Separation of Methanol-Tetrahydrofuran Mixtures by Heteroazeotropic Distillation and Pervaporation

Giuseppe Genduso, Antonio Amelio, Patricia Luis, and Bart Van der Bruggen
Dept. of Chemical Engineering, Process Engineering for Sustainable Systems (ProcESS), KU Leuven, W. de Croylaan 46, Leuven B-3001, Belgium

Steven Vreysen
Thomas More University College, Kleinhoefstraat 4, Geel B-2440, Belgium

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The experimental investigation of the separation of tetrahydrofuran-methanol by heteroazeotropic-batch-distillation and methanol-hexane by pervaporation is presented. In particular for this last task, four different specialty commercial membranes were tested (varying feed concentration and temperature). The "pore filling" PolyAn membranes show methanol permeance values higher than 5100 GPU (Typ M2®); separation factor of 19; and a selectivity of about 119 (Typ M1®). From the results, a coupling phenomenon was observed. An assessment of the temperature effect in the pervaporation process corroborates the hypothesis of the presence of a coupling phenomenon. Finally, a discussion is made on two industrial scale units for the separation of the same mixture: a system of a distillation column integrated with a decanter and stand-alone pervaporation unit. The energetic comparison shows that when using pervaporation a large reduction of the energetic consumption compared to a conventional distillation system (up to 29%) can be obtained.

Keywords: separation techniques, methanol pervaporation, heteroazeotropic batch distillation, membrane separations

Introduction

In the industrial framework, the separation of azeotropes in continuous systems occurs by azeotropic or extractive distillation,[1] in which a third component, the entrainer, is added to break the azeotrope. In general, a second conventional energy intensive distillation step is needed to purify one of the obtained solvent phases and recover the entrainer.[2,3]

Many fine chemicals and specialty chemicals are produced in batch processes, which generate solvent mixtures as "waste." These are often azeotropic mixtures. Therefore, these solvents cannot always be easily recovered by conventional distillation, hence, usually these mixtures are incinerated instead. The recovery of these solvents would be a direct cost saving for many chemical manufacturing companies and a large benefit for the environment. In particular, when treating a methanol-THF (waste) stream with a unit composed of a batch heteroazeotropic distillation column coupled with a decanter and using hexane as methanol entrainer, a methanol-hexane azeotropic mixture (again as waste stream) is obtained from the decanter (detailed information is given in Results section). Thus, when attempting to separate methanol-hexane mixtures, not only the presence of the azeotrope (about 49 mol % methanol at about 50°C and 1 atm), which is a limit for vapor–liquid-based separation technologies but also the wide immiscibility gap[4,5] has to be taken into account. This latter characteristic is an advantage as it may be used to design a unit composed of a distillation column combined with a decanter allowing the recovery of both the compounds. Nevertheless, when the main purpose is to minimize energy consumption, pervaporation (as a low energy consumption technology[6,7]) may be considered. Moreover, as the selectivity of a pervaporative separation depends on the different transport rates of compounds, which depend on their diffusivity and solubility in a dense membrane layer, the separation is not affected by the presence of an azeotrope.[8] Thus, the pervaporative technology is the perfect candidate for the separation of azeotropic mixtures (many studies have been reported on this theme, some examples can be found elsewhere[9–12]).

Traditionally, the pervaporative separation of compounds is classified in: water removal from aqueous-organic mixtures (hydrophilic pervaporation)[13]; removal of organic compounds from organic-aqueous mixtures (organophilic pervaporation)[14]; and the separation of organic–organic mixtures (organophilic pervaporation). However, the dehydration of organic liquids is the main application of pervaporation (PV) in industry, and the pervaporative organic–organic separation involves an extra challenge related to the difficulty of finding the appropriate membranes for specific mixtures.[15] Smitha et al.[15] and Rautenbach and Albrecht[16] give a good overview of research activities concerning the separation of organic–organic mixtures by pervaporation. In particular in the recent literature, the potential of pervaporation for the separation of methanol-based mixtures (product of transesterification reactions), when using commercial membranes, has

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Correspondence concerning this article should be addressed to G. Genduso at giuseppe.genduso@cit.kuleuven.be.

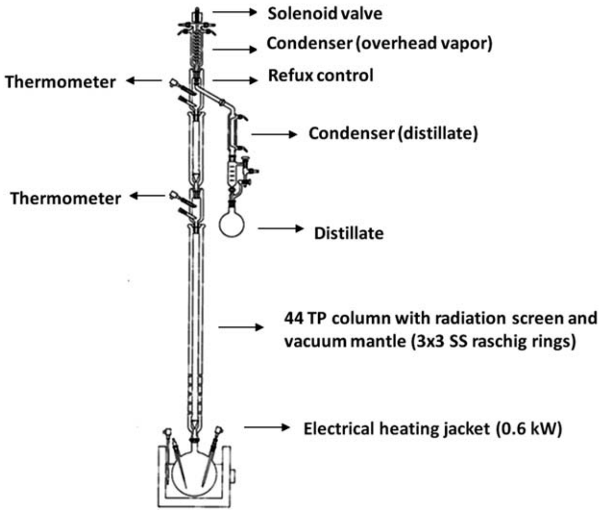


Figure 1. A labeled sketch of the batch distillation column used in laboratory.

been studied.[8,17,18] Nevertheless, the scientific literature concerning the application of pervaporation for the selective separation of methanol-hexane mixtures is very scarce. To the best of our knowledge only Cabasso[18] describes the separation of methanol-hexane mixtures by pervaporation with Nafion ion-exchange hollow fibers, for a lower feed concentration range (about 40–80 mol % methanol) than the one considered for the purposes of this article.

Hereinafter in this work, the separation of the methanol-THF mixture by heteroazeotropic batch distillation is described. Later pervaporative separation of concentrated methanol-hexane mixture is also investigated using four different commercial membranes. Using the membrane with the best performance, a stand-alone unit was simulated and then compared with a conventional separation system comprising a distillation column and a decanter, in terms of product concentration and energy duty. Indeed, the feed stream used to feed both designed units was exactly the same heavy fraction stream obtained from the decanter of the heteroazeotropic batch distillation system (detailed information is given in Materials and Methods section).

Materials and Methods

Heteroazeotropic distillation

Calculation of the azeotropic mixtures and the liquid–liquid envelops were done using Aspen Plus software and UNIF-DMD, UNIFAC, and UNIQUAC as thermodynamic models.

Figure 1 shows the batch distillation column used for the separation of the mixture methanol-THF. This distillation column is designed to have a maximal amount of theoretical plates within the available lab space. It has a length of 1.50 m and an inner diameter of 0.03 m. To minimize heat losses, the column has a radiation screen and a vacuum mantle. The column is filled with 3 × 3 mm raschig rings meaning about 44 theoretical plates. The height equivalent to a theoretical plate of the packed column and the associated plate number was experimentally defined by running the separation of a heptane-methylcyclohexane mixture.[19] The boiler was heated with an electrical heating jacket of 0.6 kW at about 40% of its maximum heating capacity. The condenser was cooled with tap water of about 10–15°C until the condensate was at room temperature (25°C) and the liquid reflux was controlled through the open/close time of a solenoid valve. Temperature was measured with a Pt-100 temperature data logger at the top of the column. In all experiments, total reflux was applied until the column reaches the steady-state-determined invariable temperature at the top of the column. Then, the distillate was drawn under a fixed reflux ratio. Several fractions were collected according to the temperature variation at the top and further analyzed by gas chromatography GC-Flame Ionization Detector (FID) (model Chrompack CP9002).

Chemicals and membranes

Reagent plus, Sigma-Aldrich THF (>99% pure), Nyssens Graphics™ methanol (99% pure), and ChemLab™ hexane 99+% (all three without further purification) were used to prepare the feed mixtures.

