Augmenting Distillation by Membranes: Developments and Prospects[*]

Ž. Olujić, P. Perez, F. T. de Bruijn, J. de Graauw, and P. J. Jansens

TU Delft, Laboratory for Process Equipment, Leeghwaterstraat 44,
2628 CA Delft, the Netherlands, E-mail: z.olujic@tudelft.nl

Dedicated to Prof. Dr. Đurđa Vasić-Rački on occasion of her 60th birthday

The growing consciousness for sustainable industrial processes has resulted in industrially developed countries in supporting research efforts toward thorough evaluation of possibilities for improving efficiency of energy intensive separations implying also significant reduction of related carbon dioxide emissions. Being inherently thermodynamically inefficient, distillation, which is by far the most widely utilised and energy intensive separation technology in chemical process industries, has become primary target of energy conservation projects in refining, petrochemical and chemical industries. Improvement is an ongoing activity, replacing still beyond comprehension and a great deal of academic effort is oriented towards augmenting distillation by combining it, where appropriate, with membranes, i.e. pervaporation or vapour permeation, which in conjunction with polymeric membranes proved to be an industrially viable alternative to conventional processes for dehydration of alcohols. Present paper addresses recent developments along this line striving for larger fluxes in alcohol dehydrations by utilising ceramic membranes, with focus on vapour permeation, as well as the potential for the recovery of organic solvents and reactants forming azeotropes with other organics.

Key words:
Distillation, hybrid processes, pervaporation, vapour permeation, ceramic membranes

Introduction

Refining, chemical and petrochemical industries depend on energy and with ever increasing energy price competing companies are increasingly looking toward finding a way to effectively reduce production costs. Certainly, improving energy efficiency of process industry implies a reduction in emissions of CO_2 and other environmentally unfriendly combustion process off-gases. However the effort and resources, chemical companies are willing to spend toward improvement in this respect, are not motivated by increased consciousness but more because of need to improve their competitive edge. Anyhow, in industrially developed countries the governments are encouraging these efforts by subsidies made available as an effective instrument to support implementation of more sustainable processes. Such a political push triggered a lot of activities and the manufacturers of bulk chemicals focus today their effort and resources on improving processes and equipment hoping however to avoid capital intensive solutions. It should be noted that after the first and second oil crises in mid 1970s and beginning 1980s, respectively, a lot of effort went into heat integration within the plants utilising effectively the "pinch technology".

Most recent developments address rather low energy efficiency of most energy intensive equipment encountered in typical petroleum refining and commodity chemicals manufacturing plants.[1]

Being most widely used and both capital and energy intensive, distillation, the work horse of process industries became the primary target of energy conservation efforts. Some 15 years ago a study of the US Department of Energy[2] came with three time-scale related scenarios, elaborated to some extent in the book by *Humphrey* and *Keller*.[3] The first, short term scenario recommended a concentrated effort to improve distillation, indicating equipment performance and process control improvement related efforts as most rewarding goals, which appeared to be particularly effective solution for US based plants employing less sophisticated technologies than their counterparts in Europe. The second, medium term approach suggested investment of considerable effort and resources into evaluation, development and implementation of possibilities for augmenting distillation by combining it in a techno-economically viable way with reactors and other separation techniques into so called hybrid processes. Combining distillation with membranes was indicated as a very promising development particularly suitable for energy efficient separation of azeotropic mixtures without involving third component or with reaction (reactive distillation) to in-

crease conversion and intensify both reaction and separation by carrying them out in a single shell. The long term scenarios count on that, that in the foreseeable future the efforts undertaken to develop new technologies which aim at replacing distillation could bring some success.

Such ambitions have been formulated in a number of formal documents which where taken as basis for installing financial support schemes for the coming years. First of such documents is so called AIChE (American Institute of Chemical Engineers) Vision 2020, 2000 Separations Roadmap.[4] The results of most recent evaluations of research needs in this respect have been summarised in a highly cited commentary paper by *Noble* and *Agrawal*.[5] Also, most recently, a similar, "Road map Separations" document has received governmental support in the Netherlands.[6] Al these documents recommend improving distillation, however strive more pronouncedly for augmenting distillation by combining it with other separations into hybrid processes in a synergetic way to arrive at energy conserving and environmentally friendly solutions for near and medium term future. Since the academic community favours and opts for the development goals providing opportunities and grants for research, development of hybrid processes involving distillation became a widely accepted subject of research interest. In the Netherlands, the TU Delft is involved with two multi-partner research efforts, sponsored by government, which strive for acquiring necessary know-how to enable cost effective implementation of membranes in conjunction with distillation into capital and energy intensive bulk chemicals separations.

A typical example of an industrial application of a hybrid process combining distillation with polymeric membranes is dehydration of alcohols. Figure 1 shows flowsheet of an ethanol dehydration plant, with permeate stream recycled to the distillation column to increase overall process yield.[7] This well established hybrid process will be used as a base case to illustrate specific features of ceramic membranes, which were introduced recently as a part of a dedicated effort to arrive at increased fluxes by employing at the feed side operating temperatures well above those used with well established polymeric membranes.[7]

In the meantime the membrane manufacturers made a strong move toward developing ceramic membranes suitable for the pervaporation or vapour permeation based recovery of solvents and reactants from organic mixtures. In the present work, the recovery of methanol in the MTBE process has been chosen as base case to illustrate the potential gains and difficulties associated with the employment of ceramic membranes for organic-organic separations on a large industrial scale.[8] Indeed, both develop-
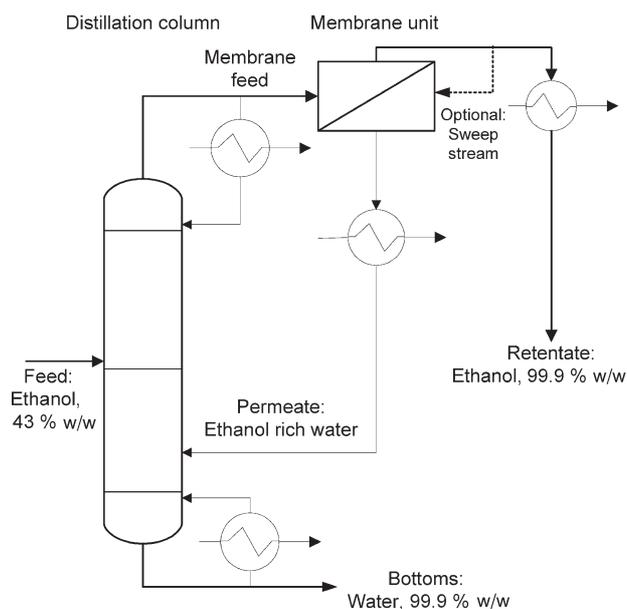
F i g . 1 – *Flowsheet of a combined distillation – vapour permeation ethanol dehydration plant*

ments along this line are interesting and promising, however, with presently available inorganic membrane materials are difficult, if not impossible to realize in an industrially viable way in practice.

Background

Regarding the state of the art of bulk chemicals separations, there is no doubt that distillation should be preferred, as long as this is affordable and possible. Namely, nothing is wrong with distillation, except that relying on heat as separating agent and due to the scale of industrial application it may be considered as both energy and capital intensive. Indeed, this is a fact, particularly in case of industrially important separations of close boiling mixtures. Certainly, decreasing relative volatility means increasing separation difficulty, i.e. dealing with large reflux and stage requirements. Another case are non ideal mixtures forming azeotropes, i.e. a thermodynamic barrier which makes impossible purifying both components in one distillation column. The typical remedy is utilising two pressures (columns) operation, where feasible, or more frequently in practice, utilising a third component (entrainer or solvent) to shift the equilibrium, i.e. to affect relative volatility accordingly (azeotropic and extractive distillations). Certainly, the third component involvement implies need for recovery and reuse which again occurs through distillation, i.e. an additional capital and energy intensive step. Besides the significant costs and energy requirements associated with building and operation of these conventional hybrid installations, the presence of third

component is generally undesired, simply because of permanent potential danger of product contamination. Therefore, combining distillation with membranes, a non-equilibrium, i.e., rate controlled separation technique, into a hybrid process was recognised early as a promising alternative for conventional, entrainer or solvent based distillation of azeotropic mixtures. The state of the art of conventional and new hybrid processes including distillation and related energy conservation aspects is summarised in recently published books by *Stichlmair* and *Fair*[9] and *Seader* and *Henley*.[10]

Building on favourable permeating properties of water, first applications in bulk chemical were dehydrations of solvents, primarily alcohols. However, there are also many interesting organic azeotropic mixtures containing solvents or reactants which require considerable effort to be separated and reused. So relying on initial success with alcohol dehydration many membrane manufacturers and/or users shifted their focus on the development of membranes for organic-organic separations.[11,12]

Membranes, modules and processes

Membranes belong to a wide family of devices employing a selective barrier, through which some components (species) from a feed mixture permeate faster than other. This is controlled by different types of resistances and driving forces.[10,13–16] Micro– and ultrafiltration are well established and widely applied techniques for isolation of dispersed solids from bulk liquid passing through a porous membrane driven by a quite large absolute pressure difference. Another well known membrane process employing a large pressure difference across the membrane, is reverse osmosis. However, in this case dense membranes permeable for the solvent, usually water, but not to dissolved salts, are used, and the pressure on the feed side has to be significantly larger than the osmotic pressure to facilitate the transport of the solvent (usually water), i.e. enable reaching reasonable throughputs. Reverse osmosis is used on largest scale for desalination of sea or brackish waters. Indeed in these applications, membranes proved to be competitive with multi-stage evaporation. Other well established membrane processes are dialysis and electrodialysis. In dialysis, which is a synonym for the artificial kidney, microporous membranes have pores of such size that only desired component can pass through, the driven by a concentration difference. Colloids dispersed in the liquid feed do not pass through the membrane. In electrodialysis an electric field in conjunction with ion-selective membranes is used for separating aqueous electrolyte feed solutions. A typical application is the desalination of brackish

water, where depending on the salt concentration range, it can compete with ion-exchange and reverse osmosis. Also, there are many other specific applications of this technique in both chemical and food industry. In all above mentioned membrane processes, liquids with or without some dispersed solid material are involved on the feed side and diluted liquids on permeate side of the membrane.

