# A New Option: Osmotic Distillation

*This novel athermal membrane-separation process retains flavors and fragrances better than thermal techniques. It promises to play an important role in the processing of foods, pharmaceuticals, and other products.*

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Osmotic distillation — a separation process in which a liquid mixture containing a volatile component is contacted with a microporous, non-liquid-wettable membrane whose opposite surface is exposed to a second liquid phase capable of absorbing that component — is nearing commercialization for the concentration of beverages and other liquid foodstuffs, and is under evaluation for the concentration of aqueous solutions of thermally labile pharmaceutical products and biologicals. Its primary advantage lies in its ability to concentrate solutes to very high levels at low temperature and pressure, with minimal thermal or mechanical damage to or loss of those solutes. The process also can enable the selective removal of a single volatile solute from an aqueous solution (for instance, ethanol from wine and other ferments) using water as the extracting solvent. Low-alcohol-content beverages have been produced in this manner with minimal losses of volatile flavor and fragrance components. Osmotic distillation (OD) promises to become an attractive complement or alternative to other athermal or low-temperature separations techniques such as ultrafiltration (UF), reverse osmosis (RO), pervaporation, and vacuum freeze drying.

## PROCESS FUNDAMENTALS

OD, which is also called "isothermal membrane distillation," is a membrane transport process in which a liquid phase (most commonly an aqueous solution) containing one or more volatile components is allowed to contact one surface of a microporous membrane whose pores are not wetted by the liquid, while the opposing surface is in contact with a second nonwetting liquid phase (also usually an aqueous solution) in which the volatile components are soluble or miscible. The membrane thereby functions as a vapor gap between the two liquid phases, across which any volatile component is free to migrate by either convection or diffusion. The driving potential for such transport is the difference in vapor pressure of each component over each of the contacting liquid phases. The mechanism is illustrated schematically in Figures 1 and 2. If the sole or primary volatile component in solution is the solvent, then evaporation of solvent from the solution of higher vapor pressure into that of lower vapor pressure will result in concentration of the former and dilution of the latter. Thus, the rate of transport of solvent from one liquid phase to the other will increase as the solvent vapor pressure over the receiving phase is reduced. If the solvent vapor pressure over the liquid being concentrated drops to a value equal to that over the receiving phase, no further transport will occur.

In most applications of practical interest, the solutions to be concentrated contain relatively low concentrations of nonvolatile solutes of moderate to high molecular weight (sugars, polysaccharides, carboxylic acid salts, proteins, and so on) which have limited stability to elevated temperatures and shear stresses. Because of the low osmotic activity of
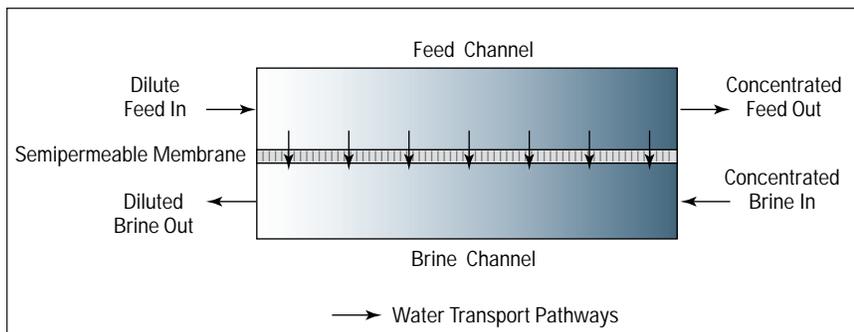
**■ *Figure 1. In osmotic distillation, a semipermeable membrane acts as a vapor gap that allows migration of volatiles in a single direction.***
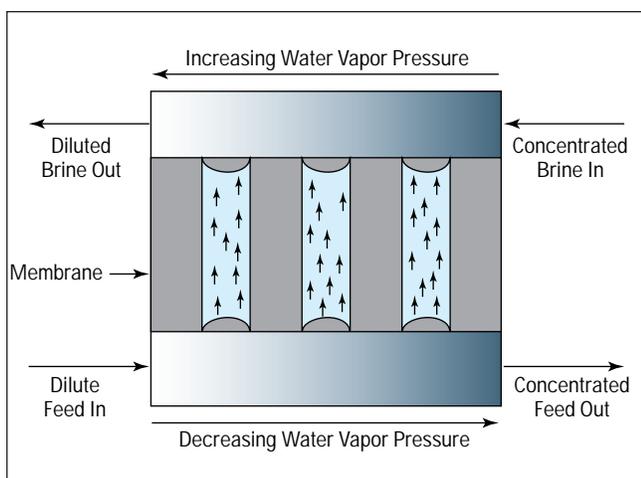


**■ *Figure 2. Mechanism of osmotic distillation through a microporous hydrophobic membrane.***
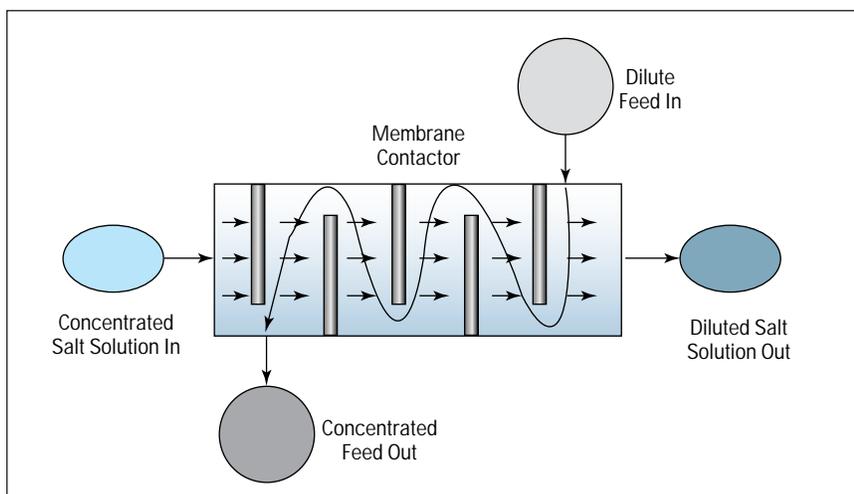


**■ *Figure 3. The basic transport process in osmotic distillation.***

such solutes, the vapor pressure of water over such solutions is very nearly that of pure water, and decreases quite slowly with increasing solute concentration. Hence, if the re-

ceiving or "strip" solution on the opposite membrane face contains a high concentration of nonvolatile solute of high osmotic activity (meaning a solute of low equivalent weight and

high water solubility), its water vapor pressure will be low and will increase slowly on dilution. This makes it an attractive candidate for favoring rapid transfer of water vapor through the membrane.

The basic transport process is illustrated schematically on a macro scale in Figure 3. OD is unique among membrane-separation processes in that it involves the transport of volatile components between two inherently miscible liquid streams, driven by differences in component activity between those streams. Its closest analogs are probably dialysis and membrane solvent extraction, although the former involves transport of solutes (whether volatile or nonvolatile) between two miscible liquid phases, and the latter transport of solutes between two immiscible liquids.

