

## Industrial application of membrane separation processes

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**Abstract** - During the past two decades membrane separation processes have been developed and optimized for even large scale industrial applications. The most important of these processes include: (i) microfiltration and ultrafiltration for purification of aqueous streams, concentration and recovery of valuable products; (ii) reverse osmosis for the production of demineralized or potable water; (iii) electrodialysis for the concentration or removal of dissolved ions; (iv) gas separation for splitting gas streams, removal or recovery of specific gases; (v) pervaporation for separation and concentration of liquid mixtures, especially of aqueous-organic azeotropes.

Whereas the first three of these processes are well established and have reached a high degree of maturity, the last two ones are still in developing stage, although development is fairly fast. Both processes, gas separation and pervaporation are very closely related with respect to their physico-chemical fundamentals. In this paper principles of the separation processes are outlined. Examples of membrane performance and applications, with the emphasis on Pervaporation processes are presented.

In general all processes used for the separation of fluid mixtures can be split into two categories:

- separation by equilibrium distribution
- separation by differences in transport rates

The most common separation processes used on large scales in the industry are based on equilibrium distribution. Evaporation, distillation, extraction, adsorption, absorption are all going back to the same principle shown in fig. 1. A first phase comprising a mixture to be separated is brought into contact with a second phase. After a certain time thermodynamic equilibrium is established between the two phases. That means both phases show the same temperature and all components have the same chemical potential in both phases. The analytical concentrations of a component in the two phases, however, may differ e.g. a component can be highly enriched in one phase and be depleted in the other one. If now the two phases are separated by appropriate means, the enriched component can be recovered usually by establishing a new equilibrium at a different temperature or pressure. Repetition of this procedure at the end will lead to a phase in which one of the components is present at the wanted purity.

If separation by differences in transport rates is to be achieved, an additional means is required. In fig. 2 such a means is a membrane, separating to phases from each other. A driving force, a gradient in pressure, concentration, temperature, electrical field is applied and has to be maintained over the membrane. Under the influence of this driving force components from the mixture to be separated, held at a higher chemical potential, migrate through the membrane to the side of the lower chemical potential. Separation between different components is effected by the difference in transport rates. The gradient in the chemical potential has to be maintained by continuous removal

