

# HYBRID PERVAPORATION-ABSORPTION FOR THE DEHYDRATION OF ORGANICS

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## ABSTRACT

A novel configuration of pervaporation and vapor permeation processes is introduced. In the suggested process the driving force for permeation is enabled by the absorption of the permeate vapors using a suitable solvent with a low vapor pressure. Thus, the refrigeration needed for condensing the permeate under vacuum can be overcome and cost savings can be achieved. Moreover, very low vacuum pressures can be reached without any permeate freezing limitations. Technical realization of this process can be achieved for organic dehydration processes by integrating the membranes into commercial scale absorption refrigerators or heat pumps with little modification. Preliminary simulations and feasibility investigations for organic dehydration with the suggested process are presented and discussed.

## INTRODUCTION

Pervaporation and vapor permeation processes have gained much attention in recent years. The coupling of such units to classical thermal separation processes in the so called 'hybrid configurations' have showed technical and economic advantages in many cases [1]. The dehydration of organic compounds is a feasible area for implementing such processes. In regions of close relative volatility and for overcoming azeotropes, the membrane process is more economic than azeotropic and extractive distillation [2-6]. Different configurations of such hybrid processes are shown in Figure 1.

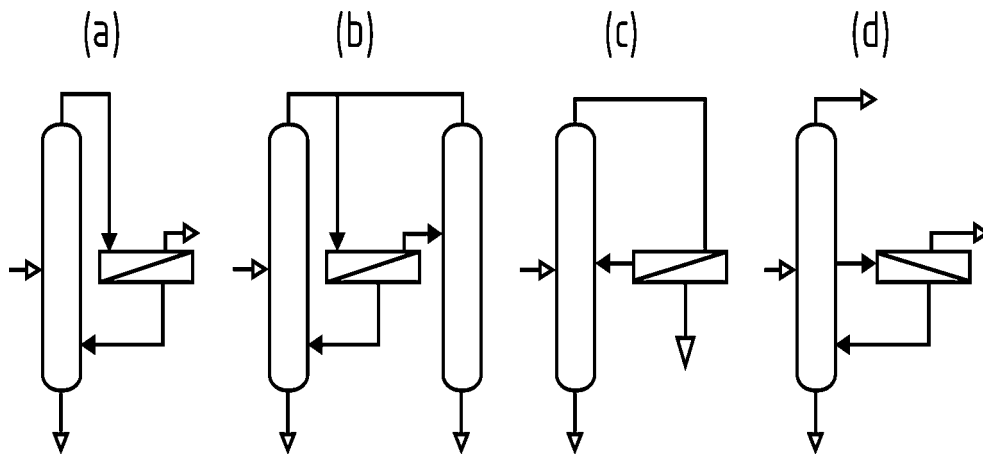


Figure 1: Membrane dehydration processes coupled to distillation

In the first scheme (a) the feed is at the water side of the azeotrope and the membrane is used for overcoming the azeotrope and for the final dehydration. Examples are the dehydration of ethanol and acetone. In the second configuration (b) the membrane is used only to overcome the azeotrope and the final dehydration is done by the second column. An example for this process is the dehydration of isopropanol or acetonitrile. The arrangement (c) is used when the original feed composition is on the organic side of the azeotrope. The column separates the feed into the high boiling organic at the bottom and a low boiling mixture close to the azeotrope at the top. The vapor from the top is passed through a vapor permeation unit which removes water to a residual concentration close to that of the original feed. Configuration (d) is used for a three component separation such as the separation of a methanol-isopropanol-water mixture [7]. In this system a minimum azeotrope that exists between water and isopropanol makes the feasible distillation separation only through azeotropic separation using a fourth component and at least three distillation column. In the alternative hybrid process, a side stream is drawn from the column and water is removed continuously by a pervaporation unit. Pure methanol can be obtained at the top and pure isopropanol at the bottom of the column.

