Novel Pervaporation Technology Using Absorption Refrigeration for Vapor Removal

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A novel process configuration for pervaporation and vapor permeation realizes the permeation driving force by absorbing the permeate vapor into a suitable solution with a very low vapor pressure. Although the suggested process design lacks an experimental demonstration, by using two well-established technologies—the separation by pervaporation and the absorption refrigeration—it can achieve technical and economic advantages over the conventional condensation technology. Vacuum pressures as low as 8 mbar can be obtained at ambient temperatures without refrigeration, as well as low vacuum ranges that are not possible by condensation without freezing. Process simulations and feasibility investigations for the suggested process are discussed.

Introduction

Pervaporation (PV) and vapor permeation (VP) processes have gained much attention in recent years. Although they offer potential solutions in a wide range of applications, they are still a niche operation with a limited number of industrial applications (Strathmann, 2001). The relatively high cost of the membrane units and the lack of extensive industrial experience built, thereby, are the main obstacles. A great deal of effort is being made to improve the membrane properties. Many research groups are working on the development of modified membrane materials and improved membrane-making technologies to achieve higher fluxes, sufficient selectivities, and stable membrane materials. Many new types of PV membranes have emerged in recent years. Many of them are reviewed in Pereira Nunes and Peinemann (2001), Feng and Huang (1997), and Zhang and Drioli (1995). Ceramic membranes with improved separation properties, even at higher prices than polymeric membranes, are likely to capture a growing share of the PV and VP membrane market (Caro et al., 2000; Coronas and Santamaria, 1999, and Okamoto et al., 2001).

Process design improvement and proper integration of the membrane units within the overall process bring additional savings to the effective cost of the membrane unit. With increasing membrane fluxes and decreasing membrane prices, the share of the membrane in the total cost of the unit is decreasing. Thus, efforts to optimize, modify, and improve the periphery equipment would be worth while.

We will start our illustration with a brief review on the state of the art of PV and VP, with emphasis on the peripheral processes and utility equipment. The limitations and the areas for potential improvements will be highlighted and investigated.

State-of-the-Art Technology

Both PV and VP processes are closely related, differing only in the state of the feed. For PV the feed is liquid and the permeate evaporates through the membrane. The heat supply to the feed stream is usually accomplished by intermediate heat-exchangers installed between a number of PV modules in series. For VP the feed is in the vapor state. This avoids the phase change across the membrane surface and leads to a less complex process. For both processes the driving force for material transport through the dense membrane is the difference in the chemical potential of the permeating components between the feed and permeate side. VP seems to be especially suitable for the purification of top streams of fractionation columns that can be used as feed directly. This combined (or hybrid) configuration of distillation and membrane separation has been studied extensively in recent years (Lipnizki et al., 1999).

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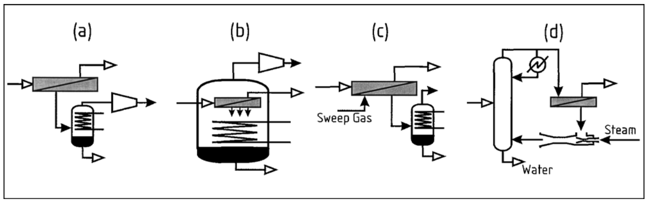


Figure 1. Different configurations for pervaporation.

The driving force for the mass transfer across the membrane is generally realized by lowering the pressure on the permeate side. The most common technique is condensing the permeate stream prior to a vacuum pump (Figure 1a, 1b). The vacuum pump removes the noncondensed compounds and the leakage air. Integrating the membrane into the vacuum condenser (Figure 1b) has the advantage of low pressure drop on the permeate side. In another technique, a sweep gas or vapor is used to lower the partial pressure of the permeating components and carry them out at the permeate side (Figure 1c). Large flow rates of sweep gases are required to achieve the same effect of condensation. It is also possible to combine both the condensation and the sweep-gas technology (Lipnizki and Field, 2001). Another suggested technique within the dehydration of organics in hybrid processes is the jet-ejection steam (Figure 1d). This method could bring cost savings within a certain range of permeate pressures (Fahmy et al., 2002).

