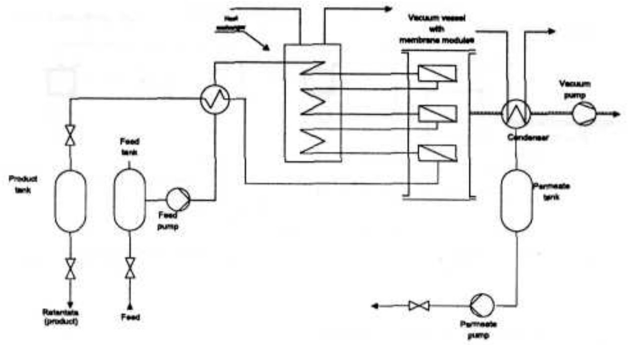


Fig. 7. Schema of a pervaporation plant.

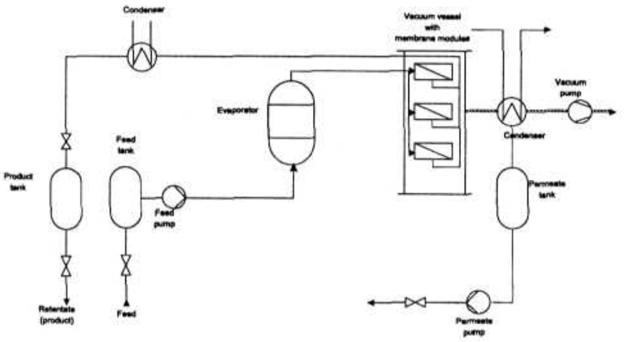
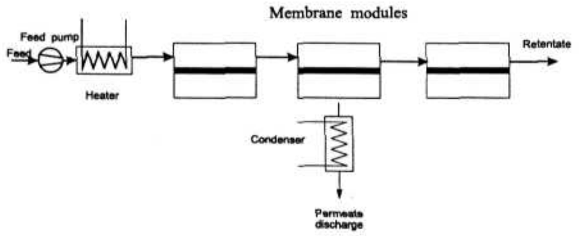
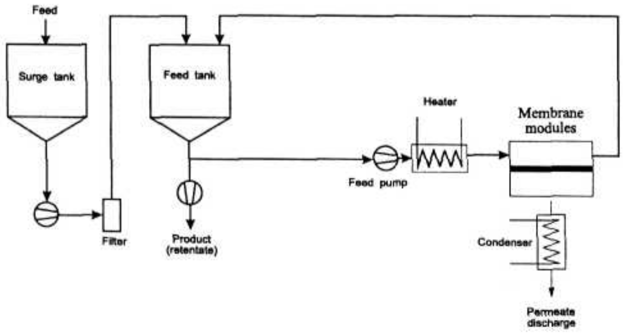


Fig. 8. Flow chart of the vapor permeation unit.



A. Straight-forward pervaporation



B. Batch pervaporation

Fig. 9. Possible operation modes of pervaporation.

A typical pervaporation plant usually includes several membrane modules in series, separated by reheaters (Fig. 7) [38, 39, 42, 44]. This multistage operation is required by the fact that 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 [10]. The reheating of feed optimizes membrane flux and, moreover, reduces membrane area needed. 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 use 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.

The flow chart of the vapor permeation plant is presented in Fig. 8 [45]. The liquid feed stream is pumped into the evaporator. If required, a small part of the feed stream may be drained from the evaporator in order to remove impurities and avoid depositions on the evaporator. The feed vapors stream is then fed to the membrane modules as a saturated vapor and the retentate is condensed after passing the membrane modules. The permeate appears also as a vapor at the downstream side of the membrane and is usually condensed at sufficiently low temperatures. Vapor permeation can offer some advantages over pervaporation because the heat required for vaporization of the permeate is not taken out of the sensible heat of the feed stream. Therefore, contrary to the pervaporation process, during vapor permeation the feed temperature and the driving force for the transport are not reduced by cooling and the feed mixtures do not need to be recirculated to the heat exchanger after passing each membrane module (Figs. 7, 8) [10]. This is especially favorable for feed streams with high water contents and thus with a large cooling effect in classical pervaporation [39,45].

Both pervaporation and vapor permeation units can operate either in the straight-forward or batch mode (Fig. 9). The straightforward mode is best applied to continuous feed streams, a relatively small amount of the component to be removed and systems for which concentration polarization is not a major problem (Fig. 9A). For small streams with large amounts of one component to separate, or with many different operating conditions, it may be advantageous to design a batch plant (Fig. 9B) with one or several modules, and a large feed circulation rate. The product is recycled to the feed tank until the required concentration is reached. This process simplifies plant design and offers maximum flexibility, however, with increased utility requirements.

