Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Membrane Pervaporation: Separation of Organic/aqueous Mixtures

H. L. Fleming[a]
[a] GFT, Boonton, New Jersey

To cite this Article Fleming, H. L.(1990) 'Membrane Pervaporation: Separation of Organic/aqueous Mixtures', Separation Science and Technology, 25: 13, 1239 — 1255
To link to this Article: DOI: 10.1080/01496399008050389
URL: http://dx.doi.org/10.1080/01496399008050389

SEPARATION SCIENCE AND TECHNOLOGY, 25(13-15), pp. 1239-1255 (1990)

MEMBRANE PERVAPORATION: SEPARATION OF ORGANIC/AQUEOUS MIXTURES

H.L. Fleming
GFT
400 Myrtle Avenue
Boonton, New Jersey 07005

ABSTRACT

The recovery of water-laden solvents by membrane pervaporation has become an *industrially-accepted* practice. A review of the technology is presented, along with discussion of the potential for removal of organics from water.

INTRODUCTION

Over the past five years membrane pervaporation has gained widespread acceptance by the chemical industry as an effective process tool for separation and recovery of liquid mixtures. It is currently best identified with dehydration of liquid hydrocarbons to yield high purity organics, most notably ethanol, isopropyl alcohol, and ethylene glycol. Due to its favorable economics, efficacy, and simplicity, it can be easily integrated into distillation and rectification processes and, depending upon the specific process, even replace them. Presently, considerable data is available on industrial scale processes utilizing pervaporation to evaluate its performance. This paper will review membrane pervaporation for the separation of organic/aqueous mixtures in view of current developments.

BACKGROUND

Pervaporation is characterized by the imposition of a barrier (membrane) layer between a liquid and a gaseous phase (Figure 1), with mass transfer occurring selectively across the barrier to the gas side.

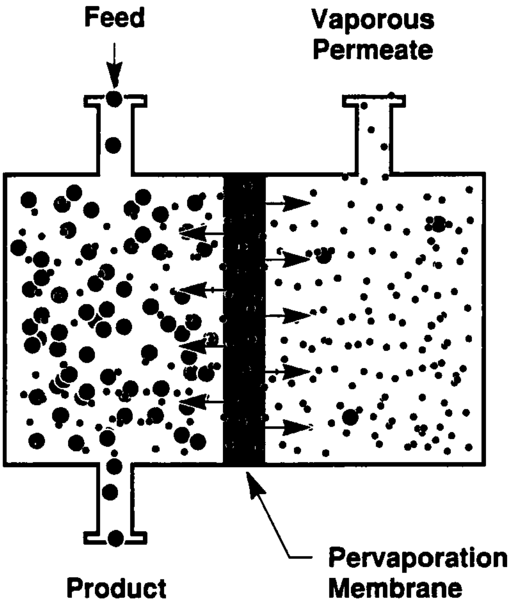

FIGURE 1
PRINCIPLE OF PERVAPORATION

Because of the unique phenomenon of phase change required of the liquid solutes diffusing across the membrane (permselective "evaporation" of the liquid molecules) the process is termed pervaporation. As different species permeate through the membrane at different rates, a substance at low concentration in the feed stream can be highly enriched in the permeate. Thus, separation occurs, with the efficacy of the separation effect being determined by the physico-chemical structure of the membrane.

Binning et al.(1,2), working in the late 1950's at Amoco were the first to recognize that a system consisting of permeable substances in the liquid phase on one side and in the gas side on the other side possessed economic potential. This was demonstrated with cost calculations for isopropanol drying, in comparison with azeotropic distillation.(3) After interest was aroused, several articles were published in the 1960's, with the focus on the separation mechanisms involved (Michaels et al.(4), Schrodt et al.(5), Long (6)). Although there was some attempt at commercialization at Ionics Inc., activity declined, with little work occurring until the middle 1970's. Traditional economics were changed by the energy crisis, and low-energy membrane processes gained popularity.