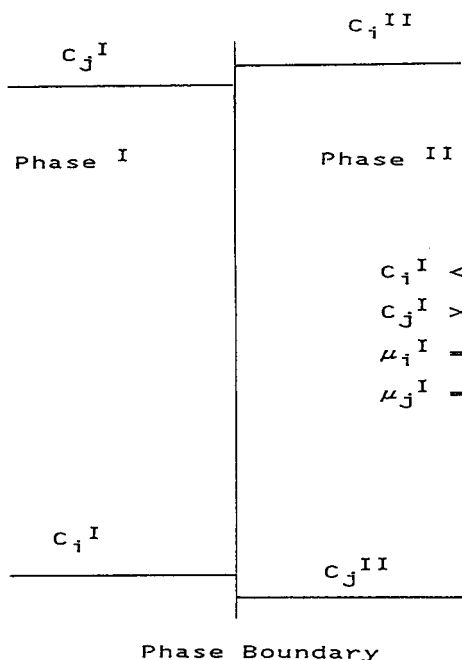


Fig. 1. Equilibrium Separation

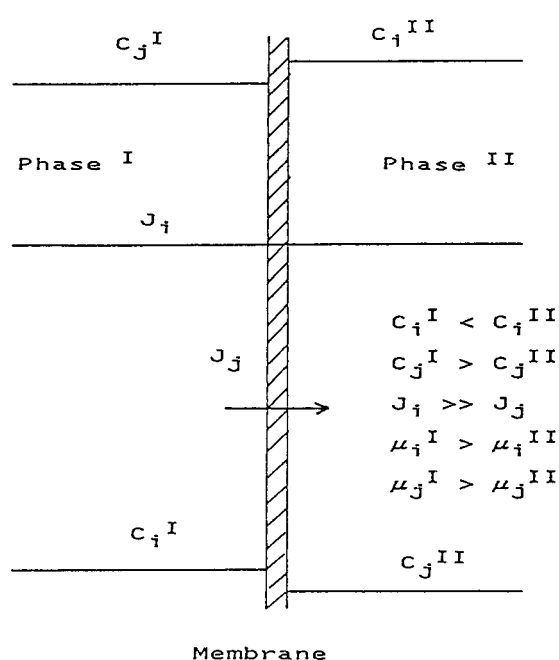


Fig. 2. Membrane Separation

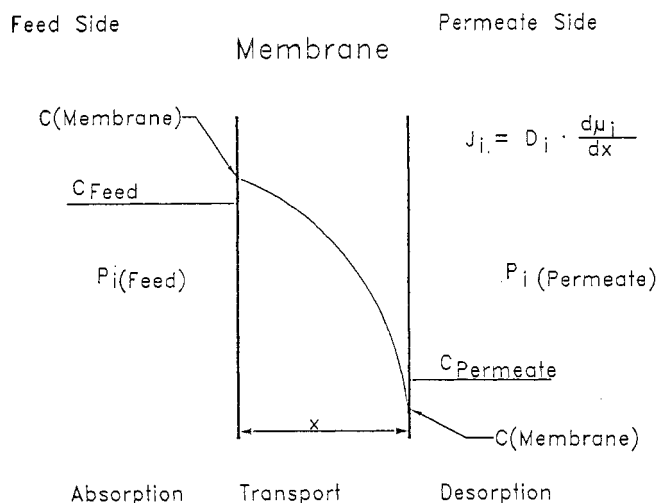
of the migrating components from the side of the lower chemical potential. If this is not done, equilibrium would be reached and no separation would occur, in most cases one of the phases would vanish.

Some mechanism must exist in the membrane which is improving the transport of one component and impeding the transport of the other. Membranes can in a first approximation be classified according to the means of such impediment.

- Porous membranes discriminate according to size of particles or molecules.
- Non-porous membranes discriminate according to chemical affinities between components and membrane materials.

In porous membranes diameter of pores vary in a large range, with several microns in microfiltration and several nanometers in ultrafiltration. A gradient in hydraulic pressure acts as the driving force. Small molecules of the solvent of a solution, usually water, can pass through the pores, whereas particles or large molecules are retained. Whatever the size of a particle, the mechanism on which separation is based is sieving or filtration.

There exist a long and tedious discussion about the distinction between porous and non-porous membranes, which eventually boils down to the definition of a pore. The best answer to this question can still be found in the classical book of Hwang and Kammermeyer (1) "There exists an unresolved question as to whether any membrane, so-called porous or non-porous, will act to some extent as a microporous medium. Even the membranes that we call "non-porous" may have a number of minute pore whose diameter will be in the 5 to 10 Å range. However, rightly or wrongly, such structures are considered non-porous, and their behaviour would seem to justify this view point".



**Fig. 3. Solution—Diffusion Mechanism**

As porous membranes are best characterized by their separating mechanism, so are non-porous membranes. Today it is generally agreed that mass transport through non-porous membranes can best be described by the so-called "Solution-Diffusion-Model". Following this model (fig. 3) the overall mass transport can be separated into three consecutive steps:

- Sorption of a component out of the feed mixture and solution in the membrane material.
- Transport through the membrane along a potential gradient.
- Desorption on the second side of the membrane.

Preferential solubility of a component of the feed mixture in the membrane material may be due to a number of different interactions: ionic-ionic interaction, ionic-dipol interaction, dipol-dipol interaction.

A membrane comprising fixed ions in its polymer matrix (ion-exchange membrane) will preferentially adsorb and "dissolve" ions of opposite charge but repel those of the same charge. Membranes with fixed ions or dipoles will preferentially adsorb and dissolve molecules with dipoles, e.g. water, but will repel non-polar molecules. Therefore, a potential classification of non-porous membranes could be found in the nature of the functional groups comprised in the membrane.

- Polar or hydrophilic membranes.
- Non-polar or hydrophobic membranes.

Another classification could follow the driving force responsible for the transport.

- Gradient in electrical potential
- Gradient in hydraulic pressure
- Gradient in vapor pressure
- Gradient in concentration

As one and the same membrane may be used for different processes it has been common practice to classify non-porous membranes rather according to processes.

The most important ones are:

- Reverse Osmosis
- Electrolysis and Electrodialysis
- Gaspermeation
- Pervaporation.

