INDUSTRIAL EXPERIENCE WITH HYBRID DISTILLATION – PERVAPORATION OR VAPOR PERMEATION APPLICATIONS

Mario Roza, Eva Maus
Sulzer Chemtech AG, Winterthur, Switzerland; E-mails: mario.roza@sulzer.com, eva.maus@sulzer.com

The last 5 years the application field for pervaporation has extended from the fine chemical and solvent recovery field into the solvent production area. A number of new and more efficient hybrid separation plant configurations in this area with distillation and pervaporation are shown. For these case stories a user added subroutine for the pervaporation has been used to simulate the plant. This subroutine has been developed by Sulzer Chemtech to run with the Pro/II® and AspenPlus® simulation packages. The subroutine uses a finite element model. The mass balance over each element is calculated using measured flux coefficients and the difference in fugacities on either side of the membranes.

Hybrid applications are presented for Isopropanol, Bio-Ethanol and Tetrahydrofurane. For these applications energy saving of more than 50% can be reached compared to traditional separation schemes.

KEYWORDS: hybrid, pervaporation, vapor permeation, distillation, IPA, THF, ethanol

SHORT INTRODUCTION TO PERVAPORATION

Pervaporation is a separation technology allowing dehydration of azeotrope-forming solvents which cannot be easily dried using distillation. Dehydration of ethanol was the first pervaporation application more than 20 years ago. Nowadays there are more than 130 pervaporation and vapor permeation units running worldwide. A typical configuration of a pervaporation unit which processes a liquid feed is shown in Figure 1.

Pervaporation is characterized by the following features compared to other conventional dehydration technologies:

- The process is simple and easy to automate which reduces personnel costs (labor and training requirements, supervision of the unit).
- The process is inert since no additional chemicals are introduced. There are no material handling or liability problems.
- Pervaporation can easily process known contaminants present in bio-ethanol or Isopropanol such as fusel oils, esters, ethers, ketones and acetic acid. For alternative drying technology such as azeotropic distillation these contaminants can pose problems as the can accumulate in the system.
- A given pervaporation unit can dehydrate a wide variety of chemicals, thus adding flexibility and giving additional operating options.
- Neither evaporation nor superheating of the feed is required i.e. pervaporation has in many cases 50–70% lower energy consumption than other technologies.

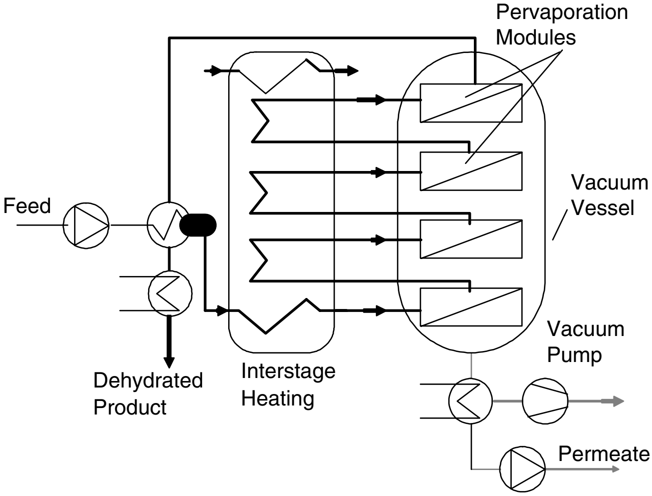

Figure 1. Typical configuration of a pervaporation unit

- Flexible operation is possible in terms of capacity vs. water contents (0.5, 0.2 and 0.1 % water can be reached with the same system).

Vapor permeation units often process the overhead vapor product of a distillation product. In this manner the water has only to be evaporated once by the column reboiler and energy consumption of the whole system is minimized.

SIMULATION OF PERVAPORATION UNITS

USER ADDED SUBROUTINE FOR PERVAPORATION

Sulzer Chemtech has developed a simulation module, a so called User Added Subroutine (UAS), to simulate a pervaporation unit. This UAS can be used with the two major flow sheet simulators ProII® and AspenPlus® used in the chemical and petrochemical industry [2].