Inasmuch as the strip solution, following its dilution by water transferred from the feed stream, must be reconcentrated by evaporation so that it can be recycled and reused in the OD operation, it is important that the strip solute itself be thermally stable to quite high temperatures — and also preferably nontoxic, noncorrosive, and of low cost. Water-soluble salts are the most attractive prospects for this purpose; those that have been most frequently employed are the alkali and alkaline earth metal halides (particularly sodium and calcium chloride). Sodium chloride, however, has relatively low water solubility and a rather low temperature coefficient of solubility, while calcium chloride is sensitive to precipitation in the presence of carbon dioxide; both are quite corrosive to ferrous alloys at elevated temperature. Salts that display large increases in solubility with temperature are desirable, because they can be evaporatively concentrated to very high levels without danger of crystallization in the evaporator or during storage prior to recycle.

We have found that, for osmotic concentration of foodstuffs and pharmaceutical products, the most attractive strip solutes are the potassium

salts of ortho- and pyrophosphoric acid. These have quite low equivalent weights, very high water solubilities, and very steep positive temperature coefficients of solubility. They also have the advantage of being normally present in biological fluids and, thus, safe for food or drug use when present in low concentrations.

The vapor pressure/concentration relationships for a representative feed to be concentrated (for example, an aqueous sucrose solution) and several candidate brines as strip solutions are shown in Figure 4. The equivalent weights of the salts increase in the order $NaCl > CaCl_2 > K_2HPO_4$, as do their water solubilities. Because the "osmotic activity" of a salt is determined by the ratio of its water solubility to its equivalent weight, this in part accounts for the attractiveness of concentrated dipotassium orthophosphate brine for this application.

## Process thermodynamics

The water transport process across the membrane takes place in three consecutive steps: (1) evaporation of water at the liquid meniscus at a pore entry; (2) diffusional or convective transport of water molecules as vapor through the membrane pore; and (3) condensation of water vapor on the brine-side liquid meniscus at the pore exit. The evaporative process requires the supply of the latent heat of vaporization at the upstream meniscus; this only can be provided as sensible heat via conduction or convection from the bulk upstream liquid, or via conduction across the solid phase comprising the membrane. Conversely, at the downstream face of the membrane, condensation of water vapor into the strip requires removal of the heat of condensation by the same mechanisms. Supplying or removing this energy by conduction/convection from the bulk liquid phases would, of course, cool the feed and heat the strip, thereby reducing the driving force for water transport.

Fortunately, however, the thermal conductance of the membrane is suf-



■ *Figure 4. Generalized vapor-pressure relationships for sugar and salt solutions at 25°C.*
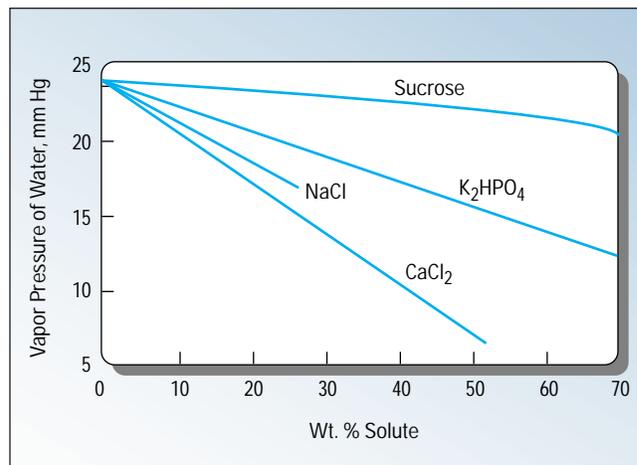
ficiently high that virtually all the energy of vaporization can be supplied by conduction across the membrane at a quite low temperature gradient. As a consequence, under normal operating conditions, the temperature difference between the liquids on opposite sides of the membrane ("temperature polarization") is quite small — seldom greater than 2°C. Hence, the process is essentially isothermal with respect to both liquid streams. For this reason, membranes prepared from solids of high thermal conductivity and of minimum practical thickness are desirable. It is interesting that the situation is exactly the opposite for the process of "membrane distillation," where a warm solution to be concentrated is separated via a microporous membrane from a cold liquid into which condensation is to occur. In that case, a membrane of very low thermal conductance is necessary to prevent heat flow by conduction from the warm to the cold liquid stream.

Many liquid feeds whose concentration is desired (such as fruit and vegetable juices, and vegetable extracts such as tea or coffee) also contain small concentrations of essential volatile, lipophilic organic solutes (flavor and fragrance components), the loss of which would make the product unpalatable and unmarketable. While such products can be concentrated by evaporation, losses

of these essential volatiles with the water vapor are severe. Condensation of the vapor mixture, followed by rectification to recover these volatiles for reblending with the concentrate, can offset this somewhat — but worsens thermal deterioration of these components and results in a significant incremental processing cost.

With OD, several factors make it possible to achieve concentration by *selective removal of water* without significant depletion of these important flavor/fragrance components. First, if the concentration is carried out at low temperature, the vapor pressure of these components (relative to that of water) is substantially depressed, reducing the driving force for transmembrane transport of these solutes. Second — and perhaps more important — the solubilities of these lipophilic solutes are substantially lower in concentrated saline solutions than in pure water; as a consequence, the vapor pressures of these solutes when present in any given concentration in such a solution are much *higher* than they are over water at the same concentration. Thus, the vapor-pressure driving force for vapor-phase transfer of these solutes from the feed to the strip is far lower than that encountered in simple evaporation. Additionally, because the molecular weights of these solutes are far higher than those of water, their diffusive permeabilities through the

membrane are much lower. The end result of these factors is that volatile flavor and fragrance losses from such feeds during OD often are too low to be significant. Indeed, concentrate, when rediluted with distilled water to its original volume, is organoleptically very similar to that of the original feed; this, of course, makes OD particularly attractive for food and beverage processing.

## Membrane transport kinetics

For successful operation of OD, it is essential that (1) liquid is prevented from penetration into and passage through the membrane pores, and (2) unimpeded vapor-phase transport of volatile components from feed to strip solution can occur. The first requirement can be satisfied if the membrane surface is sufficiently hydrophobic such that neither the feed nor strip solutions can wick by capillary forces into the pores (requiring an angle of contact between the liquid and solid phases of greater than 90°), and the surface tensions of the liquid phases are sufficiently high that the capillary penetration pressure of liquid into a pore is well in excess of the maximum pressure difference across the membrane that might be encountered in operation. Liquid penetration into the pores will lead to unacceptable gross mixing of feed and strip solutions.

The critical penetration pressure is defined by the classical Kelvin Equation:

$$\Delta p = 2\gamma \cos \theta / r \qquad (1)$$

where $\Delta p$ is the pore-entry pressure, $\gamma$ the liquid surface tension, $\theta$ the contact angle, and $r$ the pore radius. Thus, the higher the surface tension of the liquid, the larger the contact angle (in excess of 90°), and the smaller the pore radius, the greater the intrusion pressure. For most concentrated aqueous solutions of mineral salts, the surface tension far exceeds that of pure water; so, intrusion of such solutions into microporous hydrophobic membranes is unlikely at any reasonable pressures. Many

aqueous feeds of vegetable or animal origin, however, contain amphiphilic solutes that may depress the surface tension and reduce the wetting angle on hydrophobic surfaces. For such solutions, membranes fabricated from materials with very high contact angles with respect to water, and of sufficiently small pore size to meet the penetration-pressure limitation imposed by Eq. 1, will be required. Transmembrane pressure differences likely to be encountered in OD membrane modules are in the range of 140 kPa (20 psig); for a liquid with a surface tension of 50 dynes/cm and a contact angle of 110°, the maximum tolerable pore radius to prevent liquid penetration is about 250 nanometers — corresponding to a pore diameter of about 0.5 micron. Commercially available microporous membranes fall well within this range of pore dimensions. Membranes of smaller pore size than this, of course, will withstand higher hydrostatic pressures without liquid intrusion.