Dehydration of Organic Solvents by Pervaporation and Vapor Permeation

Solvent dehydration is the most common application of pervaporation [39, 42-50]. As membrane processes are not governed by thermodynamic equilibrium and selectivities are determined by the differences in sorption and

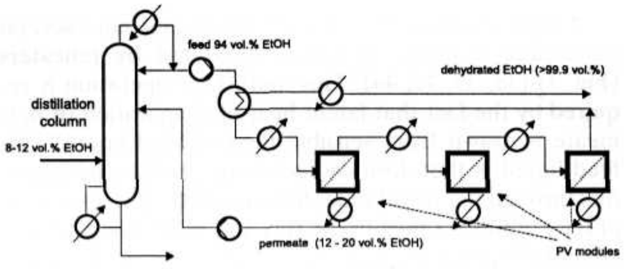


Fig. 10. Schema of the dehydration of ethanol by distilla-tion-pervaporation hybrid process.

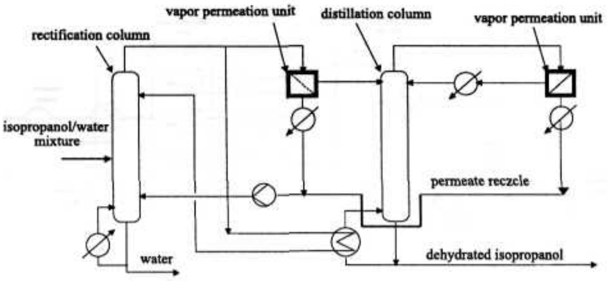


Fig. 11. Isopropanol dehydration by combined vapor permeation and above-azeotropic distillation [51].

transport rates of components through the membrane, mixtures of components with close boiling point and azeotropic mixtures can be effectively separated. As already mentioned, dehydration of ethanol by pervaporation was the first industrial scale application proposed by GFT in the 1980s. Today, more than 40 industrial pervaporation plants built by Sulzer Chemtech Membrantechnik AG (former GFT) are in operation worldwide. They are used for the dehydration of different solvents and/or solvent mixtures.

Ethanol from the fermentation broth is typically 8% to 12%, which after several stages of distillation to rectify and purify 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 a relatively expensive method and in addition there is some concern about environmental and health grounds over the use of the dehydrating agents. Pervaporation or vapor permeation are considered to be an appropriate and competitive replacement for azeotropic distillation and adsorption on molecular sieves (Fig. 10, Tab. 7).

Pervaporation is generally economic with water contents of approximately 10 wt.% and less, with final product water content of hundreds of ppm to 10 ppm attainable. To go much below these water contents it requires significantly greater installed membrane area and possibly a greater reduced pressure on the permeate side. Table 5 gives a list of organics other than ethanol currently dehydrated by pervaporation [38, 39].

Table 7. Comparison of the dehydration costs of ethanol from 94 vol.% to 99.9 vol.% by different techniques [48].

Utilities	Vapor permeation [DM/t]	Pervaporation [DM/t]	Entrainer distillation [DM/t]	Molecular sieves adsorption [DM/t]
Vapor	–	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
Replacement of membranes	9.50	15.30	–	–
Entrainer	–	–	4.80	–
Replacement of molecular sieves	–	–	–	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 vapor permeation only to break the azeotrope and to concentrate the retentate further by the above-azeotropic distillation [51]. The corresponding flow diagram of such hybrid distillation-vapor 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 vapor permeation before condensation. This concept is especially advantageous when an extremely high final alcohol concentration with a very low residual water content of less than 50 ppm and without any traces of entrainers is required.

Table 8. Organic solvents (other than ethanol) dehydrated by pervaporation [38],

Solvent	Water Content		Solvent	Water Content	
	Feed (wt. %)	Product (ppm)		Feed (wt. %)	Product (ppm)
Isobutanol	8.4	135	Ethanol/MeOH	2.9	780
n-Butanol	5.4	800	Ethanol/benzene	14.1	320
t-Butanol	10.4	581	Allylalcohol	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	Chlorothene	0.0617	12

Flexibility with respect to part load 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 9 presents the performance parameters of the multipurpose dehydration pervaporation plant with the membrane area of 120 m^2.

Table 9. Multipurpose dehydration pervaporation plant (built by GFT for Schering AG, Germany).