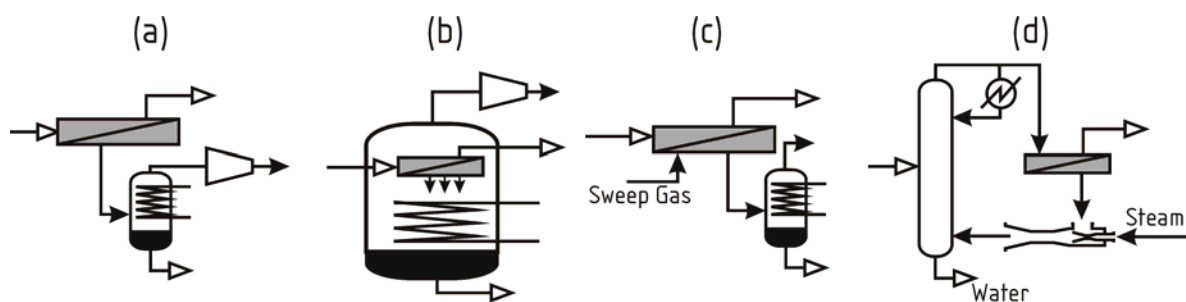


Figure 2: Different configurations for pervaporation

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 a vacuum pump (Figure 2a,b). In another technique a sweep gas or vapor is used to lower the partial pressure of the permeating components and carrying them out at the permeate side (Figure 2c). 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 [8]. Another suggested technique within the dehydration of organics in hybrid processes is the steam jet ejection (Figure 2d). This method could bring cost savings within a certain range of permeate pressures [9].

For pervaporation the feed is liquid and the permeate evaporates through the membrane. The latent heat of vaporization is usually supplied to the feed stream by intermediate heat-exchangers, installed between a number of pervaporation modules in series as shown in Figure 3(a). This configuration is necessary to keep the temperature of the feed at the highest possible level along the whole membrane area to guarantee a high transport rate. Integrating the membrane modules into a vacuum condenser has the advantage of low pressure drop on the permeate side, and is suitable for permeate-side open modules.

For vapor permeation the feed is vapor and no phase change occurs during the permeation, which makes the process less complex as shown in Figure 3(b). Vapor permeation has proven to be especially suitable for the purification of top streams of fractionation columns that can be used as feed directly. Although vapor permeation is less sensitive to concentration polarization at the feed side of the membrane, the mass transport is sensitive to the degree of superheating and to friction losses in the feed side. Little superheating lowers the transmembrane flux in the case of polymeric membranes as a result of decreased sorption and swelling.

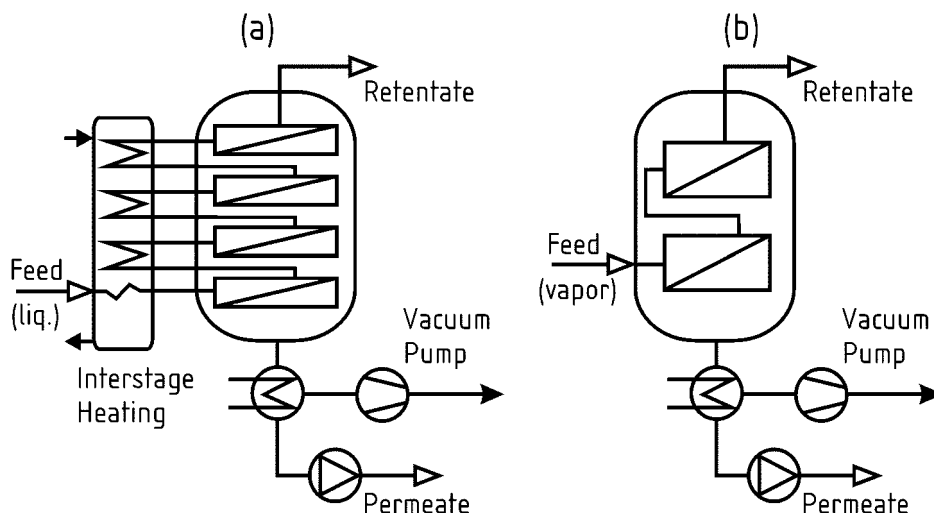


Figure 3: Technical features of pervaporation and vapor permeation

As stated above, vapor permeation is used when the feed is already available in the vapor phase. However, the evaporation of liquid in order to employ vapor permeation is accepted for small flow rates and large concentration range, which otherwise would request too many small pervaporation stages. The same is practiced when dissolved or undissolved solids are present in the feed, and an additional purification step by evaporation has to be performed anyway.