The separation of methanol-hexane mixtures has been performed by using the commercial membranes indicated in Table 1. There are strong differences in materials and structure between the dense membranes supplied by PolyAn and Sulzer Chemtech. PolyAn membranes are molecular surface engineering-based membranes. In this case, surface functionalization of an ultrafiltration polyacrilonitrile porous membrane is done by filling the pores of a porous membrane with a selected functional polymer.[20] Sulzer Chemtech membranes are multilayer composite membranes. In particular, Pervap 1201® is a polyvinyl-alcohol membrane and Pervap 2255-50® has a pore-free separation layer by using a polymer mixture, normally used for the separation of alcohols from water.[21]

Sorption experiments

As a preliminary study, the membranes were subjected to sorption analysis. Small pieces of all membrane types were weighted using a Mettler College 150 balance with an accuracy of ±0.1 mg, and their thickness was measured using a Digital Micrometer® (Cole-Parmer™ with an accuracy of 0.002 mm). Subsequently, they were immersed in three different liquids: pure methanol, a mixture methanol-hexane 91 mol % in methanol, and pure hexane. After 1 week of immersion, all sample surfaces were dried using a tissue and thickness and weight were immediately measured. When these two measurements are made immediately after the drying procedure, thickness and weight data are not affected by solvent evaporation (markedly for volatile components as methanol and hexane). Every value of thickness is the average value of at least five different measurements on the same piece of membrane.

Pervaporation experiments

During preliminary experiments with the Pervap 1201 membrane an extremely low flux was obtained, even not enough to perform chromatography measurements after 3 h of sampling time. Thus, no results concerning the Pervap

Table 1. Commercial Membranes used for the Methanol-Hexane Pervaporation Process

Supplier	Membrane
PolyAn GmbH™	Typ M1
PolyAn GmbH	Typ M2
Sulzer Chemtech™	Pervap 1201
Sulzer Chemtech	Pervap 2255-50

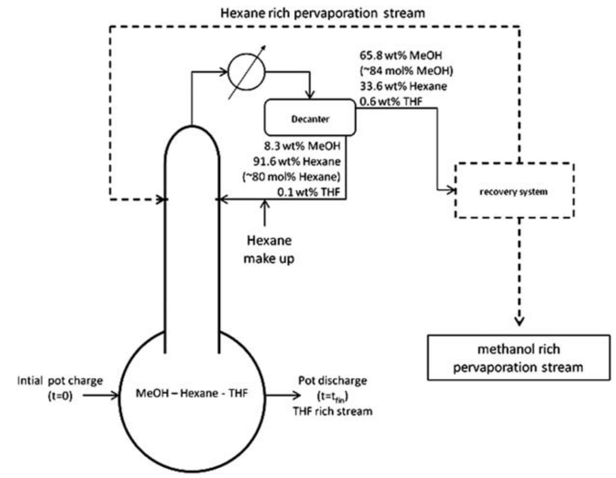


Figure 2. Schematic representation of an integrated industrial process for the separation of THF and methanol by heteroazeotropic batch distillation in which hexane is used as entrainer.

Further separation of the azeotrope hexane-methanol is required.

1201 membrane were finally included in this work and pervaporation experiments, reported hereinafter, refer to the other three tested membranes.

Pervaporation experiments were performed using a Lab Test Cell Unit from GTF-Le Carbone^{TM} (Neunkirchen-Heinitz, Germany). Feed solutions containing binary mixtures of 80, 84, 91 mol % methanol in hexane were fed into the isothermal tank of the pervaporation unit. Three different temperatures were used to run the experiments: 30, 37, and 43°C. Feed solution concentrations and temperatures were chosen in order to work in the one-phase region observed in the phase diagram[4,5] for the studied mixture (Figure 3). In addition, Figure 3 also includes the simulated data from the models: Not-Random Two-Liquid (NRTL), UNIFAC, UNIQUAC, and UNIF-DMD (which is a modified UNIFAC model), obtained using Aspen Plus v7.2. Looking at the VLE experimental data (1 atm) obtained by Raal et al. and by Vilím[22–24] and the LLE experimental data (1 atm) obtained by Hölscher et al.[4] and Alessi et al.,[5] it seems that the presence of a heterogeneous azeotrope can be excluded. Moreover, in Figure 3, Vilím data has been magnified, suggesting the presence of a minimum azeotrope. Within considered property methods, NRTL is the only one that calculates a homogenous type azeotrope. However, our experimental results clearly demonstrated the presence of an heterogeneous azeotrope as also indicated by the UNIFAC, UNIF-DMD, and UNIQUAC property methods and in contradiction with previous literature results[4,5] (more details can be found in Heteroazeotropic distillation section and in Figure 4).

At the beginning of each experiment, the actual feed concentration was in the range of 84–94 mol % methanol in hexane.

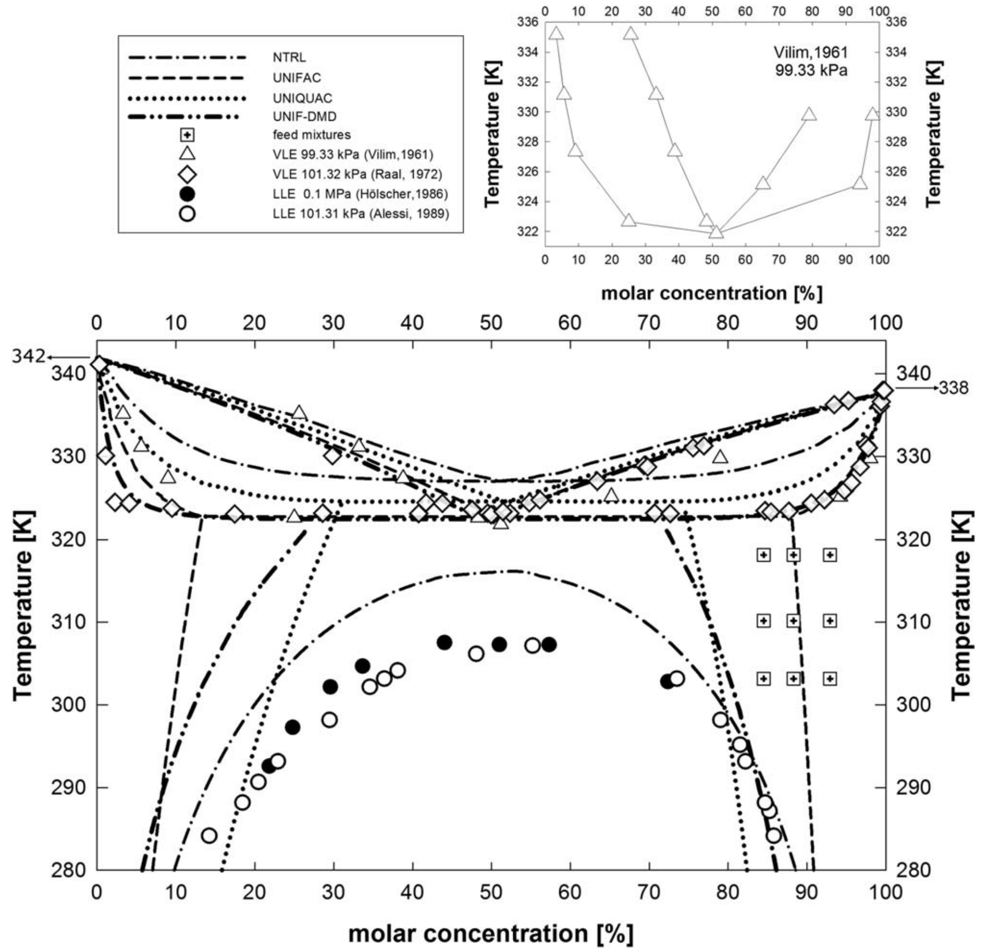
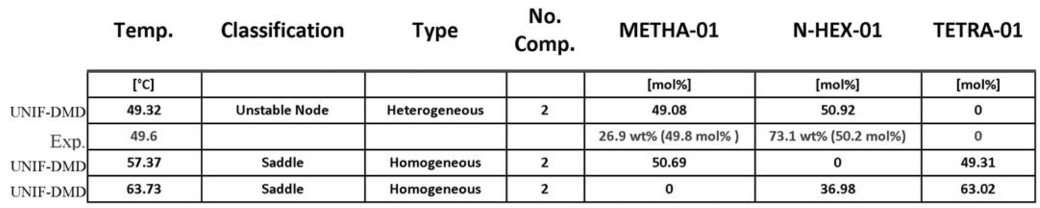


Figure 3. Experimental and simulated VLE and LLE data for the methanol-hexane mixture.

