molecular masses less than 100 000, while Sephadex G-100 is used for higher molecular mass proteins. The solutions of proteins are prepared in guanidine hydrochloride ($10\,\mathrm{mg\,mL^{-1}}$), and cytochrome-*c* ($10\,\mathrm{mg\,mL^{-1}}$) is used as an internal standard. Descending chromatography is carried out at room temperature under an inclination angle of 25° to the horizontal. After 3 h of development the quotient R_s protein/R_s cytochrome *c* is calculated for each protein–cytochrome *c* combination. A standard calibration line is obtained by plotting the log relative molecular masses of standards against protein–cytochrome quotient; the relative molecular masses of the unknown proteins are calculated from this plot.

See also **II / Affinity Separation:** Immunoaffinity Chromatography. **Chromatography:** Size Exclusion Chromatography of Polymers. **Chromatography: Thin-Layer (Planar):** Densitometry and Image Analysis; Ion Pair Thin-Layer (Planar) Chromatography; Layers; Spray Reagents. **III / Amino Acids and Derivatives:** Chiral Separations. **Impregnation Techniques: Thin-Layer (Planar) Chromatography. Appendix: 1 / Essential Guides for Isolation / Purification of Enzymes and Proteins.**

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PERVAPORATION: MEMBRANE SEPARATIONS

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Introduction

The future of membranes in liquid–liquid separation lies in their potential to replace conventional unit operations such as distillation and cryogenic separation. Pervaporation, which has elements in common with reverse osmosis and membrane gas separation, is a liquid–liquid membrane separation process that can be employed for aqueous–organic or organic–organic separations. The most developed area of pervaporation is the separation of aqueous–organic mixtures but a vast potential lies in the area of organic–organic separations, specifically in the separation of azeotropic organic mixtures, where conventional separation processes tend to be complex and uneconomical.

The first pervaporation studies were carried out in late 1950 by Binning and coworkers at American Oil. However the process was not commercialized owing to lack of technology to prepare a membrane that would withstand the commercial application. By the 1980s, membrane technology was advanced to the extent that a commercially viable pervaporation technology could be developed. However, the only commercialized applications today are the alcohol dehydration and separation of volatile organics from aqueous solutions. A few pilot-plant studies have been carried out on the industrially more significant organic–organic separations.

The applications of pervaporation can be categorized as follows: (1) dehydration of organic solvents; (2) removal of volatile organic compounds from aqueous streams; and (3) separation of organic–organic mixtures. There is a tremendous amount of literature on the first two applications. Pervaporation has been successful in these applications because the properties of organic components are very different from water and exhibit distinct membrane permeation properties. The feed solutions are also relatively non-aggressive and do not chemically degrade the membrane. However, in the case of separation of organic–organic mixtures, it is much more difficult to select membranes that would exhibit selectivities for one component over the other. This article

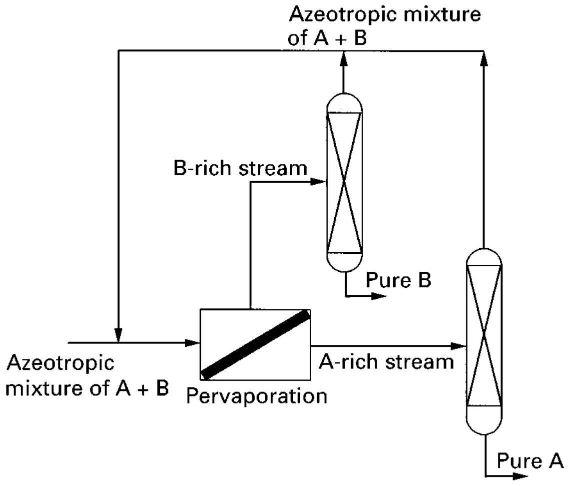

Figure 1 Schematic of pervaporation–distillation scheme for azeotrope separation.

is focused on this type of organic–organic separation. In a typical pervaporation process, even though the membrane selectivity is high, the mass flux achieved is fairly low ($2\,kg\,m^{-2}\,h^{-1}$). Thus pervaporation is most advantageously used, when combined with another operation such as distillation. A schematic of such a hybrid process scheme is shown in **Figure 1**. An azeotropic mixture A + B is subjected to one-stage pervaporation to give a permeate rich in A and retentate rich in B. Both the streams are individually subjected to fractional distillation to yield pure A and pure B, and a recycle stream of azeotropic mixture of A + B.

