PERVAPORATION & VAPOR PERMEATION PROCESSES

Pervaporation and vapor permeation have been established over the past decades as improved technologies to dehydrate organic solvents such as alcohols, ethers, esters and ketones. The optimal use can be achieved if these technologies become part of a hybrid system, for example in combination with distillation and rectification columns.

Pervaporation and vapor permeation are membrane-based thermal processes to dehydrate binary or multi-component mixtures of miscellaneous organic fluids. Dehydration of the mixtures is performed using a membrane - the pervaporation membrane. Non-porous ('dense') or microporous pervaporation membranes made of polymeric or ceramic materials exhibit different permeabilities towards different components, resulting in the desired separation of the components. The Dutch company Pervatech supplies plants, systems & membranes and provides technology for pervaporation and vapor permeation applications.

1. Dehydration by pervaporation or vapor permeation - the basics

In the dehydration process, the feed is heated up to the operating temperature and then brought into contact with the active (feed) side of the pervaporation membrane. Water preferentially passes through the membrane and is continuously removed in the form of vapor from the back (permeate) side of the membrane by using a vacuum pump or by applying a sweep gas. The continuous removal of the vaporous permeate creates a concentration gradient over the pervaporation membrane. This concentration gradient is the driving force for the separation process.

The concentration gradient is best expressed in terms of partial water vapor pressure. A few different models have been developed to describe the pervaporation or vapor permeation processes. For the sake of simplification, the mass transfer over a pervaporation membrane can be divided into three major steps:

- Adsorption of permeating components at the feed side into the membrane.
- Transport of adsorbed components through the membrane by diffusion according to Fick's law.
- Desorption at the permeate side into the vapor phase under vacuum.

Figure 2 illustrates these three steps for a pervaporation membrane.

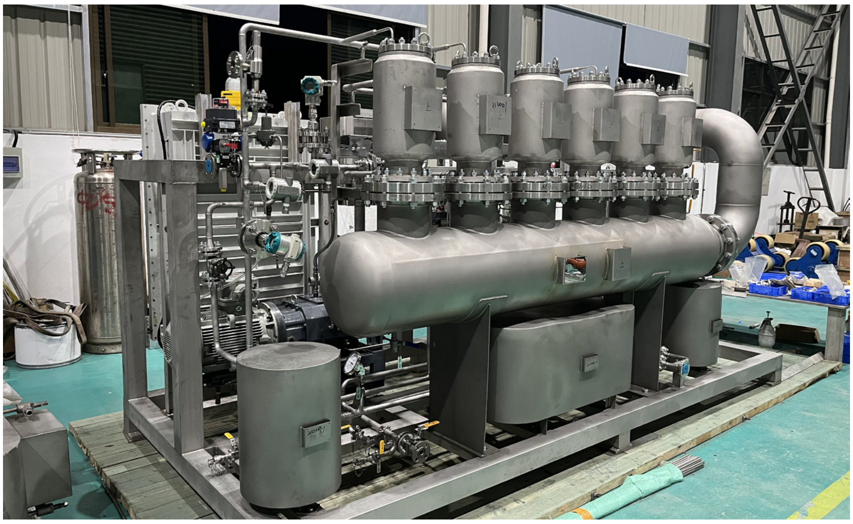

Figure 1: Pervatech's industrial scale continuous mode pervaporation plant

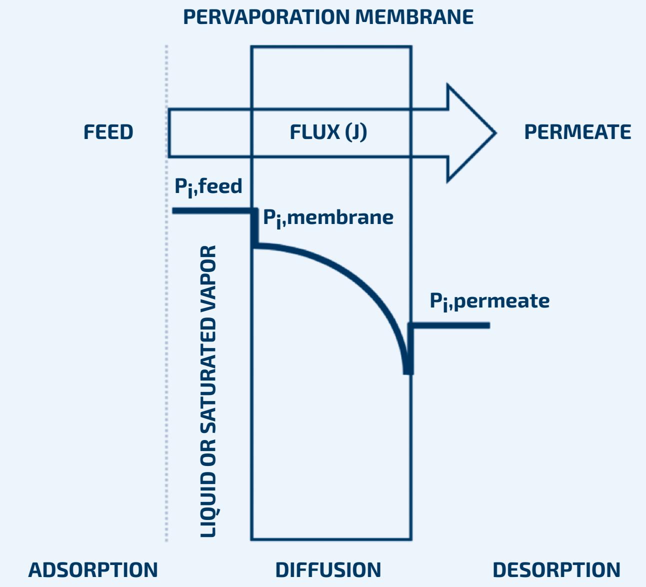

Figure 2: Principle of mass transfer over pervaporation membranes (p = partial vapor pressure, J = mass flux)

Two values characterize a membrane:

- Its *selectivity* (also called separation characteristic)
- The *permeate flux* (here: water removal rate) through the membrane.