However, the condensation technology has proven to be the most convenient method for vacuum production. Although it is relatively expensive, it is a simple and common technology with a wide range of standard units and long years of industrial experience. However, this technology has shown some limitations by its use in combination with PV and VP. One disadvantage is the exponentially increasing refrigeration cost with decreasing temperature below a certain temperature range. Another disadvantage is that the condensation temperature, and, thus, the permeate pressure, cannot be arbitrarily decreased. The freezing point of the permeate mixture sets the lowest temperature limit in the condenser to avoid solids accumulation on the heat-transfer area. This freezing limitation is shown in Figure 2 for water−ethanol mixtures. In consequence of this limitation, the permeate pressure cannot be arbitrarily lowered, and, thus, the savings in the required membrane area are also limited. This limitation is known within the attempts to achieve a very high retentate purity, where the driving force for permeation diminishes. An exponential increase in the required membrane area is expected at this concentration range. One solution, which has its cost and feasibility limitations, as just discussed, is lowering the permeate pressure toward absolute zero. Another feasible and realistic way is to use low selectivity membranes in this concentration region (Fahmy et al., 2001). An intermittent operation of the condenser with heating and melting the formed ice has also been practiced (Heckmann, 2000).

In the following sections an alternative absorption technique for carrying out the PV and VP is introduced. This process modification is evaluated and compared to the conventional condensation technique. Within case studies for the dehydration of organic compounds, the advantages and limitations of this novel technology are illustrated and discussed.

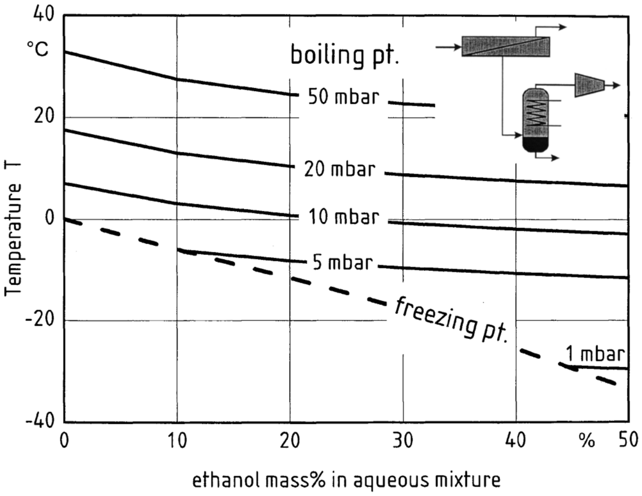


Figure 2. Boiling and freezing points for different water−ethanol mixtures.

Suggested Absorption Technology

The absorption of the permeate stream is used for vacuum generation on the permeate side. An absorbent with a high affinity for the permeate mixture is contacted with the permeate vapor. The rich absorption solution after absorbing the permeate should have a lower vapor pressure than the condensed permeate mixture at the same temperature. Thus, compared to condensation, a lower vacuum pressure can be attained by equal temperature, or the same vacuum pressure can be attained by a higher temperature. Consequently, the fixed and operating costs for the refrigeration process could be reduced, and it could be even redundant if the absorption process runs at room temperature and is cooled by normal cooling water.

The rich absorption solution is sent to a desorber where the absorbed permeate is stripped out of the solution. The required stripping energy could be attained from a low-quality energy source in the chemical plant or it can be removed from the vaporous retentate stream in the case of VP. A flow sheet of that process is shown in Figure 3. The vapor stripped out of the desorber is condensed at a higher pressure compared to the permeate. Therefore, normal cooling water can be used in all cases. The lean solution from the desorber is recycled back to the absorber. Heat is exchanged between the lean and rich solutions to reduce the energy consumption of the process.

The required area for heat transfer is realized by horizontal cooling pipes. The heat evolved by the absorption process is removed by a cooling medium, normally cooling water, flowing inside the pipes. The exiting cooling medium can then be used for another cooling step in the condenser of the stripped vapor.

Application to Dehydration Processes

An interesting application of the absorption technology is the dehydration of organic solvents. A number of hygroscopic

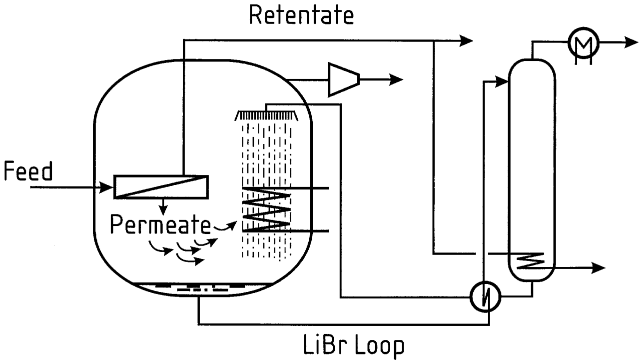


Figure 3. Absorption technology for dehydration by vapor permeation.

solutions were developed and optimized for the absorption of water for other applications. These include many well-established drying processes implemented in different fields and absorption refrigeration processes with water as a cooling medium.