Membranes used so far in industrial pervaporation plants are generally of composite type. They are prepared by coating a porous support of definite structure with a thin, dense permselective layer. In the composite configuration thus obtained, the structure of the porous support exert a significant influence on the performance of the membrane. Pores must be wide enough to avoid undesirable pressure drop in the permeate stream but not too large to prevent any deep penetration of the coating material during the formation of the membrane.

## LIMITATIONS OF CONDENSATION TECHNOLOGY

As shown in Figure 2, different techniques are used to achieve the required driving force for permeation. However, the condensation technology has proven to be the most convenient for vacuum production. Although relatively expensive it is a simple and common technology with a wide range of standard units and long years of industrial experience. However, it has shown some limitations by its use in the combination with pervaporation. 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 4 for water-ethanol mixtures. The boiling curves are calculated with “Aspen Plus” using UNIQUAC activity model. In consequence of this limitation, the permeate pressure cannot be arbitrary lowered and thus the savings in the required membrane area are also limited. This limitation emerges by trying to achieve a very high retentate purity, where the driving force for permeation diminishes. Exponential increase in the required membrane area is expected at this concentration range. A feasible way to reduce the membrane area is to use low selectivity membranes at this concentration region [10]. An intermittent operation of the condenser with heating and melting the formed ice has also been practiced [11]

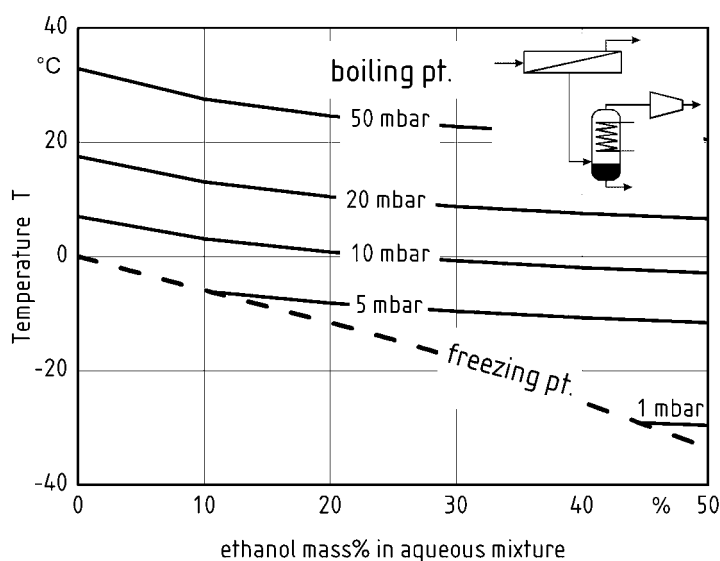


Figure 4: Boiling and freezing points for different water-ethanol mixtures

## SUGGESTED ABSORPTION TECHNOLOGY

A novel process is suggested, in which the absorption of the permeate stream is used for vacuum generation on the permeate side. An absorbent with a high affinity to the permeate mixture is contacted with the permeate vapor. The lean (dilute) 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 at equal temperatures, or the same vacuum pressure can be attained at a higher temperature. Consequently the fixed and operating cost 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 lean absorption solution is sent to a desorber where the absorbed permeate is stripped out from the solution. The required stripping energy could be attained from a low quality energy source in the chemical plant or it can be won out of the vaporous retentate stream in the case of vapor permeation. A flow sheet of that process is shown in Figure 5. The vapor stripped out of the desorber is condensed at a higher pressure compared to the permeate. Therefore in all cases normal cooling water can be used. The rich solution from the desorber is recycled back to the absorber. Heat is exchanged between the lean and rich solutions to lower 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.