Experimental data are obtained from Refs. 4,5,22–24. Crossed diamond markers show position of feed solutions used for experiments presented in this work. Vilím data[23] have also been magnified in the top-right graph for a clearer visualization.



	Temp.	Classification	Type	No. Comp.	METHA-01	N-HEX-01	TETRA-01
	[°C]				[mol%]	[mol%]	[mol%]
UNIF-DMD	49.32	Unstable Node	Heterogeneous	2	49.08	50.92	0
Exp.	49.6				26.9 wt% (49.8 mol%)	73.1 wt% (50.2 mol%)	0
UNIF-DMD	57.37	Saddle	Homogeneous	2	50.69	0	49.31
UNIF-DMD	63.73	Saddle	Homogeneous	2	0	36.98	63.02

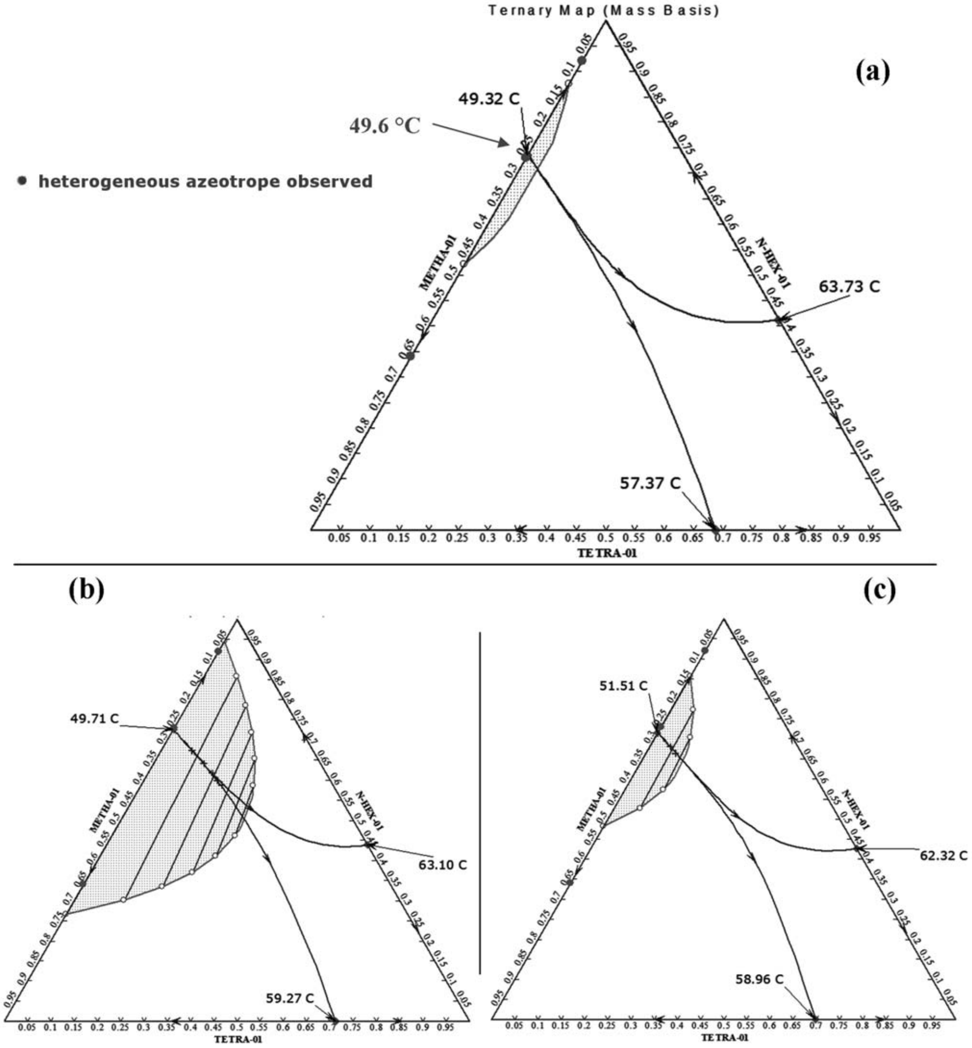


Figure 4. Residue curve maps for the ternary mixture THF, methanol, and hexane (1 atm).

Diagrammed concentrations are here expressed in weight basis. UNIF-DMD was used in (a); UNIFAC in (b); and UNIQUAC in (c). In (a), it is also reported what was experienced about the methanol-hexane heterogeneous azeotrope (of course, the whole phase envelop needs to be described by a rigorous thermodynamic experimental study).

For each experiment, the temperature was measured at the inlet of the cell. Upstream, a centrifugal pump circulated the feed/retentate stream under turbulent conditions to maintain the system well mixed. Moreover, as flow conditions in the pervaporation cell were optimized to maximize the feed side diffusion rate, the limiting step of the mass-transfer process is expected to be the diffusion through the membrane dense layer and polarization phenomenon is not expected to affect significantly the pervaporation process.[8,25,26]

At the feed side, the pressure is atmospheric (no over pressure was applied). At the permeate side, vacuum is achieved by means of a vacuum pump (values between 4 and 10 mbar were registered).

Every 10–30 min, depending on the membrane flux, permeate was collected using a liquid-nitrogen-based condenser in a glass u-tube (i.e., permeate collections were stopped just before the u-tube could be overfilled). At least three samples for each point (fixed temperature and feed concentration) were taken, observing a maximum absolute average deviation of temperature of about 2.7°C and 0.32 mbar for the pressure. Each experiment was run for more than 5 h.

Each membrane, having an active area of 19.63 cm^2, was immersed in the feed solution at least 12 h before starting the experiment to obtain an equilibrium condition between the components in solution and the same absorbed into the membrane. U-glasses used to collect produced permeate were weighed before and after each experiment by means of a Mettler Toledo AB204-S balance with an accuracy of 0.1 mg, obtaining the mass M (kg) of each pervaporation sample. The molar permeate concentration (y_i) and pervaporation feed molar concentration (x_i) were determined by gas chromatography (Perkin Elmer GC-autosystem with Headspace Sampler Turbomatrix 16 and FID detector).

Hence, the membrane flux is calculated as

$$J=\frac{M}{\Delta t\cdot A} \tag{1}$$

where A is the membrane active area.

From membrane fluxes and permeate components concentrations, partial fluxes are calculated

$$J_i=J\cdot y_i\cdot\frac{\mathrm{MW}_i}{\mathrm{MW}_\mathrm{T}} \tag{2}$$

where MW_i is the molar mass of i and MW_T is the total molar mass of the mixture.