So applying the absorption technology on the dehydration of organics with PV or VP introduced in the last section, a hygroscopic liquid is utilized for the absorption of the permeate. The lithium bromide (LiBr) solution is one of the most hygroscopic liquids found. The vapor pressure of water above the LiBr solution, as shown in Figure 4, is much lower than that of water at the same temperature. Some additives such as ethandiol or propandiol slightly increase the vapor pressure above the solution, but they lower the crystallization temperature of LiBr (Herold et al., 1996; Park et al., 1997). A vapor pressure of 8 mbar can be achieved above a 60 mass% LiBr solution at room temperature. Refrigeration to −10 or −15°C is necessary to achieve this pressure by condensing the permeate mixture.

In addition to the just stated cooling temperature advantage, lower vacuum pressures can be achieved that are not possible by condensation due to the limitation of the freezing point at low pressures. Overcoming this limitation could result in the possibility of increasing the driving force, especially in the region of a very low water content in the retentate, which would result in a considerable reduction of the required membrane area.

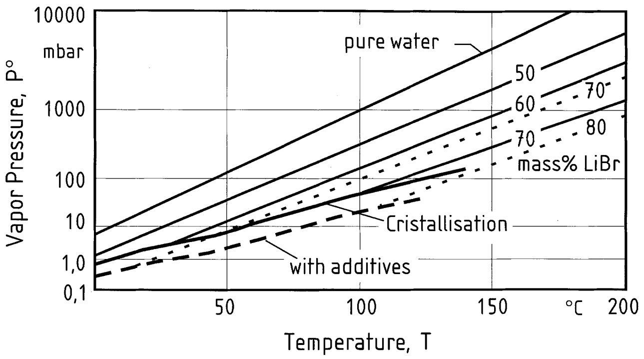


Figure 4. Vapor pressure over LiBr solutions (Herold et al., 1996; Park et al., 1997).

Integration into absorption refrigeration cycles

The absorption process just described may look more complex than conventional condensation. The absorbed solution has to be reconcentrated in the stripper. Simultaneous heat- and mass-transfer processes take place and the process has to be controlled. However, a similar process is found in absorption refrigeration units and absorption heat pumps. Generally a LiBr solution is the absorbing fluid and water is the refrigerant. There is a satisfactory amount of know-how and experience in using these refrigeration cycles. The equipment and processes are standardized and the whole cycle is available on the market as a finished product (Herold et al., 1996).

A typical cycle is shown in Figure 5a. The cooling load is drawn out of the evaporator, where water evaporates under a very low pressure. Water vapor is then absorbed by a concentrated LiBr solution at the same pressure. The level of the vacuum depends on and is realized by the absorbing solution. A small vacuum pump is also necessary for drawing the leakage and the noncondensable components out of the process. The lean solution is pumped to the desorber, where the water vapor is stripped out of the solution. The solution is recycled to the absorber and the water vapor is condensed and drawn back to the evaporator by the pressure difference. The aim of the whole cycle is to convert the heat supply to the desorber into refrigeration cooling at the evaporator. The refrigeration temperatures are not very low (4 to 6°C), as they are limited by the freezing point of the refrigerant (water). Typical pressure levels are 8 mbar for absorption and evapo-

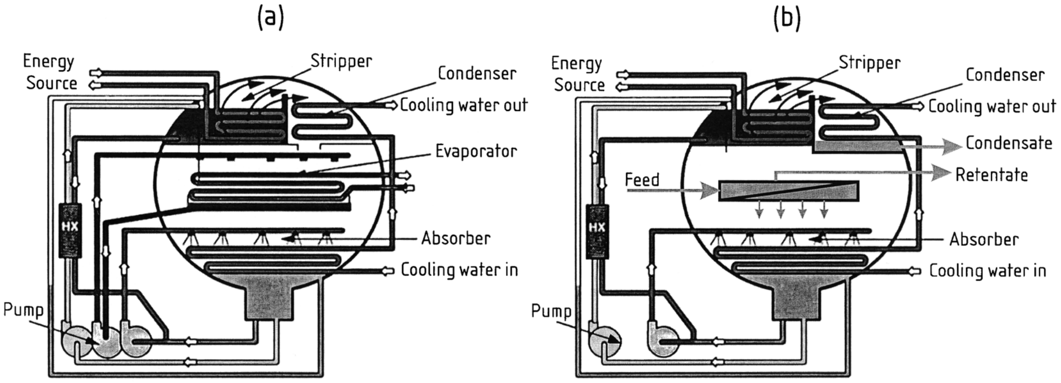


Figure 5. Integrating the membrane modules into the refrigeration cycle.

ration and 100 mbar for the desorption process (Herold et al., 1996).