Reverse Osmosis is widely used in the desalination and demineralization of saline water. The feed may be sea water and brackish water and the product drinking water or tap water may be used and pretreated in the production of deionized water. Hydraulic pressure on the feed side maintains the necessary driving force, hydrophilic membranes with high affinities towards water, but high rejections towards ions, are used.

The major application for ion exchange membranes is still found in the chlor-alkali electrolysis. Cation exchange membranes, comprising fixed anions, separate anode and the cathode compartment in an electrolysis cell. Sodium ions can pass through the membrane and form sodium hydroxyde, whereas chloride ions are repelled and cannot pollute the cathode compartment. Nearly as important is the application of ion exchange membranes in electrodialysis. Cations and anions can pass out of salt solutions through the respective oppositely charged membrane. Thus a saline solution can be split into two streams, one with a lower, the other with a higher salt content than the original solution. Both effects are utilized, the product of an electrodialysis process may be the desalinated stream, or the concentrated stream. The latter is for example important in the production of salt from sea water in Japan, as a preconcentration step.

Separation of gaseous mixtures by permeation through non-porous membranes is fairly common in specific industries. Nearly all ammonia producing plants are today equipped with a membrane system for the recovery and recirculation of hydrogen from purge gas. Prepurification of natural gas by permeation of acid components like  $\text{CO}_2$  or  $\text{H}_2\text{S}$  through membranes is another application. Air is separated by membranes into an oxygen and a nitrogen enriched fraction. Especially the production of enriched nitrogen, with purities between 95 and 99 % at small capacities has become a serious competitor for adsorption or cryogenic processes.

The most recent separation process using non-porous membranes is Pervaporation. This process is very closely related to gas separation and vapor permeation, as in all three processes the difference in partial vapor pressure is acting as the driving force for the transmembrane transport. In Pervaporation the feed side partial vapor pressure is equal to the saturation pressure, in vapor permeation, it is equal or slightly below saturation and in gas permeation it is significantly below saturation conditions.

Pervaporation can be used for a number of different applications. Hydrophilic membranes preferentially permeate water and retain less or nor polar organics. Organophilic membranes, in contrast, preferentially permeate non-polar organics, but retain water. Both types of membranes can additionally be used for the separation of more polar organics from less polar ones, especially when water is absent.

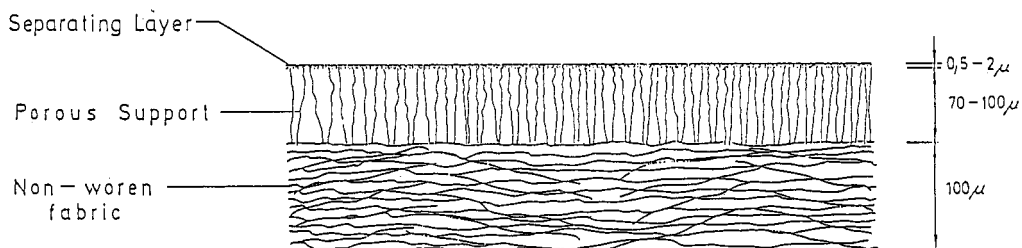


Fig. 4. Cross Section of Composite Membrane

Pervaporation membranes are usually of the composite type (fig. 4). In a composite membrane the different fractions, like separation and mechanical stability, are attributed to different layers. Thus composite membranes can combine very thin and highly selective separation layers with rigid, mechanically and thermally stable backing layers.

From fig. 5 the basic principles of a Pervaporation process are shown. The membrane separates the feed compartment from the permeate compartment. The liquid feed at a given temperature and composition is passing over the membrane. At the permeate side partial vapor pressures are maintained well below the values at the feed side. At least one of the components then is transported preferentially through the membrane, the permeate side of which it leaves as a vapor. Usually the permeating vapor is condensed at reduced pressure, the presence of non-condensable gases would hinder the transport of the permeating vapor from the membrane to the condenser. The necessary heat for the evaporation of the permeate is taken from the sensible heat of the feed mixture which is cooled down accordingly. In contrast to all other separation processes employing non-porous membranes, a phase change for the permeating substance occurs in the transgression from feed to permeate. Insofar Pervaporation is a unique process as not only matter, but also heat is transported through the membrane. The retentate leaving the membrane not only differs in concentration but also in temperature from the original feed.