Separation of mixtures, containing organic and inorganic gases or vapours or liquids is a different story. Here, so called nonporous, mainly polymeric membranes are used, which being "dense" exhibit much higher resistance and consequently much lower fluxes than porous membranes. Another distinctive characteristic is that rather small fraction of the feed, i.e. material to be removed passes through the membrane. Separations of gases, particularly those not requiring sharp separation, as for example making nitrogen or oxygen rich air, are already established applications on small to medium scale. Continuous implementation progress is made with industrially more attractive large scale separations, for instance removal of hydrogen from synthesis gas, which is well established or removal of CO_2 from natural gas, which is still under development.[14] It should be noted that here also a high pressure is required at feed side to establish large enough driving force.

This paper however is concerned with membrane processes that are compatible with distillation, i.e. pervaporation and vapour-permeation, where a saturated liquid or vapour mixture is fed to a membrane, and a relatively small fraction of feed permeated through the membrane. Vapour permeation is similar to gas permeation, and the main distinction of pervaporation, with respect to gas and vapour permeation, is in the fact that a phase change is involved during the transport of permeating material through the membrane. An experimental evaluation and comparison of these two processes in conjunction with inorganic membranes can be found in most recent publications by *Sommer* and *Melin*, addressing dehydration[17] and organic/organics separations, separately.[18] A complete overview of the patents and membrane manufacturers in this field can be found in a paper by *Jonquieres* et al.[19]

In order to be implemented in practice, membrane materials have to be arranged into techno-economically suitable configurations, i.e. membrane modules characterised by a favourable hydrodynamics. For polymeric membranes three most common configurations of a module are: plate and frame, spiral wound, and hollow fibre modules. The latter, essentially a shell and tube configuration, allows largest specific areas, because typical outer diameter for hollow fibres is bellow 0.5 mm. Hollow fibres and

spiral wound modules are preferred in gas separation applications. The commercial pervaporation plants for alcohol dehydration utilise the least suitable, i.e. plate and frame configuration, which however ensures good sealing, which is essential for continuously operating processes.[12] From the same reason, similar, plate heat exchanger based configuration was used with success for the first commercial vapour permeation plants.[20]

Membrane module reliability is still an issue and each configuration imposes certain fluid-dynamic conditions on both feed and permeate side, which can be more or less detrimental for the performance. Pressure drop due to friction losses at permeate side is a typical example, and should be accounted for appropriately, which, in turn, depends on and affects the choice of the module configuration. These merely engineering aspects of implementation of membranes are important design consideration and for all important membrane applications are discussed in greater detail in the book of *Reutenbach* and *Albrecht*.[13] In this book as well as in the monograph by *Noble*[14] and the book by *Baker*[15] detailed accounts can be found on pervaporation and its characteristics but limited to polymeric membranes. In recent articles, *Bruschke*[21] and *Bruschke* and *Wynn*[22] give a detailed overview of the pervaporation and vapour permeation technology. A detailed industrial account on vapour permeation and its relative advantages as experienced in practice with first generation of polymeric flat membranes can be found in a 1991 paper by *Sander* and *Janssen*.[20] They applied successfully plate heat exchanger type modules, which however cause a rather high pressure drop, and consequently such a temperature decrease, that intermediate compression was required to maintain the driving force. This and other first application experiences clearly indicated that the pressure drop on the feed side could become an obstacle for implementation of vapour permeation, and that other module configurations could be beneficial in this respect.

Present paper addresses engineering aspects in conjunction with implementation of ceramic membranes/modules into industrial environment, focussing on vapour permeation and its relative advantages and disadvantages with respect to pervaporation applied under the same conditions.

Pervaporation and vapour permeation

Fig. 2 illustrates schematically the separation principle of vapour permeation and pervaporation membranes, which is generally known as the perm-selective mass transfer through a nonporous top layer and a microporous sublayer of the mem-
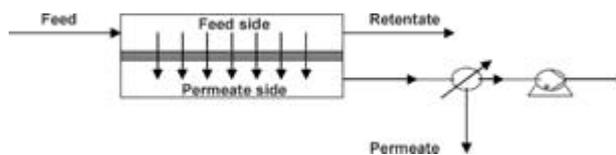
F i g . 2 – *Separation principle of PV and VP membranes*

brane. Vapour permeation (VP) implies a saturated or slightly overheated vapour feed, which means that on both sides of the membrane there is a vapour phase. In pervaporation (PV) the liquid feed is saturated or slightly sub-cooled liquid and the permeating components evaporate (flash) during the transport through the membrane. In both cases the driving force is practically the difference in partial pressures of permeating components. In order to create enough driving force vacuum must be employed on the permeate side. The pressure on the feed side is usually above-atmospheric, and the trans-membrane pressure difference should not exceed the so called breakthrough pressure, which could lead to leakage and/or damage of the membrane.

Practical purpose of PV or VP separation process is to remove a relatively small fraction of a more permeating component present in a process stream, i.e. to obtain the less permeating component called retentate at desired purity specification. In other words, in typical PV and VP applications, retentate represents the product stream.

The performance of a VP or PV membrane is characterised by its flux and selectivity. Flux determines the capacity, and the membrane selectivity the quality of the separation. Unfortunately, these two parameters are interdependent, i.e. an improvement on the flux side means less selectivity and vice versa. For bulk chemical separations the flux is more important because it determines directly the membrane area requirement and consequently the capital cost. Anyhow, the challenge for membrane manufacturers is to maximize both, flux and selectivity.

Membrane performance characterisation

Membrane selectivity

In VP and PV cases the definition of the selectivity, or the separation factor, S_{AB} (-), is similar to that of the relative volatility, α_{AB} in distillation, i.e. it represents the ratio of mole fractions of two components on both sides of the membrane:

$$S_{AB} = \alpha_{AB} = \left(\frac{\frac{y_{A,P}}{x_{A,F}}}{\frac{y_{B,P}}{x_{B,F}}} \right)_{PV} \text{ or } \left(\frac{\frac{y_{A,P}}{y_{A,F}}}{\frac{y_{B,P}}{y_{B,F}}} \right)_{VP} \quad (1)$$

where y and x denote mole fractions of a component in vapour and liquid phase, respectively. Subscripts A and B denote permeating and rejected component, and the subscripts F and P, the feed and permeate, respectively. It should be noted that here the mole fractions of the individual components on two sides of the membrane are not in equilibrium, as in the case of distillation. However, a value of relative volatility in distillation indicates directly the degree of separation difficulty involved. The selectivity of a membrane is less informative. For example, selectivity below 20 is generally considered small. A low selectivity indicates that recovery of the permeating component will not be complete, i.e. that a significant fraction of the less permeating component which is usually the product, will be lost with the permeate stream. However, this must not be a deficiency providing the permeate stream is recycled, as it is suggested in the flow-sheet shown in Fig. 1.

Membrane flux

If we assume that the mass-transfer resistance is concentrated in the membrane, the flux of the permeating component, i.e. its molar flow rate per unit membrane area, is proportional to the product of the characteristic membrane permeability coefficient and the driving force:

$$N_i = \frac{F_{i,\mathrm{M}}}{A} = \Pi_i \Delta p_i \qquad (2)$$

where N_i (kmol m^{-2} s^{-1}) is the membrane flux, i.e. molar flow rate of permeating component, $F_{i,\mathrm{M}}$ (kmol s^{-1}), per unit membrane area, A (m^2), and Δp_i (Pa), the difference in the feed and permeate side partial pressures of permeating component is the driving force. The mass transfer performance calculations are usually performed in molar units and transformed into mass based ones when equipment is dimensioned.

