


# Pervaporation Comes of Age



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This membrane process has found growing use for dehydrating organics. Uses keep increasing, mostly due to development of new, high-temperature membranes.

**A**s a separation technique, pervaporation occupies a special niche in the chemical industry — it is the only membrane process primarily used to purify chemicals. Currently, about one hundred pervaporation units are operating worldwide, most of them dehydrating solvents, such as ethanol and isopropanol. Now that pervaporation has been proven in these end-of-pipe applications, attention is turning to separations closer to the chemical reaction step — more critical to production and promising much greater benefits.

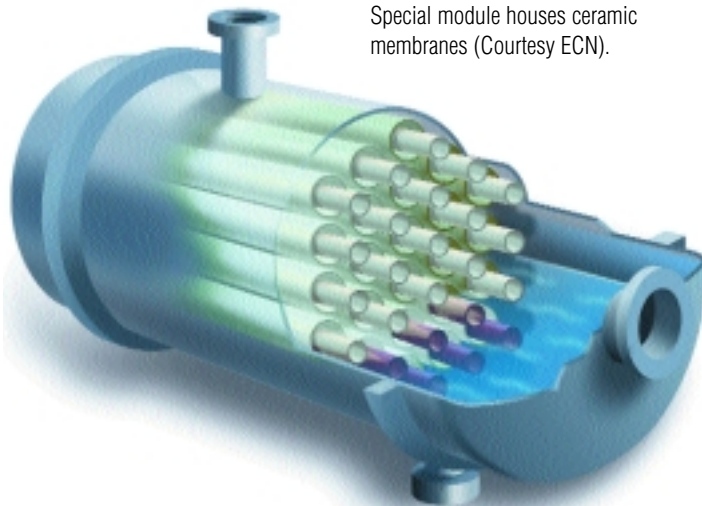
This shift in focus is accelerating the development of new, more-robust membranes with better performance that can be used at higher temperatures. Over the next few years, pervaporation will be used increasingly to enhance reactor performance, either by purifying feeds or separating reaction products. Because pervaporation is a membrane process, these separations can be integrated with the reaction step, promising quantum improvements in reaction efficiencies, yields and process economics.

In pressure-driven membrane processes, such as ultra, micro and nanofiltration, the bulk component is purified by passing it through a porous membrane that holds back the minor component. The membrane acts rather like a filter or strainer. Reverse osmosis (RO) is similar, but uses nonporous membranes. In this case, the major component selectively permeates the membrane by preferential absorption, diffusion and desorption. The solute or minor component is held back.

Pervaporation and vapor permeation processes are used in the reverse situation, *i.e.*, when the membrane is preferentially permeated by the minor component. The bulk fluid is held back by the membrane. To get a pure product stream in this situation, almost all of the permeating component has to pass through the membrane, so pervaporation and vapor permeation resort to application of vacuum to the permeate side of the membrane. Very high pressure ratios can be achieved, so the minor component can be almost completely removed without excessive pressure difference across the membrane. Undue mechanical stresses on the membrane and equipment are avoided.

Because substances that permeate nonporous membranes are reasonably volatile, application of vacuum always causes the permeate to be desorbed

Special module houses ceramic membranes (Courtesy ECN).



from the membrane in the vapor state. Hence, the term pervaporation is used if the feed to the membrane is liquid, since the contaminant appears to evaporate through the membrane. If the feed is vapor, or a gas/vapor mixture, the process is called vapor permeation.

The best-performing industrial membranes permeate water in preference to other components, so filtration and RO processes are used typically to purify water. In contrast, pervaporation and vapor permeation are commonly used to remove water from organics.