In the mid-1970's, GFT commercialized an economical pervaporation process for dehydrating ethanol and producing high purities which rivaled azeotropic distillation. Following pilot trials in Europe, the first industrial plants were built in Brazil and The Philippines for processes utilizing continuous fermentation of sugar cane, bagasse, and sweet sorghum containing 5-7% ethanol, primary distillation to a mash containing 80-85% ethanol, with vacuum pervaporation to 96%.(7) The primary driving forces for the GFT process were:

- No additives necessary for final separation
- Reduced energy demand, as only that fraction of the liquid which is to be evaporated has to be vaporized
- Only a small vacuum pump is necessary, as condensing permeate continually creates a driving force vacuum

- Closed loop operation, with only a small volume of recycled permeate
- Much lower capital cost
- Cheap cooling water, with recovery of initial thermal energy supplied as low pressure (<90 psi).

The GFT process is shown schematically in Figure 2 for ethanol dehydration. In the later 1970's, and continuing into the early 1980's, other integrated distillation/pervaporation plants were built in Europe and Asia.

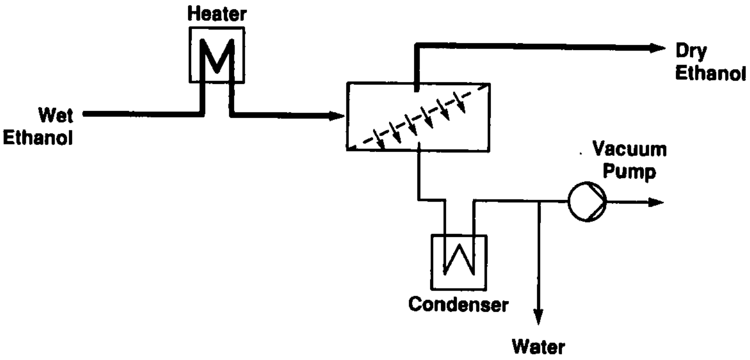

FIGURE 2

Most of these were of moderate capacity, typically 1000-50,000 liters/day ethanol recovered. As the cost of the permselective membrane module was reduced, and selectivity increased (with the corresponding capital cost decreasing), ethanol purity increased (99.85% was easily attainable), the integrated process gained industrial acceptance.

In the mid-1980's multiple membrane options were developed by GFT, all based upon novel proprietary asymmetric composite polymer technology for producing economical, chemically and thermally stable membranes in a flat plate geometry. As exemplified in Table 1, a number of composite membranes were developed, each exhibiting high selectivities (10-1000) for specific separations.(8)

TABLE 1
RELATIVE PERMEATION RULES

PVA COMPOSITES
    Water >> MeOH>EtOH>>Other Organics
SILICONE COMPOSITES
    MeOH>EtOH>Aldehydes>Ketones>>Water
    Parafins>Olefines
MODIFIED CELLULOSESTERS-ESTERS
    Aromatics>Parafins
    Olefins>Parafins
    Dienes>Olefins
    Branched Parafins>n-Parafins
    Low MW Parafins>High MW Parafins

Utilizing GFT's process, which incorporated a vacuum on the permeate, it became industrially feasible to dehydrate and recover solvents such as acetone, ethylene glycol, and tetrahydrofuran, as well as separate mixtures of liquid hydrocarbons. Today, a number of commercial pervaporation plants exist for recovery of solvents, removal of organics from wastewaters, dealcoholization of wines and liquors, as well as many more for ethanol dehydration. In fact, a 150,000 liter/day ethanol dehydration plant in Betheniville, France, went on stream in early 1988, and became the world's largest pervaporation facility.

FUNDAMENTALS

Pervaporation differs from other membrane processes in that the membrane constitutes a barrier between the feed in the liquid phase and the permeate in the gas phase. The driving force which is applied across the membrane creates a chemical potential gradient in the liquid phase, and the selectivity of the membrane is then the determining factor in the relative flow of the different components. In contrast to reverse osmosis, the osmotic pressure is not limiting, as the permeate is kept under saturation pressure.