The proportionality constant Π_i, (kmol m^{-2} s^{-1} Pa^{-1}) is generally known as the permeance, which is defined as the ratio of the permeability, P_i (kmol m^{-1} s^{-1} Pa^{-1}), to the membrane thickness, δ_{m} (m):

$$\Pi_i = \frac{P_i}{\delta_{\mathrm{m}}} \qquad (3)$$

Gas permeabilities are often expressed in a specific unit called *barrer*, named after one of the pioneers in this field *R. M. Barrer*; 1 *barrer* $= 10^{-10}$ cm^3(STP) cm cm^{-2} s^{-1} cm Hg^{-1}. STP indicates here that the gas volume is that corresponding to standard conditions (0 °C and 1 bar). Diversity of the systems and units used throughout the membrane literature requires special attention to be paid to,

when dealing with membrane performance calculations, to avoid inconsistencies which could lead to great errors. A factor 1000 error is not an exception, because, for instance, prefix k (kilo) is not used consistently. Also, the diffusion coefficients are usually reported in cm^2 s^{-1}, time in hours, and the pressure in bar, just to name some. So the relevant numbers can appear large and/or very small. Therefore, prior to starting with calculations all involved properties have to be made consistent regarding the units.

It should be noted here that the ratio of pure vapour (gas) permeabilities or permeances of two components obtained from single component measurements is known as ideal selectivity of the membrane, i.e. $S_{AB}* = \Pi_A/\Pi_B$. In the cases where permeating components do not interact strongly with each other or with membrane, and when permeate pressure is essentially zero (vacuum), ideal selectivity becomes equal to that defined by Eq. (1).[15]

Driving force

Rigorously speaking, the driving force for both PV and VP is the difference in chemical potential of the permeating component on two sides of the membrane. In the practice however it is frequently expressed as the difference of partial pressures of permeating components. Due to the fact that in case of PV the liquid is at the feed side and in case of VP a vapour phase, the working expressions for driving force differ somewhat.

VP:

$$\Delta p_i = (p_{i\mathrm{F}} - p_{i\mathrm{P}}) = (y_i f_i p)_{\mathrm{F}} - (y_i p)_{\mathrm{P}} \qquad (4)$$

PV:

$$\Delta p_o = (p_{i\mathrm{F}} - p_{i\mathrm{P}}) = (x_i y_i p_i^{\circ})_{\mathrm{F}} - (y_i p)_{\mathrm{P}} \qquad (5)$$

where x_i (-) and y_i (-) are mole fractions of permeating component in liquid and vapour, respectively, f_i (-) is the fugacity coefficient and γ_i (-) the activity coefficient of the permeating component, p_i^o (bar) is the vapour pressure of the permeating component and p (bar) is the absolute operating pressure.

With vacuum on the permeate side the vapour phase follows ideal gas law. The same can be assumed for the feed side in case of vapour permeation if the feed pressure is below 2 bar. If not then the corresponding fugacity coefficient can be estimated using one of common equations of state. Feed side liquid is generally non-ideal, which can be accounted for by employing one of the established models for estimation of the composition and temperature dependent liquid-phase activity coefficient. So the estimation of the driving force can easily be done with required accuracy, however it

appeared that the permeability for PV in conjunction with polymeric membranes depends strongly on the concentration of permeating component in the polymer, which can lead to detrimental effects, even such as inversion of selectivity.[10] Fortunately inorganic membranes do not swell, but their structure and chemistry introduce other kind of difficulties.

In order to maximize the flux, i.e. to minimize membrane area requirement the natural approach is to increase the driving force as much as possible. This can be done on either side of the membrane. Permeate side requires certain level of vacuum and the best solution in case of large scale applications is to have water as cooling medium in the condenser. This means in best case a 0.1 bar pressure at the permeate side. If this is not enough then other, more expensive cooling media/systems have to be considered. To avoid installation of expensive vacuum pumps, in large scale applications the main vacuum generating and maintaining work is obtained from permeate condensation itself, which implies employing the means for cooling of the permeate vapour down to the required dew point temperature. In this case the actual role of the vacuum pump is limited to the removal of relatively small amount of inerts and noncondensables.

In order to dehydrate organics to below 10 ppm water, vacuum below 0.1 bar is required, which is impractical. A practical remedy, i.e. way to enhance the driving force significantly is by employing a sweep stream at the permeate side by diluting the permeate accordingly. For this purpose a rather small fraction of the retentate can be effectively used (see Fig. 1) or a third, closed circuit component employed.[23] Another, even more practical possibility is to employ less selective membranes, which provides for an internal sweep. Employing a retentate or internal sweep means a certain loss of the product, however, by recycling this product to reach permeate stream to the distillation column the overall efficiency (process yield) can be maintained at the cost of slightly increased investment and operating costs. This possibility demonstrates the main advantage of a fully integrated hybrid process, such as that shown schematically in Fig. 1, which will be discussed in greater detail later on.

Another possibility, which is actually the main driving force behind the research efforts described in this study, is enhancing the PV or VP driving force by increasing the partial pressure of the permeating component on the feed side. This can be achieved if the operating temperature on the feed side is increased accordingly. A rule of thumb,[12] confirmed by own measurements, says that flux doubles roughly for each 20 °C increase in the feed

side temperature, which means that higher operating pressures/temperatures should generally be preferred when combining distillation with PV or VP. Although sometimes pushed hard, polymeric membranes already established in PV and VP applications are generally limited in this respect and, therefore, a great deal of membrane flux improvement effort during last 10 years went into the development of inorganic, mainly ceramic membranes which can sustain high operating pressures and temperatures (well above 100 °C).

Maintaining the driving force

With a high feed side temperature and a constant vacuum on the permeate side, the highest possible driving force is ensured, which however exists at the beginning of the process only. Namely, with progressing separation the fraction of the permeating component on the feed side and consequently its partial pressure decreases with the membrane length, causing effectively a decrease in the driving force and consequently a diminishing flux. This means that high purities can be reached with difficulty, i.e. that often much more membrane area is required than initially anticipated. The separations with a relatively low fraction of the permeating component (< 10 % w/w) on the feed side will suffer less in this respect than feeds rich in more permeating component. So the feed composition could affect the choice of the configuration, i.e. whether to go to the end purity or just to bridge the azeotropic point and finish the purification by distillation (second column).

Certainly, with decreasing composition at the feed side the temperature will change accordingly, however this effect can be more or less pronounced depending on the type of operation. In PV case the only source of the energy used for evaporation (adiabatic flash) is the sensible heat of the feed liquid. Removal of this heat is accompanied by a cooling effect, i.e. a significant temperature drop. A reduction in the feed temperature will inevitably cause a decrease in the vapour pressure of the permeating component and consequently further diminish the flux. Approximately, the membrane flux drops exponentially with the decrease in the temperature and linearly with the decrease in mole fraction of the permeating component on the feed side. The latter is imposed by the separation process itself (unavoidable) and the former should be avoided to make separation by PV cost effective. Practical solutions to this problem will be addressed later on.

Additional difficulty lies in the fact that the above mentioned changes in composition and temperature on the feed side are much more pro-

nounced close to the membrane surface than in the bulk of the feed flow. In other words, both the concentration and temperature of the feed mixture are higher in the bulk, than in the thin fluid layer in the immediate contact with the membrane, former due to a progressive depletion of the permeating component and the latter due to temperature drop in the membrane. These two membrane performance deteriorating effects are generally known in the membrane literature as concentration– and temperature polarization effects, respectively. However, this situation shown schematically in Fig. 3 is nothing else than a common heat and mass transfer situation encountered at heat and mass transfer interfaces, and represents typical heat and mass transfer resistances, implying that the transport through the thin boundary layer on the feed side is controlled by diffusion process.
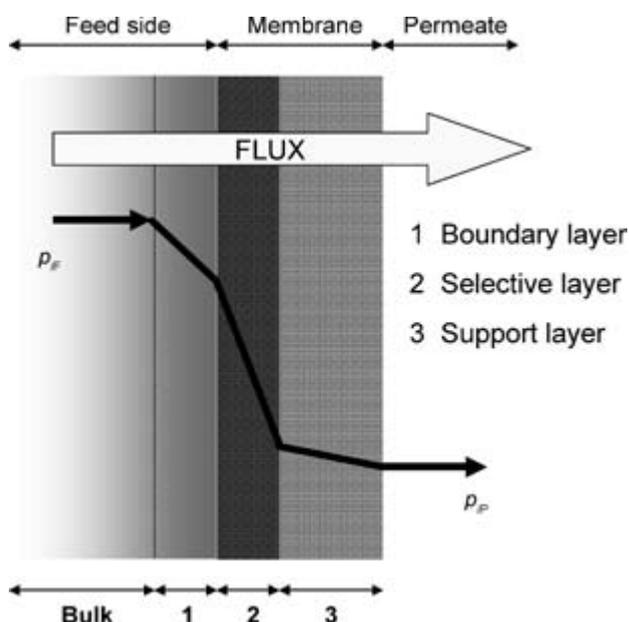
F i g . 3 – *Schematic representation of the transport mechanisms during pervaporation through a hypothetical microporous, three layer membrane*

Regarding the mass transfer process this means that on the feed side there will always be a boundary layer resistance involved, the extent of which will depend on the fluid flow configuration and conditions. As suggested in Fig. 3, there is always a membrane resistance involved, which however depends strongly on the interaction between the nature of the permeating components and the type and the configuration of the membrane. Furthermore, Fig. 3 suggests no additional boundary layer resistance on the permeate side, which is practically justified in case of PV and VP, with the vacuum pooling the vapour out of large pores (purely convective transport) into the bulk flow.