### Wide-ranging applications

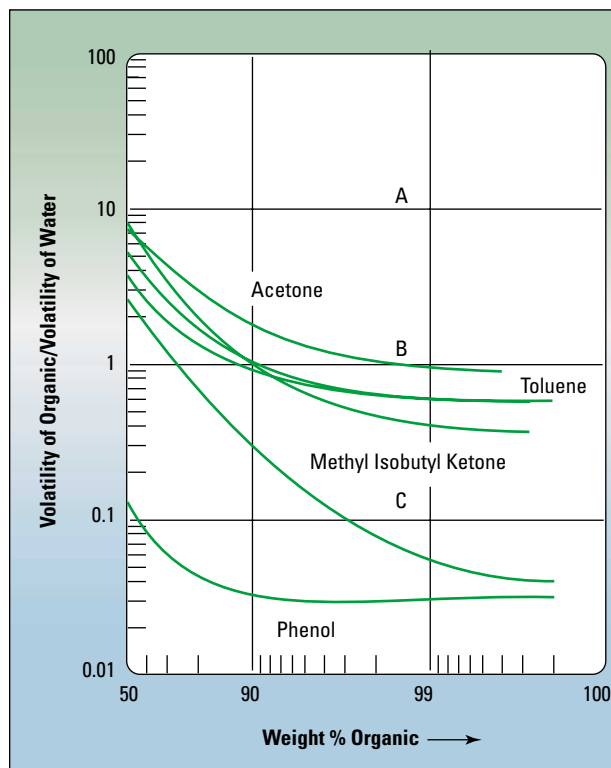
Membranes are selective either by pore size (porous membranes) or because of their chemical affinity for the permeating component. By far, the majority of pervaporation membranes in commercial use are hydrophilic. Most pervaporation membranes are therefore employed to dehydrate organics.

Although pervaporation and vapor permeation require significant driving forces to transport components through the membrane, the processes do not depend on particular vapor/liquid equilibria. Water is preferentially permeated from a stream irrespective of the other components present. In practice, pervaporation and vapor permeation are only competitive where distillation is difficult or costly.

Figure 1 shows where these processes are most usefully applied in dehydrating organics. The concentration and relative volatility of the organic are key variables.

Pervaporation is now coming of age as a separation process. Industrially, it has been introduced in end-of-pipe applications such as solvent recovery. As with other membrane processes, accumulated experience in both membrane fabrication, and design and operation of pervaporation units has matured the technology, such that it is now applied to separations that are integral to production. Although dehydrating the ethanol/water and isopropanol/water azeotropes account for the majority of all plants operating (roughly, four-fifths), most of the new plants being installed are in quite different applications.

*Methanol and ethanol removal* — Hydrophilic polymer membranes have also been developed that will permeate methanol, ethanol and, to some extent, isopropanol. (The lead photo shows a pervaporation plant for methanol treatment.)



#### Zone A : Pervaporation can save energy

Mainly volatile organics contaminated with water. Can be separated by distillation, but energy requirements are high since major component evaporates. Pervaporation requires much less energy since only the contaminant water must be evaporated.

#### Zone B: Always pervaporate

Mainly organics contaminated with water; minimal volatility differences, difficult to distill. Classic use of pervaporation or vapor permeation with hydrophilic membranes for the most economical separation. The minor component (water) is removed from the organic without problems.

#### Zone C: Special situations only

Mainly high-boiling organics contaminated with water. Strip out the water, if necessary distill. Energy requirements are low since the minor component evaporates. Pervaporation is competitive only in special situations (e.g., foaming systems or where kinetic effects dominate).

■ Figure 1. Pervaporation is mainly used to dehydrate organics.

These compounds can be removed from less polar organics, although membrane selectivity is not as high as when permeating water.

Methanol forms azeotropes with many substances, particularly esters, and often cannot be recovered from spent solvents or reaction mixtures by simple distillation. Pervaporation provides a simple way to break these azeotropes. Used alone or in combination with distillation, such units provide an economical and reliable route to recover or remove methanol.

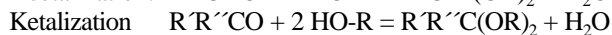
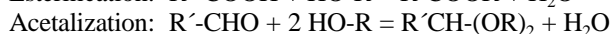
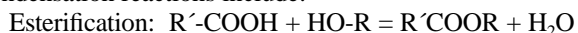
A separation scheme follows for methanol removal from a methanol-rich methanol/ethyl acetate mixture.

The mixture is distilled to the azeotrope, taking out pure methanol as bottom product. The overhead stream is passed directly to a vapor permeation unit that permeates a methanol-rich stream. This stream is condensed and passed back to the methanol column via the feed buffer.

Retentate from the vapor permeation unit, strongly depleted in methanol, can be fed directly to the ethyl acetate column. Pure ethyl acetate leaves this column as bottom product, while overhead azeotrope is sent to the vapor permeation unit.