The most suitable materials for OD membranes, thus, are apolar polymers with low surface free energies. These include the polyolefins, particularly polyethylene and polypropylene, and the perfluorocarbons, especially polytetrafluorethylene (PTFE) and polyvinylidene difluoride (PVDF). Microporous membranes fabricated from these materials are available with pore sizes and pore-size distributions in acceptable ranges for this application. For reasons to be elaborated on later, small-dia., hollow-fiber membranes with thin walls appear to be the best candidates, because they offer high area/volume ratios and do not require supports and spacers in modular geometries. Most of the studies described in this article have been conducted with microporous, polypropylene hollow-fiber modules made of Celgard (a fiber manufactured by Hoechst Celanese). These fibers are approximately 0.3 mm in external dia. with a wall thickness of about 0.030 mm; they have a mean pore diameter of about 30

nanometers (0.03 micron), and a porosity of about 40%. The intrusion pressure of water into the pores is well in excess of 100 psig. Burst strength of the fibers exceeds 200 psig; they can tolerate external pressures greater than 100 psig without collapse.

Gas and vapor transport through microporous membranes of this structure takes place principally by molecular diffusion. For pores of dia. in the nanometer range, at ambient temperature and gas-phase pressures of the order of the vapor pressure of water at that temperature (approximately 20 mm Hg or 2.7 kPa), the mean free path of gas molecules is significantly greater than the pore diameter. Under these circumstances, molecular transport occurs by Knudsen diffusion. The rate equation for such transport is approximated by:

$$dn/Ad\theta \propto \Delta p/(MRT)^{1/2} \times \varepsilon r/\tau t \qquad (2)$$

where the lefthand side of the equation is the molar flux of vapor (mol/cm²s) with $n$ the number of moles, $A$ the area, and $\Delta\theta$ the time interval; $\Delta p$ is the vapor pressure difference across the membrane, $M$ the molecular weight of the vapor, $R$ the gas constant, $T$ the absolute temperature, $\varepsilon$ the membrane porosity, $\tau$ the pore tortuosity, and $t$ the membrane thickness. For a vapor pressure difference of about 10 mm Hg (1.3 kPa) and a membrane of porosity, pore size, and thickness indicated above, the water vapor flux through the membrane is estimated to be about 5 L/m²h. Measured experimental water fluxes through this membrane under these conditions (that is, pure water on one side and a concentrated brine with a vapor pressure about half that of pure water on the other) are approximately of this magnitude.

These calculations and measurements assume that *the only gaseous species present in the pore space is water vapor*. In practice, however, both the feed liquid and brine strip are likely to be saturated with air at ambient temperature. Under these conditions, there also will be air at

about atmospheric pressure in the membrane pore space. In the presence of inert gas, the Knudsen diffusion condition no longer applies, because gas/gas collisions dominate over gas/wall collisions; water vapor, thus, will transit the pores by simple Fickian diffusion. The water vapor flux in this case will be significantly lower than that predicted by the Knudsen relation at the same vapor-pressure gradient, although it becomes independent of pore radius. Experimental measurements of water flux during OD in the presence and absence of air in the pores clearly confirm this difference: with air present at atmospheric pressure, the water fluxes are lower by a factor of two to three than in its absence.

Obviously, water vapor transport would be favored by removal of dissolved air from the liquid phases; the additional cost of air removal, however, combined with the losses of essential volatiles from many candidate feed streams consequent to air stripping, make this an unattractive option. Thus, the majority of OD operations are being carried out with noncondensable gas present (usually air, although not infrequently nitrogen or carbon dioxide), with average OD water fluxes in the range of 0.2–3.0 L/m$^2$h.

As Eq. 2 indicates, vapor transport kinetics can be improved by selecting membranes of higher porosity and smaller thickness (and also larger pore size when transport is in the Knudsen diffusion regime). Unfortunately, such changes reduce membrane strength and durability. Also, according to Eq. 1, increasing pore size reduces the pressure required to cause liquid intrusion into the membrane pores and promotes membrane "wet-out." Recent development of techniques for surface modification of microporous polymeric membranes that render their surfaces highly hydrophobic (and, thus, more resistant to liquid penetration) may yield improved membrane structures for use in this process.

The rather low permeation fluxes attainable with OD relative to those achievable via pressure-driven membrane processes such as microfiltration (MF), UF, and RO (where permeation fluxes in the range of 10–200 L/m$^2$h often are achievable) would appear to make the process economically uncompetitive with them. When, however, the product to be concentrated is a solution containing macrosolutes or hydrocolloids sensitive to shear degradation or a solution of microsolutes of moderate molecular weight (such as simple sugars), there are serious limitations to the degree of concentration achievable via these methods without significant product deterioration or costly process equipment. It is for precisely these applications where OD has important advantages.

By way of illustration, to concentrate by RO an aqueous glucose solution to 70 wt. % sugar from 20% would require a transmembrane pressure difference well in excess of the approximate osmotic pressure of sugar in that solution (about 150 atm). In contrast, the vapor pressure of water over a 70% glucose solution is only about 80% that of pure water at the same temperature; so, the OD water flux (using a concentrated brine as the stripping solution) would be only slightly depressed over that concentration range.

OD offers another potential advantage over pressure-driven membrane concentration for producing highly concentrated products, because it is a liquid/liquid transport process during which *the strip solution is undergoing dilution while the product stream is being concentrated*. Hence, if the membrane contactor is operated in *counterflow mode,* where the product stream encounters increasingly concentrated strip solution as it flows through the contactor, it is possible to maintain the vapor-pressure driving force for water transport across the membrane (and, thus, the transmembrane flux) large and nearly constant throughout the contactor. This is in

contrast to the usually rapid and marked decline in transmembrane flux experienced during UF and RO as the feed stream becomes increasingly concentrated. Thus, this mode of operation can compensate to a degree for the inherently low fluxes of OD.

## BOUNDARY-LAYER ISSUES

As is the case with all membrane separations processes, boundary-layer problems are encountered in OD and must be mitigated to achieve maximum process performance. The nature and magnitude of these problems, however, are rather different for OD than for the more common pressure-driven membrane processes — and require rather different engineering strategies.

### Polarization moduli

During concentration of aqueous solutions by OD, removal of water from the feed and its transfer into the strip creates a polarization boundary layer at the upstream membrane surface of increasing solute concentration and also one on the strip side of decreasing concentration of salt. This reduces the transmembrane water flux by depressing the vapor pressure of water over the feed solution contacting the membrane (relative to its value in the bulk liquid) and, conversely, increasing the water vapor pressure over the strip solution contacting the downstream membrane surface. The "polarization moduli" (that is, the ratios of the solute concentration at the membrane surface to that in the adjacent bulk liquid) are exponentially dependent upon the ratio of the transmembrane volume flux of liquid solvent across the membrane to the mass-transfer coefficient of the solute in the feed and strip channels. Because the inherent transmembrane fluxes in OD are low, and economics demand the use of membrane contactors with the highest possible membrane area per unit volume (such as hollow-fiber contactors), concentration polarization (because of both low transmembrane flux and

high mass-transfer coefficients) is much less important as an additional resistance to interphase transport than it is in MF, UF, and RO.