Solvent	Ethanol	THF
Concentration		
Inlet	93.5%	94.0%
Outlet	99.8%	99.9%
Capacity	200 kg/h	96 kg/h
Utility requirements		
Steam	40 kg/h	7 kg/h
Power	4 kW	4 kW
Membrane area	120 m^2	

Pervaporation Enhancement of the Chemical Reaction Efficiency

Another successful example of pervaporation is its application in the enhancement of chemical reaction efficiency [39, 42, 52-55]. There are many organic reactions which produces water molecules as one of the products. Examples of such reactions are esterification reaction or phenol-acetone condensation. These reactions often do not proceed to completion, reaching an equilibrium yield. This equilibrium point can be shifted towards higher conversions by having one reactant in excess and/or by selectively removing products from the reaction mixture. In the case of esterification or condensation reaction pervaporation can be applied for continuous water removal. Fig. 12 presents two possible solutions of the 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). The first industrial plant for the pervaporation enhanced ester synthesis was built in 1991 by GFT for BASF. Recently, research on the shifting of the equilibrium of esterification reaction by pervaporation was undertaken in Poland [55].

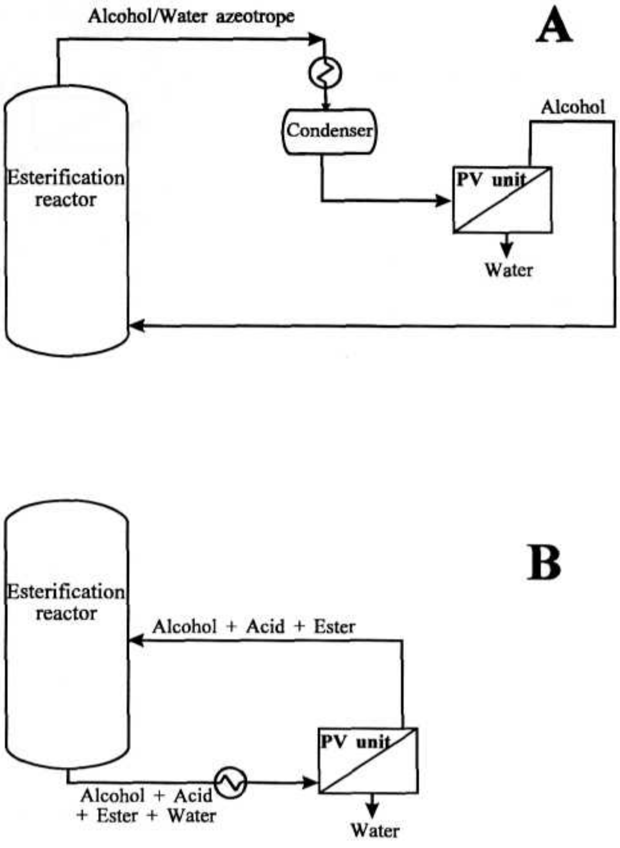


Fig. 12. Pervaporation enhanced synthesis of esters.

Solvent Recycling and Solids Recovery by Vapor Permeation

Solvent recycling and solids recovery from mother liquors is an example of the application of vapor permeation in the pharmaceutical industry [45]. Synthesized substances are precipitated from aqueous synthesis solutions by adding alcohols and then filtering. Large quantities of aqueous solvent mixtures which still contain dissolved solids are discharged to the environment. The hybrid distillation - vapor permeation process can be applied to recycle solvent and recover dissolved solids [45]. Depending on the water content of the solvent mixture, either a simple evaporator may be installed to recover the dissolved solids or a distillation column may be employed to remove the dissolved solids and provide a preliminary dehydration of the solvent down to azeotropic composition. In both cases, the solvent is finally dehydrated by vapor permeation down to a level suitable for reuse in production (Fig. 13). The advantages of this process lie in the recovery of the dissolved solids, the reuse of the solvent in production and the substantial reduction of waste streams.

Separation of Organic-Organic Liquid Mixtures

Separation of organic/organic mixtures represents the least developed and largest potential commercial impact for pervaporation, but considerable membrane material

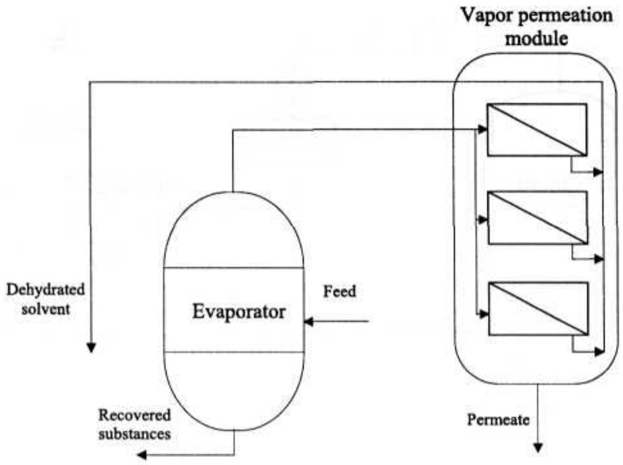
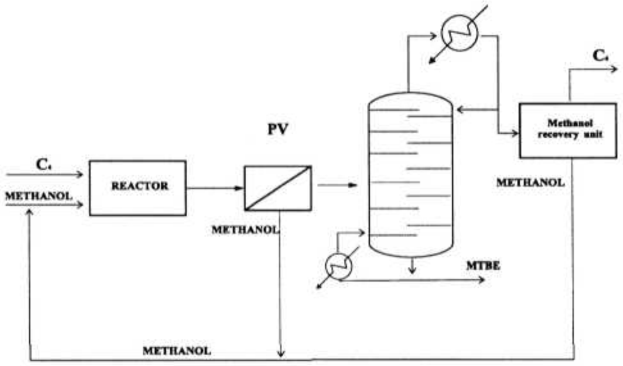