Many solvent or ester/methanol mixtures can be separated using a similar scheme. If the feed is close to the azeotrope, then the methanol column can be dispensed with. If the capacity is small, the purification column for the second component may not be required, depending on the desired purity. One of the most promising uses of pervaporation technology is removing methanol from the products of transesterifications.

*Continuous water removal from condensations* — typical condensation reactions include:



Condensation reactions are normally equilibrium-limited, so removal of coproduct water reduces production costs three ways:

- Higher yield — lower reagent consumption
- Faster reaction — greater reactor throughput
- Purer products — less effort for product purification.

However, the optimum scheme for water removal from these reactions depends upon the relative volatilities of the reactants and products, and whether the units are operated batchwise or continuously. The following examples illustrate how pervaporation or vapor permeation can be used in particular situations.

*Batch condensation of ethyl and propyl alcohols* — Unless producing volatile products, the typical procedure for

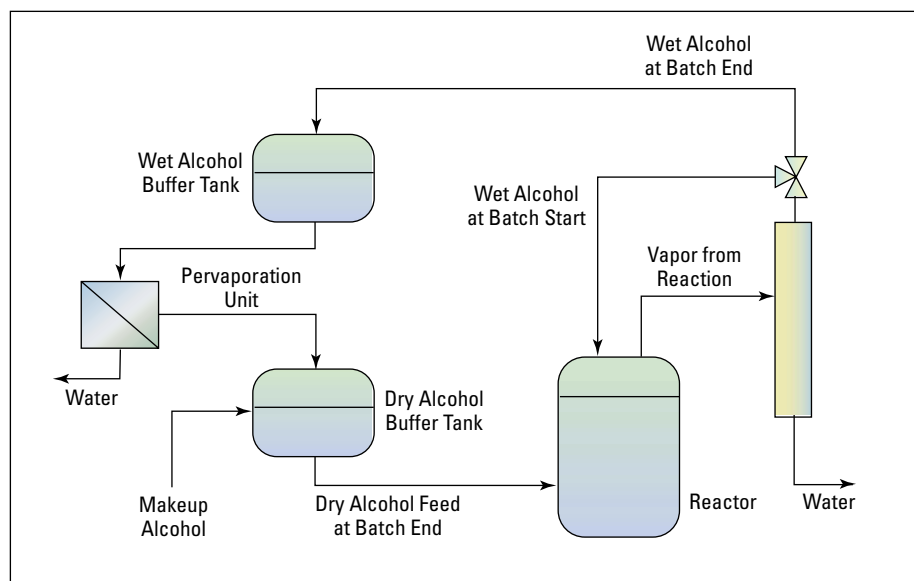


Figure 2. Reaction water removal via offline pervaporation.

these reactions is to dissolve the acid in an excess of alcohol, add catalyst, and then heat to drive off a water/alcohol mixture. This vapor is fed to a distillation column, the reaction water leaves as bottom product, and the alcohol/water azeotrope as top product. At the beginning of the reaction, the azeotropic mixture is fed back to the reaction and the reaction still proceeds at a reasonable rate. As the reaction progresses, the concentration of product in the excess alcohol approaches an equilibrium because of the water in the reactor; the reaction slows. At this point, recycle of wet alcohol is discontinued and fresh dry alcohol is added instead. Gradually coproduct water is distilled away, correspondingly more acid is reacted and a reasonably high yield is obtained, if sufficient time is available. The reaction product, excess alcohol and unused acid are then separated and a further batch is started. Normally, a batch is started with wet alcohol, generated at the end of the previous one.

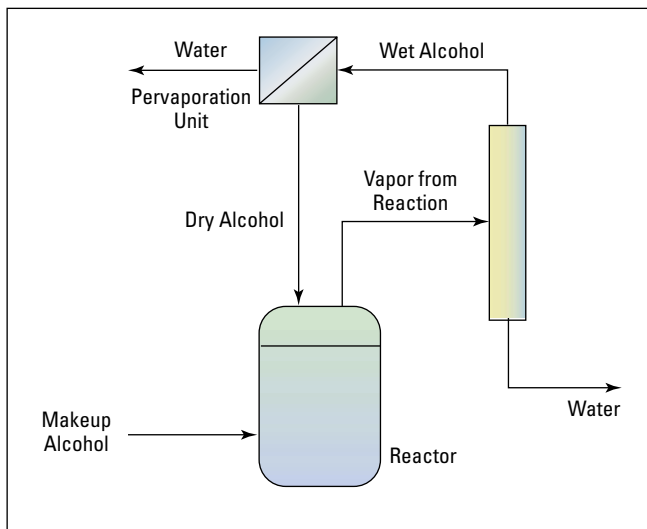
There are three ways in which pervaporation or vapor permeation can be used to enhance such reactions:

*Offline pervaporation* (Figure 2) is the simplest procedure and can be very effective. In this case, the alcohol/water azeotrope from the top of the column is collected in a tank during the latter part of the batch. The tank contents are continuously dehydrated by pervaporation and the resulting dry alcohol stored in a second tank. This material is fed to the process over the latter part of the batch. (Note: In Figures 2, 3 and 4, the horizontal line in the reactors represents a liquid line.)

*Online vapor permeation* (Figure 3) is used to remove water directly from the product of the distillation column. Dry alcohol is continuously fed back to the reaction.

*Online pervaporation* (Figure 4) replaces the distillation column altogether. The reaction mixture is continuously pumped through the pervaporation unit at a high rate and a drier stream is returned to the reactor.

In general, online pervaporation will give the most benefits, providing that the membrane is able to handle the reac-



■ Figure 3. Reaction water removal via online vapor permeation.

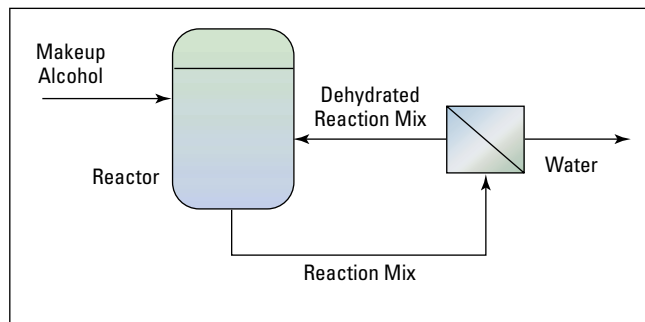
tion mix. Such units are simple, and a high pumparound rate enables water to be removed very quickly at the beginning of the batch, when it is being generated the fastest. Although highly crosslinked polyvinyl alcohol (PVA) membranes can cope with a few percent of sulfuric acid catalyst, problems can arise with aggressive catalysts (such as higher percentages of mineral acids) and with impurities in the feed. In addition, the pores in a composite membrane can become blocked if the acid or product permeate the membrane faster than they can evaporate into the permeate vapor.

Online vapor permeation avoids these problems, but the unit is constrained to operate at the reaction pressure (normally atmospheric), with the flowrate passing through the column. It is difficult to fully utilize such units throughout the cycle.

Offline pervaporation allows the membrane unit to be utilized at full capacity throughout the batch — in fact, it can also be used when the reactor is not operating. In addition, such a unit is easily coupled to other reactors. Such units enhance the economy of a batch processing operation, while providing a high degree of flexibility.

*Continuous production of ethyl/propyl esters of low-volatility acids* — The classical scheme for this is shown in Figure 5. Acid is continuously fed into a reactor containing an excess of alcohol. A product mix is continuously drawn off from the reactor containing alcohol, water, ester and some unreacted acid. Three columns are then used to remove product ester and coproduct water. Unreacted alcohol is recycled back to the reaction.

In the first column, the least-volatile component, unreacted acid, is taken out at the bottom and recycled back to the reaction. Alcohol, water and ester pass overhead to the second column. Product



■ Figure 4. Reaction water removal by online pervaporation.