As input the UAS uses the permeate pressure, the total membrane area and the membrane area for the finite element used in the calculation. Furthermore it uses the flux data for all components for the membrane of choice for the system. These flux data can be directly evaluated from pervaporation tests on bench test scale. The UAS can be used to evaluate a stand-alone PV unit but becomes of real interest when studied in conjunction with the complete flow sheet of a plant as shown in Figure 2 for an ethanol dehydration unit.

It will e.g. be possible to optimize from an energy point combinations of distillation, pervaporation and azeotropic distillation with a solvent as described in chapter 4.2.

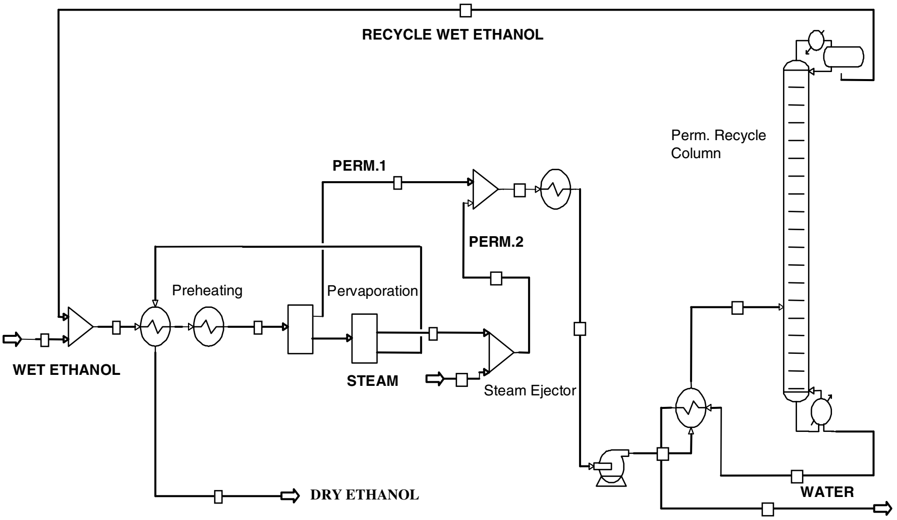

Figure 2. Typical 2-stage ethanol dehydration unit with steam ejector

It will also be possible to study what the effect of removal of water will be on the equilibrium and energy balance of a complete esterification unit with a reactor and several distillation columns.

THE CALCULATION MODEL FOR THE USER ADDED SUBROUTINE

The UAS breaks-up a membrane module in finite elements. The mass and heat balance are calculated around this element using a liquid activity model and enthalpy data available from the flow sheet program database.

As illustrated in equations (1) to (3), the driving force for a component to go from the liquid, retentate, side to the vapor, permeate, side of the membrane is calculated from the difference between the fugacities on both sides.

$$x_i P_i^0 \gamma_i \varphi_{L,i} = f_{L,i} \tag{1}$$

$$y_i P_{tot} \varphi_{v,i} = f_{G,i} \tag{2}$$

$$\Delta f_i = f_{L,i} - f_{g,i} \tag{3}$$

Where:

$f_{G,i}, f_{L,i}, \Delta f_i$	Fugacity vapor, liquid and difference between them for component i

$\varphi_{L,i}$, $\varphi_{G,i}$,	Fugacity coefficient vapor and liquid for component i respectively
γ_i	Activity coefficient of component i
P_i^0	Saturated Vapor pressure component i
P_{tot}	Total pressure permeate side
x_i y_i	Liquid or vapor mol-fraction of component i

The liquid side fugacities, the flux coefficients and the vapor pressures are taken at the inlet temperature to the element. This is satisfactory in view of the small temperature difference over the element.

The outlet temperature of an element, which will be the inlet temperature for the next element, is calculated from the heat balance over the element assuming that the element can be considered to be functioning adiabatically.

NEW AND MORE EFFICIENT PLANT CONFIGURATIONS

Using vapor permeation or pervaporation in combination with normal, extractive or azeotropic distillation can give plant configurations which would not be feasible without a membrane unit.

If the equilibrium curve of an azeotropic binary mixture allows this, distillation on both sides of the azeotrope becomes possible if a pervaporation or vapor permeation unit is used to get from one to the other side of the azeotrope.