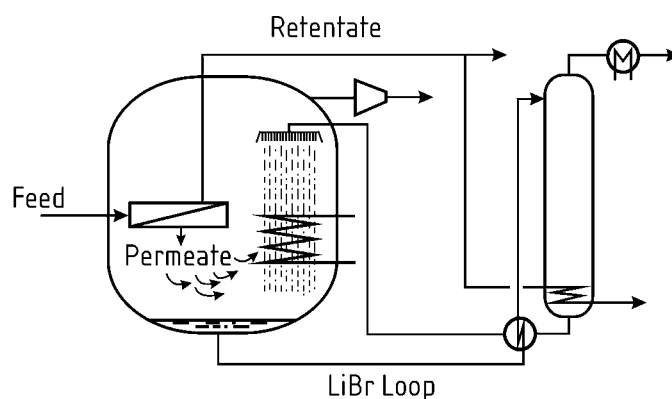


Figure 5: Absorption technology for dehydration by vapor permeation

Applying the above introduced absorption technology on the dehydration of organics with pervaporation or vapor permeation, a hygroscopic liquid is utilized for the absorption of the permeate. Lithium bromide (LiBr) solution is one of the most hygroscopic liquids found. The vapor pressure of water above LiBr solution as shown in Figure 6 is much lower than that of water at the same temperature. Some additives like ethandiol or propandiol slightly increase the vapor pressure above the solution, but they lower the crystallization temperature of LiBr [12,13]. A vapor pressure of 8 mbar can be achieved above a 60 mass% LiBr Solution at room temperature. A refrigeration to  $-10$  or  $-15$  °C is necessary to achieve such pressure by condensing the permeate mixture.

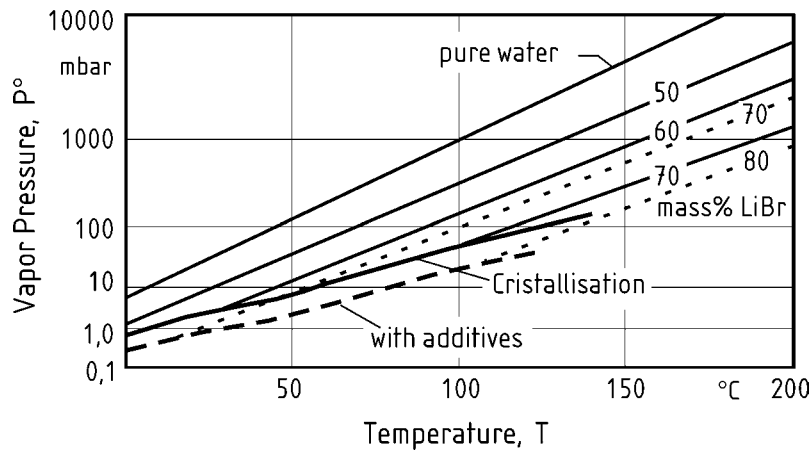


Figure 6: Vapor pressure over LiBr solutions [12,13]

In addition to the above stated cooling temperature advantage, lower vacuum pressures could be achieved that were 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 very low water content in the retentate, which would result in considerable reduction of the required membrane area.

### Integration into absorption refrigeration cycles

The above described absorption process 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 on using these refrigeration cycles. The equipment and processes are standardized and the whole cycle is available as a finished product in the market.