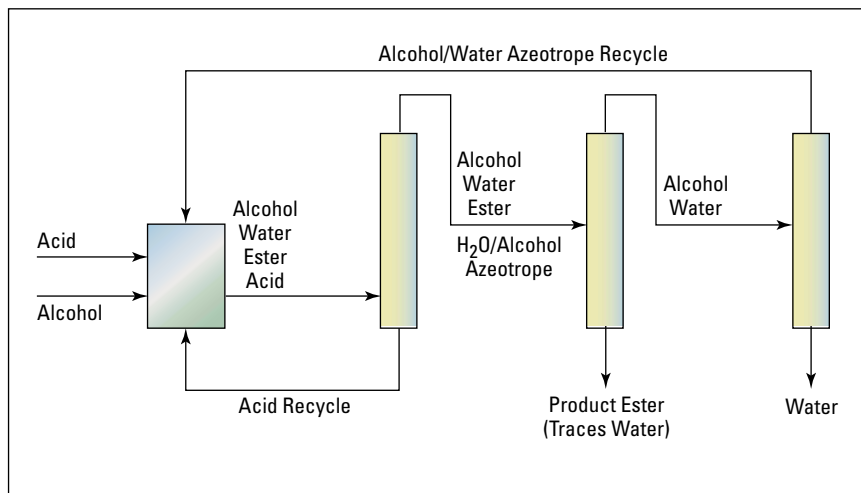
ester is taken from the bottom of this column and water and alcohol are taken overhead. The third column is used to remove water, again taken out at the bottom. The overhead product from this column is the alcohol/water azeotrope, which is recycled to the reactor.

This scheme has two major drawbacks:

- There is a high concentration of water in the reactor, requiring a large excess of alcohol to drive the reaction
- The recovered ester is contaminated with trace quantities of water, which hydrolyze the product, decreasing its purity, quality and usability in many situations.

Figure 6 shows a reaction scheme enhanced by continuously removing water directly from the reactor. In this case, the water is removed from the vapor phase. A vapor stream is sparged from the reactor and circulated through a vapor permeation membrane module, where water is selectively permeated through the membranes. The membrane unit is sized such that all of the reaction water can be removed with the water/alcohol ratio just below the azeotropic composition.

The reaction mixture is similarly passed through the first column to remove excess acid. In the second column, ester is again taken out at the bottom. However, because relatively little water is in the feed to this column, the water is entrained out with the alcohol. The ester bottom product is contaminated with traces of alcohol instead of water. It will



■ Figure 5. Classical reaction/separation for esters.

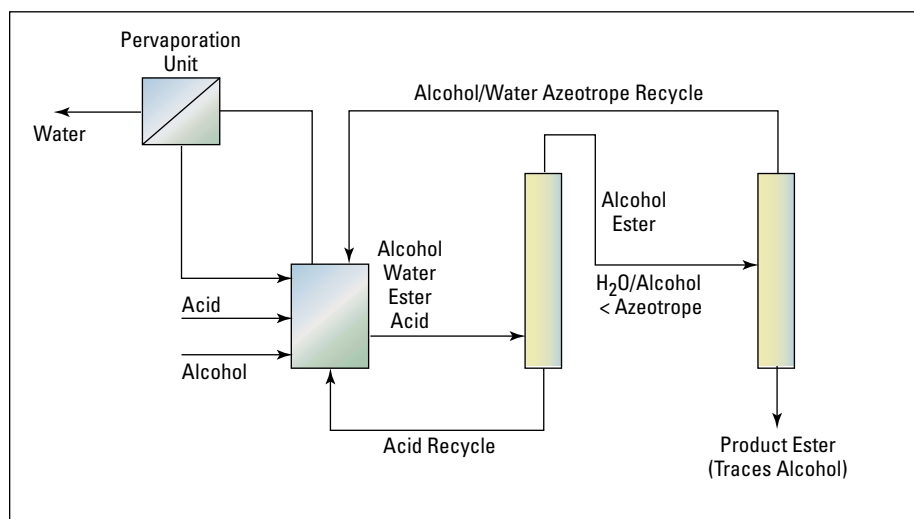


Figure 6. Enhanced reaction/separation uses pervaporation.