Our idea is to integrate the membrane modules into such processes with little modification. The membrane could be considered as the source for water vapor. It can replace the evaporator, as shown in Figure 5b. The cycle will be converted to an open system. The permeate stream is drawn out of the process as condensate.

Generally, the absorption is carried out with the highest possible solution concentration. The only limitation of this process is the crystallization limit of the salt solution. With some additives, as discussed earlier, it is possible to lower the crystallization temperature of LiBr. This has the advantage of working with highly concentrated solutions and under low temperatures.

Aqueous LiBr has been known to be aggressive to many metals, including carbon steel and copper. However, if the system is well sealed, very little oxygen is present and corrosion rates are much slower. The manufacturers of absorption refrigerators have overcome the corrosion problems, and such cycles have been used successfully in the last decades and are a well-established technology. $LiNO_3$ and Li_2MoO_4 are common corrosion inhibitors for such systems.

A small amount of octyl alcohol is added to the LiBr solution to enhance the mass transfer. Convective motions are thereby generated on the gas–liquid interface due to different surface tensions (Marangoni-effect). On the interface the liquid molecules move from regions of low to high surface tension, generating high convection rates that increase the mass-transfer coefficient.

Effect of lower membrane selectivity

The membrane selectivity for the dehydration of organics is generally very high. Ceramic membranes even offer a further increased separation selectivity. Nevertheless, a small fraction of the organic solvent will always permeate with the water to the permeate side, especially if a very pure retentate is required. However, their effect will be negligible as they are diluted further with the absorbing solution as shown later in Figure 7 by a factor 10:1. Nevertheless, for a thorough study two parameters should be investigated: the solubility of the organic part of the permeate into the absorbing solution, and the change in the vapor pressure above the solution.

It was found that LiBr and similar hygroscopic salts are soluble in most organic solvents. Many studies on the effect of different salts on overcoming the azeotropes in the water–organic distillation have been carried out (Glugla and Sax, 1985; Fu, 1996). However, a smaller decrease in the solubility of the salt in the water–alcohol solutions than in pure water is observed (Meranda and Furter, 1972; Jaques and Furter, 1972). A slight increase in the vapor pressure due to the existence of ethanol is expected but cannot be quantified at the moment. However, experimental studies on organic additives to the LiBr–water system show that the crystallization point of the solution is further decreased, which would cause a higher salt concentration (Park et al., 1997). As a result, the presence of small amounts of organic material in the salt solution has both negative and positive effects with respect to our suggested application. Thus, at this stage of basic process design we will assume that the positive effects would equal out the negative ones, and that the permeate can be considered as pure water. At further design stages, thermodynamic data for the investigated system can be experimentally determined.