Another important — and paradoxical — feature of OD that also tends to mitigate boundary-layer resistances to solvent transport is the thermodynamic consequence of changing solute concentration on solvent vapor pressure. To a first approximation, the vapor pressure of water over an aqueous solution is determined by Raoult's Law — that is, the vapor pressure is directly proportional to the mole fraction of water in the mixture. Because water is a major component of these solutions and is the lowest-molecular-weight component present, the effect of changes in *solute* concentration over moderate ranges (as likely to be encountered in the boundary layers) on water vapor pressure is quite small. Hence, polarization on either side of the membrane has *relatively little effect on the vapor-pressure difference across the membrane and, thus, on the OD flux.* Yet another factor reducing boundary resistances in OD, particularly in food and beverage applications, is that the majority of the nonvolatile solutes are compounds with relatively low molecular weight and rather high aqueous solution diffusivities, thereby contributing further to high mass-transfer coefficients.

## Viscous polarization

When highly concentrated products are desired from OD (for juices and beverages, for example, removal of 90% of the water is necessary), an unusual boundary-layer problem develops on the feed side of the membrane. This problem, which seldom is encountered in other membrane concentration processes, can have a very detrimental effect on process performance. Many of these feed streams contain hydrophilic solutes such as sugars, polysaccharides, and proteins, that, when concentrated to high levels, yield solutions of anomalously high viscosity (and, frequently, non-

Newtonian rheologic behavior). For example, sucrose solutions undergo large increases in viscosity at room temperature as the sugar concentration rises above about 50 wt. %, reaching values at a concentration of 70 wt. % about two orders of magnitude greater than that of water. Despite this enormous viscosity rise, however, the vapor pressure of water over the solution decreases very slowly; indeed, the OD flux of water out of a 70% sucrose solution of viscosity of 100 cP is not much less than that from a 20% sucrose solution with a viscosity of about 2 cP.

As such a solution passes through a membrane-bounded channel undergoing OD, solution near the membrane surface becomes increasingly concentrated and, upon reaching a critical concentration level, its viscosity begins to rise very rapidly with further water removal. Viscous transport of this layer along the channel becomes progressively slower, because it is bounded by flowing liquid of lower solute concentration and viscosity. Ultimately, stagnation of fluid in the boundary layer occurs, and the less-viscous, more-dilute solution "fingers" through the center of the channel with increasing velocity. The end result is channeling of dilute, low-viscosity feed through the centers of channels bounded by membrane coated with essentially stationary films of concentrate. Reduction in solution residence time in the contactor and blockage of access of that solution to the membrane surface lead to very large decreases in transmembrane water transport below expected performance. (This "viscous fingering" process is quite analogous to that observed in multiphase flow through porous petroleum reservoirs when the displacing fluid (water) is less viscous than that (oil) initially occupying the pore space.)

This problem, incidentally, is accentuated if an attempt is made to maximize water removal from a dilute feed stream during a single pass through a contactor. This operating

strategy maximizes the viscosity changes during transit and, thus, the degree of viscous polarization and performance deterioration attributable to it. Experience has shown that the effect can be minimized if a contactor is operated either in continuous feed-side recycle mode where the rise in solute concentration per pass can be held to modest levels, or in batch-recycle mode where the increase in concentration per pass is also small but the average solute concentration is allowed to rise to the desired final value. Fortunately, these strategies usually become necessary only when the solute concentration increases to levels (typically around 50 wt. % for most sugars) where the viscosity begins to rise very rapidly with concentration.

By far the most effective means for minimizing the "viscous polarization" is by *proper fluid management of the feed-side channel of the membrane contactor.* Fluid mechanical modeling of flows in membrane-bounded channels makes it clear that laminar flow in a channel of uniform cross-section (of even small dimensions) is a poor option to minimize viscous fingering, because there are no normal stresses to promote mixing of the viscous boundary layer with the lower viscosity fluid moving over it. Indeed, even turbulent flow at high velocities in such channels is relatively ineffective until wall shear stresses reach unreasonably high values. Experimental measurements of OD performance with such solutions in hollow-fiber reactors with feed flow through the *lumen (tube) sides* of the fibers (a strategy initially and mistakenly considered to be the best alternative) clearly support this conclusion.

If, however, the feed solution is forced to flow *normal* to the long axis of a hollow membrane fiber, in a channel designed to maintain an assembly of such fibers in uniform, relatively closely spaced array, with means for assuring uniform flow of fluid normal to all fibers, then, even in laminar flow, each fluid element is subjected to stagnation and transport

around each fiber with eddying on the downstream side before it encounters the next fiber in the array. The result is both rather efficient displacement of the boundary layer around each fiber by fresh fluid and efficient micromixing of fluid elements throughout the transit process.

Hoechst Celanese Corp. (Charlotte, NC) within the past few years has developed a hollow-fiber-membrane contactor, called Liqui-Cel, that provides a shell-side fluid channel arrangement of precisely this configuration (see Figure 5). Modules containing nominal membrane areas of 1.4, 19.2, and 135 m² (Figure 6) are commercially available. The membrane fibers first are woven into a fabric consisting of a warp of parallel hollow fibers held in fixed position by a woof of small-dia., widely spaced monofilaments, as shown in Figure 7. The spaces between the hollow fibers are about equal to the external fiber dia. This fabric is spirally wound around a perforated tube or mandrel to yield a cylinder whose central tube serves as a conduit for liquid entrance and exit, and an annulus filled with closely and uniformly spaced hollow fibers parallel to the cylinder axis. The hollow fibers typically occupy about 50% of the volume of the annulus.

Next, this cylinder is inserted into a tubular shell and the ends potted and sliced to provide access to the lumens of all fibers for fluid entry and exit. The central tube and shell are baffled so that fluid entering at one end is forced to flow radially outward through the shell annulus, along the long axis of the cylinder, and then radially back into the tube prior to discharge. As a consequence, nearly all the fluid delivered to the shell is constrained to travel normal to fiber axes.

For OD applications, the feed to be concentrated enters the shell side of the module, and the brine strip the lumen side with its flow countercurrent to the feed. Because the brine strip exhibits quite low viscosity over the entire concentration range employed, there is virtually no signifi-
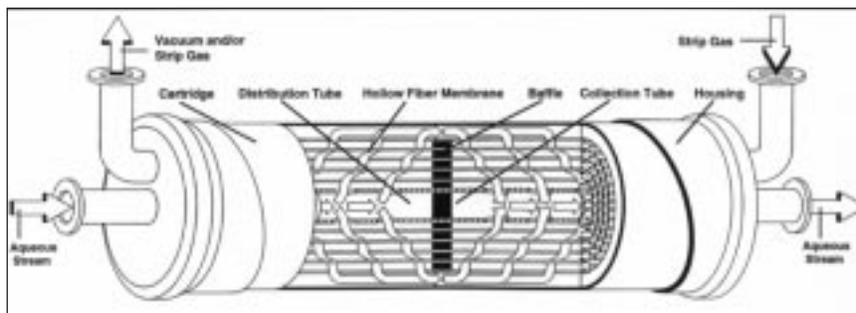


■ *Figure 5. Construction detail of the membrane contactor. (Drawing courtesy of Hoechst Celanese.)*

cant polarization on the brine side. Despite the small internal dia. of the fibers (0.24 mm), the brine pressure drop required to provide adequate brine flow for the concentration process is well within the burst limit of the fibers and below the pressure level for liquid intrusion into the membrane pores.