The separation factor is calculated as

$$\beta_{\mathrm{MeOH/Hex.}}=\frac{y_{\mathrm{MeOH}}/y_{\mathrm{Hex.}}}{x_{\mathrm{MeOH}}/x_{\mathrm{Hex.}}} \tag{3}$$

This parameter gives information about the permeate quality. However, according to Baker et al.,[25] only by eliminating the effect of driving force it is possible to see the effect of the membrane on the pervaporative separation. The driving force for pervaporation of a component in mixture is the difference of its chemical potential between the feed and the permeate side, which can be expressed as the difference in partial pressure of the component i between the two sides.[27] Thus, the permeance can be defined as

$$\frac{P_i}{l}=\frac{j_i}{(x_i\cdot\gamma_i\cdot P_i^o-y_i\cdot P_\mathrm{p})} \tag{4}$$

where l is the thickness of the active layer, γ_i is the activity coefficient of component i (estimated by ASPEN Plus UNIF-DMD property method considering the feed concentration and temperature), P_i^o is its vapor pressure at the permeation temperature (estimated by the Antoine equation[28]) and P_p is the pressure at the permeate side; j_i is the molar flux of component i, calculated following Baker et al.[25] in (cm/s) at the standard condition of temperature and pressure STP (v_i^g = 24.46 dm^3/mol) as

$$j_i=\frac{J_i\cdot v_i^g}{\mathrm{MW}_i} \tag{5}$$

For the purpose of this work, permeance values are presented in GPU ($1\ \mathrm{GPU}=1\times10^{-6}\mathrm{cm}^3(\mathrm{STP})/(\mathrm{cm}^2\mathrm{s\,cm\,Hg})=7.5005\times10^{-12}\mathrm{m\,Pa}^{-1}\mathrm{s}^{-1}$).

The membrane selectivity is calculated from the permeances of the components in the mixture

$$\alpha_{i/j}=\frac{P_i}{l}\Big/\frac{P_j}{l} \tag{6}$$

The temperature influence on separation is studied using a simple Arrhenius-Type equation

$$\frac{P_i}{l}=\frac{P_i^\infty}{l}\cdot\exp\left(-\frac{1000\cdot E_\mathrm{a}}{R\cdot T}\right) \tag{7}$$

where E_a (kJ/mol) is the activation energy of the permeation process and P_i^∞/l is the permeance for an infinite temperature (ideal value).

Separation study: Simulations

The simulation of the separation of the methanol-hexane heavy fraction were run by using Aspen Plus from Aspen Engineering Suite v7.2, in particular the UNIF-DMD property methods was used to simulate all distillation columns.

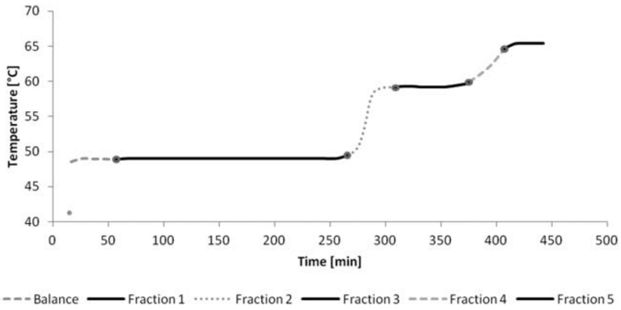


Figure 5. Variation of top temperature with time.

Experimental data from literature were used for the decanter[5] and experimental data from results obtained working with membrane PolyAn Typ M1 at a pervaporation temperature of 37°C, were used to model the pervaporation unit. The concentration of THF in the real feed stream is about 0.6 wt % (see Figure 2) but it was not considered during the simulations.

Decanter, total condenser and reboiler duties (considering only the thermal energy requirements of these units, which are the main contribution) were calculate using Aspen Engineering Suite v7.2.

The power requirement of a pervaporation unit can be calculated by summing the following contributions[29,30]

$$E_\mathrm{PV}=E_\mathrm{feed}+\frac{E_\mathrm{pump}}{\eta_\mathrm{pump}}+\frac{E_\mathrm{cond.}}{\eta_\mathrm{condenser}} \tag{8}$$

E_feed is the contribution which takes into account the pressure drop for the liquid fed in the pervaporation unit, E_pump is the energy request from the pump to maintain vacuum condition and, as effect, pumping permeate to the condenser; finally, $E_\mathrm{cond.}$ is the energy required for condensation of permeate flow. E_feed gives a marginal contribution and were not considered in E_PV calculation.

Power expressed by a PV unit vacuum pump (kW) is calculated considering isothermal expansion[30,31] as

$$E_\mathrm{pump}=n_\mathrm{tot}\cdot R\cdot T\cdot\ln\left(\frac{P_0}{P}\right) \tag{9}$$

where n_tot is the total permeate molar flow rate, R is the ideal gas constant, T is the temperature of permeation, and P_0 and P are the feed side and permeate side pressure, respectively. Thus, the efficiency coefficient (η_pump) used in Eq. 8 is the efficiency which links the energy for an isothermal expansion to the energy of the real expansion.

Power involved in permeates flow condensation was calculated according to the following equation

$$E_\mathrm{cond.}=\sum\left(n_i\cdot\left[\lambda_i\left(T_\mathrm{perm}\right)+c_\mathrm{pi}{}^\mathrm{liq}\cdot\left(T_\mathrm{perm}-T_\mathrm{cond}\right)\right]\right) \tag{10}$$

where T_perm is the temperature of permeation, T_cond is the temperature of condensation (for calculation here reported T_cond was set at the value of 25°C), λ_i is the heat of vaporization, and $c_\mathrm{pi}{}^\mathrm{liq}$ heat capacity of the liquid component at atmospheric pressure. The $\eta_\mathrm{condenser}$, used in Eq. 8, takes into account all the resistances to the heat transfer typical of a real case of industrial unit operation of condensation.

These calculations were performed using physical property of methanol and hexane reported by Perry and Green.[32] For

Table 2. Variation in Composition of the Distillate Fractions and Variation of Temperature with the Process Time

Fraction	Volume (ml)	Methanol (mol %)	Hexane (mol %)	THF (mol %)	Top Temperature (°C) Beginning	Top Temperature (°C) End	Time (h min) Beginning	Time (h min) End
Heavy phase	60	83.96	15.95	0.10				
Light phase	140	19.63	80.25	0.12				
Heteroazeotrope		49.8	50.2	–	49.6	50.30	0	3.27
Fraction 2	30	49.47	16.18	34.35	50.3	59.8	3.37	4.1
Fraction 3	40	49.75	0.13	50.12	59.8	60.8	4.1	5.15
Fraction 4	30	15.87	0	84.13	60.8	66	5.15	5.56
Fraction 5	18	0.76	0	99.24	66	66.1	5.56	6.2
Residue	125	–	–	–	–	66.1	6.2	–
Total				443				

all efficiencies used during calculations, a general value of 0.9 was considered (this is a realistic value to be used when a simple energetic calculation is proposed, as it is in this work).

Results and Discussion

Heteroazeotropic distillation

Figure 2 helps to visualize the flow scheme of the integrated system object of this work. Figure 4 shows the residue curve map for the ternary mixture THF, methanol, and hexane (concentration values are in weight basis).

Hexane forms a homogeneous azeotrope with THF and a heterogeneous azeotrope with methanol, as resulted from our experiments, in contradiction with the literature proposed by Hölscher et al.[4] and Alessi et al.[5] and in qualitative agreement with UNIFAC, UNIF-DMD, and UNIQUAC property methods. As it is possible to see from Figures 3 and 4, the composition of light and heavy phase (resulted from our experiments), is somewhere between the one predicted by UNIFAC and UNIF-DMD (Figures 4a, b). As the ternary mixture involves three binary azeotropic mixtures and no ternary azeotrope, the resulting residue curve map corresponds to the 3.0–2 class according to Serafimov's classification, with an estimated statistic occurrence of 8.4% among reported ternary azeotropic mixtures.[33] The residue curve map exhibits two unstable boundaries connecting the binary heteroazeotrope to each homogeneous binary azeotrope and dividing the composition space in three basic distillation regions. These boundaries usually restrict the separation of the components by homogeneous azeotropic distillation but not anymore in the case of heterogeneous entrainers.[34,35]

The heterogeneous binary methanol-hexane azeotrope has the lowest boiling point in the mixture and is the vapor top product, when using a column with a sufficient number of equilibrium plates. After condensation of this vapor, two liquid phases are decanted. The entrainer-rich phase is the light-liquid phase and it can be directly sent back at the top of the column as liquid reflux. The methanol-rich heavy phase is kept as distillate product.