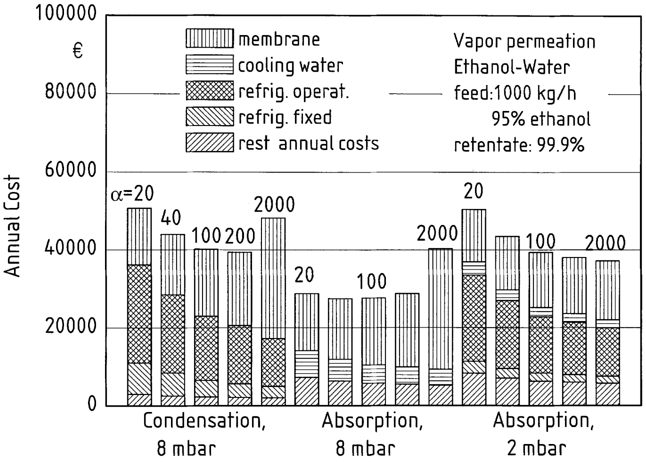
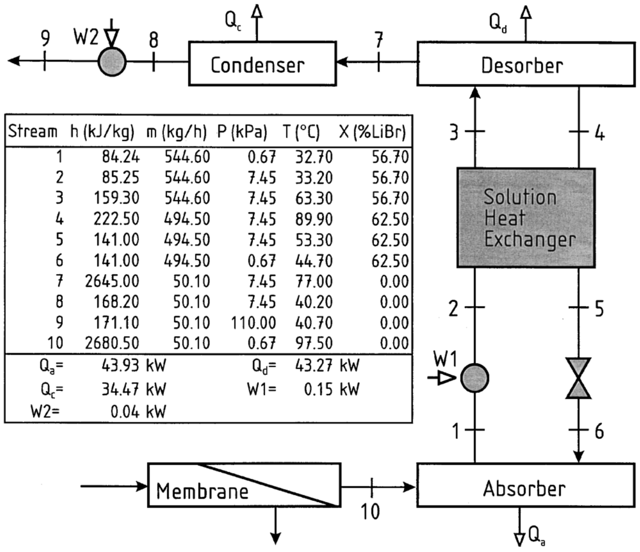


Figure 6. Comparing process alternatives on annual cost basis.

Process simulation and economic evaluation

A process simulation program is developed for PV and VP processes. It is coupled to the program system Aspen Plus as a user subroutine. Thus, the membrane unit can be simulated with all its periphery equipment. The optimum condensation temperature and vacuum pressure of the permeate, the leakage air to the unit as a function in the equipment sizes and the used vacuum, and the whole annual cost of the unit including the fixed and variable parts, can be determined on an economic basis. A simplified or a rigorous model can be used



Stream	h (kJ/kg)	m (kg/h)	P (kPa)	T (°C)	X (%LiBr)
1	84.24	544.60	0.67	32.70	56.70
2	85.25	544.60	7.45	33.20	56.70
3	159.30	544.60	7.45	63.30	56.70
4	222.50	494.50	7.45	89.90	62.50
5	141.00	494.50	7.45	53.30	62.50
6	141.00	494.50	0.67	44.70	62.50
7	2645.00	50.10	7.45	77.00	0.00
8	168.20	50.10	7.45	40.20	0.00
9	171.10	50.10	110.00	40.70	0.00
10	2680.50	50.10	0.67	97.50	0.00

Q_a= 43.93 kW
Q_d= 43.27 kW
Q_c= 34.47 kW
W1= 0.15 kW
W2= 0.04 kW

Figure 7. Mass and energy balance for the absorption–desorption cycle.

to describe the membrane. For the following calculations an empirical model based on measured permeabilities is used. The transport equation is described by

$$J_i = L_i(p_{if} - p_{ip}) \tag{1}$$

with L_i as the permeability coefficient, and p_{if} and p_{ip} the partial pressure of the permeating component on the feed and permeate sides, respectively.

The selectivity of the membrane is defined as

$$\alpha_{ij} = L_i/L_j \tag{2}$$

The transport through differential elements of the membrane is calculated. Integral calculations result in mass and energy balances and in the area necessary for separation. Details about the modeling procedure and the model assumptions can be found in Fahmy et al. (2001).

Process simulations and cost calculations are carried out for both the absorption and the condensation alternatives. A case study for ethanol dehydration is considered for technical and economic evaluation. The separation task is dehydrating 1,000 kg/h from 95 to 99.9 mass % ethanol. The permeability of water considered in the simulations is based on a modified PVA membrane of GKSS (Ebert et al., 1999, 2001). Different membrane selectivities from 20 to 2,000 are considered. The permeate pressure is 8 mbar for both alternative processes. An additional case of 2 mbar is also considered for the absorption alternative, as it is not possible by condensation because of ice formation in the condenser.

Cost functions were developed for the fixed and the variable parts. Offers from different manufacturers and data from large-scale chemical companies were the basis for these functions, which are listed in Table 1. The process alternatives are compared on the basis of the annual total cost. The membrane material is depreciated over 3 years, the membrane modules over 6 years, and the rest of the peripheral and utility equipment over 10 years. The energy costs were typical to those for a large-scale chemical industry.

The results are shown in Figure 6. The absorption alternative has shown a cost advantage over the condensation at 8 mbar. Working under 2 mbar is more expensive, as refrigeration will be required to lower the temperature of the absorption solution to achieve the vapor pressure of 2 mbar. It would be necessary if a further purification of the retentate is required. From the same figure, we can see that a certain midrange membrane selectivity seems to be optimal for the studied separation case. A very high selectivity may not be favorable for this separation task with a high retentate purity, as discussed earlier in the section on state-of-the-art technology.