In the GFT process, a vacuum pump is used to keep the permeate pressure low, supplying a sharp partial pressure driving force. The permeate is then condensed, separated, and either recovered or recycled. As mass flux, and sometimes selectivity, is enhanced by temperature gradients, the feed temperature is usually elevated as well, with heat recovery from the product liquid. The process is perpetually driven by condensation of the permeate, creating a significant vacuum and resulting in lower temperatures on the permeate side of the membrane. Compared with conventional membrane processes such as ultrafiltration or reverse osmosis, fluxes in pervaporation are generally low (< 20 kg/m^{2}h). However, selectivities can be extremely high, often exceeding 1000.

The key to successful pervaporation lies in the membrane. Selectivity, and flux to a large extent, is essentially controlled by this permselective barrier between the feed liquid and the gaseous permeate. Transport is generally described to be a series of three events: 1) preferential sorption of mixture components, 2) diffusion through the membrane, and 3) desorption on the permeate side. Sorption is controlled by specific polymer chemistry, and its interaction with the liquid mixture. Hydrophilic membranes tend to sorb hydrophilic compounds, such as water, for example. Vaporization on the permeate side is generally considered to a fast, non-selective step, except for isolated instances where the relative vapor pressures in the membrane, on the permeate side, and the feed mixture are similar (i.e., removal of trace organics from groundwaters).(9)

The choice of membrane material is critical.The key to commercialization of pervaporation has been the development by GFT of asymmetric composite membranes, each layer of which fulfills a specific requirement. The primary family of membranes for water permeation (e.g., ethanol dehydration, solvent recovery) utilize a supporting layer of nonwoven porous polyester, on which is cast either a polyacrylonitrile or polysulfone ultrafiltration membrane, and finally a 0.1 µm thick layer of cross-linked polyvinylalcohol. The PVA provides ultimate separation, with the entire structure being necessary for chemical and thermal stability, and to provide optimum transport properties. Other separations are generally accomplished using the same two sublayers, varying the top layer to modify selectivity. Polydimethyl siloxane (PDMS), for example cast upon PAN is useful for retarding polar compounds versus nonpolar, such as processes for dealcoholization of liquors. Films of cellulose esters are one example of membrane material that exhibit separation of organic/organic, such as olefin/parafins, and aromatic/parafins in petrochemical processing.

PERVAPORATION PROCESSES

Over the past few years, the number and variety of industrial pervaporation plants has dramatically increased. Many plants of a minimum of 5000 liters/day product capacity are in operation, with many more in development and pilot phases. In Europe and Asia, the primary driving forces have been: 1) reduced energy costs, 2) low overall system capital cost, and 3) superior separations possible, with no limitations imposed by thermodynamic azeotropes, relative to azeotropic distillation. In North America, the driving forces have been somewhat different: 1) pollution-free, closed loop operation, minimum wastewater and no entrainers, and 2) small, compact units with low capital costs for retrofitting existing plants to increase existing bottlenecked capacity versus distillation and adsorption with molecular sieves. Although considerably lower in pervaporation than other competing processes, energy is much less a factor in the U.S. than is pollution abatement in the selection of pervaporation or integrated pervaporation.

Commercial pervaporation processes are generally grouped into the following categories: 1) water removal from organics, 2) organic removal from water, and 3) organic/organic separations. Although there is considerable activity and interest in all three areas, dehydration processes of the former are more abundant, and account for the majority of plants built to date. In order to illustrate all three categories, examples will be given for each group.

ETHANOL DEHYDRATION

Dehydration of fermentation products directly, or following primary distillation, has become the classic example of membrane pervaporation. Because mass transport through the membrane determines the composition of the permeate and, hence, the selectivity, vapor-liquid equilibria, with the associated azeotropic effect, are irrelevant. Membrane pervaporation is especially effective in accomplishing such separations which are difficult by processes governed by thermodynamics, such as distillation.