The total amount of initial ternary mixture was 0.480 L with a total composition of 21.7 mol % methanol, 24.2 mol % hexane, and 54.1 mol % THF. The amount of entrainer was calculated by taking 20% of entrainer volume more than the theoretical composition of the binary heteroazeotrope with methanol (computed by UNIFAC model). This was done to make sure that methanol can be distilled by this heteroazeotrope, taking in account the total liquid holdup of the column. The heterogeneous azeotropic distillation process was carried out under a constant reflux ratio of 10.

Figure 5 shows the variation of the temperature at the top of the column during the batch operation and the five distillate fractions that were taken. Table 2 shows the five distillate fractions that were taken depending on the top temperature. Fraction 1 corresponded to a heterogeneous top vapor composition and constituted the main distillate fraction having 0.2 L. The next Fractions 2, 3, and 4 were the transition cuts toward pure THF into the boiler. In Fraction 5, pure THF is obtained at the top of the column. The whole process took about 450 min until pure THF was obtained in the residue.

Table 3. Membrane Thickness (mm) Measured Immediately After 1 Week of Immersion Time and Surface Drying

Membrane	Thickness Before Immersion (mm)	Thickness Before Immersion error (±)	Thickness After Immersion (mm)	Thickness After Immersion error (±)	Thickness Increase (%)	Maximal Thickness Measurement Tot. Error (± %)	Maximal Instrumental Error (± %)
Typ M1							
Pure methanol	0.220	0.011	0.217	0.008	−1.455	8.8	1.8
Pure hexane	0.245	0.007	0.236	0.010	−3.589	6.8	1.7
80% wt methanol	0.226	0.003	0.219	0.008	−3.445	4.6	1.8
Typ M2							
Pure methanol	0.198	0.002	0.202	0.002	1.894	2.1	2.0
Pure hexane	0.198	0.002	0.197	0.000	−0.303	1.1	2.0
80% wt methanol	0.200	0.001	0.201	0.002	0.902	1.4	2.0
Pervap 2255-50							
Pure methanol	0.178	0.004	0.178	0.002	−0.224	3.4	2.2
Pure hexane	0.175	0.002	0.175	0.002	−0.342	2.1	2.3
80% methanol	0.173	0.002	0.172	0.001	−0.203	1.9	2.3

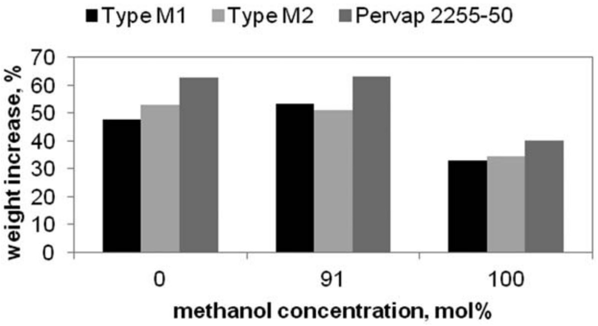


Figure 6. Percentage membrane weight increase against molar fraction of methanol in contact solution.

The heteroazeotrope (Fraction 1) was decanted at 25°C. The hexane-rich phase contains almost 20 mol % of methanol and is fed back into the column. The methanol rich phase exhibits only 84 mol % of methanol. This means that a second separation step is needed to purify methanol.

In the next sections, the use of pervaporation to purify the methanol-hexane phase will be discussed.

Sorption results

The thickness of membranes before and after immersion in pure methanol, pure hexane, and a mixture of about 91 mol % methanol are shown in Table 3. The thickness increase due to the sorption of contact solution is lower than the experimental uncertainty. This may be due to the fact that the micrometer always exerts a small pressure in surface samples, affecting the measurement even for high accuracy instruments. Moreover, the thickness of the Typ M1 membrane appeared to be not uniform (measured fluctuation from the average value of 0.227 ± 0.006 mm). In addition, due to the application of the pore filling concept, swelling was expected to be negligible for PolyAn membranes Typ M1 and Typ M2.[20]

Conversely, relevant information was obtained from the weight measurements reported in Figure 6. The weight increase is mainly due to the sorption of methanol. In addition, the weight increase of Sulzer Pervap 2255-50 is about 6–15% higher than that of the PolyAn membranes. Figure 6 also shows that for Pervap 2255-50 and markedly for Typ M1, the weight increase after immersion in 91 mol % in methanol is higher than after immersion in pure methanol or pure hexane.

Pervaporation experiments

For all the three membranes, methanol and hexane fluxes and permeances at 37°C are shown in Figure 7. Additional data at 30 and 43°C provide similar information and are, therefore, shown in Figures 8 and 9. For all the membranes and for all the studied temperatures, the methanol-hexane separation factor and selectivity toward methanol are shown in Figure 10. The highest methanol and hexane permeance (average values of about 5080 GPU and 160 GPU, respectively) were obtained using the Typ M2 membrane close to the lowest feed concentration explored (about 84 mol % methanol) and for all the studied permeation temperatures. The hexane flux was much lower than the methanol flux; the methanol permeance is one order of magnitude higher than the hexane permeance, meaning that all the three membranes are highly affine for methanol which is the fastest to be diffused. The highest values of selectivity (an average of about 116) and separation factor (about 19) were achieved using Typ M1 when working at 37–43°C and at the lower explored feed concentration (about 84 mol % methanol).

For all the membranes, Figures 7–9 show how component flux and permeance have a similar behavior. Moreover, for Typ M1 and Pervap 2255-50, in the same range of concentrations (as shown in Figures 10a, c), also the separation factor and the selectivity behave similarly and, considering that the driving force is higher for hexane than for methanol, this means once again that both from a thermodynamic (in terms of affinity) and kinetic (in terms of diffusivity) point of view, all three membranes strongly favor methanol permeation. For membrane Typ M2, Figures 7b and 9c, d show how the hexane and methanol flux and permeance decrease, above all from intermediate concentrations onward. In particular, the methanol flux and permeance curves have a more

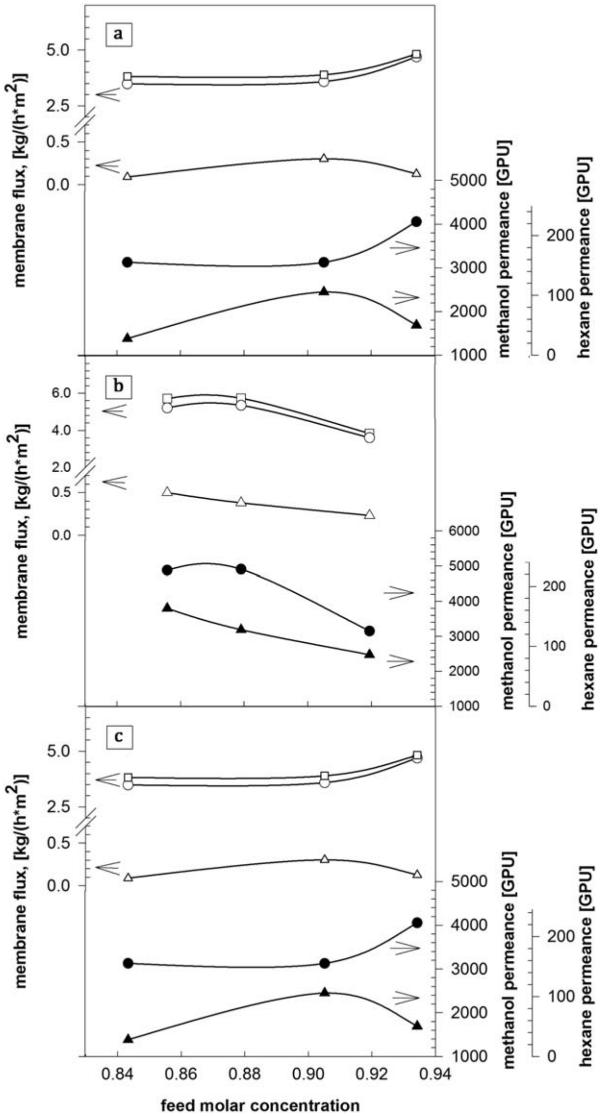


Figure 7. Variation of total flux (□), methanol partial flux (○), hexane partial flux (Δ), methanol permeance (•), and hexane permeance (▲) with feed molar methanol concentration at 37°C, for PolyAn Typ M1 (a) and Typ M2 (b) and Sulzer Chemtech Pervap 2255-50 (c) membranes.