Ceramic membranes employed

In the Netherlands two separate research and development efforts delivered commercially available ceramic membranes considered suitable for both solvent dehydration and solvent recovery purposes, accounting for specific differences by adapting in a chemical way the quality of the selective layer. The ceramic membranes offered by ECN (The Energy Centre of the Netherlands)[24] and Pervatech b.v.[25] are both actually multilayer ceramic tubes with maximum length of 1 m, with external to internal diameters of 14/10 and 10/7 (in millimetres), respectively. In case of ECN membrane, selective silica layer is outside, which implies a more favourable membrane area to volume ratio than in the case of Pervatech membrane that utilises a selective layer inside.

As illustrated in Fig. 3, the feed is always in the direct contact with the selective layer. Fig. 4 shows an ECN tubular membrane with a front cut view indicating five silica layers of different composition and thickness. The thickness of the methylated silica selective layer is around 0.1 μm, and the first, gamma-alumina support layer is 2 μm thick, while the thickness of the next two alpha-alumina layers is 30 – 50 μm. The fifth, nearly 3 mm thick alpha-alumina layer provides necessary mechanical strength. Pore size increases also from selective layer toward the coarsest support layer, as well as the size of defects. Porosity is similar for all layers (0.25 to 0.50) and tortuosity of selective and gamma-alumina layer are larger, roughly factor two than that of other support layers. For selective layer
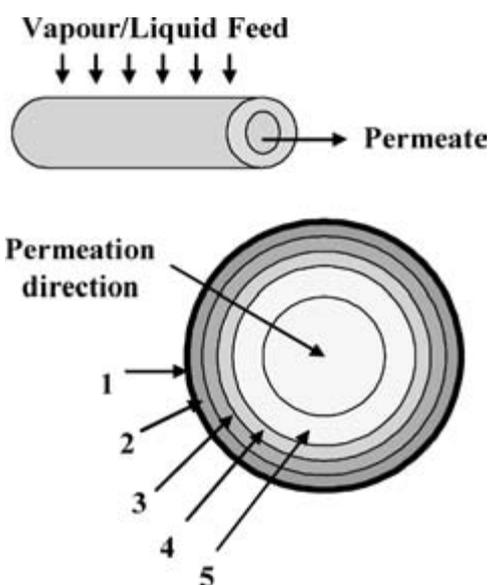
F i g . 4 – *Schematic representation of the five layer ceramic ECN membrane; the numbers refer to: (1) methylated-silica selective layer, and (2) – (5) four gamma and alpha alumina support layers of increasing thickness*

in this case, tortuosity is around 3, which means that the length of the pore is three times larger than the thickness of the selective layer. Tortuosity cannot be determined with certainty, therefore it is usually considered in detailed models as an adjustable parameter.

Ceramic membrane module configurations

For these basically tubular membranes the most suitable module configuration is that widely employed for heat exchangers, i.e. shell and tube. Fig. 5 shows photographs of an industrial and a laboratory scale shell and tube module of Pervatech. Large module delivered to TU Delft for pilot scale testing purposes contains a bundle of seven ceramic tubes arranged in triangular pitch within a stainless steel shell. The ceramic tubes are fixed on both ends by a proprietary method which should provide for both leak free operation and compensation of thermal expansion differences. The small module containing a short (< 0.2 m) ceramic tube represents the size used for typical membrane characterisation tests. The common tube length in case of Pervatech modules is 0.5 m and modules containing up to 52 tubes are available commercially. Tube length in Sulzer modules equipped with ECN ceramic membranes is 1 m. The number of tubes per shell may vary, and presently it is not exceeding 24. A clear advantage of the shell and tube configuration is that the design and operation know-how developed for heat exchangers can be directly used for design and optimization purposes. A counter-current operation is preferred, but this can be fully utilised only if an external sweep stream is employed.

Since the Pervatech membranes have the selective layer inside, the feed, liquid or vapour, is supplied at the tube side. Even with tightest arrangement of tubes the available cross sectional area for flow of vapour permeate of low density on the shell side is always big enough to allow significant pressure drop to develop. This is a practical advantage of this configuration. This may not be quite so with the shell and tube modules comprising small diameter tubular membranes with the selective layer outside, however the ECN tubes installed in Sulzer shell and tube modules developed for PV purposes have a rather large inside diameter. Therefore permeate side pressure drop is not considered as a serious treat. With the feed on the shell side care should be taken to ensure efficient operation of multi-tube modules, which can be achieved by adopting the proven method of installing baffles in the shell.

However, the commercially available Sulzer module shown in Fig. 6 differs in one respect from common situation. Instead of a bundle of membrane tubes it comprises a bundle of double-pipe membrane units. The feed side is the annular section of the double-pipe configuration, while the permeate leaves the module through the tubes. This proprietary configuration effectively eliminates the before mentioned temperature polarization effect, which is a specific wrongdoer in case of PV, by ensuring module operation under isothermal conditions, with heating fluid on the shell side. Conventional configurations include so called inter-stage heating, i.e. a heat exchanger in between subsequent modules.

From the membrane unit design point of view, the main dimension to be determined is the required membrane area. For a given molar flow rate of the permeate stream, known permeance and driving force, the required membrane area follows from Eq. (2). However, for practical design purposes also the boundary layer resistances have to be considered in addition to the membrane resistance. Therefore, following working expression for membrane area is preferred.

$$A = \frac{R \, T \, F_{i,\mathrm{M}}}{k_{\mathrm{oM}} \Delta p_i} \qquad (6)$$

where k_{oM} (m s^{-1}) is the overall membrane mass transfer coefficient, R (kJ kmol^{-1} K^{-1} = kN m kmol^{-1} K^{-1}) is the universal gas constant, and T (K) is the absolute temperature.

Since the driving force is steadily decreasing with progressing separation, the estimation of the required area is usually carried out by cutting the membrane length into a series of increments for which an assumption of constant driving force, i.e. constant composition and temperature is justified. The complexity of this, basically iterative calculation depends on the size of the increment adopted and the membrane engineering oriented research efforts focus on finding most practical solutions, i.e. a balance between required accuracy and model complexity in this respect. However, membranes are not used as single tubes but arranged in a cost effective way into modules of certain size.

Mass transfer characteristics of ceramic membrane modules

In order to determine the membrane surface area needed for the mass transfer of permeating component to occur at a specified rate (flux) and the driving force available, which is the main objective in the design of a membrane module, the value of the overall mass-transfer coefficient must be known. In a situation as encountered here, similar to that of a heat exchanger, a solid wall separates two flowing fluids, which implies existence of three main components contributing to the total mass transfer resistance. Per definition, the overall and individual mass transfer resistances are reciprocals of the mass transfer coefficients. Assuming that the resistances are additive and no resistance involved on permeate side, the working expression for the overall mass transfer coefficient is generally written as:

$$k_{oM} = \left(\frac{1}{k_F} + \frac{1}{k_M} \right)^{-1} \qquad (7)$$

where k (m s^{-1}) in conjunction with subscripts F, and M denote individual mass transfer coefficients of the vapour or liquid boundary layer at the feed side, and the membrane, respectively.

Membrane based resistances

Certainly, the resistance of the membrane itself is the key factor. The mechanisms involved are complex and depend on the nature of the membrane (type of material, its nature and structure) and its interaction with species involved. For well established non-porous polymeric membranes, the so called solution-diffusion model appeared to be capable of describing in a sound, experimentally verifiable way the relation between the driving force and flux and selectivity. Generally, non-porous or dense polymeric membranes contain no pores of the size which would allow a molecule to pass through it. The permeating component must first dissolve into the polymer and then diffuse through the polymer, driven by concentration gradient, to be desorbed at low pressure side of the membrane and as a vapour diffuse into the bulk of the permeate stream. Plainly speaking, we deal here with a combined "sorb-diffuse-desorb" mass transfer/separation mechanism, which can be even enhanced by some intrinsic diffusion affecting properties, like those due to swelling of the polymer membranes. Hydrophylic membranes favour permeation of water and therefore are used for solvent dehydration purposes. Organophilic membranes favour removal of volatile organic components from water. In both cases so called composite membranes are used, which implies a proprietary type of the combination of two materials, one as selective layer to perform separation and the other one as a carrier layer to provide for chemical, mechanical, and thermal integrity. Most detailed account on fundamental and practical aspects of membrane materials used for pervaporation and vapour permeation purposes can be found in the earlier mentioned article by *Bruschke*.[21]

Separation process relies on the difference in solubility or sorption affinity of components in the polymeric material and the rate of their diffusion through the membrane and is mainly affected by the first mechanism. Depending on the nature and structure of membrane material the conditions for diffusion process can be beneficial either for selectivity or flux (permeability), but not for both. Although solubility is a thermodynamic equilibrium controlled process, the separation process is not governed by vapour-liquid equilibrium, but by the difference in transport rates of the permeating components. This distinguishing property imposed by membrane material makes the whole difference and allows azeotropic mixtures to be easily separated, which is impossible in case of mass transfer through an open vapour-liquid interface as encountered in common distillation situations, with surface of bubbles, droplets, or films providing interfacial, i.e. contacting area.