In Figure 3 permeate compositions for a typical PVA composite

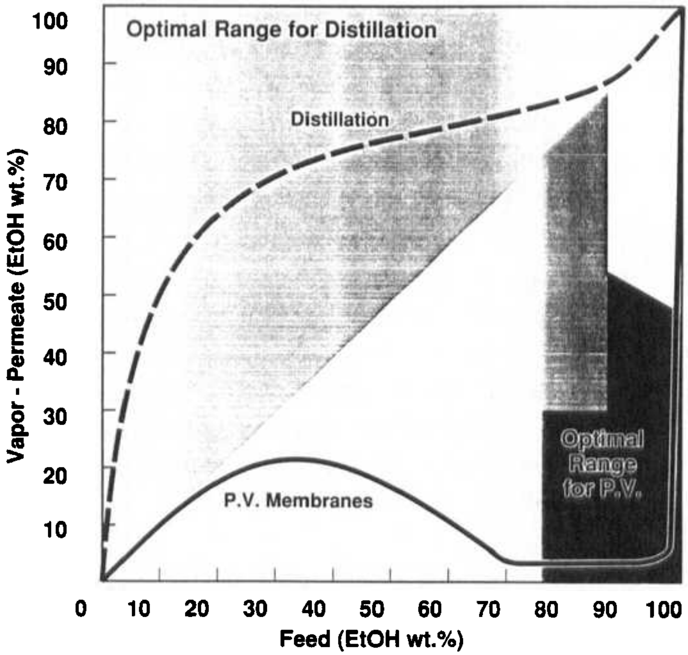

FIGURE 3

ETHANOL-WATER SEPARATION

pervaporation membrane are plotted over feed composition of ethanol-water mixtures, together with the respective vapor-liquid equilibrium curve at ambient conditions. It can be easily seen that pervaporation exhibits its highest efficiency in a concentration range of the mixture where distillation is least effective, namely at high ethanol concentrations. Conversely, at high water levels, distillation is more thermodynamically efficient.

As a result hybrid processes, integrating pervaporation with distillation, have been shown to be the most effective solution in both operating and capital costs. Such a system is shown in Figure 4. Permeate from the pervaporation membrane unit (containing 5-50 wt.% EtOH) is typically recycled back to the distillation columns. The result is an integrated system capable of continuously producing ethanol in multiple purities up to