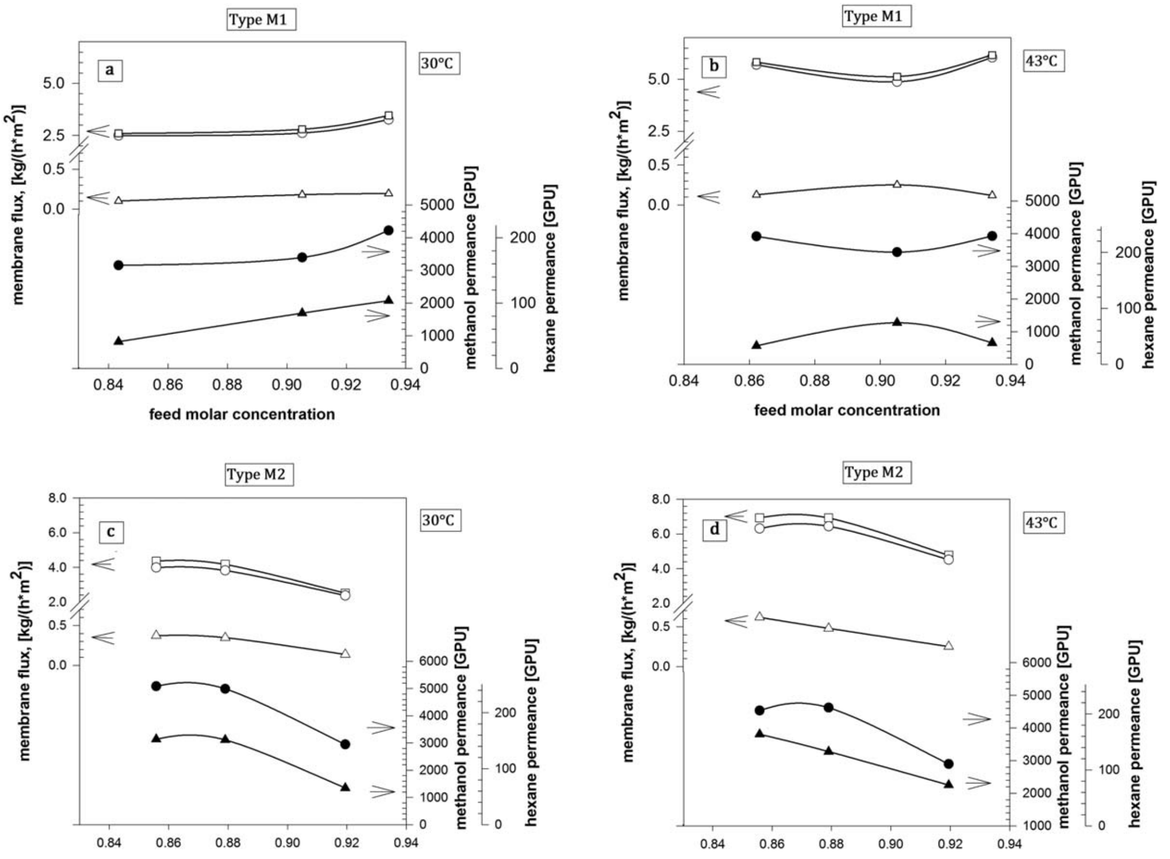


Figure 8. Variation of total flux (□), methanol partial flux (○), hexane partial flux (Δ), methanol permeance (•), and hexane permeance (▲) with feed molar methanol concentration, for PolyAn Typ M1 membrane at 30 (a) and 43°C (b), and for Typ M2 membrane at 30 (c) and 43°C (d).

marked negative slope than the hexane curves. Conversely, in the whole feed concentration range separation factors decrease slightly and the selectivity toward methanol increases slightly (Figure 10b). This means that particularly for this membrane, driving forces and probably other transport resistances (e.g., polarization resistance) become relevant, competing with the material properties of the membrane's active layer in affecting permeance of the two components.

Figure 10a suggests as at 37 and 43°C, for membrane Typ M1, separation factor and selectivity present a minimum. Of course, the values of selectivity and separation factors obtained at a feed concentration of about 91 mol % in methanol are not the two minimum values of these two curves, however, it is interesting to notice how at the same concentration, the membrane Typ M1 sorbs more liquid than in the case of pure methanol and hexane solutions (as shown in Figure 6). This phenomenon can be related to a coupling effect that links methanol and hexane during permeation affecting pervaporation performances. For organic-water mixtures, the formation of joint structures has been already reported in literature.[36] One possible explanation may be

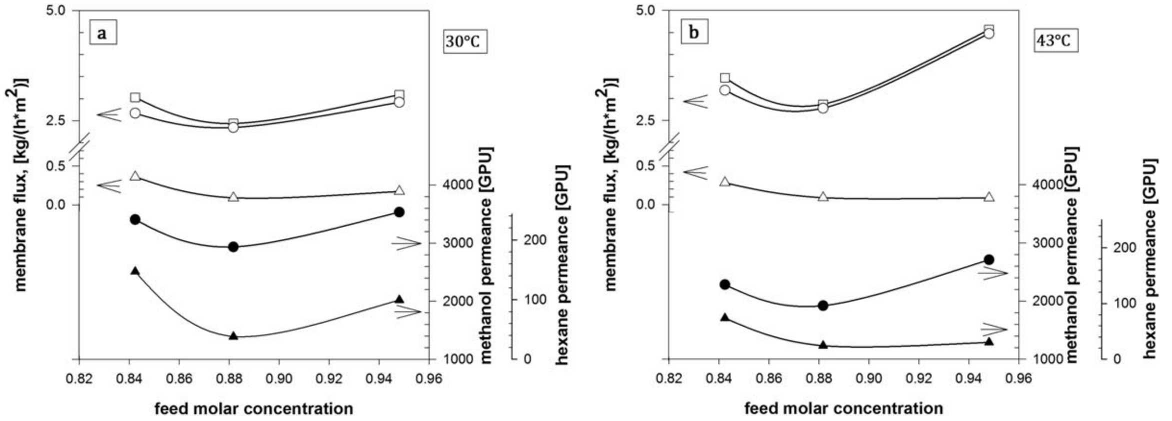


Figure 9. Variation of total flux (□), methanol partial flux (○), hexane partial flux (Δ), methanol permeance (•), and hexane permeance (▲) with feed molar methanol concentration, for Sulzer Chemtech Pervap 2255-50 membrane at 30 (a) and 43°C (b).