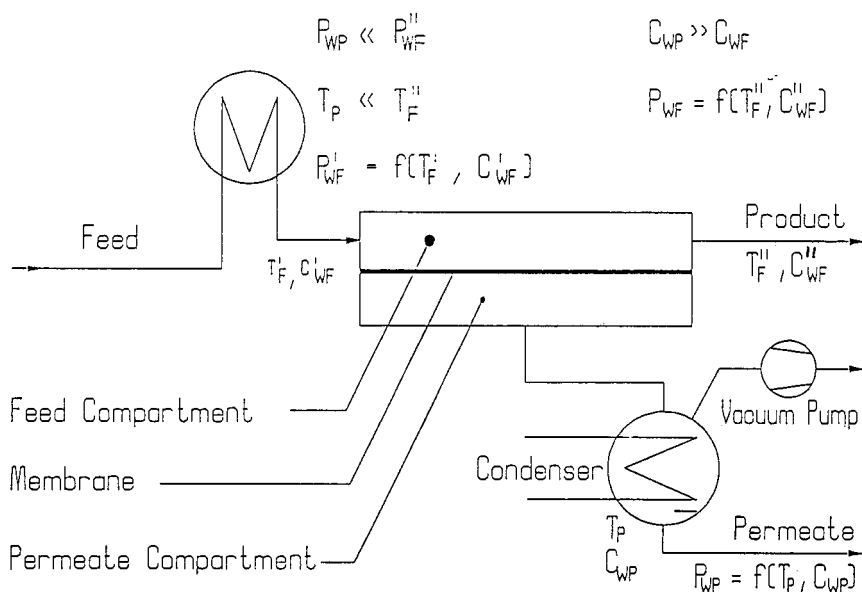


Fig. 5. Pervaporation : Basic Principles

This temperature reduction in the Pervaporation effect has two different disadvantages:

- The partial vapor pressure of the better permeable component is not only reduced by its reduced concentration in the retentate, but also by the decrease in temperature. For the retentate the driving force is lower than for the feed.
- The transmembrane flux decreases with decreasing temperature.

In order to avoid too low temperatures it has become common practice to split the total membrane area into a number of stages, as shown schematically in fig. 6. The preheated feed stream enters the first stage, where heat is lost for the evaporation of the permeate. At a lower temperature the retentate is passed through an intermediate heat exchanger where it is reheated to the original feed temperature, and fed to a second membrane stage. This procedure is repeated as many times as are necessary to reach the specified composition of the final retentate. Size and number of stages as well as allowed temperature drop over a stage are a matter of optimization in the design of any Pervaporation plant.

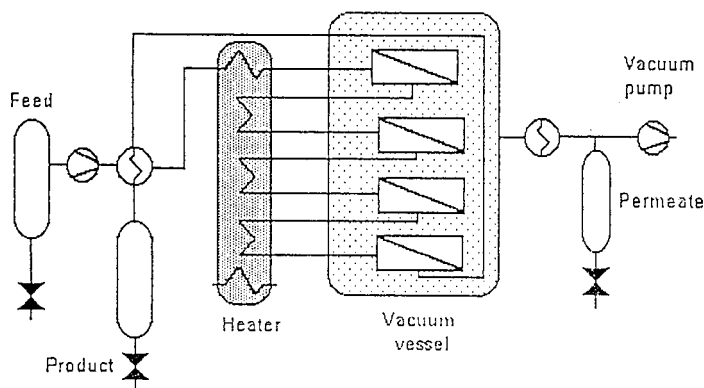


Fig. 6. Pervaporation

The Pervaporation membranes used today in industrial applications are of the hydrophilic type. They preferentially permeate water but retain nearly all organic molecules. The main application of these membranes is therefore the removal of water from its mixtures with organic liquids.