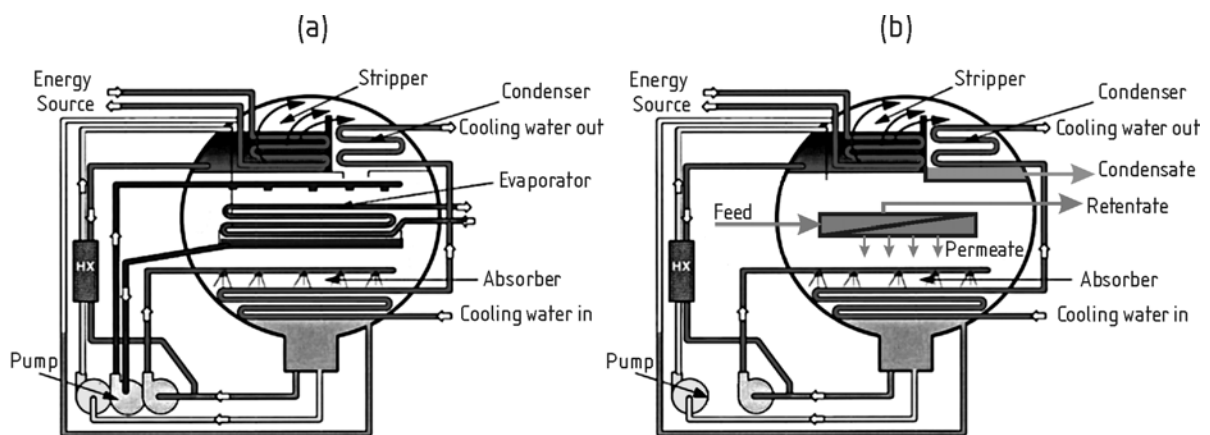


Figure 7: Integrating the membrane modules into the refrigeration cycle

A typical cycle is shown in Figure 7a. 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 the concentration of the absorbing solution. A small vacuum pump is also necessary for drawing the leakage and the non-condensable 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 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 evaporation and 100 mbar for the desorption process [12].

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 7b. The cycle will be converted to an open system. The permeate stream is drawn out of the process as condensate.

## **PROCESS SIMULATION AND ECONOMIC EVALUATION**

A process simulation program is developed for pervaporation and vapor permeation 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 can be determined on an economic basis. Details about the modeling procedure and the model assumptions can be found in [10].

A case study for ethanol dehydration is considered for technical and economic evaluation. The separation task is dehydrating 1000 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 [14]. Different membrane selectivities from 20 to 2000 are considered. Both absorption and condensation alternatives running under a permeate pressure of 8 mbar are compared. An additional case of 2 mbar is also considered for the absorption alternative since it is not possible by condensation due to ice formation in the condenser. Functions for fixed and variable costs were developed on the basis of offers from different manufacturers and data from large scale chemical companies. 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 results are shown in Figure 8. The absorption alternative has shown 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 a vapor pressure of 2 mbar. It would be necessary if a further purification of the retentate is required. From the same figure one can derive that a certain mid-range membrane selectivity seems to be optimal for the studied separation case.

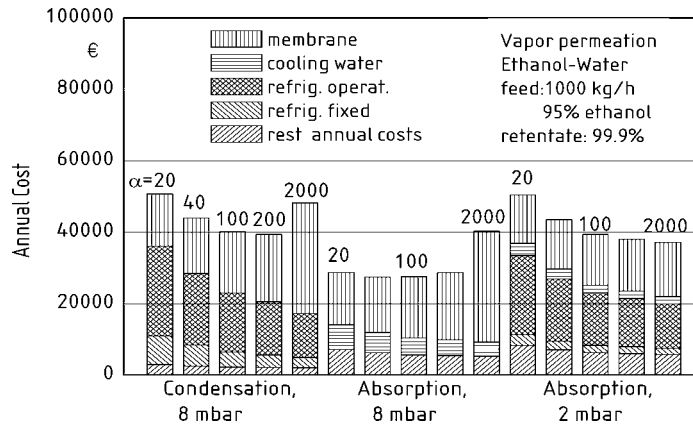


Figure 8: Comparing process alternatives on annual cost basis

At a permeate pressure of 8 mbar the permeate contains 1.1 and 9.8 mass % ethanol when using a membrane selectivity of 2000 and 200 respectively. This amount is then diluted in the absorbing solution to be 0.1 and 0.89 % in the effluent solution. The permeate is assumed to be free of ethanol in our present calculations. This assumption is discussed further in the next section. Results for mass and energy balance calculations for the Absorption cycle are illustrated in Figure 9. The permeate flow in the presented results is based on a membrane selectivity of 200.