On the shell side, the hydraulic resistance to feed flow — even for high-viscosity concentrates — is low enough to allow adequate flow rates with pressure drops in the 2–5 psi (20–50 kPa) range. Despite the low mass velocities in the shell space (and, thus, low Reynolds numbers), boundary-layer turnover and micromixing are sufficient to achieve transmembrane OD fluxes within one-half to two-thirds of those predicted from base-line measurements using pure water as the feed — even for juice concentrates containing as high as 70 wt. % sugar. The flux losses attributable to viscous polarization, thus, are sufficiently low to render the process both technically and economically feasible for production of such high-solids concentrates.

OD membrane contactors generally are operated with a slightly higher pressure on the shell (feed) side of the module than on the lumen (strip) side, so that the pressure difference across the membrane at all points in the contactor is greater on the shell side. This is to insure that, in the event of a fiber failure or liquid intrusion into the membrane pores, feed liquid will leak into the strip, and not *vice versa*. This avoids



■ *Figure 6. Membrane contactors are available in 1.4-, 19.2-, and 135-m² modules. (Photo courtesy of Hoechst Celanese.)*
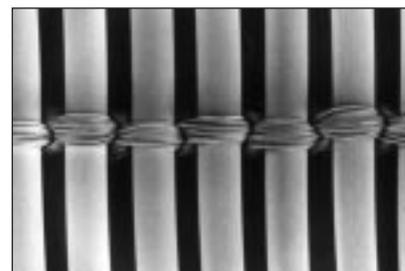


■ *Figure 7. Photo enlargement of a section of a hollow-fiber array. (Courtesy of Hoechst Celanese.)*

contamination of the product with the strip solute. In most instances in practice, such leakage is too small to have a detectable impact on product yield. Periodic sampling of diluted strip and analysis for a specific feed component can be used to detect leakage; before leakage becomes serious, it can be corrected by module replacement.

## PROCESS DESIGN

The objective of an OD process for concentration of an aqueous feed is to remove water from the feed via transfer of a large fraction of the
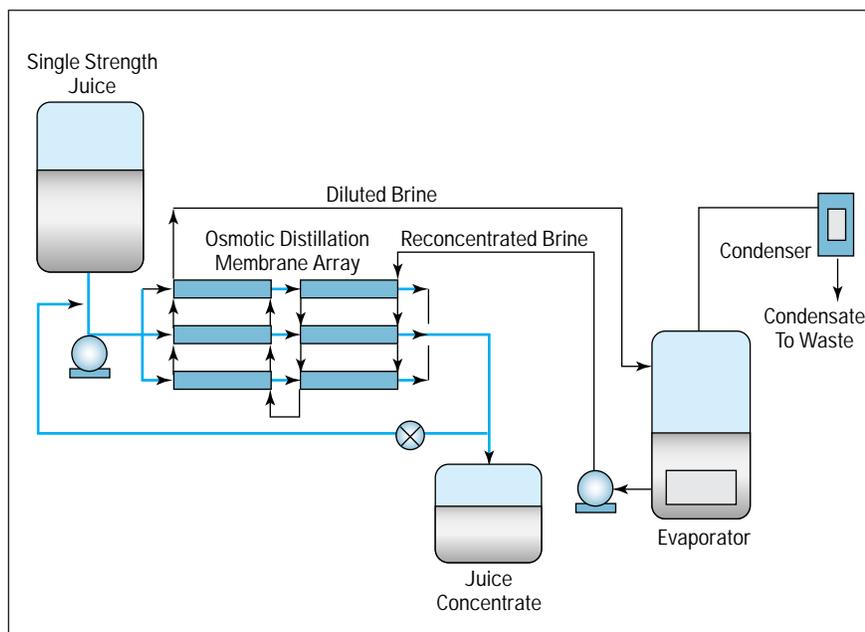
water into a saline strip solution, yielding a product of the desired solute concentration and a diluted strip. The essential design parameters are: (1) the required plant capacity in daily volume of feed to be concentrated, (2) the solute concentrations in the feed and final concentrate, (3) the water vapor pressure/concentration relationship for the feed stream, (4) the water vapor pressure/salt concentration relationship for the strip solution, and (5) the intrinsic water vapor permeability of the OD membrane, expressed as liters of water transmitted per sq. m. of membrane area per unit of water vapor-pressure difference across the membrane. These relationships allow determination of the maximum and minimum concentrations of salt in the strip, and the average rate of removal of water from the feed. Then, the mode of feed and brine supply to the membrane contactors (for instance, single-pass or feed/bleed recycle of the feed or strip streams) can be selected; this, in turn, enables computation of the membrane area and strip volume requirements, feed- and strip-pump capacities, and the evaporative load for strip reconcentration.

A schematic for a simple juice-concentration unit is shown in Figure 8. The process employs partial batch recycle on the feed side (to minimize large feed viscosity changes through the membrane contactors) and continuous countercurrent recycle plus evaporative reconcentration of the brine strip. The feed side of the system usually operates in batch mode for food and pharmaceutical products, because such products typically are processed in batches, and periodic cleaning, sanitizing, and sterilization of equipment are essential.

The contactors can be arranged in a series, parallel, or series-parallel array, as process requirements dictate. Because feed-side viscous polarization results in OD flux decline with increasing feed-side solution viscosity, economics usually favor a tapered series cascade with increasing numbers of contactors in parallel toward the feed-discharge end. This results in an elevated average OD flux and, thus, greater water-removal capacity per unit membrane area.

## Feed- and strip-solution pretreatment

The flow channel dimensions in the Liqui-Cel contactors are quite small (on the order of 200–300 microns). Liquids containing suspended particles (or that may precipitate such particles during concentration) may plug those channels — particularly on the feed (shell) side of the module where the fiber fabric behaves in many respects as a deep-bed filter. Hence, prefiltration of both feed and strip prior to delivery to the OD array is a necessity. Cartridge or sheet-membrane filters capable of removing particles larger than 5 microns have been found to be adequate, although secondary backup with a 1-micron filter is a recommended precaution. Obviously, only feed streams with very low concentrations of such particulates (such as clear juices and vegetable extracts, and drug or biological solutions devoid of suspended cells or cell debris) are amenable to processing in this manner. Feeds containing high concentrations of suspended solids can be concentrated by OD, but require different pretreatments, as will be discussed later.

Certain clear solutions contain dissolved solutes of limited water solubility that, in the course of OD concentration, will precipitate or crystallize during transit through the contactor and deposit on or in the membrane. An important example is grape juice, many species of which contain potassium bitartrate. Such precipitates or crystals may form obstructive layers on the membrane surface or, in some cases, actually nucleate and grow into the membrane pores where they can promote wet-out and liquid leakage through the membrane. The problem can be eliminated by restricting the degree of concentration of the feed to a level just short of the saturation solubility of that solute at the processing temperature. Another approach that appears to be effective is to concentrate the feed to the solubility limit via OD, collect and chill the concentrate to allow precipitation to occur in the storage vessel, and then decant or filter, rewarm, and return the solution to the OD unit for further concentration. Sometimes, the

rate of precipitation during concentration is sufficiently slow that it does not occur during transit through the contactor — in such instances, providing a holding tank for the (supersaturated) concentrate to allow precipitation to take place *external to the contactor*, and then prefiltering or cyclone separating the precipitate prior to recycling the supernatant for further concentration may be effective.