Figure 3 for the binary system isopropanol-water can be used to demonstrate the selectivity of a pervaporation membrane in comparison to the vapor-liquid equilibrium as used in distillation, the 'workhorse' of industrial chemical separation. In conventional distillation, the difference in boiling point (relative volatility) of the components is the basis for separation: a lower-boiling component will evaporate more than a higher-boiling component, resulting in a higher fraction of the lower-boiling component in the vapor mixture, compared to the liquid mixture. However, distillation performance is highly limited at the azeotropic composition of the mixture, where the liquid mixture has the same composition as the vapor mixture. Above this azeotropic composition, volatility-based separation is no longer achievable since this composition will not be changed any further by conventional distillation.

In Figure 3, the composition of the permeate is plotted against the composition of the feed. Included in the diagram is the composition of the vapor, in equilibrium with the liquid mixture (red curve). In contrast to this equilibrium curve, water is the more permeable component at nearly all feed concentrations (blue curve). Permeate qualities for organic solvents comparable or larger in size than isopropanol range between 95-99 wt% water, resulting in a low organic loss.

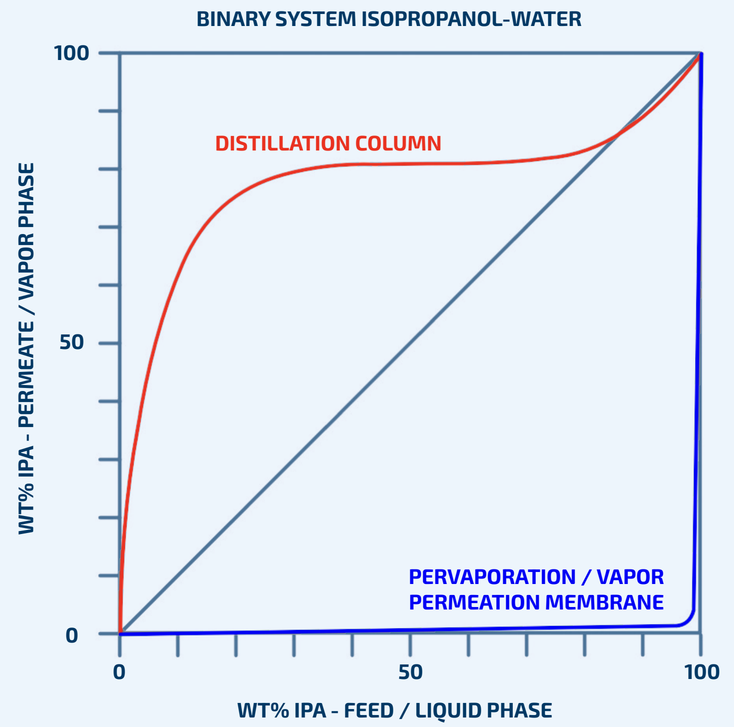

Figure 3: Distillation and pervaporation characteristics for the binary system isopropanol (IPA) - water