Fig. 13. Flow diagram of a hybrid process consisting of an evaporator followed by vapor permeation module for solids recovering and liquids recycling [45].

Fig. 14. Pervaporation enhanced MTBE production [58].



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: alcohols/ethers (methanol//MTBE, ethanol/ETBE), 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) [21-23, 35, 56-60].

The first industrial application of pervaporation to organic/organic separation was the separation of methanol from methyl t-butyl ether (MTBE) stream [58]. MTBE is an octane enhancer for motor fuel. In the conventional MTBE production process, methanol in the 20% excess is used to achieve a high conversion of isobutene and to minimize side reactions. Unfortunately, methanol forms azeotropes with both MTBE and unreacted isobutene, which is difficult to separate by distillation. The conventional process scheme is to take this azeotropic mixture to a butanizer to produce a MTBE bottom product and a binary methanol/C4 azeotrope overhead. This stream is then subjected to a water wash to remove the excess of methanol from C4s[58]. Methanol/water mixture is distilled to recover the methanol for recycle. This conventional process is energy intensive and creates additional wastes. In 1989 Air Products proposed the pervaporation TRIM™ process for methanol recovery from methanol/MTBE/C4 mixture (Fig. 14). The success of this application lies in 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.

Removal of Volatile Organic Compounds (VOCs) from Water and Soil

Contamination of groundwater and soils with volatile organic compounds (VOCs) is a problem at many industrial and government sites [1, 36]. Soil contamination by VOCs is a source for continuous air pollution and is also a source for groundwater pollution. The level of volatile organic compounds allowed in discharged wastewater or drinking water is lowered every few years. Examples of contaminants are petroleum hydrocarbons, methyl t-butyl ether, chlorinated hydrocarbons such as trichloroethylene and carbon tetrachloride. Many of VOCs are potential carcinogens [61, 62]. 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. 15) [17]. Some of them can generate secondary wastes. This, coupled with a growing interest in recycling both for economical and environmental reasons, opens new opportunities for membrane technologies like pervaporation. Pervaporation can be used for effectively removing VOCs from water, concentrating them for economical disposal or recycle/reuse using specially designed hydrophobic membranes. Membranes in these applications are rubbery polymers such as silicone rubber, polybutadiene, polyether copolymers, polydimethylsiloxane (Tab. 2). The separation achieved is determined by the individual rates of

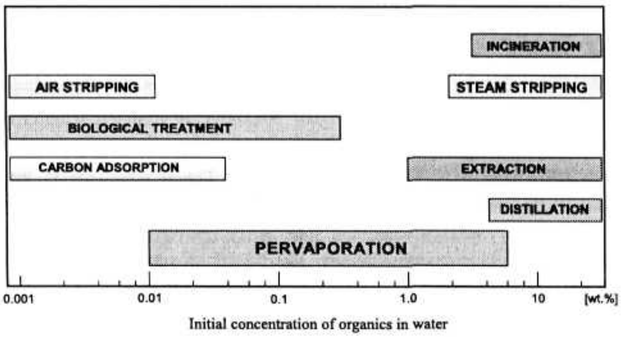


Fig. 15. Comparison of the separation methods for VOCs removal from water [39].

permeation through the membrane and the relative volatility of the components of the feed mixture. Usually the VOCs permeate through hydrophobic membrane orders of magnitude faster than water, as a result of which the VOCs are highly concentrated (Table 10).

Table 10. Typical pervaporation separation factors (a) for VOCs removal from water [17].

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 t-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.

Methyl acetate (MeAc) and MTBE are the examples of VOCs which can be found in the effluents from many chemical, pharmaceutical or petrochemical factories in Poland. MTBE, widely used as an octane enhancer, has relatively high water solubility and vapor pressure MTBE is very toxic and is also suspected for its carcinogenic properties [61, 62]. Recently, MTBE has been detected in lakes, reservoirs, and groundwater used as potable water supplies in concentrations exceeding, in some cases, allowed levels for taste, odor and human health [61].