In fig. 7 the vapor liquid equilibrium curve for the system 2-propanol (IPA)-water is plotted. The upper line in the diagram indicates the composition of the vapor in equilibrium with the liquid, the bottom curve gives the composition of the permeate of a Pervaporation process. It has to be kept in mind that this composition is not in equilibrium with the liquid mixture but is obtained at a specific difference or ratio of the vapor pressures of water at the feed and permeate side of the membrane. Although water is the less volatile component, it is enriched in the permeate over the whole concentration range. Even the azeotrope, clearly visible in the vapor-liquid equilibrium is not reflected in the permeate composition. In contrast it seems that the Pervaporation process reaches a maximum separation with the feed at the azeotropic composition. From this diagram the preferred application of a Pervaporation membrane is clearly understandable. At high water concentration a Pervaporation process could be used, but would not be very efficient. A large portion of water had to pass through the membrane, enrichment of IPA in the vapor is even higher than enrichment of water in the permeate, and in a distillation process at least the heat of evaporation could be partially recovered.

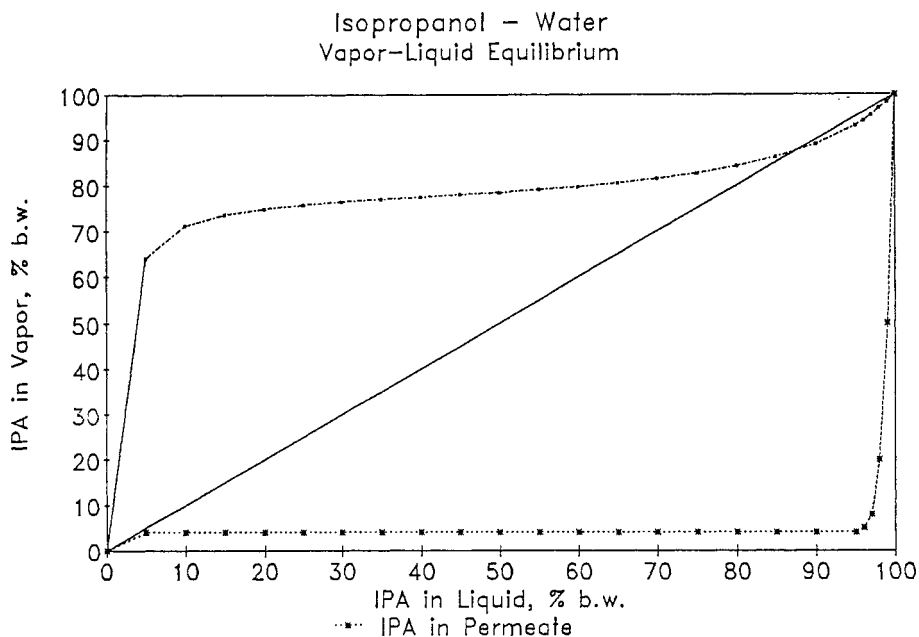


Fig. 7

At low water concentration, however, distillation becomes less and Pervaporation more and more effective. For the purification of isopropanol from its mixture with about 50 % of water, as obtained in normal IPA production, the best means is then a combination of distillation and Pervaporation. In a distillation step the mixture is pre-concentrated close to the azeotropic composition, then it is further dehydrated by Pervaporation to a final water content of 0,5 % (fig. 8). Any lower water content could be reached, simply by adding membrane area to the Pervaporation step. In fig. 9, costs for such a hybrid system are presented, clearly showing the advantage of the hybrid system.

Similar considerations as for the IPA-water system are valid for a large number of other aqueous organic mixtures. Ethanol, for example, is dehydrated using the hybrid scheme today in large plants.