In pervaporation, the liquid mixture is brought in contact with one side of the membrane and permeated product is removed from the other side by applying vacuum (**Figure** 2A). Alternatively, the vapour product can also be removed by use of a carrier gas (**Figure** 2B). The permeate is then cooled and the organic phase condensed and collected to obtain the product.

The ability of a pervaporation membrane to perform separation is usually characterized by a separation factor defined as:

$$\alpha_{ab} = \frac{Ca_p/Cb_p}{Ca_f/Cb_f} \qquad [1]$$

where, Ca, Cb are concentrations of A and B, and the subscripts p and f designate permeate and feed, respectively. The separation factor depends upon the operating conditions of the pervaporation processes and the solubility and affinity of the compounds in the feed solution towards the membrane. The selectivity can be of two types: solubility selectivity and diffusivity selectivity. In most of the organic separations, dense membranes are employed and the diffusivity selectivity is generally low. Hence, of importance here is the solubility selectivity. For high solubility, membranes should have high affinity for one component and little affinity for the other component. However, excessive affinity for one component causes significant swelling of the membrane leading to loss in selectivity and mechanical strength. In the case of organic–organic separations, the membrane selection is particularly difficult. Several different methods such as polymer alloys, crosslinking, concentrated emulsion polymerization, microphase separation, copolymerization, and plasma graft filling polymerization have been proposed to prepare the membranes with the desired properties.

Selection of Membrane for Pervaporation

The choice of membrane to perform a particular separation is determined by the membrane's stability, productivity, and selectivity. Membrane productivity is the measure of the quantity of a component that permeates through a specific area of membrane in a given unit time and depends on the intrinsic permeability and the thickness of the membrane. The ability of a membrane to separate the desired component is characterized by its selectivity. Selectivity depends on the preferential sorption and relative permeability of the components. There is usually a trade-off between membrane permeability and selectivity. In 1993, Huang and Feng introduced a composite number called a pervaporation separation index (PSI) to take into account both these aspects.

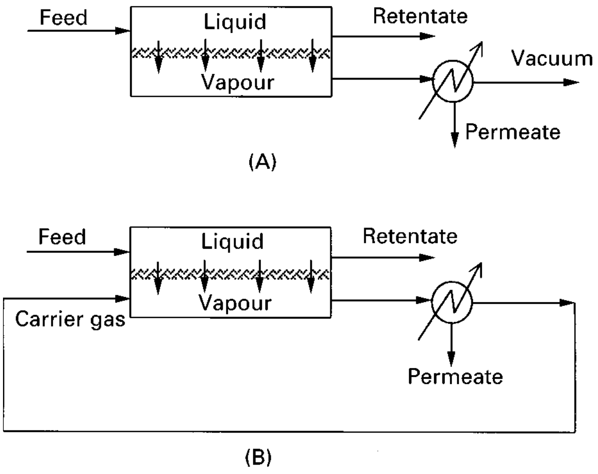

Figure 2 Schematic of pervaporation process. (A) By vacuum. (B) By carrier gas.

The stability of the membrane strongly depends on chemical, mechanical, and thermal properties of the membrane and the type of the environment.

Although the use of pervaporation for the separation of organic–organic mixtures represents a large opportunity for energy and cost savings, it is the least developed application of pervaporation. This is because of problems associated with the choice of proper membrane for the concerned application. Organic–organic separations involve relatively harsh conditions and the stability of the membranes under these conditions is often low. The polymeric membranes that are commonly used for aqueous systems are not stable in organic environment. This is an area of active research.