The present paper deals with performance characteristics of microporous ceramic membranes, comprising a selective and several support layers with thickness and pore size increasing toward the permeate side. The separation mechanism of this family of membranes is considered to be more complex than that associated with polymeric membranes, including molecular sieving effects and specific molecule-surface interactions, which may play

a decisive role, i.e. determine whether at all and to which extent a component will be able to pass the membrane. However, this is a field of interest of membrane specialists and here we would like to concentrate on the engineering aspects only, i.e. at developing and utilisation of engineering models to be able to predict and analyse performance of commercial inorganic PV and VP membranes.

Two inorganic (ceramic, silica) membranes considered here are microporous membranes and can be used for both PV and VP. For micro-porous silica membranes considered here, with a pore size of around 0.4 nm in a selective layer with a thickness of around 0.1 μm, mass transfer process is governed by combination of (surface) adsorption and diffusion mechanisms, with the selective diffusion occurring mainly in the selective layer, accompanied by Knudsen diffusion mechanism prevailing in the support layer adjacent tot the selective layer. In the latter case, gas molecules do not see each other, they collide only with pore walls, being instantly adsorbed and desorbed, i.e. thrown out in a random direction. Since in PV and VP applications volatile (condensable) components are involved, Knudsen diffusion is normally accompanied by surface diffusion of less volatile components and in case of temperature drop excessive condensation can occur leading to capillary condensation which closes pore for more permeable (more volatile) component. All this is very complex. Therefore, it is difficult to describe in an exact and still practical way the link between the nature of the membrane material and the membrane permeation properties. Our ongoing research effort is expected to make a significant contribution in this direction. It should be noted that it is still difficult to make the ceramic membranes defect free, therefore some "leakage" (loss of selectivity & increase in flux) by normal convective (viscous) flow can be expected, which generally prevails in support layers with pores larger than 0.1 μm.

In order to estimate the overall mass transfer resistance created by a micro porous ceramic membrane following practical expression can be used:

$$k_M = \left(\frac{1}{R\,T\,\Pi_i} + \frac{\delta_m}{D_{Kn}} \right)^{-1} \tag{8}$$

where k_M (m s^{-1}) is the membrane mass transfer coefficient, Π_i (kmol m^{-2} s^{-1} Pa^{-1}) is the permeance, D_{Kn} (m^2 s^{-1}) is the Knudsen diffusion coefficient, and δ_m (m) is the support layer, i.e. membrane wall thickness.

Second term on the right hand side of Eq. (8) represents the support layer resistance, with the

Knudsen diffusion coefficient for the flow through porous media defined as

$$D_{Kn} = \frac{d_p}{3} \sqrt{\frac{8RT}{\pi M_W}} \left(\frac{\varepsilon}{\tau} \right) \tag{9}$$

where d_p (m) is the representative pore diameter, M_w (kg kmol^{-1}) is molar mass of the permeating component, ε (-) is the porosity, and τ (-) is the tortuosity. Porosity represents the fraction (%) of the total membrane area occupied by pores in which the Knudsen flow may occur. Therefore its value is always well below 1. On the other hand, the lowest value for the tortuosity is 1, which implies that the length of the pore is equal to the thickness of the selective layer(s). Usually, tortuosities are in between 1 and 3. This means that in the worst case the value of the Knudsen coefficient for the flow through porous media is three times smaller than that for the single pore.

It should be noted that in case of large fluxes (rather high vapour volumes transported through support layers at high speed) the related pressure drop may be detrimental to flux to a certain extent.[26]

The membrane permeance is usually determined experimentally at pressures and temperatures expected under actual conditions. Within a certain range of temperatures, membrane permeance and consequently flux appeared to exhibit an exponential dependence on the feed temperature, described appropriately by Ahrenius type-equation:

$$\Pi_i = \Pi_i^o e^{\left[\frac{E_i^o}{R} \left(\frac{1}{T^o} - \frac{1}{T_F} \right) \right]} \tag{10}$$

where T_F (K) is the feed temperature, Π_i^o (kmol m^{-2} s^{-1} Pa^{-1}) is the permeance of the permeating component at the reference temperature, T^o (K), and the E_i^o (kJ kmol^{-1}) represents the corresponding energy of activation, which, besides the activation energy for diffusion includes also the heat of adsorption.

Permeance and activation energy at reference temperature are calculated from fluxes and compositions determined from devoted membrane characterisation experiments carried out within the temperature range of interest at a number of constant temperatures with different feed compositions. In present cases, the membrane characterisation experiments were carried out with short single tube membranes (length < 0.2 m) under laboratory conditions. This means that the obtained performance may generally be considered to be on the optimistic side. Pilot scale experiments carried out with modules as that shown in Fig. 5, containing several tubes of normal length, with a tube bundle imposed fluid dynamics and consequently mass transfer af-

fecting effects, are expected to be more realistic with respect to overall performance achievable under actual conditions.

Feed side boundary layer resistance

As indicated schematically in the Fig. 3, there is always a resistance associated with the transport of permeating component from the bulk of the feed stream to the membrane surface. The permeating component has to pass through a stagnant boundary layer to reach the surface of the selective layer. It is not just the thickness of the laminar boundary layer, but also its composition which affects the extent of resistance involved. Due to the progressive depletion of the permeating component there is an accumulation of rejected component near the membrane surface. This implies a rather low concentration of permeating component at the membrane surface with respect to that in the bulk of the feed. Unfortunately, this tendency increases with both increasing flux and increasing selectivity.

This concentrated boundary layer exerts a pronounced resistance toward mass transfer which is in the membrane technology community generally known as concentration polarisation. In fact, it is practically nothing else than what chemical engineers know as boundary layer mass transfer resistance, which depends strongly on the flow regime on the feed side. Certainly, stagnant flow should be avoided and a pronounced turbulence will be beneficial, because of its tendency to reduce the thickness of the laminar boundary layer and providing opportunity for concentrated, heavier or less permeating component to back-diffuse into the bulk, making more area available for the access of the permeating component.

Unfortunately, this mechanism, as well as earlier mentioned degradation of driving force is inherent to both VP and PV. Since the diffusion through liquids is much slower ($\approx$ 1000 times) than through vapours it can be concluded that, in general, PV suffers much more from concentration polarisation than VP. On the other hand, with the tendency to increase feed side pressure to increase the driving force in VP, the vapour is expanded over a rather large pressure ratio, which could cause certain temperature drop due to so called Joule-Thompson effect, just enough to cause some of the vapour to condense, turning a part of VP membrane effectively into a PV unit with all limitations of it.[21] This means that a temperature polarization effect could under certain conditions occur in a VP application, introducing a much stronger concentration polarisation effect than anticipated.

Boundary layer thickness of liquid films is smaller than that of vapour or gas flows and both

can be significantly reduced by providing enough turbulence in the flow on the feed side. As it will be demonstrated later on, suppressing the flux decline due to concentration polarisation effect by adopting a certain degree of turbulence on the feed side is an important membrane module design consideration.[28]

The mass transfer coefficient for the transport through the boundary layer on the feed side can be estimated, depending on the flow regime, using following well established Sherwood number based expressions for closed conduits.[29,30]

A quadratic interpolation expression covers the whole range of laminar and turbulent flows:

$$k_{\mathrm{F}} = \sqrt{k_{\mathrm{F,lam}}^2 + k_{\mathrm{F,turb}}^2} \qquad (11)$$

For laminar flow following expression can be used:

$$k_{\mathrm{F,lam}} = \left(\frac{D_{\mathrm{F}}}{d_{\mathrm{h,F}}}\right)\left[3.66 + 1.62\, Re_{\mathrm{F}}^{1/3} Sc_{\mathrm{F}}^{1/3}\left(\frac{d_{\mathrm{h,F}}}{l}\right)^{1/3}\right] \quad (12)$$

where D_{F} (m^2 s^{-1}) is the feed side diffusion coefficient, $d_{\mathrm{h,F}}$ (m) is hydraulic diameter of the flow channel (tube or annulus), l (m) is the length of the flow channel. The characteristic Reynolds and Schmidt numbers are defined as

$$Re_{\mathrm{F}} = \frac{u_{\mathrm{F}}\, \rho_{\mathrm{F}}\, d_{\mathrm{h,F}}}{\mu_{\mathrm{F}}} \qquad (13)$$

and

$$Sc_{\mathrm{F}} = \frac{\mu_{\mathrm{F}}}{\rho_{\mathrm{F}} D_{\mathrm{F}}} \qquad (14)$$

where u_{F} (m s^{-1}) is mean superficial velocity and μ_{F} (Pa s) is the viscosity of the feed stream. For small diameter tubes, i.e. capillaries, like hollow fibres, Sherwood number assumes a constant value, $Sh_{\mathrm{F,lam}} = 3.66$, provided velocity and concentration profiles are fully developed.