CASE STORIES

ETHANOL

Ethanol dehydration was one of the first applications of pervaporation. Numerous units in solvent recovery plants are in operation. As one of the possibilities to increase the percentage of fuels from renewable sources there is lot of activity in the bio-ethanol field. Bio-ethanol plants also require a dehydration step to get to the final water specification.

Pervaporation is especially of interest if the wet ethanol source for the bio-ethanol is liquid. If this is the case, the energy requirements using pervaporation will be, dependent on the type of cooling medium used, only a quarter of the energy consumption of a traditional dehydration plant using molecular sieves. Main reason for this saving is that molecular sieves have to be fed with a superheated vapor to avoid operating problems. This means that the whole feed has to be evaporated. In a pervaporation plant only the heat of vaporization for the water removed and for a small amount of ethanol which also passes through the membranes has to be provided.

In Figure 2 a simplified flow sheet for a typical 2 stage pervaporation unit for ethanol dehydration is shown. This scheme is generated using a flow sheet simulation program with the User Added Subroutine for a pervaporation unit as described in chapter 2.

The permeate side of the first stage of the plant is operated at a vacuum level which still allows normal cooling water to be used for the permeate condensation. For the second stage bringing the ethanol to its final water contents a relatively low vacuum level is required on the permeate side. In order to be able to condense the second stage permeate there are two possibilities:

- Using a refrigerant in a separate second stage condenser or
- Compressing the second stage permeate to the level of the first stage using a steam ejector and condensing first and second stage permeate together in one permeate condenser. This configuration is shown in Figure 2.

In general using refrigerant for the condensation is most interesting from an overall energy consumption point of view while using a steam ejector gives a lower investment for the dehydration unit.

A molecular sieve plant generally has two or more vessels filled with molecular sieves. At a certain moment in time, one operates in the dehydration mode while the other operates in the regeneration mode. One vessel is fed with super-heated wet ethanol vapor and adsorbs the water. In the other vessel the water is removed from the molecular sieves.

In many cases this is done by a combination of employing a moderate vacuum and feeding a small amount of dry ethanol product to the vessel. The vapor from the vessel in the regeneration mode is fed to the recycle tower which also serves to evaporate the wet ethanol feed to the super-heater.

In Table 1 a comparison is made between a molecular sieve drying unit and a pervaporation unit for a typical Ethanol dehydration unit capacity. This comparison includes the duties for the recycle tower for both plant types. For pervaporation it shows both options. One using a steam ejector to compress the second stage permeate and one using refrigerant to condense this permeate.

Table 1. Energy requirements for a 75 kt/y, 2840 hl/d ethanol dehydration plant with pervaporation and with molecular sieves

Equipment name		Pervaporation with ejector	Pervaporation without ejector	Molecular Sieves
Reboiler steam	t/hr	0.49	0.36	5.45
Ejector steam	t/hr	0.63		
Pervap./Super-heat steam	t/hr	1.08	0.99	0.38
Total steam	t/hr	2.19	1.34	5.83
Recycle/permeate cond. CW	m^3/hr	95	34	92
Perm. cond. with refrigerant	MW		0.191	
Product/column cond. CW	m^3/hr	23	17	226

Base data for the comparison: Feed 92.5 wt% ethanol, steam saturated 5 bara, cooling water (CW) temperature difference 10°C, recycle tower has 18 theoretical stages.

For the sake of comparison it is assumed that the steam quality required for all units is the same i.e. saturated steam with a pressure of 5 bara. For the molecular sieve unit which operates at temperatures around 170°C this pressure is advisable. For the pervaporation unit which runs around 110°C also lower quality steam can be taken. Only the ejector requires a steam pressure of at least 5 bara.

As can be seen from Table 1 the molecular sieve unit requires about 49 kg steam/hl Ethanol (EtOH). The pervaporation requires 19 kg steam/hl EtOH with a steam ejector and 11 kg steam/hl EtOH without ejector. This is an energy saving of more than 75%.

ISOPROPANOL

The most common configuration to dehydrate Isopropanol (IPA) in production plants is azeotropic distillation using an entrainer like Cyclohexane or Di-Ispropylether (DIPE). These units consist of:

- A normal distillation tower bringing the mixture close to azeotropic composition i.e. containing 12–15 wt% water.
- An azeotropic distillation using an entrainer.
- A decanter separating the organic phase which serves as reflux to the azeotropic distillation and a water phase.
- Sometimes a small stripper column removing the entrainer and dissolved IPA from the water phase.