## Feed pretreatment of particulate suspensions

Many feed streams that are candidates for OD processing contain rather high concentrations of particulate solids that neither the OD contactors nor conventional prefilters can handle properly. These include pulpy fruit and vegetable juices (citrus, pineapple, tomato, and the like), and fermentation broths containing microbial cells or cell debris. In some cases, the suspended solids are important components of the final concentrate; in others, they are contaminants. The most convenient means for preprocessing such feeds is *tangential or vortex-flow MF or UF*, to yield a particle-free permeate for delivery to the OD contactor array, and a retentate of high-suspended-solids content. This process does not alter the composition of the suspending medium. OD concentration of the permeate then can be carried out as with any clear solution.

If the suspended solids must be included in the concentrate, then the retentate labelled as "concentrated suspension" in Figure 9 would be reblended with the product concentrate. This, of course, will cause dilution of the final concentrate by the (unconcentrated) serum present in the retentate, the extent dependent upon the relative volumes of the two streams. This two step process necessarily limits the achievable degree of concentration (as well as increases the processing cost) and, thus, may be inappropriate for certain pulpy juices.

If, on the other hand, the suspended solids are contaminants, the reten-

tate generated on pretreatment can be discarded as waste, as indicated in Figure 9. It, of course, will contain product in solution; the fraction of product lost will approximately equal the ratio of the retentate volume to that of the original feed. Usually, this fraction is too small to be worth recovering. If its recovery is desirable, this easily can be accomplished by diafiltration of the retentate in a second cross-flow-filtration stage, with the permeate so produced delivered to the OD contactor array for addition to the main permeate stream prior to concentration.

## Hybrid processes

As mentioned earlier, OD is inherently more costly for concentration of aqueous mixtures than such conventional processes as evaporation, UF, or RO. Its advantage stems from its ability to selectively remove water relative to other low-molecular-weight solutes (volatile or nonvolatile) and, thus, to yield concentrates of superior quality. It also allows preparation of more concentrated products than are achievable by

RO. On the other hand, RO, where it can be carried out at relatively low pressure, is among the least costly means for water removal for feeds of low solute concentration. Although using RO will cause losses in volatile and nonvolatile flavors, fragrances, and other essential microsolutes, such losses can be minimized by *limiting the fraction of water removed*. Test results indicate that, with most liquid foodstuffs, acceptable concentrates not exceeding 30 wt. % solids can be produced economically in this manner. Therefore, a *hybrid process*, involving preconcentration of the feed by RO followed by further concentrating the RO retentate by OD, should yield a high-solids product concentrate of quality comparable to that achieved by OD alone, but at significant reduction in processing cost.

This hybrid process is also illustrated in Figure 9. Optimization calculations indicated that RO preconcentration of an 18° Brix (18 wt. % sugar) fruit-juice feed to about half its original volume (yielding ≈30° Brix retentate at a permeation flux of about 10 L/m²h) would cut the amount of
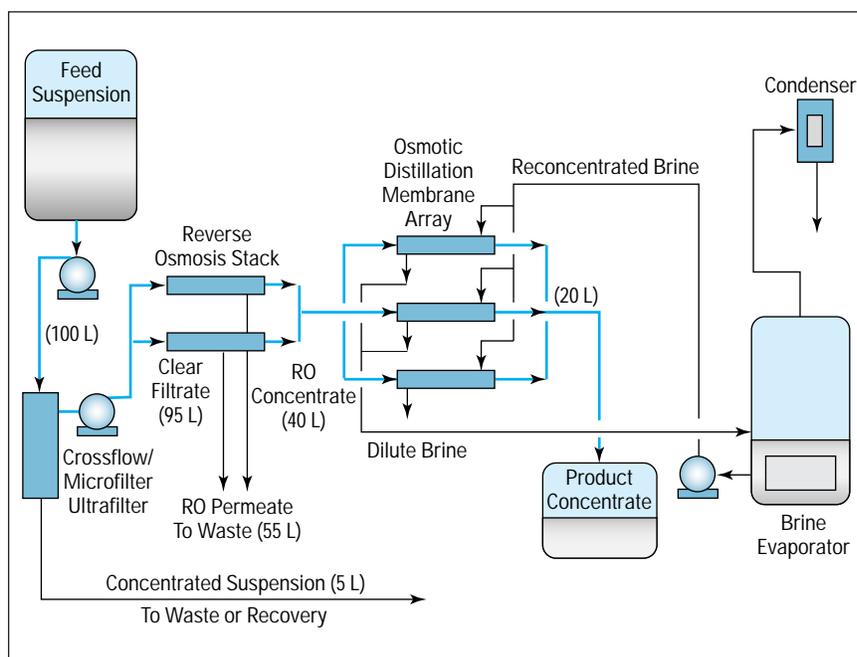


■ *Figure 9. Hybrid concentration system for food and pharmaceutical products containing suspended solids utilizes UF, RO, and OD.*

water to be removed by OD to deliver a 68° Brix concentrate by about 56%, with undetectable change in concentrate quality. This reduces the evaporator capacity requirements by one-half, and membrane area for OD by over 30% — leading to a decrease in capital and operating costs that far more than compensate for the incremental cost of the OD pretreatment stage. Obviously, for feeds of lower sugar or solute content, removal of larger fractions of the water by RO is practical, with even further improvement in process economics. Pilot-scale operations with this hybrid system have confirmed these predictions.

Thus, it appears that a hybrid RO/OD system is probably the most economic choice for feeds whose primary solutes are retained by RO membranes. A first-stage UF treatment for removal of suspended solids and colloids is also generally desirable to minimize possible fouling of either the RO or OD units. For feeds containing only macromolecular or intermediate-molecular-weight solutes (such as solutions of biologicals or pharmaceuticals), preconcentration by UF (in this case, discarding the permeate) without intermediate RO concentration may suffice.

## APPLICATIONS AND LIMITATIONS

At present, the most thoroughly evaluated and successfully demonstrated application of OD has been the concentration of fruit and vegetable juices, conducted in pilot-plant facilities located in Mildura and Melbourne, Australia. The Melbourne facility is a hybrid plant (consisting of UF and RO pretreatment stages, an OD section containing two 19.2-m$^2$ Liqui-Cel membrane modules, and a single-stage brine evaporator) designed and fabricated by Zenon Environmental (Burlington, Ont.). This unit can concentrate fresh fruit juices at an average throughput of 50 L/h to yield a 65–70° Brix (65–70 wt. %) concentrate, and has evaporative ca-

pacity for brine reconcentration of about 100 L/h. Each membrane stage is mounted independently on its own wheeled chassis with quick-connect sanitary fittings and flexible-hose connections between stages, to facilitate changes in system layout for differing feedstocks. The system occupies about 400 ft$^2$ of floorspace and requires headroom of about 12 ft.

This pilot facility has been used principally to develop operational parameters and economic data for the design of full-scale plants and, secondly, for the production of sample concentrates from feedstocks supplied by potential customers for their testing and evaluation.