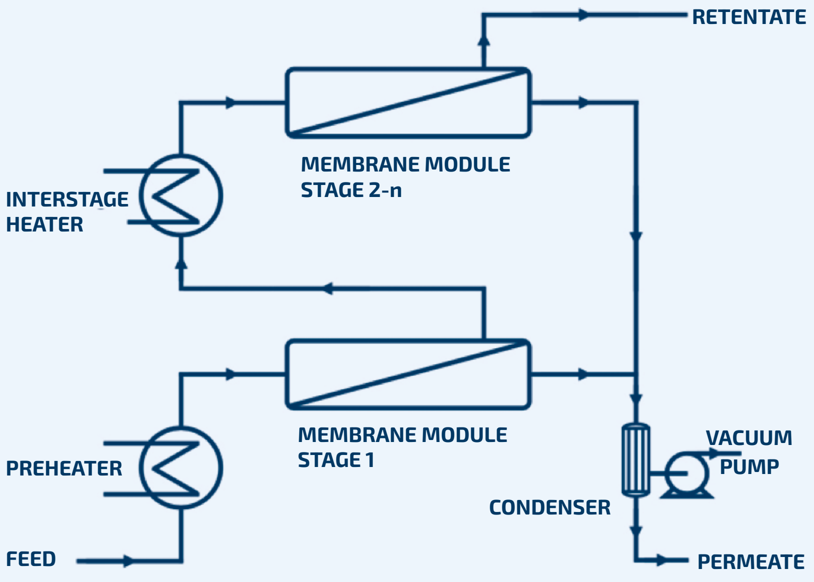

Figure 4: Pervaporation process

2. Practices

2.1 Pervaporation process

In the pervaporation process, as depicted in Figure 4, a liquid feed stream is first preheated to operating temperature and then routed to a membrane module. The permeate transported through the membrane is evaporated at the permeate side of the membrane and heat is dissipated from the feed. As the partial pressure of the transported component, and with it the driving force for mass transportation, decreases at declining temperature, the feed mixture has to be re-heated. Therefore, for larger plants and high permeate rates, it may be necessary to provide for several small membrane modules with upstream heat exchangers. The vaporous permeate leaving the membrane module is condensed under vacuum.

2.2 Vapor permeation process

In the vapor permeation process, illustrated in Figure 5, saturated vapor instead of a liquid feed solution is passed through the module. Vapor permeation is advantageous if the feed mixture contains non-volatile or undissolved constituents (such as salts) and any of its constituents that tend to precipitate out can be separated as bottom product in the evaporator.

3. Feed materials

Please find below an overview of some important compounds that can be treated by pervaporation or vapor permeation:

- Alcohol dehydration, such as ethanol, propanol, butanol, and higher linear alcohols, as well as higher alcohols such as glycol, glycerin and glycol ether.
- Dehydration of ketones such as acetone, methyl ethyl ketone (MEK) and methyl isobutyl ketone (MIBK).
- Ether dehydration such as diethyl ether, di-isopropyl ether, tetrahydrofuran (THF) and dioxan.
- Ester dehydration such as ethyl acetate, butyl acetate and isopropyl propionate.
- Dehydration of hydrocarbons such as benzene, toluene and xylene (in most cases in mixtures with other solvents), as well as chlorinated hydrocarbons such as trichlorethylene.
- Organic acid dehydration, such as acetic acid, propionic acid and higher acids; these can be dehydrated using PERVATECH Hybrid Silica HybSi® Acid Resistant membranes.
- Aprotic solvent dehydration, like DMF, DMSO or NMP. Note: these solvents will attack polymeric pervaporation membranes but can be dehydrated by means of *ceramic* pervaporation membranes such as PERVATECH Hybrid Silica HybSi® Acid Resistant membranes.
- Winning of organics from aqueous solutions, such as biobased components (e.g. Aacetone-butanol-ethanol or n-butanol) made by fermentation or other biological process, flavor and fragrances.

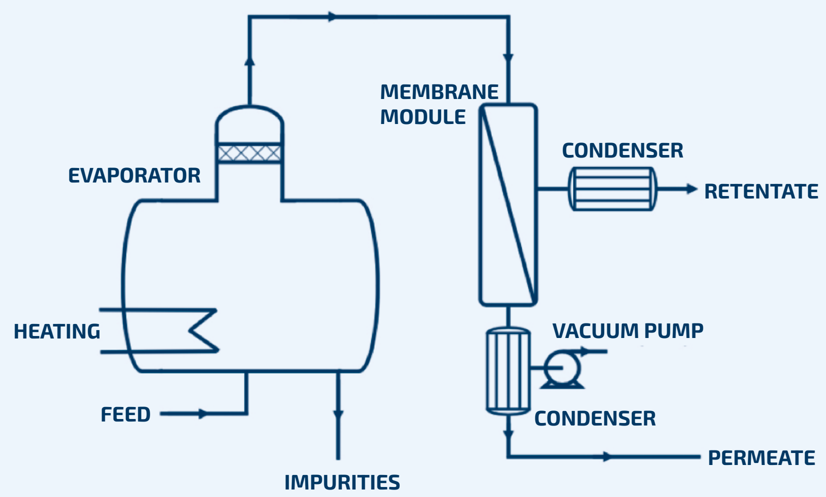

Figure 5: Vapor permeation process

Figure 6: a) Pervatech's industrial membrane module holding tubular PERVATECH Hybrid Silica HybSi® Acid Resistant pervaporation membranes. b) Membrane stack

4. Major applications

Typical applications for pervaporation and vapor permeation include:

- Removal of water from organics / concentration of aqueous solutions
- Removal of organics from water
- Separation of organic mixtures (such as MeOH/DMC)

With respect to the number of installations, installed membrane area and economic advantages, the removal of water from organic solvents and solvent mixtures is the most important pervaporation and vapor permeation process. Membranes, modules, and process know-how are fairly well developed and allow the installation and operation of industrial plants with large capacities. See 4.1 Solvent dehydration processes for more details.