The combination of the two larger towers is energy intensive as the required reflux ratio to get close to azeotrope is high and the required amount of entrainer which is circulating and needs to be evaporated is significant. In Figure 3 an IPA dehydration with an integrated pervaporation unit is shown.

In this configuration the outlet concentration of the distillation does not have to be the same as the inlet concentration of the azeotropic distillation. The energy consumption of the distillation tower can be reduced by increasing the water contents in the overhead product. The energy consumption of the azeotropic distillation can be reduced by decreasing the water contents in feed to the tower. The membrane unit brings the water concentration from the outlet of the distillation to that of the inlet of the azeotropic distillation. In this manner the loads in both towers can be decreased independently by varying the membrane area. Energy savings of 20% compared to the conventional configuration can be reached by integrating a pervaporation unit in the system.

When it is possible to run the distillation column at slightly elevated pressure i.e. about 1.8 bara overhead pressure it is also possible to integrate a vapor permeation unit directly fed from the partial condenser of the tower in the plant. This would give an additional 10% energy saving. Return on investment based on energy saving and costs for the skid mounted membrane unit installed in an existing IPA plant is usually less than 2 years.

The described configuration can also be used to increase the capacity of the plant. In Table 2 a comparison is made between a conventional IPA plant with three columns

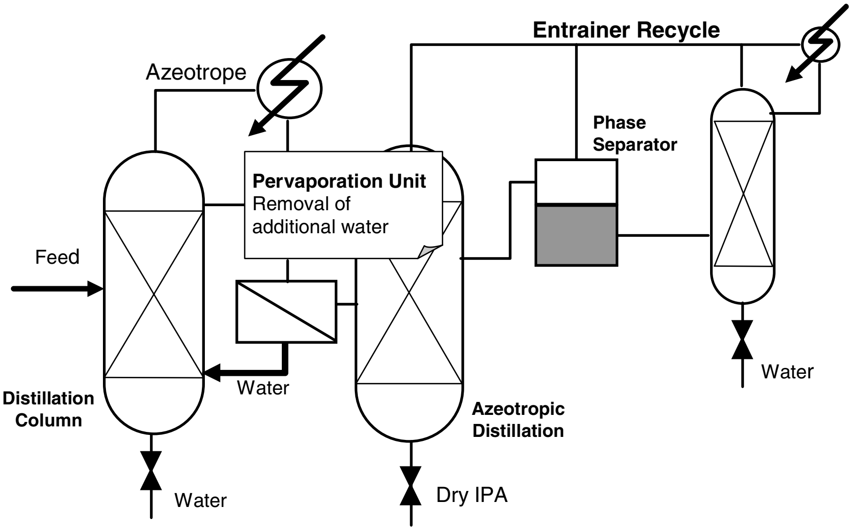

Figure 3. Typical configuration of an Isopropanol dehydration unit with a pervaporation [1]

Table 2. Energy requirements for an IPA dehydration plant processing 6.6 t/h without membrane unit and a plant with a membrane unit processing 8.9 t/h crude IPA

Without membrane unit, feed 6.6 t/h 30 mol% IPA					
Equipment name		Rectification column	Azeotropic column	Stripper column	Pervaporation
Condenser duty	MW	−2.13	−1.66	−0.59	0.00
Reboiler duty	MW	2.32	1.59	0.65	
With membrane unit, feed 8.9 t/hr 30 mol% IPA					
Equipment name		Rectification column	Azeotropic column	Stripper column	Pervaporation
Condenser duty	MW	−1.99	−1.61	−0.62	−0.60
Reboiler duty	MW	2.33	1.58	0.64	0.53

Base data for the comparison: feed 59 wt% IPA, distillation tower has 30 theoretical stages, azeotropic distillation tower with cyclohexane has 30 theoretical stages.