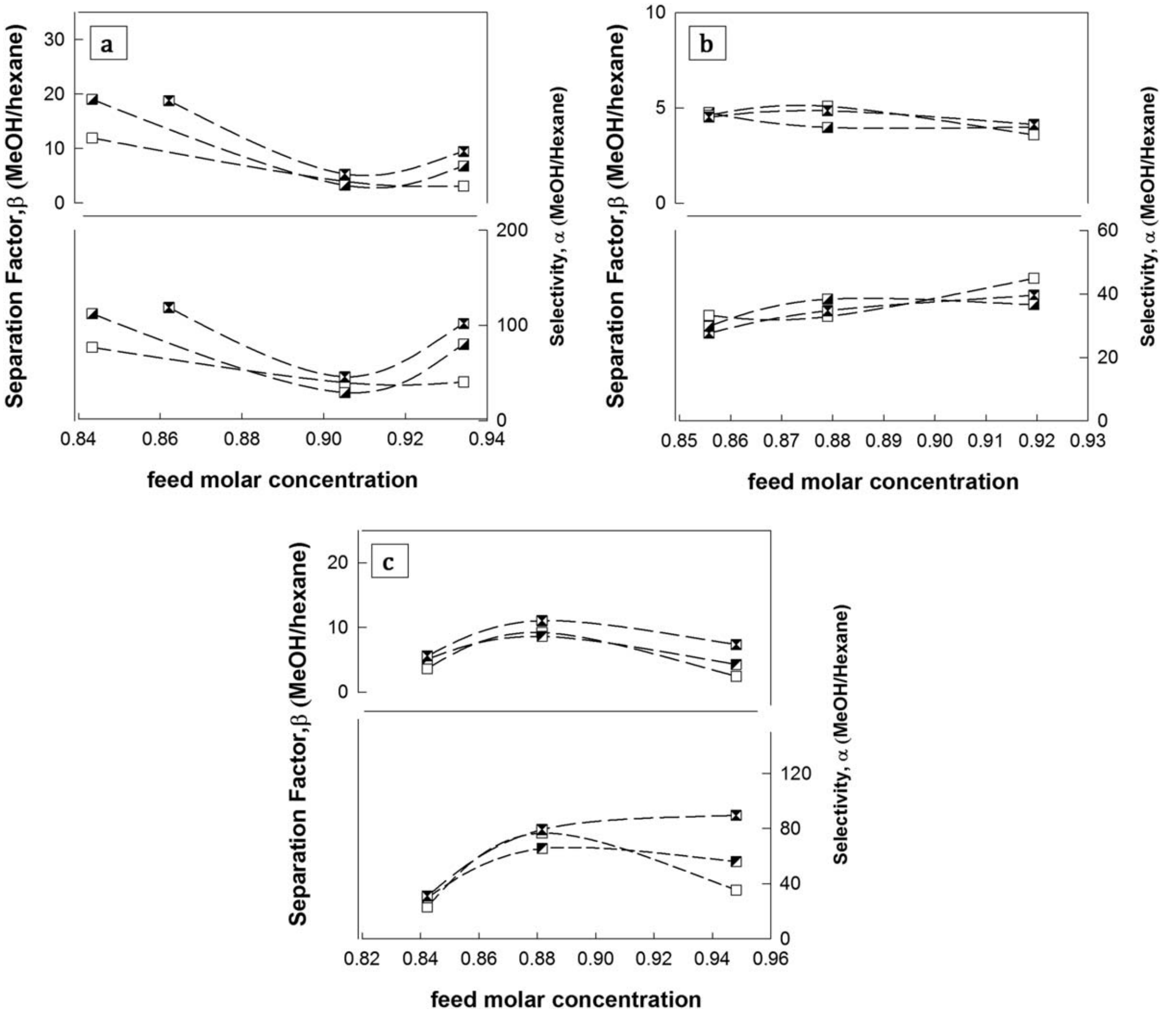


Figure 10. Variation of separation factor and selectivity with feed molar concentration of methanol at 30°C (□), 37°C (◩), and 43°C (⧗) for membrane PolyAn Typ M1 (a), Typ M2 (b) and Sulzer Chemtech Pervap 2255-50 (c).

related to the difference between the number of methanol molecules and hexane molecules in mixture (the ratio is about 9:1), in the sense that a certain number of methanol molecules surrounds some hexane molecules (bigger than methanol ones) forming a big polar entity, kept together by electrostatic forces, and then drag them through the membrane. A coupling phenomenon can be also the explanation of the trend shown by the separation factor (a maximum around the middle of the feed concentration range) and by the selectivity curves of membrane Pervap 2255-50 (Figure 10c). The effect of coupling is not unique but depends on all factors which dominate diffusion into the active layer of a membrane.[37] In other terms, as also shown by Van Baelen et al.[36] in the case of formation of joint structures, the interactions between feed components and the membrane, and between the different feed components have a consequence on the pervaporation behavior of the different components, thus, affecting flux and selectivity. For membrane Typ M1, this coupling effect decreases the permeate quality and methanol selectivity of the membrane (resulting in a minimum for both the curves), differently for membrane Pervap 2255-50 it increases permeate quality (separation factor curves present a maximum) and together with temperature effect also membrane selectivity (see also next section).

Table 4. Estimated Activation Energies and Preexponential Factors for all Studied Commercial Membranes

	Membrane	MeOH $E_{a'}$(kJ/mol)	P_i^{∞}/I, (GPU)	Hexane $E_{a'}$(kJ/mol)	P_i^{∞}/l, (GPU)
Low feed concentration range explored	Type M1	12.9	503832.9	−15.0	9.8E-02
	Type M2	−7.7	242.5	4.8	1040.0
	Pervap 2255-50	−46.5	0.0	−26.7	8.7E-02
Medium feed concentration range explored	Type M1	−0.4	2795.9	−4.3	1.6E+01
	Type M2	−4.7	765.1	−9.2	3.8
	Pervap 2255-50	−29.0	0.0	−27.6	5.3E-02
High feed concentration range explored	Type M1	−4.1	819.7	−57.3	1.3E-08
	Type M2	−0.9	2094.8	6.7	991.3
	Pervap 2255-50	−14.7	11.0	−65.5	5.7E-10

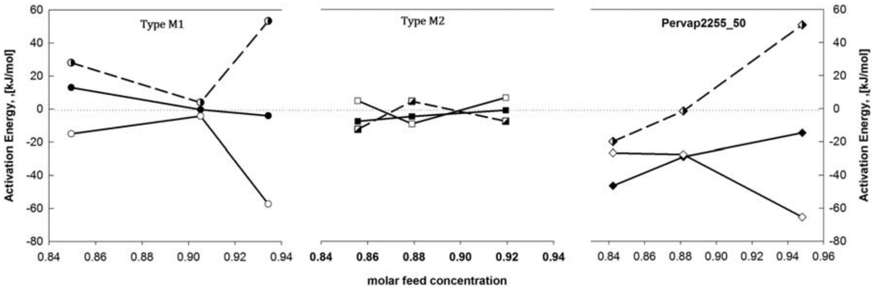


Figure 11. Variation of activation energy of permeance with feed molar concentration of methanol.

Circular symbols refer to membrane Typ M1, square symbols to membrane Typ M2, and diamonds symbols to Pervap 2255-50. Full symbols refer to methanol permeance and empty ones to hexane permeance. Partially full symbols and dashed lines refer to difference between methanol and hexane activation energy.

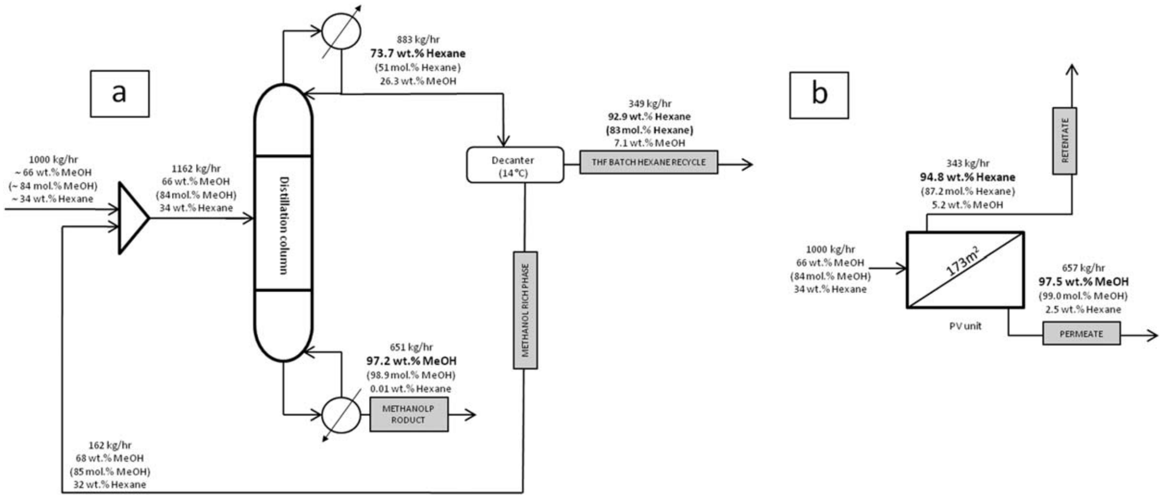


Figure 12. Picture (a) shows the proposed distillation system.