At a permeate pressure of 8 mbar the permeate contains 1.1 and 9.8 mass % ethanol when using a membrane selectivity of 2,000 and 200, respectively. This amount is then diluted in the absorbing solution to be 0.1 and 0.89% in the effluent solution. As discussed in the subsection on the effect of lower membrane selectivity, the effect of the presence of ethanol is neglected. Hence, the simulation of the absorption cycle is based on an ethanol-free permeate at this basic design phase. Results for mass and energy balance calculations for the absorption cycle are illustrated in Figure 7. The permeate flow in the presented results is based on a membrane selectivity of 200.

Discussion

The presented process for carrying out the pervaporation and vapor permeation processes combines both the selectivity of the membrane and the high affinity of the permeate toward the absorbing solution. It should be separated from other membrane absorption processes where a porous membrane is utilized as a contacting medium between the feed and the absorbing solution. In the presented configuration the membrane is not a contacting medium, but it is a selective barrier between the feed-side mixture and the absorbing solution. The absorption process takes place outside the membrane module.

As illustrated earlier, the suggested process configuration could bring cost savings in the case of the dehydration of organic solvents. This should not rule out its feasibility in other membrane separation applications. The presupposition is the availability of a low vapor pressure solvent with a strong affinity toward the permeate mixture.

The presented modification in the LiBr absorption cycles turns it from a closed cycle to an open one. The use of the LiBr absorption cycle as an open cycle has been reported as a feasible option for waste energy management. In such processes the exhaust gases of the power plants are directed to similar absorbers, where the latent heat of its water vapor is

Table 1. Developed Functions for the Estimation of Annual Costs

	Estimated Cost Function in Euro/year	Notation
Membrane material	$80A/3$	A = membrane area, m^3
Membrane module	$250A/6$	A = membrane area, m^3
Condenser	$1{,}300Q^{0,7}/10$	Q = condenser duty, kW
Refrigeration	for 25°C < t < −5°C	Q = cooling duty, (kW)
	Fixed cost: $\{1{,}036 + 2{,}870 \exp[-(t+25.4)/3.6)]\} Q^{(0.97+0.01t)}/10$	
	Operating cost: $\{149 + 214 \exp[-(t+23.6)/19.2]\} Q$	t = refrigerant outlet temp., °C
Vacuum pump	Fixed cost: $230V^{0.8}/10$	V = volumetric flow rate, m^3/h
	Operating cost: $9.6V$ (per year)	
Electricity	0.03 Euro/k Wh	
Cooling water	0.05 Euro/m^3	
Adsorption refrig. unit	Between 10 and 100 kW	Q = refrigeration effect, kW
	$(15{,}000 + 1{,}035\, Q^{0.9})/10$	

caught by the hygroscopic solution. The heat of absorption is utilized in different process configurations (Bittrich and Hebecker, 1995; Fratzscher and Stephan, 2000).

Although the suggested process design has not been demonstrated experimentally, it rests on two well-established technologies: the separation by pervaporation and absorption refrigeration. The presented process is a combination of both processes in a new configuration. The process evaluation and the feasibility study will encourage researchers to proceed with experimental investigations. The most important point that has to be investigated experimentally is to quantify the effect of the membrane selectivity on the process as stated in the subsection on the effect of lower membrane selectivity. Moreover, test runs and parametric studies on a pilot-scale unit would be necessary to make it more understandable and to adjust the suggested process to guarantee a reliable design and operation.

Conclusion

A novel process configuration for pervaporation and vapor permeation is presented. In this process the permeation driving force is realized by absorbing the permeate vapor into a suitable solution with a very low vapor pressure. The refrigeration needed for condensation in the conventional process can be overcome and cost savings can be achieved. Very low vacuum pressures can be reached without any permeate-freezing limitations. Preliminary simulations and feasibility studies for the suggested process are presented. The presented results should be considered qualitatively rather than quantitatively, as the utility costs are unique for each industry and in each plant. The presented process could be considered as an additional optional process scheme for chemical plants that are going to run membrane dehydration units.

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Literature Cited

Bittrich, P., and D. Hebecker, “Abluft- und Brüdenwärmenutzung mit Sorptionskreisläufen,” *Chem.-Ing.-Tech.*, **67**, 766 (1995).