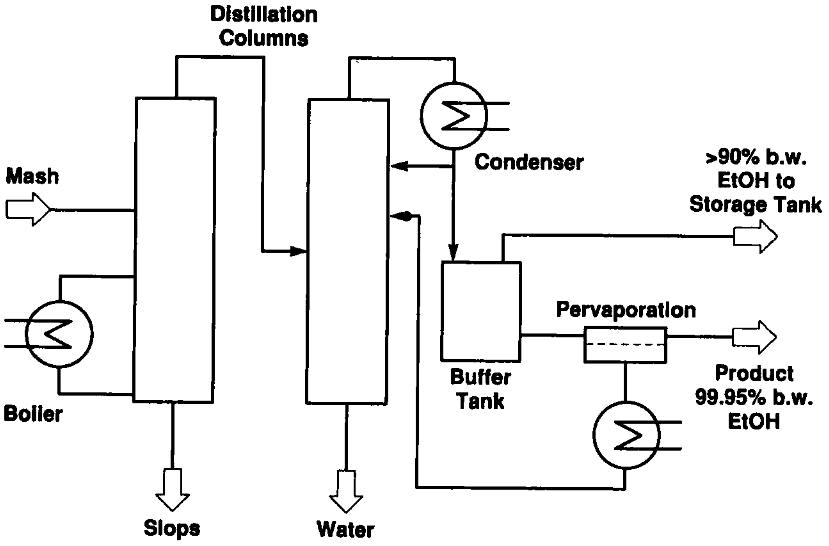

FIGURE4
INTEGRATED DISTILLATION/PERVAPORATION

99.95 %, with low energy consumption, almost no wastewater generation, and no chemical additives as entrainers required. No additional heat input is necessary, as the still overheads are fed directly to the membranes. The spent mash preheats the recirculating permeate and feed. Because of the continuous recycling, ethanol losses are close to zero (averaging 4% for conventional azeotropic distillation), with virtually no environmental pollution. The cost of entrainer is also not to be minimized. A 140,000 liter/day ethanol plant may use 120,000-150,000 liters of benzene. At the current price of $0.95/liter delivered, a net savings of approximately $120,000 annually is seen on this moderately sized plant. Typically, 2,000 BTU/gal water of low quality steam is required for pervaporation, versus the 11,200 BTU/gal required for azeotropic distillation.

Typical capital system costs for skid-mounted, stand-alone pervaporation systems for ethanol production may be quite attractive. It has been seen that there is some economy of scale at higher volume systems, as membranes comprise more of the cost, with ancillary equipment costs decreasing. Capital costs for pervaporation tend to be roughly equal to azeotropic distillation at large scale green field facilities, and cheaper at reduced scale and retrofits. The same is true of regenerative adsorption, with adsorption capital costs roughly equivalent at small scale and 10-20% cheaper at larger scale. However, these figures for adsorption are misleading, as operating costs including energy, adsorbent replacement, and disposal of spent adsorbent are much higher, and do not exist for pervaporation.

DEHYDRATION OF LIQUID HYDROCARBONS

Removal of water from liquid organic mixtures now accounts for the largest segment of new industrial pervaporation plants. This is even more true in the U.S. than in Europe or Asia because capital costs and environmental issues are of primary concern, and fewer ethanol plants are being built. In the chemical process industry there are literally unlimited numbers of organic streams which become contaminated with small (<10

%) amounts of water. In most cases, it is economically desirable to remove this water to ppm levels prior to the next processing step. Even if distillation is possible (many multicomponenet azeotropes formed) it becomes prohibitively expensive to remove small amounts of water. Adsorption with desiccants such as aluminas and zeolites are typically employed.

Although capital costs of adsorption are usually low (assuming existing beds are in place), operating costs including adsorbent replacement, high energy of regeneration, adsorbent disposal, and hazardous gaseous effluents are significant deterrents in many cases. Further, very small volume streams (<10-20 gpm) require small, modular plants because of space requirements, with simple, unattended operation. This feature is considered a strength of pervaporation systems relative to adsorbers. Membrane pervaporation has made major contributions to these applications and is now a conventional process option for dehydration of liquid hydrocarbons.

TABLE 2
INDUSTRIAL EXAMPLES OF SOLVENT DEHYDRATION

SOLVENT	WATER CONTENT FEED (WT.%)	PRODUCT (PPM)
1-Butanol	8.4	350
n-Butanol	1.41	800
t-Butanol	10.4	810
Acetone	3.8	90
THF/Benzene	0.255	220
Xylene	0.04	18
Methanol/IPA	0.21	302
Methanol/BTX	1.1	40
Caprolactam	10.3	171
Ethanol/IPA	0.6	610
Ethanol/MeOH	2.9	1800
Ethanol/Benzene	14.1	120
PFP	4.2	120
Allylalcohol	4.85	62
Trichlene	0.01	80
MEK	4.0	22
Methylene Chloride	0.20	14
Ethylene Dichloride	0.22	10
Chlorothene	0.0617	12

The list of organics which are currently dehydrated and recovered given in Table 2 serves to illustrate the strength of pervaporation. The degree of water removal is primarily dependent upon the desired economics. Generally, 200-1000 ppm levels of water in the product are easily attainable. To approach 1 ppm or less requires much more membrane surface and, in some cases, reduced permeate pressure with a larger vacuum pump. Because of reduced solubility and increased chemical potential driving force, water fluxes tend to be even greater for solvent dehydration than for ethanol. While dependent upon feed concentration, 1-10 kg/l-hr are not unusual, resulting in reduced membrane requirements and capital and operating savings. Feed water contents of 0.1-10 wt.% are economical with pervaporation. Greater water is best separated with extraction or other bulk techniques, while at lower water contents, adsorption may become competitive.