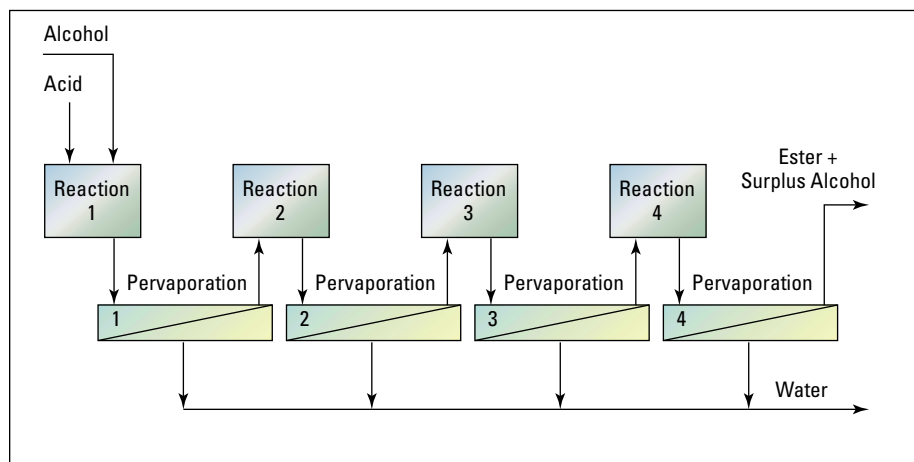


Figure 7. Four-stage reaction/pervaporation cascade.

not hydrolyze, so premium product quality is assured.

Removing reaction water directly from the reactor improves reaction conditions — the reaction runs faster, lower residence times suffice, equipment costs are minimized and side reactions are reduced. No third column is required and product quality is better. A win on all counts.

**Continuous esterification with a heterogeneous catalyst** — Some condensation reactions are carried out using heterogeneous catalysts. Continuously removing water from such systems brings concrete benefits, particularly in yield.

Figure 7 shows a scheme for removing water from a continuous esterification process that uses a heterogeneous catalyst. The process runs in four stages. Each stage includes a reactor where the components are brought close to equilibrium over the catalyst. The mixture then flows through a pervaporation stage, where water generated in the reaction step is removed, shifting the reaction equilibrium. In the next reaction step, equilibrium is reestablished and again the reaction water is removed. In four such stages, the reaction will be pushed

far over to the right and consume nearly all of the feed supplied. Such a procedure not only maximizes reagent usage but also minimizes the separation work required to purify the product. A number of such plants are operating and more are under construction.

**Transesterifications using methyl esters** — Many esters are made using transesterification, because the milder conditions prevailing permit the reaction of components containing additional functional groups. In alcoholysis, a complex alcohol is reacted with a methyl ester, forming a complex ester and methanol. These reactions are all equilibrium-limited, so the reaction only proceeds if product or coproduct is removed. Commonly, the reaction mix is distilled to remove the methanol. However, methanol forms azeotropes with many methyl esters, so driving out the methanol also removes a reactant.

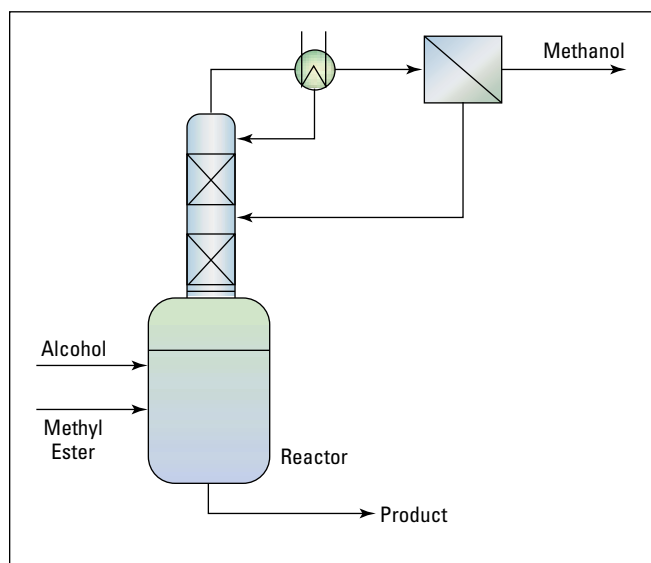
Separation of these azeotropic mixtures by traditional means is difficult. However, polymer membranes with a low degree of cross-linking can be engineered that will preferentially permeate methanol.

Figure 8 shows a vapor permeation unit installed to remove methanol from the top of a column, treating the boil-off from a transesterification reactor. The column is operated to condense overhead product close to the azeotropic point. Condensed liquid is refluxed through the column. Net overhead vapor is passed through the vapor permeation unit, which is sized to permeate methanol at the rate that it is generated in the reaction. The recovered ester is recycled to the reaction. In the example shown, membrane area is saved by feeding ester only partially depleted in methanol back to the column. The remaining methanol is stripped from the stream as it passes down the column to the reactor.