Once the stable membrane material is identified, attention should be focused on obtaining maximum separation with large production rate. As mentioned earlier, separation is achieved by virtue of the difference between the permeability or the solubility (affinity) values of the component in the membrane. The permeability in the membrane depends on the molecular size, and small molecules tend to permeate faster through the membrane. However, their permeation can be restricted by selecting a membrane material that offers less solubility to these components. Hence, the polarity of the membrane can conveniently be manipulated in such a way that it offers preferential treatment for the components to be separated on the permeate side. For instance, to improve the permselectivity towards certain non-polar organics, the membrane can be filled with organophilic adsorbents.

Materials used for pervaporation membranes are normally polymeric in nature. Polymeric membranes can be classified in three different categories: glassy polymer membranes, elastomeric polymer membranes and ionic polymer membranes. Glassy polymers are water-selective whereas elastomeric polymers are organo-selective. However, for organic–organic separations, the selection of material becomes highly system-specific and is based on relative polarity and molecular size of the components to be separated. Hence, all the polymer membrane types have shown selectivity to certain components in organic–organic mixtures. Hydrophilic–hydrophobic composite membranes containing polystyrene as the dispersed phase and polyacrylamide as the continuous phase have shown tremendous selectivity towards aromatic difluoride compared to aliphatic ones. Membranes made from cellulose esters, polyethylene, and poly(vinylidene difluoride) modified to contain various Werner complexes, have been successfully used on a laboratory scale for separation of isomer mixtures such as *p*-xylene–*o*-xylene. Ionic membranes of perfluorosulfonic acid have been found to be effective for the selective pervaporation of relatively polar organic compounds such as alcohols. A list of organic–organic separations attempted by pervaporation is shown in **Table 1**.

In the interest of improving the membrane productivity, either membrane structures are modified or a different configuration such as a hollow-fibre membrane is used. The membrane structure can be altered by introducing an asymmetry during the membrane preparation procedure and most industrially important membranes are asymmetric. These membranes have a thin dense selective surface layer supported on a much thicker microporous layer. When the support material and layer material are different, then the membranes are called composite membranes. One of the advantages of the com-

Table 1 Examples of organic–organic separation by pervaporation

Type of system	*Example*	*Membrane(s) used*[a]
Aromatic–alcohol	Benzene–methanol, ethanol, propanol	Polyethylene, cellulose acetate
	Toluene–*n*-butanol	Polypropylene, polyethylene
Aromatic–naphthalene	Benzene–cyclohexane	PVA, acrylonitrile copolymers, plasma grafted, composite
Aromatic–paraffin	Benzene–*n*-hexane	Polyethylene
	Toluene–*n*-heptane	Polyethylene
Mixture of isomers	*o,m,p*-xylene	Polyethylene, PVF
Alcohol–paraffin	Ethanol–hexane	PTFE–PVP
Alcohol–naphthalene	Ethanol–cyclohexane	PTFE–PVP
Alcohol–ketone	Methanol–acetone	PTFE–PVP
Halogenated hydrocarbons	Dichloroethane–trichloroethylene	Polystyrene–butadiene
Reactive systems	Methanol–MTBE	Organophilic plasma polymerized
	Ethanol–ETBE	Organophilic plasma polymerized
	Methanol–dimethylcarbonate	Organophilic composite

[a] PTFE–PVP: poly(tetrafluroethylene)-*N*-vinylpyrrolidone; PVF: poly(vinylidene difluoride) modified by including Werner complexes.

posite membranes is that different polymers may be used as the barrier layer and the porous support, which allows a combination of properties that may not be available in a single material. The hollow-fibre membrane configuration is constructed similarly to a shell-and-tube heat exchanger. This configuration provides advantages over a flat plate-and-frame configuration such as large membrane area per unit volume, self-supporting ability, etc.

Applications

We will discuss here a few commercially important organic–organic systems that have potential of adapting pervaporation-assisted separation schemes.