In case of turbulent flow, entrance effects are usually neglected and following expression used:

$$k_{\mathrm{F,turb}} = \left(\frac{D_{\mathrm{F}}}{d_{\mathrm{h,F}}}\right)0.023\, Re_{\mathrm{F}}^{0.8} Sc_{\mathrm{F}}^{1/3} \qquad (15)$$

Pressure drop

Equations developed generally for flow of fluids through pipes and along or around tube bundles are used here. For flow through membrane tubes:

$$\Delta p = \xi \frac{l}{d_\mathrm{h}} \frac{\rho u^2}{2} \qquad (16)$$

where ξ (–) is the friction factor, which depends on the flow regime, l (m) is the length of membrane tube(s), and d_h (m) is hydraulic diameter. The latter is, for the feed inside simply the inner diameter of the tube. For laminar flow: $\xi = 64/Re$, and for turbulent flow in smooth tubes: $\xi = 0.3164/Re^{0.25}$. All expressions are valid for both liquid and vapour (gas) flow, on feed and/or permeate side. Expressions suitable for estimation of the pressure drop of a fluid moving through a bundle of tubes are those recommended for conventional shell and tube heat exchangers.[31]

Configuring membrane unit

The required total membrane area is often larger than that which can be accommodated in one module. Due to present constructional limitations the largest modules containing ceramic tubes for PV and VP applications provide less than 2 m² active area per module. This means that the total membrane area as required according to Eq. (6) divided by single module area will deliver information on the number of modules required for a certain separation task. This means that for a given industrial scale application, the membrane unit will consists of a number of modules connected both in parallel and in series. The number of modules connected in parallel depends on the chosen operating fluid velocity, i.e. Reynolds number and the density of the fluid. This practically means that in case of PV, i.e. a liquid feed less modules will be connected in parallel than in case of VP, with vapour, i.e. much larger fluid volume on feed side. Consequently, in case of PV much more modules will be connected in series than in case of VP.

In case of larger fractions of permeating component it may be that the number of modules connected in series needs to be reduced toward the end, in order to preserve the constant fluid velocity over the whole length of the membrane unit. This membrane unit configuring process is a typical engineering consideration. Also, if the modules are considered as single stage separators, than in analogy with cascading the single distillation stages various configurations can be arranged utilising co-, counter-, and cross flow couplings. This approach to lay-out of multistage membrane configurations is elaborated in great detail in the book by Hoffman.[32]

Simulation studies

The main task for a hybrid process designer is to shape a membrane unit to be combined with a distillation column in an integrated way. To perform this task effectively, a reliable predictive model is required, which allows simulation of the performance of a shell and tube module containing tubular membranes with selective layer on either outer or inner side of the tube. This means dealing with and quantifying appropriately the mass transfer resistances involved.

Simulation tools

With the equations mentioned above, representing the working heart of a predictive model, the performance of membrane modules can be simulated using any of the available mathematical frameworks, for instance Matcad or even more practical Excel. The latter one is preferred because it can easily be combined with latest versions of established process simulation packages like ASPEN Plus, CHEMCAD and the like. In order to be able to simulate the performance of the whole integrated process simultaneously, to couple a membrane module model with a rigorous programme for distillation column performance calculation into a flowsheet with permeate stream recycled to the column, a user subroutine has been written in Fortran and implemented in ASPEN Plus, version 11.1.[32]

For the membrane module model, product (retentate) quantity and composition are input variables and the calculation proceeds in two subsequent steps. First the feed and permeate flow rates are estimated, i.e. the material balance of the module fixed (iterative procedure). With known membrane feed the distillate flow rate and composition are fixed as well as that of the permeate, which is considered here as second feed stream. With bottoms specification the input for distillation column is fixed and the fine tuning is obtained by running the simulation of the whole integrated process with known recycle stream. This avoids convergence problems. In other words, starting with specified membrane product flow rate and composition, the mass balance of the whole process is back-calculated, which implies that for different membranes and membrane feed conditions different process mass and energy balances are obtained, as well as different equipment dimensions and membrane areas.

Parametric study

For process engineers considering practical implementation of hybrid processes, it is interesting to be able to simulate the performance of the membrane modules, i.e. to study the relationship between governing variables and the performance of the module. The gained knowledge can then be used as a guide to design and optimize the mem-

brane units. This implies arriving at most suitable configuration with a minimum number of modules connected in parallel and in series.

The usefulness of the membrane module simulation tool will be demonstrated first, using ethanol dehydration case as example. The vapour permeation in conjunction with Pervatech tubular membrane, with selective layer inside, is considered, relying on experimental values for selectivity and permeability determined in a laboratory experiment,[7,33] which are shown in Table 1.

T a b l e 1 – *Selectivity and permeance data used in this study*

	Selectivity	Permeance, Π/kmol m^{-2} s^{-1} Pa^{-1}
ethanol dehydration – VP	43	$4.70 \cdot 10^{-9}$
methanol recovery – PV and VP	39	$5.57 \cdot 10^{-11}$

Fig. 7 illustrates the relative magnitude of individual resistances for three different flow conditions for a fixed tube size. The resistance due to support layer is practically negligible and the concentration polarization, i.e. feed side boundary layer resistance dominates at low Reynolds numbers, indicating that turbulence on the feed side is needed to suppress this performance deteriorating effect. From Fig. 8, which shows the concentration polarisation imposed resistance as a function of Reynolds number, the large diameter tubes are much more sensitive than the small ones. For 10 mm tubes, Reynolds numbers well above 10 000 are required to minimize this effect. However, as illustrated also in Fig. 8, this is accompanied by increasing pressure drop, which in case of tubes with diameters around 1 mm (ceramic fibres) may become prohibitive.
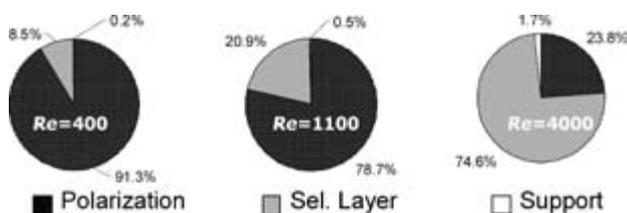
F i g . 7 – *Effect of the Reynolds number on the relative magnitude of mass transfer resistances*

So, a typical chemical engineering trade-off situation between mass transfer and pressure drop is encountered here. Unfortunately, the tube diameter is not a variable, because presently the tubular ceramic membranes are delivered with fixed in-
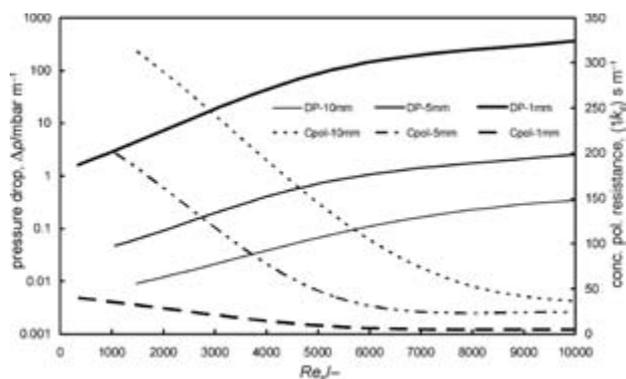
F i g . 8 – *Concentration polarisation and pressure drop as a function of the Reynolds number and the membrane tube diameter*

ner/outer diameter and it is difficult to believe, that variations in tube diameters will be available soon. Talking of tailor made approach means here more influencing the properties of the selective layer than the macro geometry of membranes. Therefore, further design considerations will be based on ECN and Pervatech ceramic tubes available commercially and a shell and tube configuration for the module in both cases.

Design base cases

Two industrially interesting applications were chosen as base cases, both involving azeotropic mixtures. First case is already mentioned, the dehydration of ethanol, and the other one is recovery of methanol from a mixture containing methanol, methyl-tert-buthyl-ether (MTBE), dimethylether and isobutylene.