The versatility of the pervaporation process for solvent dehydration is illustrated in Figure 5. Vapor-liquid equilibria for acetone/water binary mixtures are given at ambient conditions. The performance of two commercial GFT pervaporation membranes are also plotted on the same scale. It is seen that the hydrophilic polyvinylalcohol composite membrane is highly selective for permeating water preferentially over most of the concentration range, with the ability to obtain solvent with extremely low water content. Conversely, the organic-selective polymethoxysilane membrane exhibits virtually the opposite behavior, permeating acetone selectively from water. Both types of processes are industrially feasible within certain concentration ranges, and both are much more selective that processes such as distillation which rely on thermodynamic equilibria as their mechanism of separation.

The typical dehydration process is illustrated by purification of dichloroethylene in Figure 6. In this pilot plant data, saturated EDC at 0.2 wt.% from a condenser is preheated and sent to the pervaporation stack containing PVA membranes. Purified EDC containing <10 ppm water is obtained in one pass. The permeate, in this case containing 45-50 % water,

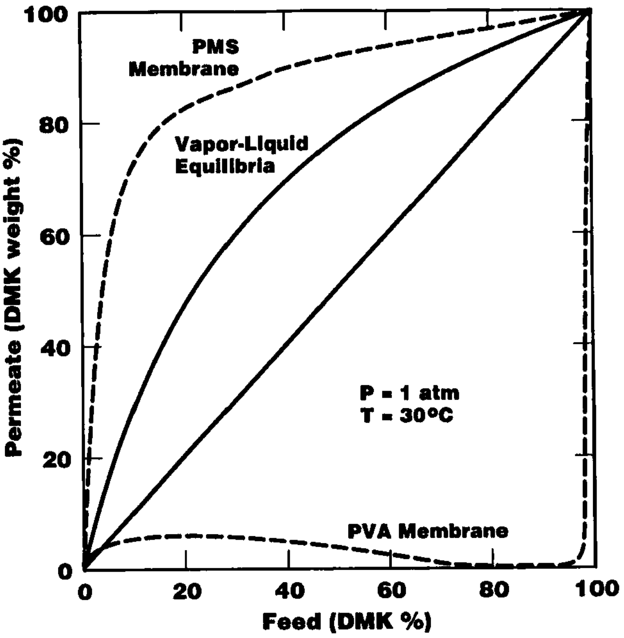

FIGURE 5

ACETONE-WATER THERMODYNAMICS

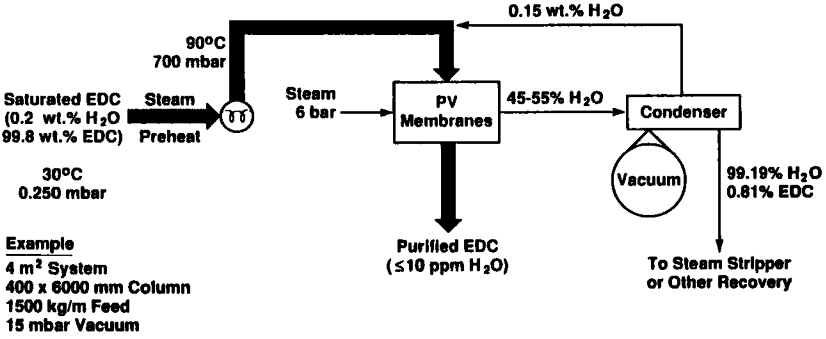

FIGURE 6

PURIFICATION OF DICHLOROETHYLENE

is condensed. Phase separation occurs, with the organic-rich phase recycled to the pervaporation membranes for further purification, and the aqueous phase sent to an existing steam stripper or disposed.