Picture (b) shows the recovery system constituted by a PV stand-alone unit.

Temperature effect on pervaporation

The temperature dependence was studied by considering the permeation activation energy (using Eq. 7), which is mainly composed of two contributions: $\Delta H_{\mathrm{sorb},i}$ is the enthalpy of sorption and $E_{\mathrm{d},i}$ is the activation energy of diffusion.[38] The latter contribution is generally positive and the former negative for exothermic processes.[38,39] Table 4 resumes these estimations together with calculated preexponential factors (permeance value at infinite temperature).

This analysis is graphically resumed in Figure 11, which shows that for all the three membranes, the variation of the activation energy for methanol with feed molar concentration is linear; whereas the activation energy trend for hexane is a discontinuous curve that almost merges with the curve for methanol (in between 88 and 91 mol % methanol). Thus, along the whole feed concentration range, methanol permeates always in the same way, but the permeance of hexane is affected by temperature and by methanol permeation, confirming the presence of the mentioned coupling phenomenon. For membrane Typ M2, this study shows that the membrane is also affected by coupling and that its selectivity is slightly favored by decreasing temperature. In fact, the overall average difference between methanol and hexane activation energy, which corresponds with the activation energy of membrane selectivity toward methanol permeation (also reported in Figure 11), is low and negative (an average of about −5 kJ/mol).

For membrane Pervap 2255-50 (as already described in the previous section), differently from membrane Typ M1, the coupling between methanol and hexane has a positive effect on selectivity and permeate quality. Furthermore, as shown in Figure 11, increasing the temperature helps to maintain this positive effect on the pervaporation performance. For membrane Typ M1, similarly to the trend of selectivity curves (Figure 10a), the difference in methanol-hexane activation energies shows a minimum (Figure 11), suggesting

Table 5. The Best Four Methanol-Hexane Separation Results Achieved by Using all Three Tested Membrane and Considering a Methanol-Hexane Feed Stream Entering the PV Unit with a Concentration of about 84 mol % in Methanol

Membrane	Separation Factor	MeOH/Hexane Selectivity	MeOH Flux * MeOH/Hexane Selectivity (kg/h m^2)	Total Flux (kg/h m^2)	Working Temperature (°C)	Estimated Permeate Concentration (mol %)
Typ M1	19.0	112.4	391.9	3.8	37	99.0
Typ M2	4.5	28.0	174.4	6.3	43	95.9
Pervap 2255-50	5.6	31.0	98.6	3.5	43	96.7

Table 6. Comparison of Power Requirement and Membrane Area of all Different Methanol-Hexane Separation Processes Proposed

	Product Composition		Total Condenser Thermal Duty	Total reboiler Thermal Duty	Decanter	Pervaporation Total Duty	Total Duty
	(mol%)		(KW)	(KW)	(KW)	(KW)	(KW)
	MeOH Product	Hexane Product					
Distillation system	98.9	83	−274.2	156.1	−18.8	–	499.0
PV unit	99.0	87.2	–	–	–	318.2	353.5

that in the edge of the whole feed concentration range selectivity is positively conditioned by the highest temperatures.

Discussion over two energetically relevant unit configurations

During the last 10 years, some cost optimization works concerning PV stand-alone or hybrid membrane system have been published. More often, results obtained came from simplifying assumptions (more information can be found elsewhere[40–44]). A fundamental turning point came from Sørensen and coworkers' outcomes.[45,46] They used genetic algorithm methods to run high efficiency cost optimizations of structured unit designs and configurations. Nevertheless, the following discussion has not the ambition to propose any unit to be implemented in industry, as an optimization based on cost analysis is needed. Conversely, two designs are proposed for an energetic comparison: a distillation column separated by a decanter (high energy consumption technology) and a simple pervaporation stage.

Hence, by simulation of an integrated system of a distillation column (operated at 1 atm) and a decanter, treating a methanol-hexane feed flow of 1000 kg/h with a concentration of about 84 mol % methanol (as shown in Figure 2), good product streams can be obtained (see the flow sheet of Figure 12a). In particular, a methanol product with a purity of 98.9 mol % methanol and a hexane product with a purity of 83 mol % hexane (adherent to expected concentration of 80.2 mol % in hexane, see Figure 2), were obtained.

To reduce the energy consumption, the distillation system can be replaced by a simple PV step. Therefore, the best membrane and working temperature, to be used for the design of this pervaporation-based recovery unit were selected based on the product of methanol flux and selectivity. These data are summarized in Table 5 together with the corresponding values of separation factor, selectivity, total flux, and permeate product quality. The membrane Typ M1 has the best performance (at the temperatures of 37 and 43°C). To minimize the energy consumption of the pervaporative recovery units, only Typ M1 membrane data obtained at 37°C were used for the simulations [a total flux of $3.8\ \mathrm{kg}/(\mathrm{h\ m}^2)$].

Based on the energetic calculation reported in Table 6, the use of a simple PV stand step permits a 29% of energy saving compared to the proposed conventional system of separation (i.e., a distillation column coupled with a decanter).

It has to be remarked that these energetic considerations were made on a continuous operation mode of these two units. Indeed, a batch operation mode may eventually make the system more complex, but the indication about the energetic consumptions still remains valid.

Finally, it has also to be noted that the PV stand-alone unit needed an active area of 173 m^2. This value is maximum value that could be reduced as a consequence of a cost-optimization analysis which, in turn, could lead to a more complex unit configuration (hybrid, perhaps).

Conclusions

Due to its azeotropic nature, the methanol-THF mixture cannot be separated by simple distillation. The residue curve map of the ternary mixture methanol-THF-hexane showed that the methanol-THF mixture could be separated by using hexane as entrainer in a heterogeneous azeotropic distillation (the heteroazeotropic nature of the methanol-hexane mixture was experimentally proved defining a substantial disagreement with past literature works). This separation was experimentally verified. According to our knowledge, this is first contribution of the separation of methanol-THF mixture by using this heterogeneous azeotropic distillation process. In this process, the entrainer rich light phase was sent back to the column, while the methanol rich heavy phase was purified using pervaporation.

The Sulzer Chemtec Pervap 1201 membrane showed a too low flux through the membrane for a practical application. The highest values of methanol and hexane permeances have been obtained with the PolyAn Typ M2 (average value of about 5080 GPU). Conversely, the highest values of selectivity (an average of about 116) and separation factor (about 19) were achieved using PolyAn Typ M1 membrane. The membrane Sulzer Chemtec Pervap 2255-50 showed a maximal separation factor of about 11 and selectivity values of about 90, close to the ones demonstrated by the PolyAn Typ M1 membrane.

At the tested temperatures of 37 and 43°C, the membrane PolyAn Typ M1 membrane allows obtaining medium-high fluxes [average of $4.6\ \mathrm{kg}/(\mathrm{h\ m}^2)$] and high quality permeate products (a purity of 99.0 mol % methanol). This membrane was used for the design and simulation of a stand-alone pervaporation recovery unit to be compared with a conventional system comprising a distillation column and a decanter. These two separation systems (working in batch), coupled with a heteroazeotropic-batch-distillation column, allow the recovery of the feed stream compounds (THF, methanol, and hexane). In particular, the best quality of the products (99.0 mol % for methanol product and 87.2 mol % for recycled hexane) and the lowest energy duty (less than 29% in respect to the system of a distillation column and decanter) were obtained by using the stand-alone pervaporation configuration. However, for this simple configuration, a large membrane area is required. The final consideration is that a PV-membrane network could eventually better perform the separation with a much lower overall membrane area requirement.[46] This is left as future work to be assessed before any industrial implementation may be proposed.

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