Removal of organics from water, using organophilic pervaporation membranes, is applied in e.g. the production of ABE and n-butanol by fermentation and other biological processes. These products are utilized as bio-based building blocks for sustainable production of chemicals and materials. Another application is the winning of valuable flavors and fragrances from aqueous natural feed stock.

Separation of organic mixtures by pervaporation/vapor permeation is a growing sector. Membranes have been developed and are reportedly tested on a pilot plant and industrial scale, for example to separate methanol from dimethyl carbonate (DMC) in the industrial DMC synthesis (see 5.3 Solvent recycling and organic/organic separation for more details).

4.1 Solvent dehydration processes

When conventional distillation is practically feasible, pervaporation or vapor permeation will usually not be economically favorable. However, where distillation requires entrainers / pressure swing to split azeotropes or a large number of theoretical separation stages or high reflux ratios, the employment of pervaporation or vapor permeation in a hybrid configuration results in high energy reductions. Such hybrid configurations have been described in literature. [Harvianto et al. 2016]. have modelled a number of possibilities in their review paper and found that clever combinations between distillation and pervaporation can lead to savings up to 77%.

Figure 8 illustrates a typical process with pre-distillation, extractive distillation and entrainer recovery for the purification and dehydration of polluted solvents, for example for an isopropanol-water system. How such a standard process can be improved by integration of a pervaporation or vapor permeation unit (process intensification) is shown in the example in Figure 9.

A pervaporation or vapor permeation process will show the greatest advantages in hybrid systems for the separation of those mixtures in which the organic component has been pre-concentrated by distillation to a certain degree. The optimum pre-distillation depends on the nature of the organic component but is often a sub-azeotropic concentration.

Figure 7: PERVATECH pilot pervaporation plant for organics recovery from aqueous feed

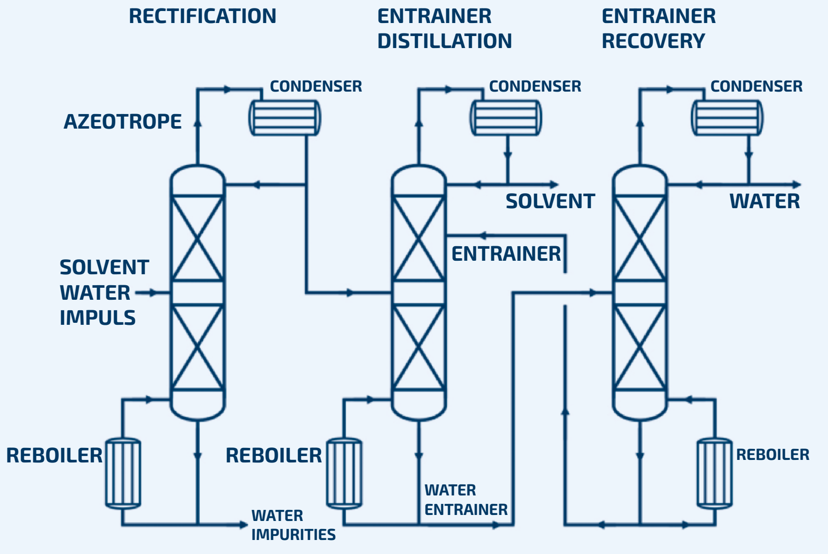

Figure 8: Standard process with entrainer distillation

Furthermore, during pre-distillation the untreated raw feed mixture is also pre-purified for removal of non-volatile impurities. As with all membrane processes, the feed stream to a pervaporation membrane should be free of undissolved particles and should not contain dissolved substances, which could precipitate out during the concentration process. Such particles otherwise could block or even destroy the membrane. The pre-distilled product (azeotropic concentration) is drawn from the head of the first column and then fed to the pervaporation unit. During the pervaporation process, the feed mixture will be dehydrated above the azeotropic point and then proceeds to a second column for final dehydration/ purification purposes. The water-rich, vaporous permeate can be condensed and recirculated to the pre-distillation column to minimize losses of the organic solvent if necessary. However, this comes at the expense of energy consumption. This hybrid process is also applicable to systems such as tetrahydrofuran-water and pyridine-water, for example.