Figs. 16 and 17 present the efficiency of two commercially available hydrophobic membranes (Sulzer Chemtech) in the removal of MTBE/MeOH and MeAc/MeOH mixtures from water [63]. PERVAP-1070 is a composite membrane with a selective toplayer made of PDMS filled with hydrophobic zeolite. The toplayer of PERVAP-1060 membrane is made of PDMS. Both membranes shows very high efficiency toward less polar components of the ternary mixture at moderate temperatures.

Pervaporation with organophilic membranes can also be applied in the treatment of wash waters used to remove organics from solvent-laden airstreams (Fig. 18). 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, to recycle to the air scrubbing unit.

Removal of Volatile Organic Compounds (VOCs) from Gas Streams

Many industrial processes which handle volatile solvents produce air streams contaminated with organic

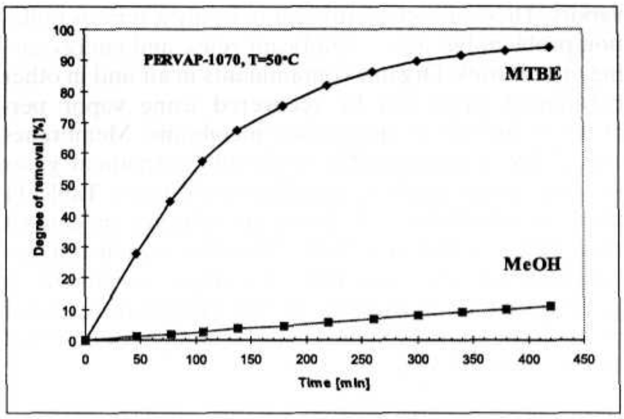


Fig. 16. Batch mode pervaporation. Removal of MTBE and MeOH from water using PERVAP-1070 membrane. Feed volume to membrane area ratio 120 dmVm^2. Initial organics concentration: MeOH: 2%, MTBE:1%.

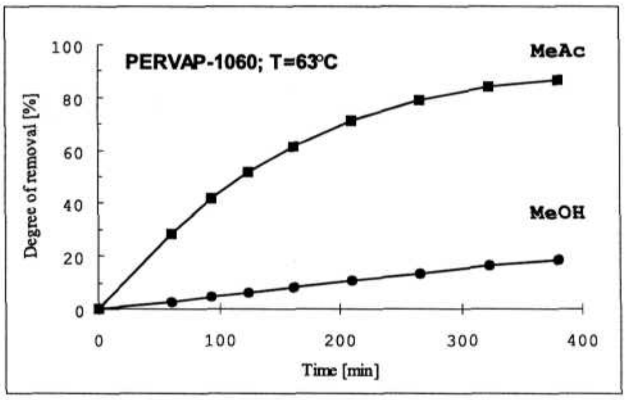


Fig. 17. Batch mode pervaporation. Removal of MeAc and MeOH from water using PERVAP-1060 membrane. Feed volume to membrane area ratio 120 dm^3/m^2. Initial organics concentration: MeOH: 6.4%, MeAc: 1.6%.

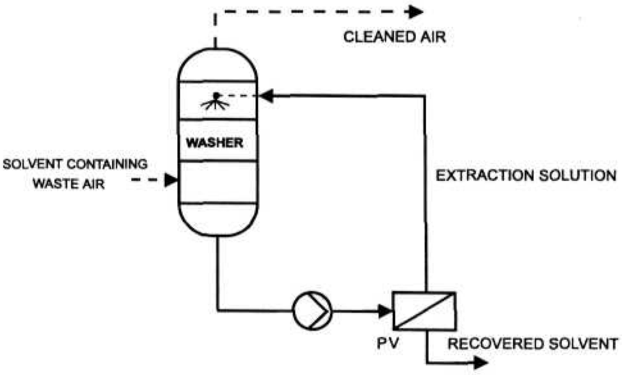


Fig. 18. Removal of solvents from waste air [37, 39].

vapors. These streams represent not only a serious pollution problem but also a significant reuse and energy saving opportunity. Organic contaminants in air and in other permanent gases can be recovered using vapor permeation through an appropriate membrane. Membranes are relatively impermeable to air and permanent gases and are usually made from rubbery polymers. Table 11 presents selectivities of chosen membranes in contact with vapors of organic solvents. The typical industrial applications of vapor recovery are off-gas treatment in gasoline tank farms, gasoline station vapor return, end of pipe solvent recovery in the chemical and pharmaceutical industry [38, 39, 46].

Table 11, Separation of organic solvents by vapor permeation from air or N_2 if stated [39].