Caro, J., M. Noack, P. Kölsch, and R. Schäfer, “Zeolite Membranes —State of Their Development and Perspective,” *Microporous Macroporous Materials*, **38**, 3 (2000).

Coronas, J., and J. Santamaria, “Separations using Zeolite Membranes,” *Sep. Purif. Methods*, **28**, 127 (1999).

Ebert, K., D. Fritsch, O. Stange, and A. Wenzlaff, “Hydrophile Kompositmembran zur Entwässerung organischer Lösungen,” European Patent No. DE 199 25 475 (1999).

Ebert, K., O. Stange, and K. Ohlrogge, “Dehydration of Organic Solutions by Vapor Permeation with Temperature Stable Polymeric Membranes,” 6th World Congr. of Chemical Engineering, Melbourne, Australia (2001).

Fahmy, A., D. Mewes, and K. Ebert, “Design Methodology for the Optimization of Membrane Separation Properties for Hybrid Vapor Permeation/Distillation Processes,” *Sep. Sci. Technol.*, **36**, 3287 (2001).

Fahmy, A., D. Mewes, and K. Ohlrogge, “On the Integration of Jet-Ejectors into Hybrid Dehydration Processes,” *J. Memb. Sci.*, **196**, 79 (2002).

Feng, X., and R. Huang, “Liquid Separation by Membrane Pervaporation: A Review,” *Ind. Eng. Chem. Res.*, **36**, 1048 (1997).

Fratzscher, W., and K. Stephan, *Strategien zur Abfallenergieverwertung*, Chap. 4, “Regionale Objektbereiche und Entwicklungsstrategien, 1st ed., Friedr. Vieweg Verlag, Berlin, p. 165 (2000).

Fu, J., “Salt Containing Model for Simulation of Salt-Containing Extractive Distillation,” *AIChE J.*, **42**, 3364 (1996).

Glugla, P., and S. Sax, “Vapor Liquid Equilibrium for Salt-Containing Systems: A Correlation of Vapor Pressure Depression and a Prediction of Multicomponent Systems,” *AIChE J.*, **31**, 1911 (1985).

Heckmann, M., “Die Verbesserung der Destillation durch hybride Systeme,” *Vak. Forsch. Prax.*, **2**, 108 (2000).

Herold, K., R. Radermacher, and S. Klein, *Absorption Chillers and Heat Pumps*, 1st ed., CRC Press, New York (1996).

Jaques, D., and W. Furter, “Salt Effects in Vapor-Liquid Equilibrium: Testing the Thermodynamic Consistency of Ethanol-Water Saturated with Inorganic Salts,” *AIChE J.*, **18**(2), 343 (1972).

Lipnizki, F., and R. Field, “Integration of Vacuum and Sweep Gas Pervaporation to Recover Organic Compounds from Waste Water,” *Sep. Purif. Technol.*, **22/23**, 347 (2001).

Lipnizki, F., R. W. Field, and P.-K. Ten, “Pervaporation-Based Hybrid Process: A Review of Process Design, Applications and Economics,” *J. Membr. Sci.*, **153**, 183 (1999).

Meranda, D., and W. Furter, “Vapor-Liquid Equilibrium in Alcohol-Water Systems Containing Dissolved Halide Salts and Salt Mixtures,” *AIChE J.*, **18**, 111 (1972).

Okamoto, K., H. Kita, K. Horii, K. Tanaka, and M. Kondo, “Zeolite NaA Membrane: Preparation, Single-Gas Permeation, and Pervaporation and Vapor Permeation of Water/Organic Liquid Mixtures,” *Ind. Eng. Chem. Res.*, **40**, 163 (2001).

Park, Y., J.-S. Kim, and H. Lee, “Physical Properties of the Lithium Bromide + 1,3-Propandiol + Water System,” *Int. J. Refrig.*, **20**, 319 (1997).

Pereira Nunes, S., and K.-V. Peinemann, *Membrane Technology in the Chemical Industry*, 1st ed., Wiley-VCH, Weinheim, Germany (2001).

Strathmann, H., “Membrane Separation Processes: Current Relevance and Future Opportunities,” *AIChE J.*, **47**, 1077 (2001).

Zhang, S., and E. Drioli, “Review: Pervaporation Membranes,” *Sep. Sci. Technol.*, **30**, 1 (1995).

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