Depending on the nature of the solvent, overall capacity, and product quality, it might be more economically favorable to remove the second dehydration/purification column and apply the pervaporation unit for final dehydration as well. This process variation is illustrated in Figure 10. Pervaporation down to 0.1-1 percent of water is very well possible. As a rule of thumb, it will take just as much membrane surface area to dehydrate from 20 % to 0.2 % water as the membrane surface area needed to dehydrate from 10 % to 0.1 % water.

Summarizing: pervaporation is a flexible technique which can also be used in combination with traditional drying techniques to enhance the performance of these drying systems.

5. Case studies

5.1 Chemicals

Case 1: IPA dehydration in a hybrid process - economics

A binary IPA and water mixture forms a minimum-boiling azeotrope at 87 wt% IPA (80 °C). Breaking of this azeotrope via entrainer or pressure swing distillation leads to high CAPEX and OPEX investments. These costs can be reduced by means of a hybrid process. The economic evaluation has been widely studied in literature. [Van Hoof et al. 2004] compares and evaluates the processes shown in Figure 8 and 9 of this white paper. They found that combination of distillation with ceramic pervaporation is the most promising and leads to total costs reduction of approximately 49%. The paper was published in 2004; since then, the costs for energy have increased tremendously, and in addition CO_2 emissions have a cost as well. The need of the industry to reduce CO_2 emissions and limit their