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
p-Xylene	Polyimide	460
	PDMS	68
m-Xylene	Polyimide	513
1,2-Dichloromethane	PDMS	142
Chloroform	Polyimide	24
1,2-Dichloroethane	Polyimide	52
	PDMS	103

One of the practical applications of vapor permeation is its use for gasoline vapor return at gasoline stations. Gasoline apors contain hydrocarbons (like butane, pentane or benzene) and octane enhancers like MTBE or ethanol. Organic vapor emission to the atmosphere can be substantially reduced by applying the appropriate vapor return system. Fig. 19 presents the schema of a gasoline station vapor return system recently developed by the GKSS company (Germany) [46]. The average efficiency of this system varies from 70 to 95% depending on the type of car and particular solution applied. The air/gasoline vapor mixture from the vehicle's fuel tank is sucked by an internal vapor channel back to the vapor permeation module. By means of a membrane module this mixture is split into an organic vapors enriched stream which is directed back to the storage tank and a depleted stream which is vented to the atmosphere.

Another interesting example of industrial application is VOCs recovery by compression-condensation and vapor permeation method, presented schematically in Fig. 20. This is a schema of the process operating in ANWIL (Wloclawek, Poland) 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 vapor/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.

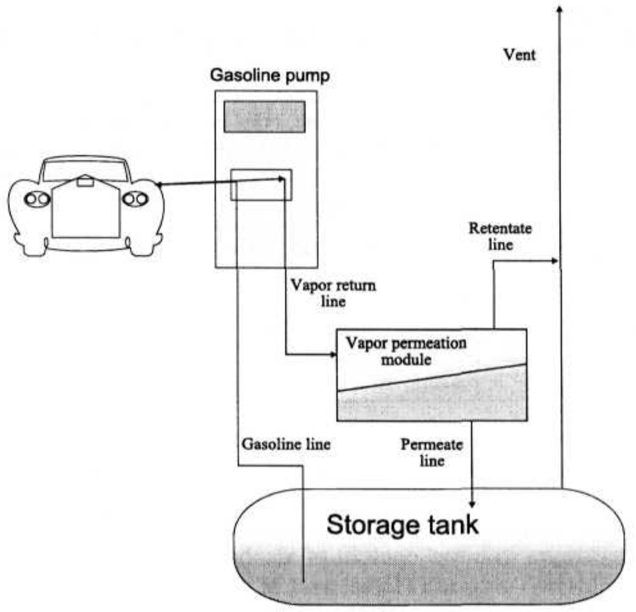


Fig. 19. Flow scheme of GKSS vapor return system [46].

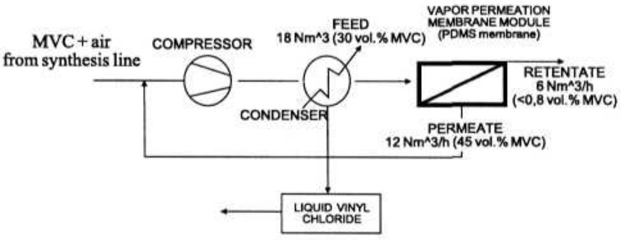


Fig. 20. Flow diagram of compression/condensation and membrane separation for MVC recovery [39].

Conclusions

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

There are several practical advantages of pervaporation and vapor permeation 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 also several areas of the techno-economical success of pervaporation and vapor permeation:

- the separation of small amounts of water or a 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 vapor from streams of permanent gases.

In general, pervaporation and vapor permeation will especially be used in those cases where a small quantity has to be removed from a large quantity.

In all the above applications, the most successful processes require integration with existing conventional separation unit operations. Nevertheless, pervaporation and vapor permeation have been identified as areas of vast potential for future research and commercial development.

