Even though we prefer not to use them, solvents are indispensable to many processes in fine chemicals, pharmaceuticals, petrochemicals and printing. Most of these processes involve:
• a feed of a high purity, anhydrous solvent
• introduction of water into the solvent, e.g. as a reaction by-product
• contamination of the solvent with other materials, resulting in a waste stream

LIMITATIONS OF DISTILLATION
Distillation has long been the standard technology for solvent recovery. Both dissolved solids and higher boiling components such as water can be removed.

Distillation is uncomplicated as long as the solvents are easy to distill from water, i.e., if they lend themselves to concentration (Fig. 1, curve a). It becomes more difficult with low water content, if the difference between the equilibrium vapour and liquid concentration narrows (curve b). Once the equilibrium vapour and liquid phase concentrations are identical, i.e. the azeotropic point has been reached, further distillation serves no purpose because there can be no further concentration (curves c and d).

Pervaporation takes over where conventional distillation comes up against its limits. The membranes which are used easily separate water, methanol and ethanol from organic solvents.

The last traces of water can only be separated from a solvent with great effort (curve b, top right). The azeotropic point limits where distillation can be used (curves c and d).
Every process engineer looks for a way round this problem. In rare cases it may be possible to modify the production process to use aqueous solvents. Another solution could be to eliminate the azeotropic point by adding an additional substance such as an entrainer or a dessicant, although this risks contaminating the solvent.

**Pervaporation breaks the barrier**

Having taken over the activities of the German-based GFT membrane separation business, Sulzer Chemtech is now able to offer pervaporation technology as an ideal complement to distillation. Pervaporation membranes, assembled in patented plate and frame modules, are at the core of a pervaporation plant and provide the desired separation. The membranes are able to absorb certain substances which have a chemical affinity for the membrane and reject substances which have less affinity (Fig. 2). Hydrophilic membranes are available for separating water from solvents, and organophilic membranes are used to remove organics from water.

A substance needs a driving force to pass through the membrane. In the case of pervaporation, this is provided by the partial pressure difference across the membrane for the component being removed. The partial pressure of a component is proportional to its concentration and the vapour pressure of the pure substance at the operating temperature. The partial pressure of the permeating component is increased on the front (feed) side of the membrane by heating and reduced on the back (permeate) side by applying vacuum and cooling. The operating temperature of the feed mixture is typically around 95°C. On the permeate side, temperatures from +20 down to –20°C may be needed to condense the permeate, depending on how thoroughly it is desired to remove the permeating component (typically water).

This principle offers enormous advantages for separating materials:

- It can be applied regardless of the vapour-liquid equilibrium.
Azeotropes can easily be broken without adding additional substances; components with the same volatility can be separated.

**VALUABLE ADJUNCT TO DISTILLATION**

The effectiveness of distillation is determined by vapour-liquid equilibria. These properties are not a factor in pervaporation. What matters here is the differential absorption and diffusion of the components through the membrane. This is why pervaporation is such a valuable adjunct to distillation, allowing distillation towers to be designed for less stringent operating conditions for example, while a subsequent pervaporation stage pushes the separation to completion.

The term pervaporation is used when separating liquids. If a saturated vapour mixture is to be separated, the process is called vapour permeation, although it is essentially the same.

**INCREASING THE YIELD OF REACTIONS**

The production of esters by reacting acids with alcohols is a commonly used process in the chemical industry. Water is generated in the process, and its removal increases the yield of ester.

If the ester has a high boiling point, water can be separated by heating the reaction mixture so that the lower boiling alcohol evaporates with the water while the higher boiling ester remains in the reactor. Water and alcohol are then separated in a downstream column, though this is possible only up to the azeotropic point. Recycling the azeotropic alcohol-water mixture into the reactor again is possible, but has limitations because water addition shifts the reaction equilibrium unfavorably. Up to now it has only been possible to optimize the reaction by the additional use of anhydrous alcohol.

Using vapour permeation immediately after the tower allows the operator to dehydrate the alcohol azeotrope and recycle the anhydrous alcohol back into the reactor (Fig. 3). This enables the reactor to keep operating until the feedstock is completely converted. The amount of excess alcohol can be reduced, and there is no aqueous alcohol requiring disposal. Ester separation is simplified too, since the ester has only to be separated from the alcohol.

**RECOVERING SOLIDS AND SOLVENTS**

Solvent recovery from mother liquors is another example of the use of vapour permeation. In many industries such as pharmaceuticals, valuable substances are precipitated from aqueous synthesis solutions by adding solvents such as alcohol. Large quantities of aqueous solvent mixtures which
still contain dissolved solids are left after precipitating and filtering out these substances. Here again, Sulzer Chemtech’s technology can help. Depending on the water content of the solvent mixture, either a distillation tower may be employed to remove the dissolved solids and at the same time provide preliminary dehydration of the solvent down to the azeotrope, or else a simple evaporator may be installed to remove the dissolved solids. In both cases, the solvent is subsequently dehydrated by vapour permeation down to a level suitable for reuse in production (Fig. 4). The chief advantages lie in the recovery of the dissolved solids and their valuable constituents, the reuse of the solvent in production and the reduction of waste streams. Sulzer Chemtech has already supplied a plant of this kind to a pharmaceutical producer in Portugal, where 300 kg/h of dehydrated solvent are produced at 88% recovery (Fig. 2). **UP TO 98% RECOVERY**

Solvent recovery in such printing and coating operations that still need to use solvents is a common practical application. The usual process for recovering the solvent is adsorption onto activated carbon, which is periodically regenerated with steam. This results in recovered solvent heavily diluted with water. This poses disposal problems and is usually incinerated at some cost. Recycling is the better method. Here Sulzer Chemtech has adopted the hybrid process. In Italy, a leading producer of adhesive tapes uses one of the plants supplied by Chemtech to recover isopropanol (IPA). Regeneration of the activated carbon with steam produces an effluent with 20 - 30% IPA, which is treated using Sulzer Chemtech technology. The first process stage is preparation and concentration of the IPA in a distillation tower with structured packing (Mellapak®). In the second stage, the azeotrope vapour containing 86% IPA passes into a vapour permeation plant, where it is concentrated to 99.5% (Fig. 5). The permeate, which contains a small quantity of IPA, is recycled back to the tower in order to make the IPA recovery as complete as possible. With the resulting 98% IPA no incineration is necessary, purchase of new solvent is cut to a minimum, and the effluent water can be discharged to a treatment pond. **FOR MORE DETAILS**

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**5 Flow diagram of a hybrid plant (distillation plus vapour permeation).**