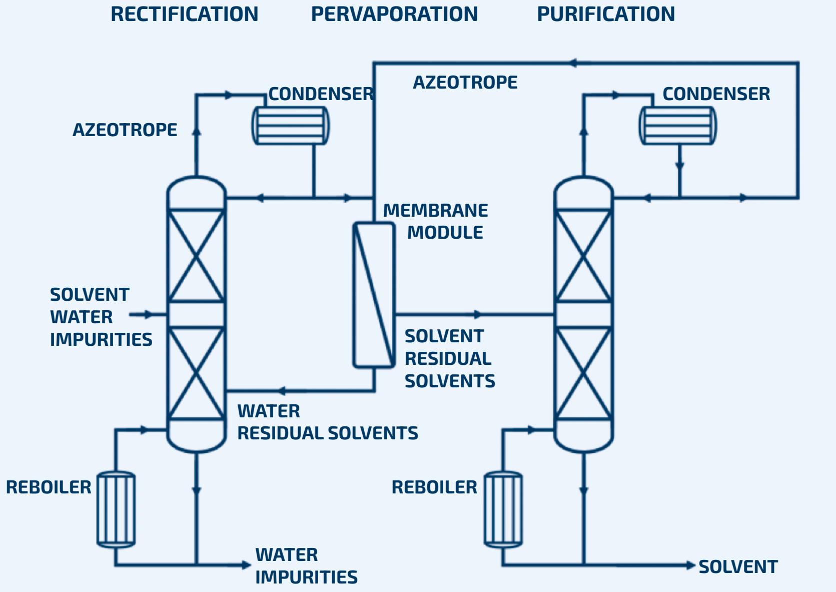

Figure 9: Hybrid process with pervaporation for azeotrope-splitting

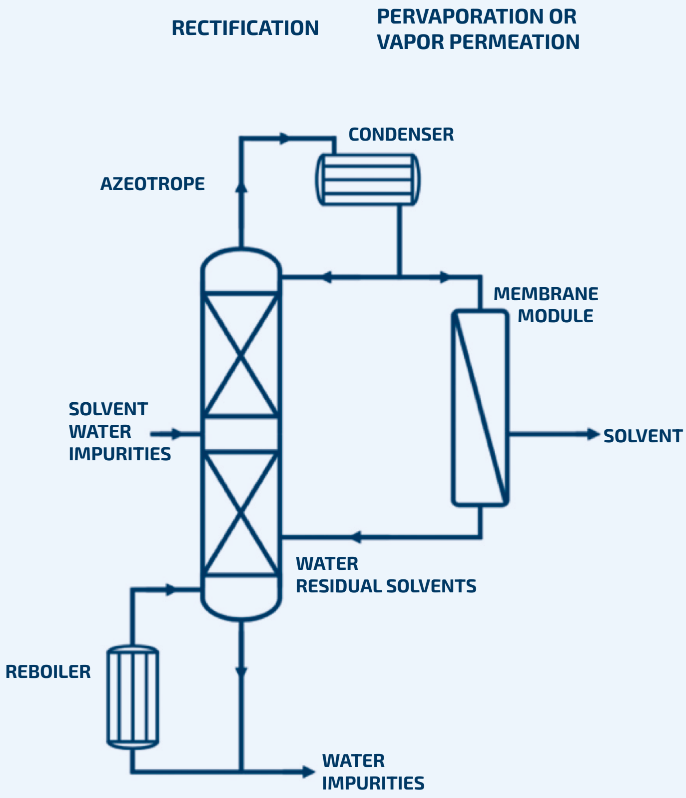

Figure 10: Hybrid process with pervaporation or vapor permeation for azeotrope-splitting and final dehydration

solvent use is significantly more relevant, both for economic reasons as well as the pressure from society for a more sustainable industry.

Case 2: Full-scale IPA dehydration by vapor permeation in a hybrid process

The economic evaluations in scientific literature, especially the modelling performed by [Harvianto et al. 2016], have also been proved at larger scales. Pervatech supplied a vapor permeation plant containing 21 m^2 of PERVATECH Hybrid Silica HybSi® Acid Resistant membranes to an end-user in the Netherlands who wanted to recover their isopropanol. This solvent was used in their extraction process where water dilutes the solvent, making it impossible to re-use. An external treatment was rejected because of logistical reasons and overall costs for handling and treatment. Dehydrating such alcohols by distillation/rectification requires a complex and space-consuming process unit as well as an entrainer, leading to impurities in the dehydrated solvent.

Solvent recovery is performed by means of a simple distillation column, which dehydrates the IPA to the azeotropic composition. Part of the vapor coming over the top is refluxed back into the column and another part is sent to our vapor permeation skid. The membranes are able to remove the final amount of water enabling the IPA to be re-used by the customer. Such membrane systems are compact, for example, they can easily be incorporated in any existing infrastructure on-site and are simple to operate (once-through process). As such, the IPA dehydration plant shown in Figure 10 has dimension of approx. 10 x 4 x 4 meters.

The business case is mainly driven by reduction in solvent waste costs and purchase costs of the solvent. Furthermore, the customer has a continuous supply of IPA and is therefor less dependent on suppliers. This plant is designed to produce 8000 tons of IPA annually.

Case 3: Lithium recovery

Enrichment of Li-containing brines can be achieved by pervaporation using PERVATECH Hybrid Silica HybSi® Acid Resistant membranes. The process has been developed by Agua Dulce Technologies, Littleton, USA. The complete process is patented [Kasaini 2020].

Figure 11: Industrial vapor permeation plant for IPA dehydration with PERVATECH Hybrid Silica HybSi® Acid Resistant membranes

5.2 Pharmaceuticals

Case 4: Solvent dehydration in a continuous mode process

Continuous mode dehydration of solvents using Pervatech's membrane separation skid (MSS) as shown in Figure 1 and 13 is currently applied in several industrial cases. This skid-mounted pervaporation plant is able to dehydrate many solvents continuously and is perfect for pilot-scale testing. The unit is easily transported between sites as all the components for pervaporation are available on the skid. Heating and cooling of the feed is integrated inside the skid, so no pressurized vessel is required. The feed is supplied at ambient conditions and the product is returned at ambient conditions.

Depending on the size of the industrial process, the unit is also able to recover the solvent for you continuously. Annual production capacity of the MSS is between 1200-6000 tons of solvent.

THF, di-chloromethane acetone, NMP, ethyl lactate, isopropanol, acetonitrile, acetic acid and 1-propanol have been already dehydrated using the MSS. However, the list of recoverable solvents is more extended. Please refer to 3. Feed materials of this white paper.