Such enhancements directly impact the quantity of reagent required and so have a direct impact on the bottom line. Payback times for the separation equipment are typically short.

## Continuous drying of reactor feed streams: Replacing molecular sieves

In a typical solvent recovery application, dehydration is only required down to 0.5% water or, in some cases, 0.1% water. At this water content, the solvent will perform al-



■ Figure 8. Methanol removal from a transesterification.

most as well as a completely dry solvent. Conventional pervaporation plants have no problem reaching such end water contents.

However, some special situations arise when water should be completely removed from an organic stream. At most, only a few ppm are tolerated because whatever water is left in the organic will react in later processing steps and consume, for example, an expensive catalyst. Although molecular sieves have traditionally been used for these dehydration duties, pervaporation can also be applied and is now emerging as a strong competitor.

The perceived problem using pervaporation for ultra-drying is generating a sufficiently high vacuum on the permeate side of the membrane to remove all of the water from the retentate side. At 100°C, 10 ppm of water in ethanol generates a partial vapor pressure of only 0.01 mbar. Maintaining this level of vacuum on the permeate side of a pervaporation unit is hardly practical.

In practice, this problem can be avoided if tailored membranes are used. Composite polymer membranes are tailored by modifying the degree of crosslinking of the polymer in the thin separation layer. Highly crosslinked membranes exhibit high selectivity, but low flux; with weakly crosslinked membranes, the situation is reversed. During ultra-drying, a considerable amount of organic will copermutate with the water if the selectivity of the membrane is not too high. In fact, when removing water to the 10 ppm level, the permeate will be mostly organic — water will only be present at maybe 500 ppm. In this situation, maintaining a total pressure of 10 mbar on the permeate side will result in a partial vapor pressure of water of 0.005 mbar, *i.e.*, water will continue to permeate across the membrane and dehydration will proceed. Properly designed pervaporation plants with tailored membranes can easily reach ppm or even ppb levels of water.

Ceramic membranes allow extremely low water contents to be reached simply by operating the membrane at a higher

temperature. Operating at 200°C instead of 100°C will increase the partial pressure of contained water by a factor of around 15, and drive correspondingly more water through the membrane.

Because pervaporation is a continuous process, the drying operation is much simpler and less error-prone than when drying with molecular sieves. There is no regeneration step, no nitrogen is required for regeneration, there is no off gas, product quality is consistent, and control is trivial.

### New membrane developments

The use of polymer membranes is restricted by temperature limitations and, to some extent, by their geometry. Most polymer membranes will be damaged by temperatures in excess of 110°C, which sets a limit on the vapor pressure that can be used to drive pervaporation. In addition, polymer membranes are fabricated in sheet form or as hollow fibers. Neither of these forms can be easily assembled into modules with optimum heat and mass transfer characteristics.

Much effort has been devoted to the development of tubular ceramic membranes suitable for pervaporation. An initial focus was on zeolite A membranes, which have pore diameters of around 4 Å. Such pores allow the passage of water molecules, but, in the absence of defects, are too small to pass molecules such as ethanol and isopropanol. Despite intensive promotion over the past decade, these membranes have found only minimal industrial acceptance. Their Achilles heel is the sensitivity of zeolite membranes to even the slightest acidity. At pH values below 6, the zeolite layer is irreversibly leached from the ceramic substrate. Such membranes are really too delicate for industrial service.

Subsequent work has been directed to materials with better chemical resistance. In particular, the Netherlands Energy Research Corp. (ECN) has developed a range of ceramic porous membranes based on microporous silica. These membranes are mechanically and chemically robust. Stability in acidic conditions is well demonstrated: 90% acetic acid has been dehydrated. Not only are the membranes stable in a normal industrial environment, but they also can be used to remove water from condensation reactions such as esterification, where strongly acidic conditions predominate.

*Performance of microporous silica membranes* — The performance and durability of ECN's silica membranes has been exhaustively tested. Some of the solvents successfully dehydrated include methyl ethyl ketone and glycols. Extremely high normalized water flux rates can be realized. Flux rates can be maximized by operating at elevated temperatures. The driving force for pervaporation is the partial vapor pressure of the permeating water and, as a rough guide, this doubles for every 20°C increase. Because the silica membranes can operate at up to 240°C, the operating temperature is dictated by restrictions on the fluids being processed, rather than the membrane material.

