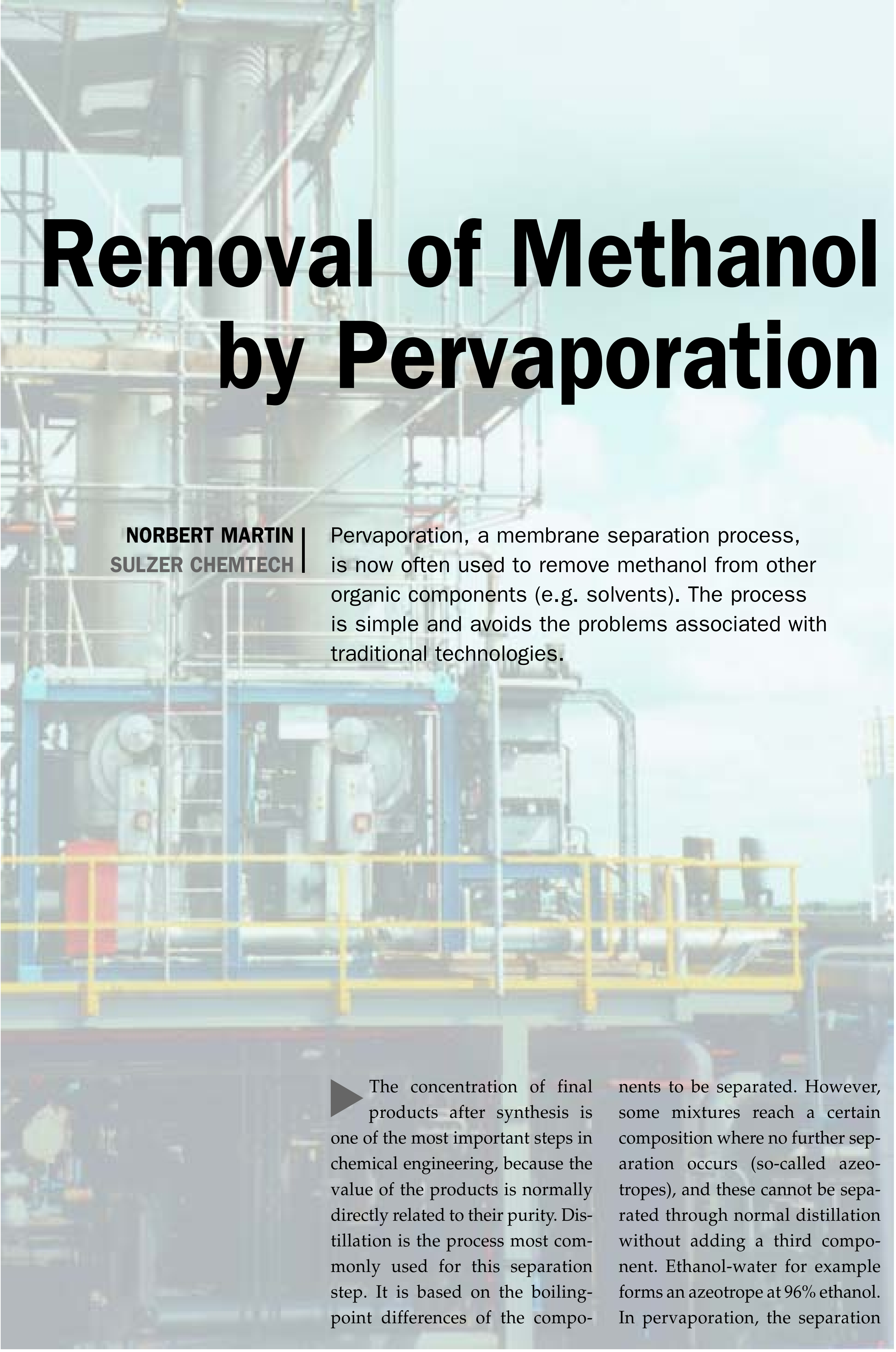

Removal of Methanol by Pervaporation

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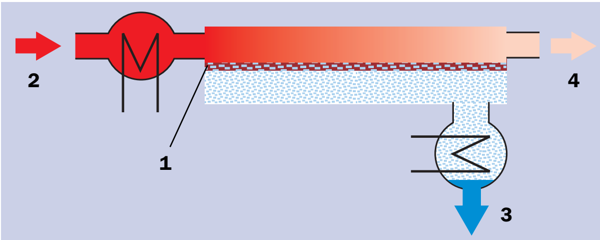
Pervaporation, a membrane separation process, is now often used to remove methanol from other organic components (e.g. solvents). The process is simple and avoids the problems associated with traditional technologies.

The concentration of final products after synthesis is one of the most important steps in chemical engineering, because the value of the products is normally directly related to their purity. Distillation is the process most commonly used for this separation step. It is based on the boiling-point differences of the components to be separated. However, some mixtures reach a certain composition where no further separation occurs (so-called azeotropes), and these cannot be separated through normal distillation without adding a third component. Ethanol-water for example forms an azeotrope at 96% ethanol. In pervaporation, the separation



1 The principle of pervaporation: By means of a semi-permeable membrane (1), water or methanol (3) is removed from the feed mixture (2) to provide a purified product (4).

mechanism is the difference in the diffusion rate of the components through a semi-permeable membrane. This technique works well to separate azeotropic mixtures. The separation of water from organic solvents by pervaporation is by no means new (see STR 3/1998, p. 12). Sulzer Chemtech is now also applying this process successfully for the separation of methanol from other organic solvents.