Figure 12: a) Permeation plant PERVATECH Hybrid Silica HybSi® Acid resistant membranes for Li recovery and b) Membrane stack

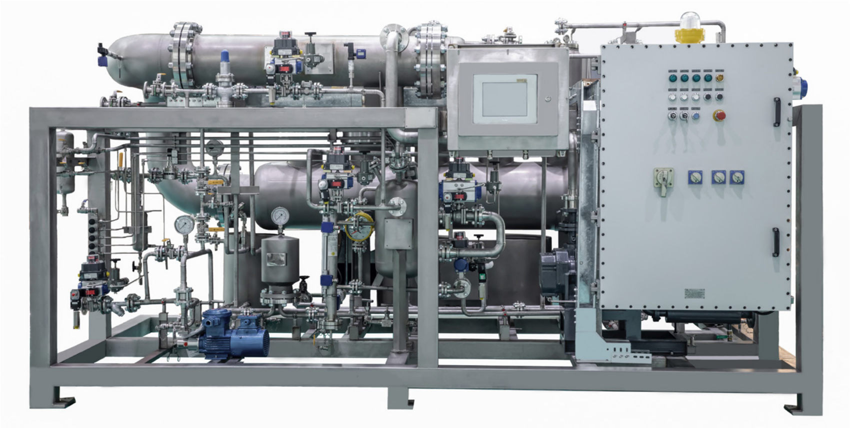

Figure 13: Pervatech's continuous mode membrane separation skid (MSS)

Case 5: Ternary mixture dehydration

The aim was to recover pure solvents (a purity of at least 99 %) from a ternary mixture of ethanol (approx. 70-80 %), xylene (approx. 2-15 %) and water (approx. 15-20 %) contaminated with dissolved and undissolved solids as well as traces up to several 100 ppm of higher-boiling components, fats, and several organic chemicals/pharmaceuticals.

Ethanol and xylene both build azeotropes with water and therefore cannot be separated or dehydrated by simple distillation. Dehydration of the ternary azeotropic mixture by pervaporation technology now permits economic separation of both solvents.

A three-stage hybrid system distillation-pervaporation-distillation was installed to purify, dehydrate and separate both solvents up to more than 99 %. At the start, a simple distillation column generated a purified ternary ethanol-xylene-water mixture. Following this, a pervaporation system removed the water from the purified ternary mixture. This membrane process allowed an easy separation of the remaining binary ethanol-xylene mixture in a simple distillation column. The solvent recovery plant was designed as a multi-purpose system and was also used to treat an isopropanol-xylene-water mixture (composition as before).

5.3 Solvent recycling and organic/organic separation

Case 6: Batch dehydration by pervaporation

A company who recovered solvents from different industrial sources required a technology to dehydrate volatile organic solvents such as alcohols, esters, ethers, and ketones. The majority of these solvents built azeotropes with water or required a large number of theoretical stages for dehydration by distillation/rectification. Since feed volume as well as solvent composition and water concentration of the incoming raw solvent mixtures varied significantly, a flexible, multi-purpose and easy-to-operate system was requested.

A simple stand-alone batch pervaporation plant could dehydrate binary and multi-component solvent mixtures with 2-20 % water down to any desired final water concentration. A batch tank was used, and a feed stream was circulated from the batch tank through the membrane unit and back to the tank until the final water concentration was reached, typically 0.1-1.0 %. The membrane area was arranged in several stages with relevant feed re-heaters to balance the temperature drop while handling solvents with high water concentrations.

Case 7: Solvent separation by pervaporation

Like water, **methanol** also forms azeotropes with a lot of commonly used solvents. Pervaporation is also able to remove methanol from these solvent mixtures. The effective use of pervaporation membrane technology in methanol / dimethyl carbonate (DMC) separation is clearly demonstrated in the work of [Baik 2024]. The conventional process is based on pressure swing distillation (PSD). PERVATECH HybSi® pervaporation membranes were highly effective in removing methanol selectively from a MeOH/DMC mixture (even) at the azeotropic composition in a hybrid configuration.

The process performed best at conditions with relatively high temperatures and high methanol concentrations in the feed stream - as is the case in industrial dimethyl carbonate synthesis. Pilot tests gave a typical total permeate flux of 15 kg/m^{2}h @ 105 °C @ 8 bar @ 600 mbar. This concept resulted in a potential reduction in purification cost of 45%.

See also our white paper on 'Methanol / dimethyl carbonate (MeOH/DMC) separation by pervaporation' for more details [Pervatech 2024].