References

1. SIKDAR S.K, GROSSE D., ROGUT I., J. Mem. Sri., **151,** 75-85, **1998.**
2. HO W.S.W., SIRKON K.K. (Eds.); Membrane Handbook, Van Nostrand Reinhold, New York **1992.**
3. RAUTENBACH R.; Procesy Membranowe, WNT Warszawa **1996.**
4. NAREBSKA A. (Ed.), Membrany i Procesy Membranowe, UMK Torun **1997.**
5. BODZEK M., BOHDZIEWICZ J., KONIECZNY K., Techniki membranowe w ochronie srodowiska, Wydawnictwo Politechniki Slaskiej, Gliwice **1997.**
6. MULDER M.H.V.; Basic principles of membrane technology; Kluwer Academic Publishers; Dordrecht, Boston, London, **1991.**
7. APTEL P., CUNY J., JOZEFOWICZ J., NEEL J.; J. Appl. Polym. Sci., **16,** 1061, **1972.**
8. NEEL J.; Introduction to Pervaporation; in: Pervaporation Membrane Separation Processes; R. Y. M. Huang (Ed.); Amsterdam, **1, 1991.**
9. MEARES P., The Sorption and Diffusion of Vapours in Polymers, Proc. Ill Int. Conf. on PV Proc. in the Chem. Ind., Nancy, France 1988 , R. Bakish (Ed.), Bakish Materials Corporation, Englewood, 12, **1988.**
10. ITO A., FENG Y., SASAKI H.; J. Membr. Sci, **133,** 95, **1997.**
11. BODDEKER K.W.; J. Membr. Sci, **51,** 259, **1990.**
12. KOOPS G.H, SMOLDERS C.A.; Estimation and Evaluation of Polymeric Materials for Pervaporation Membranes; in: Pervaporation Membrane Separation Processes; R. Y. M. Huang (Ed.); Amsterdam, 253, **1991.**
13. RAUTENBACH R, MEYER-BLUMENROTH U.; Desalination, **77,** 295, **1990.**
14. BELL CM, GERNER F.J, STRATHMANN R; J. Membr. Sci, **36,** 315, **1988.**
15. BERGDORF J, Proc. 5th Int. Conf. on PV Proc. in the Chem. Ind, Heidelberg Germany 1991, R. Bakish (Ed.), Bakish Materials Corporation, Englewood, 362, **1991.**
16. LIPNITZKI F, FIELD R.W, TEN P.-K.; J. Membr. Sci, **153,** 183, **1999.**
17. ATHAYDE A.L, BAKER R.W, DANIELS R, LE M.H, LY J.H.; Chemtech. **1,** 34, **1997.**
18. PAUL H, PHILIPSEN C, GERNER F.J, STRATHMANN H.; J. Membr. Sci, **36,** 362, **1988.**
19. KIMMERLE K, BELL CM, GUDERNATSCH W, CHMIEL H.; J. Membr. Sci, **36,** 477, **1988.**
20. MECKL K, LICHTENTHALER R.N.; J. Membr. Sci, **113,** 81, **1996.**
21. MULDER M.H.V, FRANKEN A.C.M, SMOLDERS C.A.; J. Membr. Sci, **23,** 41, **1985.**
22. WESSLING M, WERNER U, HWANG S.T.; J. Membr. Sci, **57,** 257, **1991.**
23. ROIZARD D, JONQUIERES A, LEGER C, NOEZAR I, PERRIN L, NGUYEN Q.T, CLEMENT R, LENDA H, LOCHON P, NEEL J.; Sep. Sci. Technol. **34,** 369, **1999.**
24. KONDO M, KOMORI M, KITA H, OKAMOTO K.; J. Membr. Sci. **133,** 133, **1997.**
25. VELTEROP F.M, Pervatech selective ceramic membranes; Information leaflet, Pervatech, **1999.**
26. M. ZHOU, M. PERSIN, W. KUJAWSKI, J. SARRAZIN - "Electrochemically Synthesised Polypyrrole Membranes for the Separation of Organic Mixtures by Pervaporation" - Proc. 7th Int. Conf. on Pervaporation (Reno, Nevada USA, 1995); R. Bakish (Ed.), Bakish Material Co, New Jersey USA, 193, **1995.**
27. M. ZHOU, M. PERSIN, W. KUJAWSKI, J. SARRAZIN; J. Membr. Sci. **108,** 193, **1995.**
28. SANDER U, SOUKUP P, Practical experience with pervaporation systems for liquid and vapor separation, Proc. Ill Int. Conf. on PV Proc. in the Chem. Ind, Nancy, France 1988, R. Bakish (Ed.), Bakish Materials Corporation, Englewood, 508, **1988.**
29. KUJAWSKI W, WACZYNSKI M, LASOTA M.; Sep. Sci. Technol, **31,** 953, **1996.**
30. TOCK R.W, CHEUNG J.Y.; Sep. Sci, **9,** 361, **1974.**
31. HUANG R.Y.M, XU Y, JIN Y, LIPSKI C, Proc. Second Int. Conf. on PV Proc. in the Chem. Ind, San Antonio, USA 1987, R. Bakish (Ed.), Bakish Materials Corporation, Englewood, 225, **1987.**
32. KUJAWSKI W, NGUYEN Q.T, NEEL J, Pervaporation of Water-Alcohols Mixtures Through Nafion 117 and Poly(Ethylene-co-Styrene Sulfonate) Interpolymer Membranes, Proc. Ill Int. Conf. on PV Proc. in the Chem. Ind, Nancy, France 1988 , R. Bakish (Ed.), Bakish Materials Corporation, Englewood, 355, **1988.**
33. FEATHERSTONE W, COX T.; Brit. Chem. Eng. Process Technol, **16,** 817, **1971.**
34. KIMURA S, NOMURA T.; Maku, 8, 177, **1983.**
35. GROOT W.J, van der Lans R.G.M, LUYBEN K.Ch.A.M.; Pervaporation of fermentation products, Proc. 3rd Int. Conf. on PV Proc. in the Chem. Ind, Nancy, France 1988 , R. Bakish (Ed.), Bakish Materials Corporation, Englewood, 398, **1988.**
36. KUJAWSKI W.; Pervaporative Removal of Organics from Water Using Hydrophobic membranes. Binary Mixtures, Sep. Sci. Technol, **1999** in press.
37. KITA H, INOUE T, ASAMURA H, TANAKA K, OKAMOTO K.; Chem. Commun, 45, **1997.**