Pervaporation–Distillation

Pervaporation–distillation process for MTBE production Methyl-*t*-butyl-ether (MTBE) is manufactured through the reaction of isobutylene from the C_4 fraction with methanol. The reaction is limited by equilibrium. The current technologies use a combination of reaction and either normal distillation or reactive distillation. The former process can exploit the potential of pervaporation before, during or after the distillation step to recover methanol from the reaction mixture. **Figure 3** shows the two possible configurations, which use pervaporation as an intermediate step in MTBE manufacture.

The first configuration uses pervaporation to separate methanol from the reactor effluent (**Figure** 3A). The methanol-rich permeate is fed back to the reactor. This increases the overall conversion and also reduces the load on the methanol recovery unit. Moreover, this modification is easily possible in an existing MTBE plant without any major investment. The second configuration involves the withdrawal of a side-stream from the rectifying section of the distillation column to subject it to pervaporation (**Figure** 3B). Methanol from this stream can be separated and the retentate is again fed back to the distillation column. By doing this, the load on methanol recovery can be substantially reduced. Both configurations have been proved to be beneficial in view of reducing the investment cost by about 5–20%. The second configuration appears to be attractive compared to one that incorporates pervaporation before distillation. It involves low flow rates, low amount of methanol to be separated and a large driving force owing to high methanol concentration. Hence a membrane with a small surface area serves the purpose. A variation of the second scheme is also possible where the top product of the distillation column is liquefied and fed to the pervaporation unit to separate the methanol. The methanol-rich permeate is recycled back to the reactor. A highly permselective asymmetric aromatic polyimide membrane is used with a separation factor greater than 200. As a separate methanol recovery unit is not required, the process is more promising than the two options mentioned above.

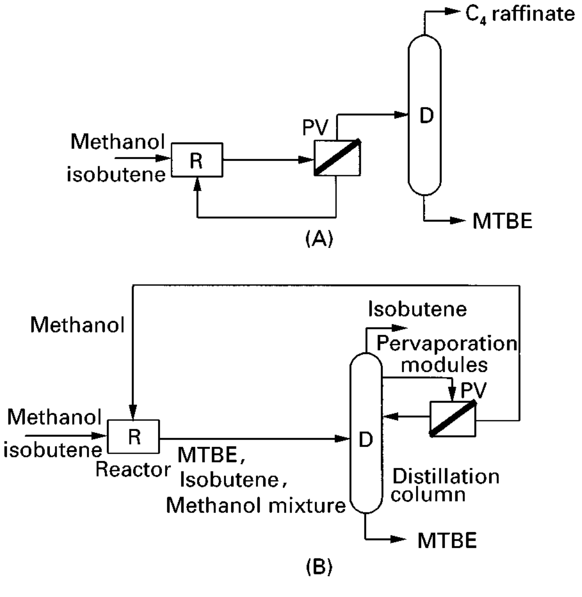

Figure 3 Different configurations of hybrid pervaporation-based MTBE processes.

A general advantage that is realized by adopting the hybrid process using pervaporation is the considerable savings in energy (especially steam) consumption. An organophilic (methanol-philic) plasma-polymerized PERVAP 1137 membrane (Sulzer Chemtech/GFT) has been suggested for this operation.

Pervaporation–distillation process for ETBE production Typically ethyl *t*-butyl ether (ETBE) is produced by acid-catalysed etherification of isobutylene with ethanol. The products are separated by distillation, the top product being the C_4 fraction and the bottom consisting of ethanol and ETBE. Pervaporation can be incorporated into this process to purify the bottom of the distillation column wherein ethanol is separated from ETBE (**Figure 4**). An organophilic (ethanol-philic) copolymer PERVAP 2051 membrane is used for this purpose and this brings down the ethanol content in the ETBE product stream to less than 1% w/w. A significant reduction in operating cost is realized with the help of the hybrid process. Pervaporation can also be used to recover ethanol from the top product of distillation. The liquid retentate may be fed back to the distillation through

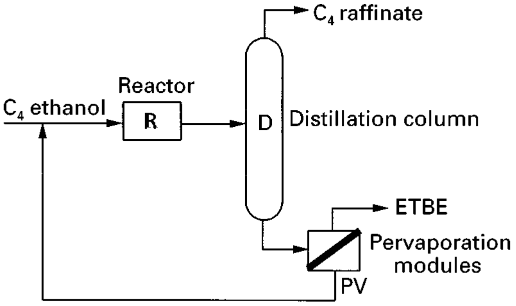

Figure 4 Hybrid pervaporation process for ETBE.

the column feed. The hybrid process is more economical than the conventional process.