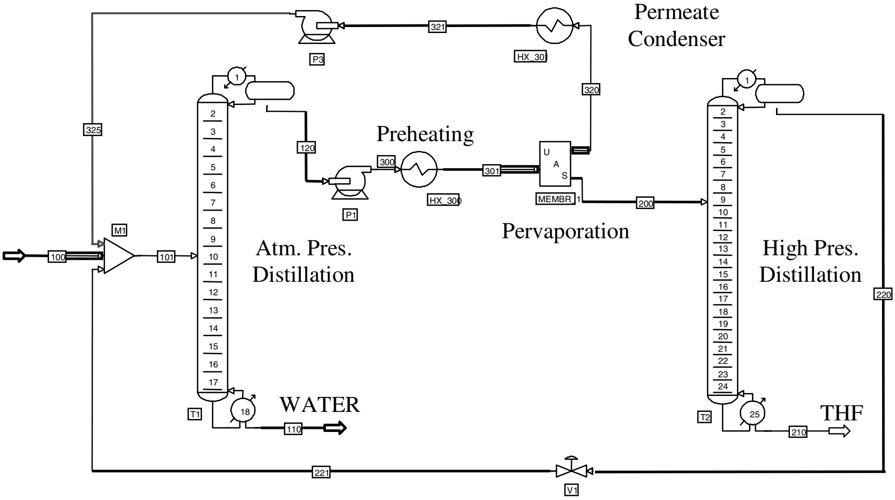

Figure 4. THF-water separation using a distillation/pervaporation hybrid system

processing 6,6 t/h of crude IPA with 41 wt% water and a plant with a vapor permeation processing 8.9 t/h of the same crude IPA as shown in Figure 4.

As can be seen in Table 2 for the configuration with the vapor permeation the energy requirements and the corresponding internal vapor and liquid loads in the towers remain constant despite a capacity increase of nearly 35%.

TETRAHYDROFURANE

Tetrahydrofurane (THF) is a largely used solvent. In many cases it is dehydrated by making use of the pressure dependency of the water-THF azeotrope [3].

In a first column working at atmospheric pressure water is removed at the bottom of the column. The composition of the overhead stream of the atmospheric column should be as close as possible to that of the azeotrope. After the atmospheric column, the azeotropic mixture is fed to the second column operating at 6–8 bara. As at the higher pressure the azeotrope forms at a lower THF concentration, the THF can be removed as a pure bottom product from this column.

The main problem of this so called two pressure distillation is the large recycle stream from the pressure column to the atmospheric column which leads to an increase of the physical size of the column and thermal requirements. This can be resolved by placing a pervaporation unit treating the THF-Water azeotrope coming out of the atmospheric tower and separating the feed into a water rich permeate and THF-rich retentate that is fed to the high pressure column. With this configuration, the recycle stream becomes much smaller and energy savings are substantial. The process flow diagram of the

Table 3. Energy requirements for a 28 kt/y THF production with and without PV unit between the distillation columns

Without PV			With PV		
Steam 4 bara	MW	t/hr	Steam 4 bara	MW	t/hr
Reboiler T-1	1.78	3.01	Reboiler T-1	1.18	1.99
Reboiler T-2	1.22	2.05	Reboiler T-2	0.30	0.51
			PV Stage	0.20	0.34
Total steam	3.00	5.06	Total steam	1.68	2.84
Cooling water 10 °C Δt	MW	m^3/hr	Cooling water 10 °C Δt	MW	m^3/hr
Cond. T-1	1.33	114	Cond. T-1	0.58	50
Cond. T-2.	0.91	78	Cond. T-2.	0.21	18
			Perm. Cond.	0.14	12
Total CW	2.67	192	Total CW	1.42	80

Base data for the comparison: Feed 35 wt% THF, THF product >99.97 wt% THF, Waste water >99.9 wt% water.

combined distillation-pervaporation system is presented in Figure 4 and an energy savings comparison in Table 3.

With the pervaporation unit an energy saving of more than 40% can be reached.

REFERENCE

1. Hybrid Processes by Coupling Distillation and Pervaporation/Vapour Permeation, Dr. H.E.A. Brüschke, E. Maus, 27th International Exhibition-Congress, Achema 2003.
2. Process Simulator Toolkits for Pervaporation and Vapour Permeation, Nick Wynn, 27th International Exhibition-Congress, Achema 2003.
3. Debottlenecking Pressure Swing Column Systems by Pervaporation. Norbert Martin, 27th International Exhibition-Congress, Achema 2003.