Ethanol dehydration

Dehydration of ethanol is first and largest commercial application of pervaporation. Indeed, water, as rather small molecule appeared to have good permeating properties so that in conjunction with common chemicals large fluxes were obtained which, as mentioned before, could significantly be enlarged if operated at higher feed temperatures, well above those employed with hydrophilic polymer membranes. In conjunction with ceramic membranes ethanol dehydration could be performed at higher pressures, which means that membrane unit would receive feed at temperatures well above 100 °C. Since in case of alcohol dehydration the vapour which leaves the top of the distillation column is at a near azeotropic point, vapour permeation should be a natural choice for these applications. However, due to inevitable pressure drop in the supply line to the membrane unit, temperature of vapour could drop and cause a certain amount of vapour to con-

dense upon entering the module. Creation of a thin liquid film in between vapour and the membrane wall transforms VP partly or fully into PV, which could have catastrophic consequences for membrane performance if not accounted for appropriately. A practical measure is to consider a certain degree of overheating the vapour before entering the membrane unit. However, this should be kept low to avoid introduction of other performance deteriorating effects (transformation of vapour into gas, density decrease, etc.). A detailed discussion of relative benefits and drawbacks of vapour overheating can be found elsewhere.[21]

If we consider the flow-sheet shown in the Fig. 1 as basis for production of 23 000 ton per year of dry ethanol, with vapour containing 82 % w/w of ethanol leaving the top of the column delivered slightly overheated at 5 bar to the membrane unit, following membrane unit configuration would be required. As the basic unit (assumed configuration for this purpose) a module is chosen with shell diameter of 0.2 m containing 55 Pervatech tubes of 1 m length, and the inner and outer diameters of 7 and 10 mm, respectively, with the selective layer inside. The tubes are arranged in a square pitch with a distance between tubes equal to two outer tube diameters. With this arrangement and tube dimensions, the installed area per module is 1.2 m². Assuming a constant permeate side pressure of 0.1 bar, the membrane unit would require 114 modules to produce required purity (99.6 % w/w of ethanol), arranged into 9 parallel trains each containing 13 modules in series. The shell side pressure drop is negligible and the tube (feed) side pressure drop is below 0.1 bar, which is acceptable.

At the moment, it is difficult to estimate related capital expenses accurately because there is still no industrial manufacture of ceramic tubes, which means that rather high capital costs have to be taken into account, some 3000 Euro per meter square area, with roughly 2000 Euro for tubular membranes, and 1000 Euro for stainless steel module. Since there is still no certainty about the life span of ceramic membranes a conservative estimate is that every two years the membranes should be exchanged. Manufacturers of ceramic tubes claim even double of that, but proper answer can be expected from experiences with first industrial applications. In any case, this implies much higher investment than usually anticipated.

In case of isopropyl alcohol (IPA) and heavier alcohols, the azeotrope shifts toward larger concentrations of water, which means that membrane unit is more probable to be used to break the azeotrope only, and final purification left to the second distillation column. This means that area requirement will be generally on the low side. Encouraging in

this respect is the fact that due to a larger concentration of permeating component in the feed, significantly higher water fluxes can be expected.

Similarly, rather small quantities of alcohol or other organics can be effectively separated from water; however these applications require use of organophilic membranes.

Methanol recovery from organic mixtures

A typical example of an important large scale industrial process amenable for considerable process intensification through combination of distillation with pervaporation or vapour permeation processes, is the manufacture of the MTBE. Hoemmerich and Reutenbach[34] give a detailed account on this opportunity for membranes related to so called Hulls MTBE process. Fig. 9 shows the flow-sheet of a similar, Lyondell process, indicating that debutanizer column side-draw stream is recycled to the reactor section, which in addition to unreacted methanol contains some 65 % w/w of MTBE, which forms an azeotrope with methanol and therefore cannot be separated within the distillation column. This means that a rather large fraction of the column feed is recycled to the reactor section (indicated by dotted line) and being mainly inert material it just runs in a closed circuit occupying valuable space. If the debutaniser side stream would be directed to a membrane unit, as suggested in the flowsheet shown in Fig. 9, then unreacted methanol could be separated from the main stream containing mainly MTBE and some isobutylene and recycled to the reactor. The retentate stream could be recycled to the appropriate tray or, even better, fed to another distillation column to separate MTBE from C4 components and add it to main MTBE product stream coming from the bottom of the debutaniser column. Both schemes reduce the size of recycle stream considerably and consequently offer potential for significant capacity increase.

Figure 10 shows composition and temperature profiles of debuthaniser column indicating that at the third and fourth stage methanol is at maximum concentration in the liquid and vapour streams, respectively. This means that both vapour permeation and pervaporation can be considered. However, taking liquid as a side draw is easier and this could be in favour of pervaporation, but which phase and where to take is not an easy decision. For instance, the liquid phase concentration of methanol is largest at third stage, but the corresponding temperature (100 °C) is much lower than that of the stage four (115 °C). In turn the concentration of the methanol on stage four is lower, so in both cases a beneficial factor in combination with a detrimental factor. Similar situation is in general with VP, but in this
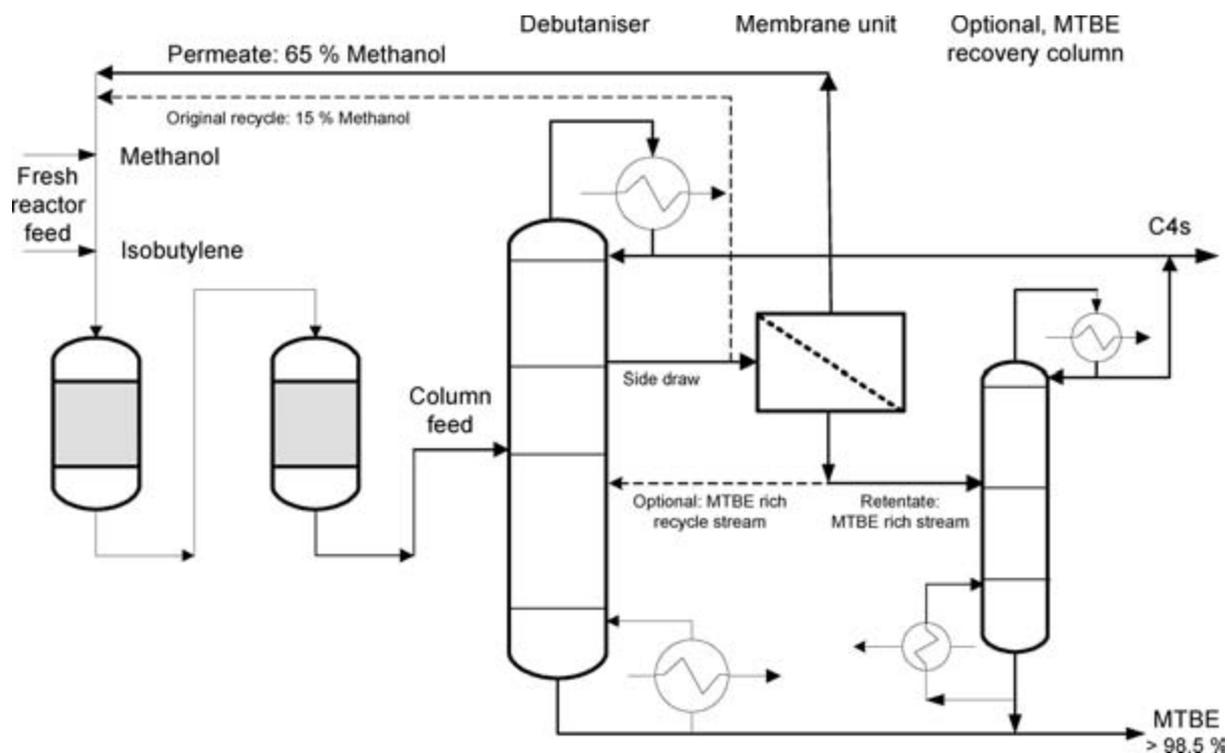
F i g . 9 – *Flowsheet of a plant for manufacture of MTBE with an integrated membrane unit for separation/recovery of MTBE and methanol*
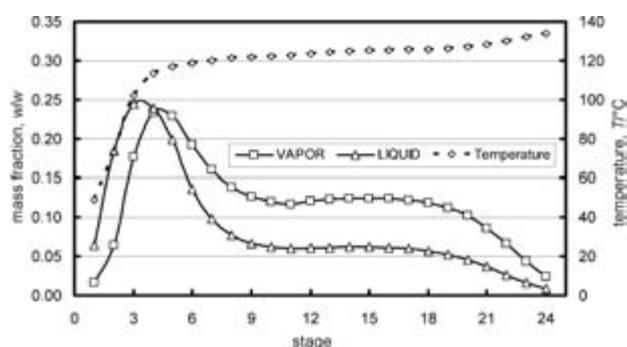
F i g . 1 0 – *Composition and temperature profiles of the de-butaniser column in an MTBE plant*

particular case at stage four the maximum feed concentration of methanol comes in combination with a high temperature.

Simulations of the flow-sheet shown in Fig. 9 indicated that by recovering MTBE from the recycle stream could result in a production capacity increase of up to 20 %, which is, regarding the scale of production, such a large increase of production that it would justify even capital intensive debottlenecking scenarios. Since no sharp separation is required the membrane area requirement as well as related capital cost could be on the low side.