Separation of Benzene–Cyclohexane

Cyclohexane is industrially produced by hydrogenation of benzene. They have close boiling points (within 1°C) and also form an azeotrope and hence cannot be separated by simple distillation. With the right choice of membrane, the separation can be achieved via the pervaporation route. However, the similar molecular size of benzene and cyclohexane makes the selection of a pervaporation membrane challenging. Poly(vinyl alcohol), acrylonitrile/methyl methacrylate, acrylonitrile/vinyl acetate, polymer metal complex membranes, plasma-grafted polymer membranes, and composite membranes of acrylic acid/styrene have all been employed with each having their own advantages/disadvantages. The process has been successfully demonstrated on a laboratory scale but there is no commercial process so far. Rautenbach and Albrecht made a comparative study of different separation schemes for this system. A comparison of a cascade of pervaporation processes with extractive distillation using furfurol shows that the pervaporation process is more capital intensive. However, the conventional two-column extractive distillation process does not give the desired purity of the benzene and cyclohexane stream. A hybrid pervaporation–extractive distillation process shown in **Figure 5** proves to be the economically attractive alternative and gives the highest purity product. Furfurol is used as an extractive carrier to carry benzene down in the first column. The bottom of the first column contains benzene and furfurol, which are separated to obtain 99.5% pure benzene in the second column. The top product of the first column is subjected to a one-stage pervaporation where benzene is selectively removed to obtain 99.2% cyclohexane. The hybrid process can save up to 20% of the overall costs of the extractive distillation process.

Dimethyl Carbonate–Methanol Separation

Dimethyl carbonate (DMC) finds use in gasoline products as a fuel oxygenate and can be blended with alcohols or MTBE. It can serve as an MTBE substitute or as a phase enhancer in gasoline containing alcohol. DMC is prepared industrially by the reaction of methanol with carbon monoxide and oxygen. The process produces a mixture of methanol and DMC, which cannot be separated by simple distillation owing to the formation of an azeotrope. In the conventional process, a two-pressure distillation scheme is employed to split the azeotrope. The degree of separation achieved is nevertheless insufficient to meet the product specifications so a supplementary physical separation process such as crystallization is needed to obtain the desired product purity. Another route is to employ extractive distillation, where water is preferably used as an extractant. This means the separation of water–methanol needs to be carried out to recover the methanol. Owing to the high specific and latent heat of water, this process becomes very energy intensive.

Pervaporation combined with distillation can be advantageously employed to separate the methanol–DMC azeotrope as shown in **Figure 6**. The azeotropic methanol–DMC mixture is subjected to pervaporation. The retentate is 45% DMC, which is further separated by a distillation column into 99% DMC at the bottom and a near-azeotropic methanol–DMC mixture at the top. The top stream is recycled to the pervaporation. The further advantage of this scheme is that the top composition at the distillation column is not required to be azeotropic. This further brings down the number of stages required in the rectifying section of the column. This, combined with the elimination of high-pressure column, brings down the investment cost by 60% from the conventional process to the pervaporation–distillation hybrid process. Organophilic composite

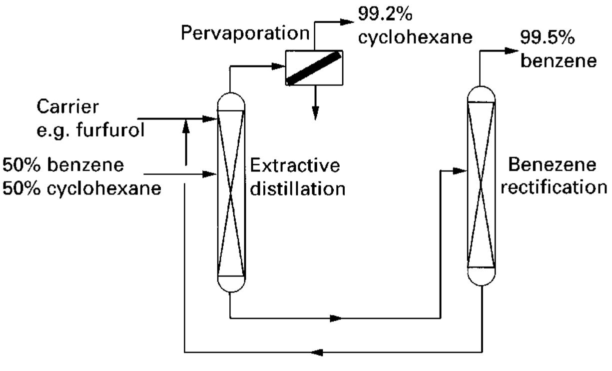

Figure 5 Hybrid process for separation of benzene–cyclohexane.