The primary focus to date has been on the concentration of varietal grape juices used for the production of high-quality vintage varietal wines (Chardonnay, Cabernet Sauvignon, Merlot, Sauvignon Blanc, and the like). These are clear juices requiring relatively modest pretreatment to remove suspended particulates or hydrocolloids. Concentrates of these juices are of great interest to premium winemakers, because they can be stored for long periods without deterioration and can be used as blending stocks to adjust the sugar content of freshly harvested grapes to minimize variations in alcohol content of the resulting wine from vintage to vintage. Another important advantage of concentrates is that they can be shipped over long distances at relatively low cost and used to produce high-priced varietal wines in locations and at times where local grape supplies are unavailable, inadequate, or too costly.

An important economic motivation for the use of varietal-grape-juice concentrates for winemaking is the extraordinarily high cost of such grapes in many areas of the world and the wide disparity in cost from region to region. Fresh juices frequently sell in the range of $0.50–$1.50/L. As one liter of fresh juice yields about 200 mL of 70°

Brix concentrate, the base value of concentrate is between $2.50 and $7.50/L. The total processing cost of OD concentration (at commercial-scale production levels) is estimated to be well below $1.00/L of concentrate. There are, therefore, opportunities for high profits to be derived from producing quality varietal-grape-juice concentrates by OD from fruit available at low cost and shipping and selling concentrate to winemakers serving high-price markets.

Other fruit and vegetable juices that have been concentrated by OD in this facility include high-value clear tropical fruit juices, as well as apple and carrot juices. Interest also has developed in the use of the process for preconcentration of coffee and tea prior to relatively costly freeze drying.

Concentration of citrus and other pulpy juices has sparked some interest, but it is uncertain whether depulping and recombination after concentration will be technically and economically feasible, and whether the resulting concentrate would be sufficiently superior in quality to justify its higher cost. Moreover, citrus juices contain peel oils and other highly lipophilic flavor components that reduce their surface tension and promote wetting of hydrophobic surfaces. Such fluids, in most cases, will promote wet-out and liquid penetration into polypropylene OD membranes. Development work currently is underway to attempt to produce hollow-fiber microporous membranes from more hydrophobic polymers such as PTFE or PVDF or to make laminate membranes that will prevent liquid intrusion without impeding vapor transport. Success in this area should broaden the utility of OD for feedstocks of this nature.

### Pharmaceuticals and biologicals

Many manufacturing operations in the drug and biologicals industries produce relatively dilute solutions of macromolecular products (such as

vaccines, peptide hormones, recombinant proteins, enzymes, and nucleic acids) or of intermediate-molecular-weight products generated by fermentation (like antibiotics, fungicides, and oligopeptides). Most of these products exhibit rather poor thermal stability or are susceptible to denaturation and inactivation with changes in their solution environment. Isolation and recovery of these products in the dry state often is essential to maintain their activity and shelf stability for extended periods. Today, preconcentration of these products by RO, nanofiltration, and UF is in wide use, although the degree of concentration achievable without product activity loss via these techniques frequently is limited. Second-stage concentration of these solutions by OD may allow the production of bioactive product concentrates from which solids can be more easily recovered (by crystallization or extraction).

By far the most successful means of producing a stable solid product from these solutions is lyophilization (vacuum freeze drying). Lyophilization, however, is a very costly and tedious process, because it usually requires the removal of water by ice sublimation at very low temperatures — where the sublimation rate is exceedingly slow and the energy requirements for maintaining the necessary low pressures and temperatures are substantial. In addition, the capital and maintenance costs of industrial-scale units are quite high.

There is growing interest in the possibility of employing OD as a preconcentration step for such products prior to lyophilization, to remove a significant fraction of the water from solution without product deterioration and, thus, to reduce the water-removal load during freeze drying. Efforts currently are underway to evaluate, in small-scale tests, OD concentration of a vaccine or biological solution, the bioactivity of the resulting concentrate, and the final activity and stability of the dry product made by lyophilizing this concentrate.

## Dealcoholization and removal of volatile solutes

Another potentially important application of OD is the selective removal of a volatile solute from an aqueous solution. Here, the solute of interest is evaporated from the feed at the membrane surface, transported by vapor diffusion through the membrane pores, and condensed into a strip liquid on the opposite face of the membrane. Most commonly, the stripping liquid is pure water or an aqueous solution containing a lesser concentration of the solute being transferred. This process more precisely can be described as "evaporative pertraction." It functionally resembles dialysis, but is selective only for volatile solutes.

The primary application now under active evaluation is the removal of ethanol from fermented beverages such as wine or beer. There is considerable worldwide interest today, for health reasons, in a method for selective removal of alcohol from such beverages without adversely affecting their taste, odor, or mouthfeel. For wines, which typically contain 11–15 vol. % ethanol, evidence suggests that reducing the alcohol content to about 6% will yield a beverage that closely resembles in organoleptic properties the original ferment, so long as the flavor and fragrance volatiles (principally organic acids,

ketones, aldehydes, alcohols, and esters) are retained. Decreasing ethanol to below 6% in a wine may drastically alter its taste and aroma.

OD of a high-alcohol-content wine at a temperature of 10–20°C using plain water as the stripping liquid can rapidly reduce its alcohol content to levels down to 6% with minimal loss of its flavor and fragrance components. (Of course, the process permits removal of nearly all the ethanol, if that is desired.) The mechanism of the process, as illustrated in Figure 10, takes advantage of three factors: (1) ethanol is the most volatile component in the wine and the most rapidly diffusing species across the membrane, (2) the vapor pressure of the flavor/fragrance components is low and, thus, so is their OD flux, and (3) the solubilities of the flavor/fragrance components in alcohol/water solutions are substantially higher (and their vapor pressures correspondingly lower) than they are in plain water. As a consequence of this last property, the driving force and transport rate of these components from wine to strip is reduced even further. In addition, because the vapor pressures of water over the wine and over the strip solution are nearly identical, there is virtually no traffic of water from the strip into the wine. The variations in vapor pressures of ethanol and water over ethanol/water solutions are illus-



■ *Figure 10. Mechanism of selective alcohol removal by evaporative pertraction.*
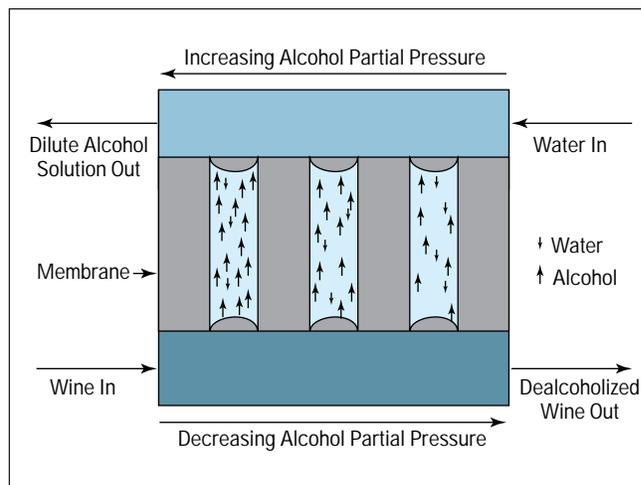
trated in Figure 11, from which the relative OD fluxes of alcohol and water during dealcoholization can be easily visualized.