An estimate of the size of membrane unit was done, assuming that performance obtained under laboratory conditions with ECN membranes (selective layer outside) will hold in practice. The single, short membrane tube based experimental values,[35] for permeance and selectivity observed under PV and VP conditions, were similar and for the purpose of this study they are taken equal (see Table 1). For the industrial base case the membrane feed is around 20 t h^{-1} then, containing 24 % w/w of methanol, entering the shell side of membrane modules at a temperature of 110 °C. A module containing 24 tubes, with a length of 1 m and inner and outer diameters of 8 and 14 mm, respectively, was chosen as building unit for the membrane unit. With the selective layer outside this means slightly more than 1 m^2 area per module. The results of membrane unit sizing calculations performed assuming no concentration polarization effect (Re = 10000), and a constant driving force, are summarised in Table 2. The discrepancy in the estimated membrane areas for PV and VP can be attributed to the difference in the rate of the decline in the driving force which seems to be more pronounced in case of VP.

T a b l e 2 – *Area requirement and module configuration for the membrane unit in the MTBE base case plant*

| | Modules (#) | | | |
	in parallel	in series	total	area, A / m^2
PV	5	218	1090	1150
VP	74	18	1332	1406

Although, the total area requirement is not so different, striking is the difference in the configuration. With the liquid on the feed side much less cross sectional area is required to arrive at desired flow conditions. Therefore, a rather long train of modules connected in series is required in case of PV to reach desired product specification. Opposite is with the VP. In order to accommodate appropriately the large volumetric flow of feed vapour, the VP unit requires much more modules connected in parallel, however, much less membrane length is needed to get the desired product specification. Indeed, the configuration of the module unit, i.e. the distribution of modules is dictated by the density of the fluid on the feed side.

On the other hand, the pressure drop on the feed side of a PV unit is larger and a quite complex manifold is required to keep the permeate side pressure drop low. Another worrying factor, when thinking of implementation in an actual plant of a multi-module unit, is that in case of PV after each module a heat exchanger should be installed to compensate for inevitable feed side temperature drop caused by adiabatic evaporation of the permeate. Certainly, intermediate heating is not needed if isothermal modules as that shown in Fig. 6, are used. For VP the pressure drop involved on both sides is rather small, however, placing such a large number of modules in parallel requires certain pressure drop to get feed vapour uniformly distributed, which was not accounted for in this study.

In order to reduce the overall pressure drop, lower Reynolds number operation could be considered, which means adding more parallel trains. This, in turn, creates conditions for appearance of concentration polarization, which, in case of PV would require more than the doubling the membrane area to compensate for it. So, although a larger area is required for VP under given conditions, being practically insensitive to concentration polarisation and associated with a negligible pressure drop, VP seems to be a better candidate for this application.

Again, further effort is needed to evaluate and balance properly advantages and disadvantages of two membrane processes. First of all the performance data should be obtained under pilot scale conditions with full size modules, and operating continuously under actual conditions. Also the progressive loss of driving force should be rigorously accounted for when estimating the membrane area requirements.

Choosing VP and assuming the same estimate for unit membrane area cost, the purchased cost of a VP unit for the MTBE plant capacity considered here would be above 4.000.000 Euro. With at least two membrane replacements during the plant economic life this could more than double. Furthermore, this will more than double as installed cost, however, the amount of money required as investment is well below the profit expected from increased capacity (assume a 10 t h^{-1} gain), which, according to a recent peak in the MTBE price (around 900 Euro t^{-1}, November 2005) would be above 70.000.000 Euro per year, which means a pay-back time of few months. Even with a significantly lower MTBE price, there is more than enough economic incentive for considering implementation of membranes in MTBE and similar bulk chemicals manufacturing plants. However, dealing with such capacities means also a correspondingly high sensitivity to failures to perform properly, i.e. without causing an unplanned plant stop, which usually leads to a great, irreparable financial loss. Therefore membrane reliability plays main role in considerations whether a new technology will be implemented within a complex industrial plant. When this moment arrives (a challenge for membrane developers), stand alone and end of pipe applications will be more suitable candidates for this daring step, but existing uncertainties, summarised in what follows, have to be understand and dealt with appropriately.

Performance uncertainties

Besides the basic performance data (permeability and selectivity), the information on the chemical and mechanical stability of the membrane as well as fouling tendency with time is essential for practitioners. Although the ceramic tubes look to be robust enough they are sensitive to damages of the selective layer as well as the leakage at the connections between ceramics and metal due to mechanical and thermal stresses, which, if excessive, can lead to the breakage of tubes. At the moment it looks that the performance stability, i.e. flux deterioration with time, as well as chemical, thermal and mechanical vulnerability are the main barrier for a successful implementation of ceramic PV and VP membranes in the practice. In addition, present ceramic membrane costs based on manual manufacture can be considered also as a prohibitive factor in this respect. So there is still a considerable research effort needed, mainly on material side, but also on module manufacturing side, to get ceramic membranes to be seriously considered for industrial application et all. However, without some daring in this respect and lessons learned from first larger scale applications, it is difficult to expect that ceramic membranes could reach the level of application the well established polymer membranes achieved so far in industrial practice.

Concluding remarks

Regarding the present trends for more sustainability in process industries, there is more than enough incentive to consider implementing ceramic pervaporation and vapour permeation membranes into existing industrial processes, but there seems to be still a great deal of uncertainty around performance characteristics and stability of ceramic membranes. Zeolite membranes seem to be promising in many respects, but here also a further devoted effort is needed to ensure enough chemical stability and to arrive at manufacturing process which will allow making reproducible membranes in the sizes suitable for industrial applications.

Engineering aspects that should to be taken into account when designing hybrid processes, including a suitable combination of distillation with pervaporation or vapour permeation ceramic membranes, have been outlined and discussed.

The main issues have been discussed and qualitatively resolved, indicating the need for experimental support which should be revealing not only with respect to achievable permeability and selectivity but also to more practical performance indicators such as flux stability, fouling tendency, cleaning, and mechanical integrity.

Regarding the overall performance of shell and tube modules containing ceramic tubular membranes, in case of PV isothermal operation it should be ensured to avoid performance degradation due to thermal polarisations. For PV, and to a lesser extent also the VP, the real practical wrongdoer is the concentration polarisation, i.e. the resistance concentrated in the feed side boundary layer. Therefore, high enough Reynolds numbers are required on feed side to limit the total resistance to that of the membrane itself, but pressure drop should not be compromised.

Certainly VP and PV differ to some extent, and VP should be preferred if the feed is available as vapour, however relative advantages and deficiencies should be analysed thoroughly before the final choice between PV and VP is made, because this is also something strongly application depending.

When designing PV or VP membrane units to be combined with distillation, it is essential to account appropriately for the strong decline in the flux due to progressive depletion of the permeating component on the feed side.

Linear scale up, inherent to membrane based contactors, can be practical, but never economical and therefore it should not be considered as an advantage.

Present high costs related to manufacture of ceramic membranes can be considered as the main obstacle for their wider acceptance and consequently further development and implementation in practice.

Symbols

A – membrane area, m^2

D_F – feed side diffusion coefficient, m^2 s^{-1}

D_{Kn} – Knudsen diffusion coefficient, m^2 s^{-1}

$d_{h,F}$ – hydraulic diameter for the feed side, m

d_p – pore diamater, m

E_i – energy of activation, kJ kmole^{-1}

E_i^o – energy of activation at reference temperature, kJ kmole^{-1}

f_i – fugacity coefficient, –

k_{oM} – overall gas phase related mass transfer coefficient, m s^{-1}

k_F – feed side mass transfer coefficient, m s^{-1}

k_M – membrane mass transfer coefficient, m s^{-1}

l – length of (membrane) flow channel, m

$F_{i,M}$ – molar flow rate of permeating component, kmol s^{-1}

M_w – molar mass, kg kmol^{-1}

N_i – molar flux of permeating component, kmol m^{-2} s^{-1}

P_i – permeability, kmol m^{-1} s^{-1} Pa^{-1}

p – operating pressure, Pa

p_i – partial pressure, Pa

p_i^o – vapour pressure, Pa

R – universal gas konstant, kJ kmol^{-1} K^{-1}

Re_F – Reynolds number of the feed fluid, –

S_{AB} – membrane selectivity, –

Sc_F – Schmidt number of the feed fluid, –

T – temperature, K

u – fluid superficial velocity, m s^{-1}

x – liquid phase mole fraction, –

y – vapour phase mole fraction, –

w/w – percent on weight basis

Greek letters

α_{AB} – relative volatility, –

Δp_i – partial pressure difference, Pa

δ_m – membrane or layer thickness, m

γ – activity coefficient, –

μ – fluid viscosity, Pa s

Π_i – permeance, kmol m^{-2} s^{-1} Pa^{-1}

ρ – fluid density, kg m^{-3}

ξ – friction factor, –

ε – porosity, –

τ – tortuosity, –

Superscripts

o   – reference conditions

Subscripts

A   – more permeating component
B   – less permeating component
F   – feed side
G   – gas or vapour
i   – permeating component
L   – liquid
lam   – laminar flow
P   – permeate side
turb   – turbulent flow

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