The latter points out another strength of the pervaporation process, namely the ability to use the limited solubility of water in organics to phase separate the permeate. In many systems, a secondary phase separator in line allows much greater organic recovery, as well as a major reduction in the volume of aqueous water. In most cases, the aqueous phase is dilute enough to allow disposal in a nonhazardous manner. This example with dichloroethylene is typical for numerous organic systems of industrial interest, and is employed extensively. Commercial examples include treatment of halogenated refrigerants and jet engine fuels.

Another example of industrial interest is that reported by Texaco(10) for dewatering isopropyl alcohol. As shown in Figure 7, Texaco utilized

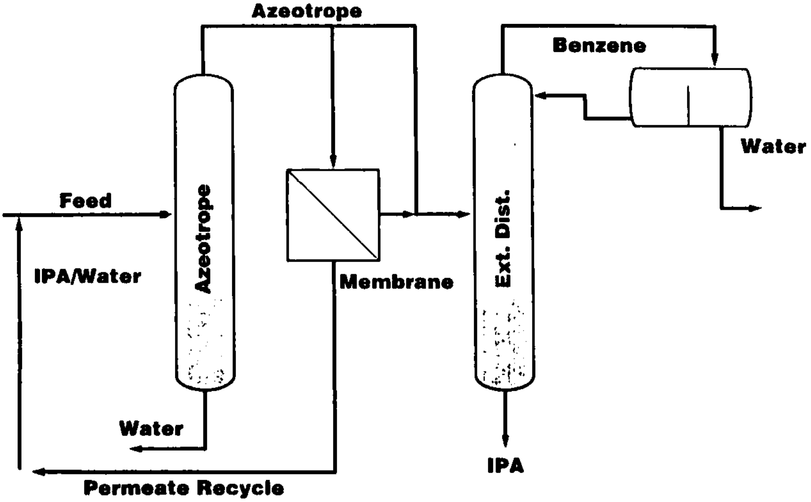

FIGURE 7
IPA RECOVERY PROCESS

pervaporation for retrofitting an existing azeotropic/extractive distillation system. In this process pervaporation debottlenecks IPA plant capacity by taking IPA at 85 % up to 95% prior to feeding to the extractive distillation column. Only a small pervaporation system is necessary because of the large driving force and low water load. Yet, it eliminates capital requirements for additional extractive distillation capacity. Further, a more desirable entrainer than benzene can be used because of the lower water load on the extraction column.

ORGANICS FROM WATER

Only in the past year have membranes and processes become commercially available for selectively permeating organics from aqueous streams. Because of the associated requirements for good chemical and thermal stability in solvents, most hydrophobic membrane materials, those which are most selective to organics, are not compatible. Currently available composite materials which have been developed for this application are a compromise, with good chemical properties are limited separation abilities. However, some processes are now commercially viable, while others are developing rapidly.

The best known of the commercial processes is the GFT process for dealcoholization of beers, wines, and liquors. Using PMS or PDMS-type membranes, reduction or removal or ethanol has been demonstrated in various alcoholic beverages. As in the pilot-scale example in Figure 8 for beer, selective permeation of ethanol is straightforward, with alcohol reduction to 0.7 wt.% for "alcohol-free" beer easily accomplished. Reduction is currently limited to around 0.1 wt.% as membrane selectivity is not as good as with the PVA-based materials. Also, numerous contaminants are present. Fusel oils (amyl and propyl alcohol fractions) may also be separated in the process and recovered. Depending upon the choice of membrane, permeate quality can be controlled from 15-55 % ethanol, so that in many cases the permeate is a useful product. In production of low alcohol wines, for example, the permeate is useful as a saleable brandy.(11)