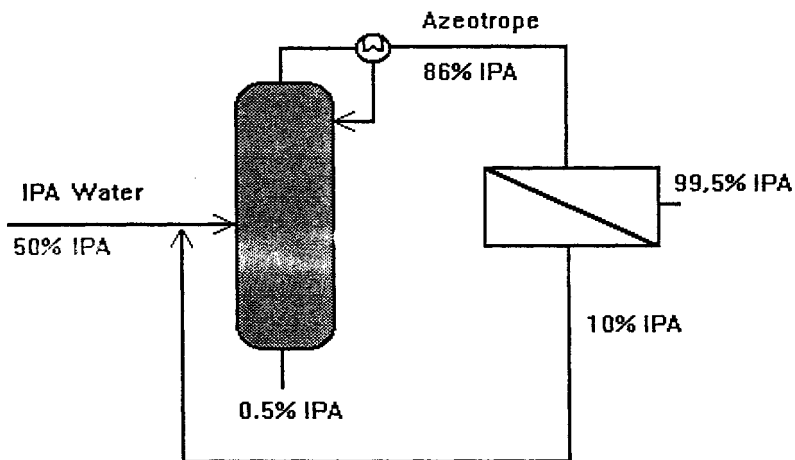


Fig. 8. Hybrid Process

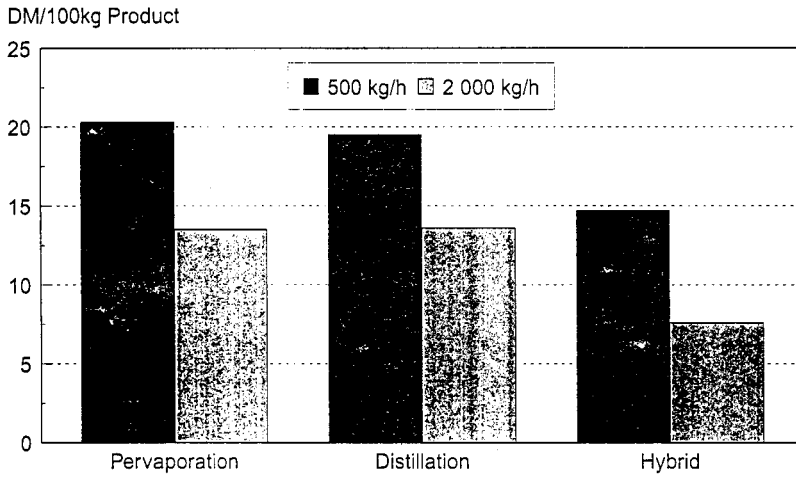


Fig. 9. Operation Cost : 50% — 99,5% IPA

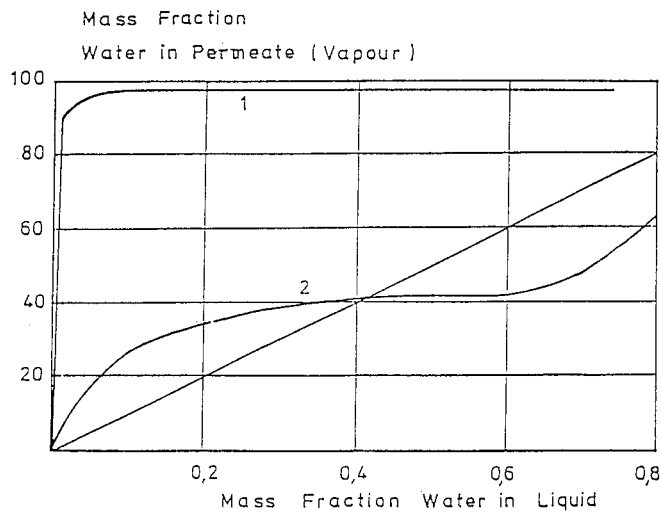
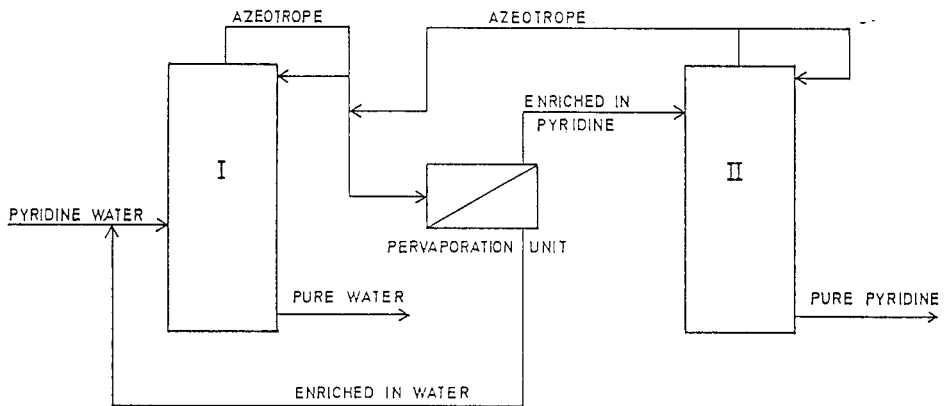