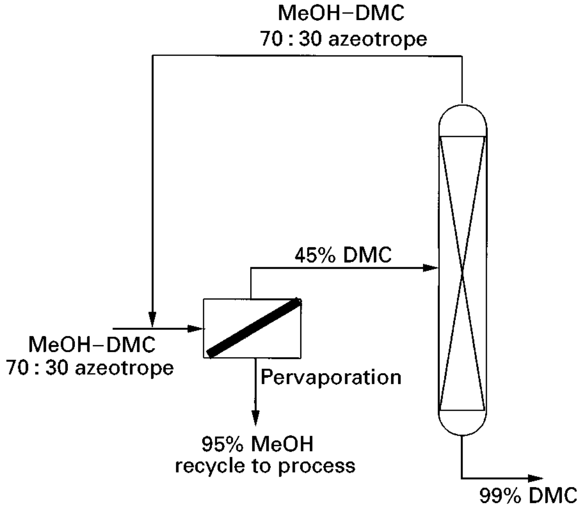

Figure 6 Pervaporation–distillation hybrid process for DMC.

membranes are used to carry out the pervaporation separation.

Separation of Aromatics–Saturates

The separation of aromatics from saturates is of considerable importance in the petrochemical industry. The boiling range of the aromatics and saturates is the same and hence simple distillation fails to separate the products. Pervaporation can be efficiently employed for this separation. A copolymer of polyimide–aliphatic polyester is advantageously used as a membrane. The polyimide provides the stability at high temperature whereas the polyester provides for the selectivity to aromatics. Other membranes that can be used for this application are polyurea urethane, polyurethane imides, and polyester imides. The process shown in **Figure** 7 gives high selectivity towards the aromatics. A part of the aromatic permeate (25–40%) is recycled back to the pervaporation stage where it is mixed with the fresh feed. This scheme gives unexpectedly high selectivity than when the feed is exclusively either fresh feed or recycle permeate. Heavy cat naphtha can be separated by the above process into aromatic-rich permeate for high-octane gasoline use and aromatic lean retentate suitable for diesel fuel. The process can also be applied to intermediate cut naphtha, diesel oil, gas oil, and light aromatic streams boiling in the C_5 range.

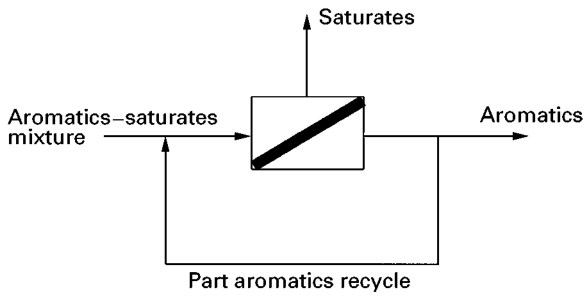

Figure 7 Pervaporation scheme for the separation of aromatics–saturates.

Conclusion

Pervaporation of organic–organic mixtures has the great potential of replacing conventional processes. The key areas of applications are separation of azeotropes and close boiling mixtures. However, the challenge for pervaporation to prevail in organic–organic separation is enormous, as there is a lot of inertia of the industry to change from the conventional distillation processes. Finding a suitable membrane is the most important hurdle in devising a pervaporation system. Hence, the major thrusts in this field should be towards developing new membranes with high flux, selectivity, and stability. At the same time, to warrant commercialization, high surface area modules must be developed. With emerging trends in membrane research and newer techniques such as asymmetric and composite membranes, the day is not too far off when pervaporation will be the preferred process. As outlined earlier, pervaporation combined with conventional separation is the way forward in most of the applications. Hence, overall integrated process development needs to be given equal importance. Ultimately, in order to achieve a complete success, membrane development efforts should be backed by more theoretical research for a better understanding of the complicated phenomenon of pervaporation.

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