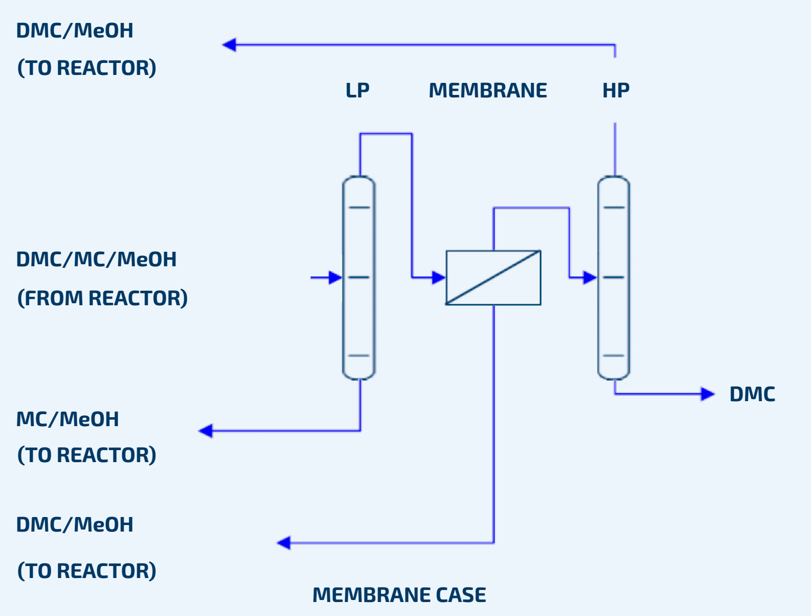

Figure 14: Hybrid PSD-pervaporation process for MeOH-DMC separation using PERVATECH Hybrid Silica HybSi® AR membranes

5.4 Food industry

The use of pervaporation membranes in the dehydration of beverages showed promising results. The economic incentive for dehydration of these natural products is mainly driven by the increase in shelf life and the reduction in transport efforts, warehousing, and packaging. However, the net added value is highly dependent on the final quality of the dehydrated compounds. Product degradation during the dehydration process will have a negative impact on the net added value.

PERVATECH Hybrid Silica HybSi® Acid Resistant membranes are essentially molecular sieves. Due to their relatively small kinetic diameter, water molecules can permeate through the membrane pores and larger molecules are retained. Therefore, this membrane can be used for solvent dehydration as is described above. Moreover, large (organic) molecules responsible for flavors and fragrances of these natural products are also retained by the HybSi® membrane, which results in maintaining the same flavor profile for the dehydrated product as compared to the original feed.

Since pervaporation may also be operated at lower temperatures, any issues with the Maillard reaction in food processing can be prevented. The Maillard reaction causes browning of the feed in the presence of sugars and amino acids, and its reaction rate is strongly temperature dependent.

Case 8: Whiskey and coffee dehydration

PERVATECH HybSi® membranes showed highly positive results in testing a dehydration step in whiskey processing. Dehydration, which took place at low temperatures, occurred very fast. Due to the membrane selectivity and the low operating temperature, the flavor and fragrance of the product was retained. Other technologies, including reverse osmosis, were found to be unsatisfactory for this application.

For a coffee manufacturer, these HybSi® membranes were successfully applied in dehydrating an aqueous coffee aroma feed. The client tested the final product and found the taste to be similar to the original product.

6. In summary: main advantages

In conclusion, the above examples show that pervaporation and vapor permeation, especially when using PERVATECH Hybrid Silica HybSi® Acid Resistant membranes, are ideally suitable for applications within chemical, pharmaceutical and food industry. Low process temperatures, high membrane selectivity and the membrane's acid resistance are key enablers in this respect.

The main advantages of a pervaporation or vapor permeation process are summarized as follows:

- Significantly **reduced energy consumption** for hybrid systems (pervaporation and vapor permeation in combination with distillation or rectification), up to 45% energy savings compared to distillation.
- **Breaking the azeotrope** - mixtures which form azeotropes and/or require many theoretical stages (like the dehydration of acetone) in conventional distillation can easily and **economically be separated** by pervaporation. **High product purity** is obtained (no entrainer required as in extractive distillation), and no additional environmental pollution occurs (no entrainer emitted).
- **Multi-component mixtures** even with just small differences in boiling points can be dehydrated effectively and economically. There is a high degree of **flexibility** regarding the feed mixtures that may be accommodated (multi-purpose systems, various feed mixtures can be treated in one unit), throughputs, and final product qualities. The feed mixtures to be treated may be supplied in either liquid (pervaporation) or vapor (→ vapor permeation) form.
- Pervaporation and vapor permeation systems are **simple to operate** and can be started-up and shut-down rapidly. Due to the modular design of the membrane system, even small units can be operated economically.
- Dehydration of food products such as vinegar and whiskey is very effective since **flavor and fragrance molecules are retained**, and therefore taste and smell is unaffected. The feed for the pervaporation membrane can be supplied in any water concentration level, showing excellent **hydrolytic stability**.

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