Disadvantages of Conventional Processes

Methanol is found as a reactant or reaction product in many different processes (esterification, transesterification) where it is more difficult to separate it from other organic compounds than from water. Methanol forms azeotropes with numerous organic compounds.

There are various conventional processes for the removal of methanol. Selection of the process is dependent on the specific characteristics of the mixture to be separated. They all have greater or lesser disadvantages:

- In the case of water-washing followed by distillation, the water is introduced into a previously water-free mixture and cannot be removed completely afterwards. In addition, this process requires three distillation columns and thus a relatively large amount of space. Furthermore, it consumes a large amount of energy and generates wastewater that has to be treated.
- Although it is simple to extract methanol with alkali salts, it entails a risk with regard to the product quality, because the presence of a certain amount of salt in the final product cannot be avoided. The treatment of the separated salty phase also necessitates additional equipment and energy. Moreover, it is labor-intensive due to the handling of solids, causes corrosion and creates environmental problems.

2 If a pervaporation plant is skid-mounted, installation on the site is simplified.

Development of a New Membrane

Pervaporation avoids the aforementioned disadvantages. It is now regarded as the latest state of the art in the chemical industry, where separation is concerned. The most frequent application is the removal of water from organic compounds with hydrophilic membranes. Typical applications are the splitting of azeotropes and the final dehydration of the product.

The separation principle of pervaporation (Fig. 1) is based on the difference in the polarity of the compounds to be separated, their molecular size, and the affinity of the most polar substances for the interface of the membrane. The more polar and smaller a molecule is, the easier it can be absorbed and passed through the membrane. Since water is the smallest and most polar molecule, the separation of water from organic compounds functions the best. The driving force for the separation is the difference in the partial pressure of the water vapor between the feed and rear side of the membrane. The necessary partial pressure difference is attained by feeding the mixture to be separated to the membrane preferably with a high temperature, while a vacuum at low temperature is created on the rear side of the membrane. The substance passing through the membrane – the so-called permeate – is then condensed there.

As far as the polarity is concerned, methanol is water's closest neighbor. Based on the experience gained with the separation of water, Sulzer Chemtech has developed a new generation of membranes which can remove methanol from organic substances. This constitutes a further field of application for pervaporation – the first plants are already in operation.

The use of pervaporation dramatically simplifies the separation of mixtures containing methanol. The azeotrope is fed to the membrane unit, and the methanol selectively permeates the membrane. The retentate – depleted in methanol – is either condensed (providing the methanol concentration is low enough) or passed as a vapor to a downstream column, where even higher purities are attained. The methanol-rich permeate is recycled back to the process which produces the azeotrope to remove the methanol. This process can be employed for new plants and also for the revamping of existing installations.

High Purity – Lower Energy Consumption

The advantages gained through the separation of methanol by pervaporation are obvious: No additional water or salts that have a negative effect on the product quality are required. The membranes are inert and do not release any substances to the solvent mixture. There is no impact on the environment, since neither wastewater nor salt solutions containing methanol have to be treated.

Furthermore, the membrane process is characterized by its low energy consumption. If the mixture can be taken directly off a column as a saturated vapor with a temperature of approximately 90 °C, no additional energy is required to pass the methanol through the membrane. And should an evaporator have to be installed, the retentate can be fed directly to the column as a vapor to save energy.

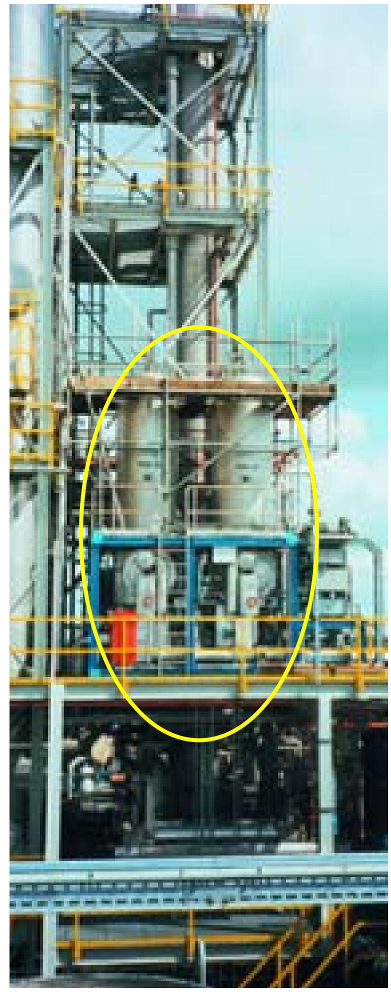
Successful Operation

Pervaporation plants are delivered as skid-mounted units. They contain all the necessary components (heat exchangers, pumps, valves, etc.), as well as the internal pipework and the instrumentation (Fig. 2). This minimizes the installation costs and the time needed for the installation on the site. Since the process is simple, the skids are easy to install and require relatively little space.

Sulzer Chemtech has already installed two of these plants, which are both being operated successfully by the customer. The first plant (Fig. 3) was installed in a fine-chemicals plant in the Netherlands in 1997 to accommodate a capacity expansion as well as replace the existing salt extraction. Since then, the customer has been using the fully automatic process and achieves a higher product quality.

The second plant, which separates methanol from methyl acetate, was installed in Spain at the end of 2000. The customer insisted on a water-free end product with a specific methanol content. The membrane process was able to fulfill both these requirements.

A third plant – for the separation of methanol from acetone – was supplied to another customer at the end of 2002. Thus, Sulzer Chemtech was able to demonstrate the suitability and benefits of pervaporation yet again. ◀



3 The vapor permeation plant supplied to the Netherlands in 1997 was integrated in an existing plant complex.

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