*Special modules to house tubular ceramic membranes* — In all membrane installations, membranes are housed in

modules, which support and seal the membrane in the face of the pressure difference required to drive the process, allow feed to flow uniformly over the membrane surface and collect, and keep separate the retentate and permeate streams. For a specific application, a number of modules are connected together according to the membrane surface required. Both plate-and-frame and spiral-wound modules are used to house flat sheet polymer membranes. Hollow-fiber membranes are housed in cartridge modules.

In practice, the chemical process industries use only plate-and-frame modules for pervaporation. These units are sealed with graphite compression gaskets that universally resist organic liquids. Spiral-wound and hollow-fiber modules require adhesives, which are not resistant to all solvents.

Special modules, tailored to the high-performance membranes, are an important part of the ECN technology. The actual membranes are externally coated on ceramic tubes installed inside of the tubes of a unit like a shell-and-tube heat exchanger (see illustration, top of p. 67). When feed flows through the annular passage between module tube and ceramic tube, water is sucked through the membrane by the vacuum maintained inside the ceramic tube. This module geometry includes two key features:

1. By connecting the annular passages in series, the long path-length results in a high annular flowrate, creating high fluid turbulence. This prevents concentration polarization/depletion of the permeating component at the membrane surface when one component permeates a membrane quickly, so the driving force is maintained, even under very high fluxes.

2. By feeding the steam to the module shell, the heat of evaporation of the water permeating the membrane is supplied directly to the pervaporation site. Optimum temperature, permeation driving-force and flux rates are maintained by operating the module isothermally. Intermediate heating, normally required between pervaporation modules, is unnecessary.

### Future developments

The emerging applications outlined here use existing membranes with proven industrial performance. Development of new and better membranes, *i.e.*, with higher fluxes, better selectivities and broader chemical resistance, is being pursued in a number of companies and institutions. These efforts will expand the areas where pervaporation is viable. Parallel developments in module design are also opening up new opportunities. In particular, tubular ceramic membranes allow the use of module geometries with superior heat- and mass-transfer characteristics.

Where will these developments have an impact? Reaction enhancement will be a major beneficiary, but a look at the simpler field of solvent dehydration shows that the innovation process is very application-dependent.

Pervaporation (with vapor permeation) is progressively displacing other techniques in solvent dehydration. Initially replacing entrainer distillation for drying ethanol and iso-

propanol, pervaporation is now always preferred when a third component must be added to shift equilibria. The handling of entrainers or calcium chloride or caustic with the attendant environmental risks and costs is no longer a viable option.

Pervaporation has also made inroads in drying solvents in which phase separation facilitates drying by distillation. Drying esters this way requires high reflux ratios, so pervaporation is easily cost competitive. If the solvent mix includes alcohols, then the phases will not separate and distillation will not work at all.

The use of tubular ceramic membranes is the current wave of innovation. Existing pervaporation applications are benefiting from the more-robust membranes. Continuous pervaporation plants can run isothermally and are considerably simpler. Dehydration of hydrocarbons and chlorinated hydrocarbons by pervaporation is now cost-competitive with molecular sieves, and operation is continuous and consistent. There are no beds to regenerate, no regeneration streams to dispose of, and no perturbations in product dryness. The field of reaction enhancement is more complex and developments are more difficult to predict.

The ability of ceramic membranes to run at higher temperatures greatly increases the number of reactions that can be considered as enhancement candidates. These reactors can be further enhanced, for example, by using a ceramic tube to support a catalyst, as well as a membrane. Equipment of this type is already under development.

External factors are also pushing the development and adoption of better technology. Higher oil prices impact reagent costs and, especially, solvent costs. Environmental pressures are pushing companies to recover solvents in-house, without using additional chemicals. Ongoing globalization increases the competitive pressure to maximize product quality and consistency at minimum cost, *e.g.*, by improving reagent efficiency.

As these forces drive the adoption of new technologies such as pervaporation, chemical engineers will need all of their skills to select the very best applications and maximize the benefits to their plants.

**CEP**

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