38. FLEMING H.L., SLATER C.S.; in ref. 2, chapter **III:** Pervaporation, 103.
39. SCOTT K., Separation of Liquid Mixtures/Pervaporation, in: Handbook of Industrial Membranes, K. Scott (Ed.), Elsevier, Oxford, 331, **1995.**
40. KUBICA J., STELMASZEK J.; Zastosowanie blon polimerowych do rozdzialu mieszanin azeotropowych i bliskowrzacych; Politechnika Wroclawska, Wroclaw **1973.**
41. BINNING R.C., LEE R.J, JENNINGS J.F, MARTIN E.C, Ind. Eng. Che. **53,** 45, **1961.**
42. ABOUCHAR R, BRUSCHKE H.; Biotechnology Today, 148, **1992.**
43. BRUSCHKE H.; Pure and Applied Chem. **67,** 993, **1995.**
44. BRUSCHKE H., SOUKUP P., Chem. Plants Proc, **5,** 86, **1991.**
45. MARTIN N.; Sulzer Technical Review, **3,** 12, **1998.**
46. OHLROGGE K., BROCKMOELLER J, WIND J, BEHLING R.-D.; Sep. Sci. Technol, **28,** 227, **1993.**
47. KUJAWSKI W.; Env. Prot. Eng, **25,** 49, **1999.**
48. SANDER U, SOUKUP P.-B.; J. Membr. Sci, **62,** 67, **1991.**
49. RAUTENBACH R, KLATT S.; State of art of PV. 10 years of industrial PV; Proc. Sixth Int. Conf. on Pervap. Proc. in the Chemical Industry; Ottawa **1992.**
50. SANDER U, JANSSEN H.; J. Membr. Sci, **61,** 113, **1991.**
51. RAUTENBACH R, Vapor Permeation of Water-Organic Mixtures. Module and Process Design, Proc. **Ill** Int. Conf. on PV Proc. in the Chem. Ind, Nancy, France 1988, R. Bakish (Ed.), Bakish Materials Corporation, Englewood, 287, **1988.**
52. KITA HI, SASAKI S, TANAKA K, OKAMOTO K, YAMAMOTO M.; Chem. Letters, 2025, **1988.**
53. Okamoto K, Semoto T, Tanaka K, Kita H.; Chem. Letters, 167, **1991.**
54. BAGNELL L, CAVELL K, HODGES A.M., MAU A.W.-H, SEEN A.J.; J. Membr. Sci, **85,** 291, **1993.**
55. KRUPICZKA R, KOSZORZ Z.; in: Euromembrane '97, "Progress in Membrane Science and Technology", University of Twente, the Netherlands, p. 332, **1997.**
56. LUO G.S, NIANG M, SCHEATZEL P.; J. Membr. Sci, **125,** 237, **1997.**
57. OGONOWSKI J, SIKORA E.; Przemysl Chemiczny, **75,** 135, **1996.**
58. CHEN M.S.K, MARKIEWICZ G.S.; AiChE Symp. Ser, **85,** 82, **1989.**
59. NAM S.Y, LEE Y.M.; **J.** Membr. Sci, **157,** 63, **1999.**
60. HOEMMERICH U, RAUTENBACH R, J. Membr. Sci, **146,** 53, **1998.**
61. BELPOGGI F, SOFFRITTI M, MALTONI C; Toxicology and Industrial Health, **11,** 1, **1995.**
62. SQUILLACE O.J, ZAGORSKI J.S, WILBER W.G, PRICE C.V.; Environmental Sci. Technol, 30, 1721, **1996.**
63. KUJAWSKI W, in: Proc. 2nd National Science Conference "Membranes and Membrane Processes in the Environmental Protection", Wydawnictwo Politechniki Slaskiej, Gliwice, Part **2,** 5, **1997.**