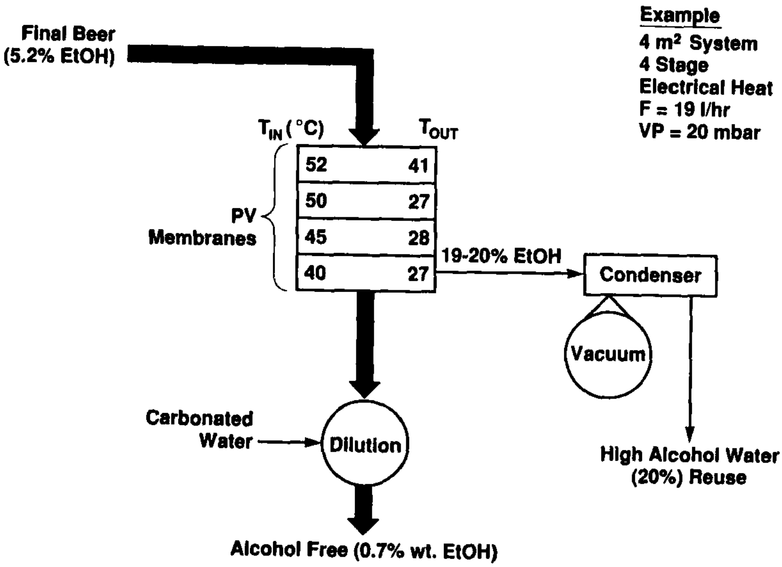

FIGURE 8

ALCOHOL REDUCTION IN BEER

Pervaporation of other organics from water is also commercially viable. Removal and recovery of trace organics from groundwaters and industrial wastewaters is underway and are commercially available.(12,13) It is being suggested that pervaporation is extremely economical for recovery in such streams as ethyl acetate, the various carboxylic acids-citric, lactic, and acetic, as well as aromatics such as phenol and benzene. decontamination of groundwaters with dioxins, trihalocarbons, and other pollutants is possible. However, the driving force for separation is low in the latter case, requiring more membrane area. Also, more sophisticated condenser and recovery systems are necessary because of the permeate volatility. Such systems have been demonstrated, however, and the total amount of material permeated is small, so that economics remain attractive.

CONCLUSIONS

Membrane pervaporation is a rapidly emerging technology for the separation of numerous organic-aqueous systems. Although not described here, hydrocarbon/hydrocarbon separations are also being conducted, and appear promising.(14) With numerous demonstrated commercial successes in Europe and Asia, it is only now finding commercial application in North America. Because of its great versatility, and inherent capability, it is rapidly taking its place among the conventional techniques utilized by the chemical separations community.

BIBLIOGRAPHY

1. Binning, R.C., et al., ACS Division Petroleum Chemistry, Preprints 3(1), 131(1958)
2. Binning, R.C., et al., Ind. Eng. Chem., 53, 45(1961)
3. Binning, R.C., and F.E. James, Petrol. Refiner., 37, 214(1958)
4. Michaels, A.S., et al., Ind. Eng. Chem.Proc. Des. Dev., 1, 14(1962)
5. Schrodt, V.N., Sweeny, R.F., and A. Rose, ACS National Mtg, Div.Ind.Eng.Chem., Los Angeles (3/63)
6. Long, R.B., ACS National Mtg, Chicago (9/64)
7. Ballweg, A.H., et al., Fuel Alcohol Conference, New Zealand (1982)
8. Bruschke, H.E., et al., U.S. Patent 4,769,140 (9/88)
9. Aptel, P., et al., J. Membrane Science, 1, 271(1976)
10. Bartels, C.R., et al., Third Int.Conf. on Pervaporation Processes, Nancy, France (9/88)
11. Escudier, J.L., and M. LeBouar, Third Int.Conf. on Pervaporation, Nancy, France (9/88)
12. Bengston, G., and K.W. Boddeker, Third Int.Conf. on Pervaporation, Nancy, France (9/88)
13. Kaschemekat, et al., Third Int.Conf. on Pervaporation, Nancy, France (9/88)
14. Rautenbach, R., and r. Albrecht, J. Membrane Science, 7, 203(1980)