Fig. 10. Pyridine—Water : 1, Pervaporation; 2, Liquid—Water Equilibrium



PYRIDINE WATER SEPARATION  
COMBINATION AND DISTILLATION , AZEOTROPE - SPLITTING BY PERVAPORATION

Fig. 11



In some cases where the azeotrope point is not close to one side of the VLE-diagram, final dehydration of the organic liquid might not be the optimal way. An example is given in fig. 10 for the pyridine-water system. The azeotropic mixture comprises fairly equal concentrations of pyridine and water. Here, a scheme as shown in fig. 11 might be more feasible. The azeotrope from the top of both columns is split by Pervaporation into a water rich and pyridine rich fractions, which are then passed to the respective columns. Again, optimized design of the columns and the Pervaporation system are necessary.

Another application of hydrophilic Pervaporation membranes is schematically shown in fig. 12. In a chemical reaction, e.g. an esterification, water is a by-product. Continuous removal of this water will shift the equilibrium of the reaction to the side of the product and eventually total conversion of one of the educts can be reached. Improved productivity and reduced effort for the purification of the product are the main advantages of this scheme. A medium size plant, operated in batch mode, has been started about 16 months ago and is producing different esters by this scheme. A much larger plant, producing an ester in a straight-forward process, using a series of reactors and Pervaporation stages, is under construction.

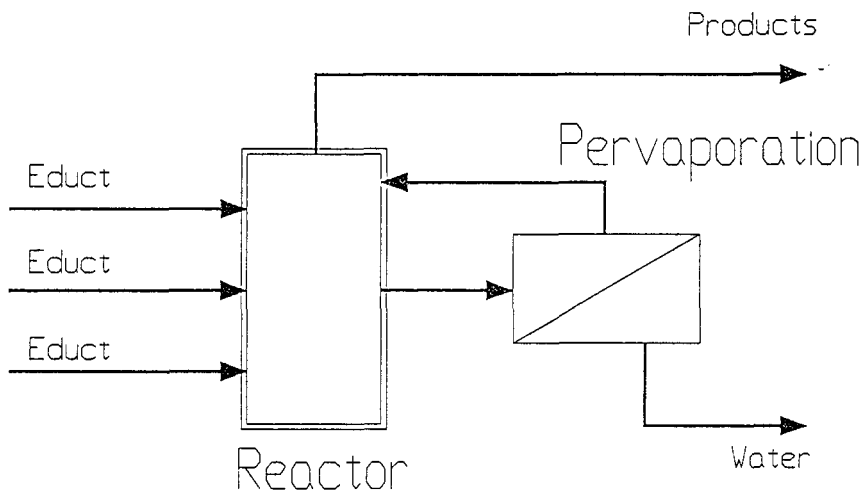


Fig. 12

Pervaporation plants employing organophilic membranes, are much less numerous than those with hydrophilic membranes. The larger number of plants for organic removal are, in fact, not really Pervaporation plants but using air, laden with organic vapors, as feed streams. For this process the term "vapor permeation" is used. The differences to a Pervaporation process are found in the fact that cooling of the retentate is avoided, as the permeating component is already supplied as a vapor. Furthermore, the feed side partial vapor pressure of organics may reach in a few exemption the saturation level, but will usually be below this value. Vapor permeation thus can be regarded as a process in between Pervaporation and gas separation, partially overlapping with both.

Organic-organic separation by non-porous membranes has been in the fiftieth the subject of intense investigations, especially in the US. Today, first membranes are available at least for the removal of more polar organics, like methanol and ethanol, from their mixtures with less polar organics. A first pilot plant for one of these applications is supposed to start its operation at the end of this year.

Separation of fluid mixtures by means of membrane process today already plays an important role in various industries, especially in biotechnology, gas treatment, water treatment and chemical industry.

Regarding the fact that the first membranes applicable for industrial processes have been developed about 25 years ago, and new membranes and applications are produced and found, it can be expected that the role of membranes in separation processes will continue to improve. Membrane processes, however, will probably not displace more classical separation processes, but in hybrid systems will supplement them and lead to technically, economically and environmentally more efficient separation.

- 1) S. T. Hwang, K. Kammermeyer  
Membranes in Separation, Wiley and Sons  
New York, 1975, p. 67