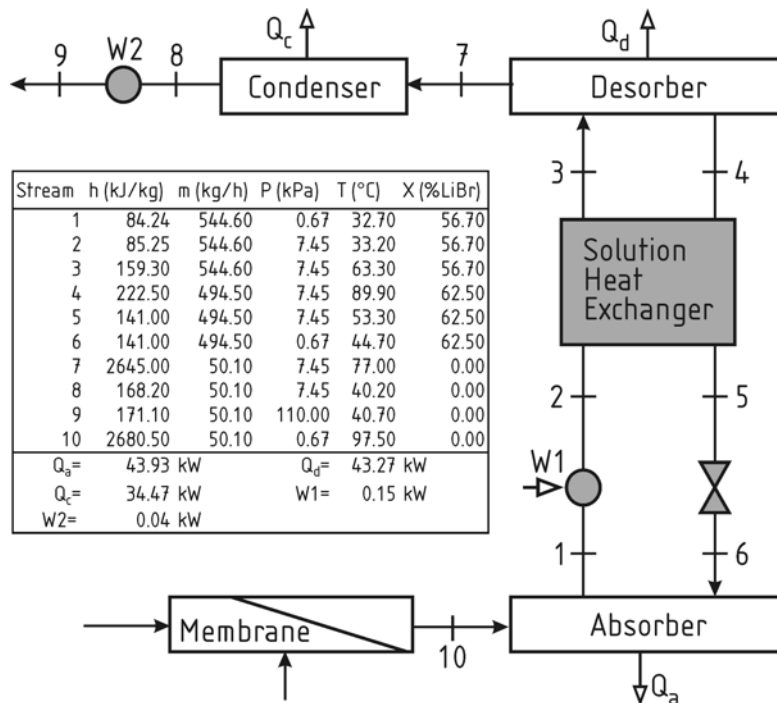


Figure 9: Mass and energy balance for the absorption-desorption cycle



## DISCUSSION

The presented process for carrying out pervaporation and vapor permeation processes combine both the selectivity of the membrane and the high affinity of the permeate towards the absorbing solution. It should be differed 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 rather a selective barrier between the feed side mixture and the absorbing solution. The absorption process takes place outside the membrane module.

As illustrated above, 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 towards the permeate mixture.

The membrane selectivity for the dehydration of organics is generally very high. However, 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 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 were carried out on the effect of different salts on overcoming the azeotropes in the water-organic distillation [15]. However, a slight decrease in the solubility of the salt in the water-alcohols solutions compared to pure water is observed [16]. 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 allow to implement higher salt concentration [13]. As a result the presence of small amounts organic material in the salt solution has negative and positive effects with respect to our suggested application. Thus at this stage of basic process design we assumed that the positive effects would adjust 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.

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 the 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 caught by the hygroscopic solution. The heat of absorption is utilized in different process configurations [17].

Although the suggested process design lacks an experimental demonstration, it rests on two well established technologies, the separation by pervaporation and the absorption refrigeration. The presented process is a combination of both processes in a new configuration. The process evaluation and the feasibility study will encourage 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. Moreover, test runs and parametric studies on a pilot scale

unit would be necessary to give more comprehension and to adjust the suggested process to guarantee a reliable design and operation.

### Nomenclature

h	[kJ/kg]	specific enthalpy
m	[kg/h]	mass flow rate
P	[kPa]	pressure
Q	[kW]	heat duty
T	[°C]	temperature
W	[kW]	pumping work
X	[-]	mass per cent

### Subscripts

a	of the absorber
c	of the condenser
d	of the desorber

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### **KEYWORDS**

Pervaporation, Vapor Permeation, Hybrid, Absorption, Dehydration