Another advantage of this process is that it generates a strip solution from which food-grade (190 proof) ethanol can be recovered by rectification. This is a potential blending stock for production of fortified wines, liqueurs, and whiskeys.

Such a system for controlled dealcoholization is suitable for wineries of any size, and is very simple and nearly foolproof to operate. The essential features of the system are shown in Figure 12. Wine from a chilled storage tank is continuously recycled through the shell side of the OD contactor array, while strip solution (water) from a second storage tank is continuously recycled through the lumen side. The volume of water provided to the storage tank is adjusted so that, when the concentrations of alcohol in the strip and wine reach equality, the wine will have the desired alcohol content. Thus, a 10,000-L tank of 15%-ethanol wine treated with 15,000 L of water will yield 10,000 L of 6%-ethanol wine and 15,000 L of 6% ethanol. This system can run unattended, except for occasional analysis of the strip for ethanol, until the transfer stops.

Winemakers also encounter situations where a dry-season vintage provides high-sugar-content grapes which, on fermentation, yield inordinately high-alcohol-content wines. Such wines are considered "hot" to the palate and, so, have reduced market value. Dilution with water can correct this, but is considered adulteration in many jurisdictions. Thus, there is a need for a means for "trimming" the wine — that is, removing alcohol selectively to a level of ≈12% without altering its flavor and fragrance characteristics. Trimming by OD dealcoholization, using a small relative volume of strip water, accomplishes this task rapidly and readily.

The cost of OD dealcoholization (per liter of ferment processed) is



■ *Figure 11. Vapor pressure relationships for evaporative pertraction of ethanol.*
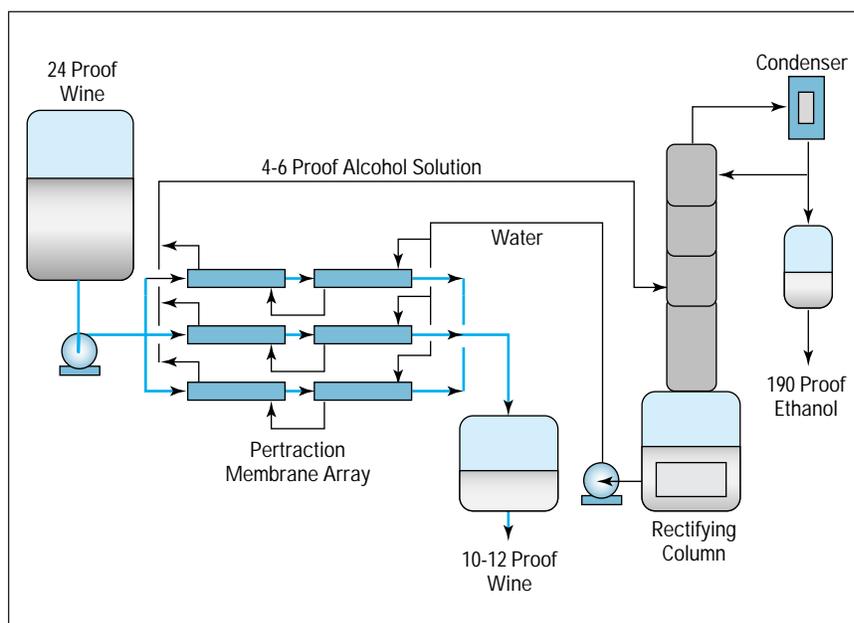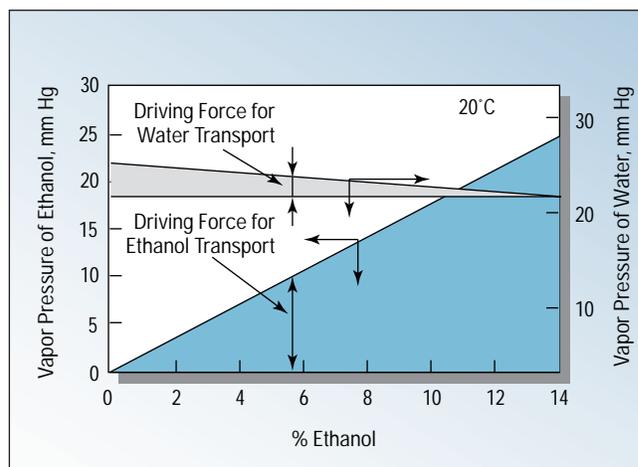


■ *Figure 12. Dealcoholization of ferments by evaporative pertraction.*

considerably below that of OD concentration, because the vapor traffic per liter of feed is much lower, pumping and instrumentation requirements are minimal, and the ancillary costs of feed pretreatment and brine reconcentration are avoided. Moreover, rates of transmembrane permeation of ethanol are far higher than those of water; so, OD membrane-area requirements are much reduced. Recovery of marketable food-grade azeotropic ethanol is another cost benefit.

Opportunities also exist for selec-

tive removal of organic volatiles from aqueous solutions in the drug industry. For example, miscible solvent extraction of intracellular products from whole fermentation broths is widely employed today. After separating out the biomass from this mixture, it often is necessary to remove and recover part of the organic solvent from the product-rich supernatant. This frequently needs to be done at low temperature to protect the product from thermal degradation. Solvent removal by OD using water as the strip solution is a convenient means for accom-

plishing this. The solvent-containing strip then can be rectified to recover the solvent in high purity, leaving clean water for recycle.

Similar needs exist in the isolation and purification of antibiotics, hormones, and biologicals by hydrophobic or inverse-phase chromatography, which frequently employs water/organic solvent mixtures as eluting solvents. Eluant cuts containing products of interest can be processed by OD to remove and recover the organic cosolvent without product damage, providing an aqueous solution of the product for final recovery.

## Commercial status

Over the past year, process development studies with the pilot plant now operating in Melbourne, and production in that facility of test quantities of juice concentrates and dealcoholized ferments for customer evaluation have confirmed the reliability and economic feasibility of the process for such applications and the superior quality of the resulting products. Design and costing of a commercial-scale hybrid OD plant recently has been finished and construction of such a unit is scheduled for completion later this year. Negotiations currently are underway to establish a collaborative advanced-commercial-development and product-marketing program with a major international producer of wines and fruit juices that has U.S. production facilities for varietal-grape and other fruit-juice concentrates and low-alcohol wines.

As noted above, the process appears to have considerable promise for the concentration of heat-sensitive pharmaceutical and biological products such as vaccines and antibiotics. Selective removal and recovery of volatile organic solutes from aqueous solution by OD also may have promising applications in the pharmaceutical industry for recovery and isolation of thermally labile bioactive substances. The pilot OD facilities now available are expected to be used for evaluations of such applications in cooperation with several pharmaceutical manufacturers who have expressed interest in this technology.

It should be emphasized that OD is a relatively more costly process for water removal from solution than more-conventional processes such as distillation, UF, and RO. Therefore, it is unlikely to compete with these conventional concentration processes if the concentrates they produce are adequate. Its unique ability, however, to produce highly concentrated solutions of heat- or stress-sensitive products with minimal deterioration appears to make the incremental cost justifiable for many high-value products. Hybrid processes, involving the use of pressure-driven membrane-preconcentration processes such as UF and RO, promise to reduce the overall costs of OD concentration and broaden its utility. **CEP**

## Further Reading

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