Basic Principles of a Hybrid Distillation and Pervaporation Unit in a Single Column: an Analytic Tool

Juan A. León, Javier Fontalvo*

Universidad Nacional de Colombia, Sede Manizales, Departamento de Ingenieria Quimica, Laboratorio de Intensificacion de Procesos y Sistemas Híbridos – LIPSH.
jfontalvoa@unal.edu.co

Distillation-Pervaporation Hybrid Systems (DPHS) are a relatively novel technology for separating multicomponent azeotropic mixtures, due to pervaporation is not limited by the liquid-vapor (LV) equilibria. However, conventional Distillation-Pervaporation Hybrid Systems, where the pervaporation unit is externally connected to the distillation column, have several drawbacks in the pervaporation unit, for instance high resistance to heat and mass transfer and an inter stage heating system is required between the pervaporation modules. Distillation-Pervaporation in a Single Unit (DPSU) is a novel concept where the pervaporation membrane is located inside the distillation column working as a packing bed in a section of the column. Due to it is a new concept, there is little data about its separation behavior. However, DPSU is able to overcome distillation boundaries. In this work, a simplified model is used to evaluate the separation of ternary homogenous azeotropic mixtures and thermodynamic conditions in a DPSU column. A pervaporation sections located in rectifying and stripping sections were studied. Two topological types, based on Serafimov's topological classification, were selected as case studies: acetone-isopropanol-water (1.0-2) and ethyl acetate-ethanol-methanol (2.0-2b) mixtures. The effects of the DPSU column on the mixture topology, such a perturbation of stationary points, are studied. It is possible to overcome distillation boundaries using a selective membrane but also new stationary points in middle of the composition space appear.

1. Introduction

Distillation-Pervaporation Hybrid Systems (DPHS) are an alternative to separate azeotropic mixtures, since pervaporation is not limited by the liquid-vapor equilibrium as distillation (Skiborowski et al., 2013). In a conventional DPHS, the membrane is located outside the distillation column. However, pervaporation is affected by temperature and concentration polarization (Nagy, 2010). In addition, an inter stage heating system between the pervaporation modules is required to compensate the retentate temperature drop and avoid a drastic loss of membrane flux (Baker, 2012).

Fontalvo et al. (2007) proposed a hybrid Distillation-Pervaporation system in a Single Unit (DPSU) where pervaporation is located in a section of the column. In the pervaporation section, distillation and pervaporation (and vapor permeation depending on membrane wettability) occur simultaneously. In a DPSU the feed to the membrane section (MS) is a two-phase stream (internal distillation flows) that, due to its turbulence, reduces temperature and concentration polarization where reductions of 33% and 50%, respectively are reported (Fontalvo et al., 2006). Additionally, the vapor phase works as an internal energy source for the pervaporation process. So, the thermal energy required for pervaporation is compensated by the column reboiler.

Although this technology is promising to separate multicomponent azeotropic mixtures, the behavior of the DPSU in not well known. Haelssig et al. (2012) proposed a similar system to a DPSU for ethanol dehydration, called Membrane Dephlegmation Process (MDP). The pervaporation membrane was located over the inner wall of a distillation column. The liquid wets the wall, forming a liquid film that flows downwards and vapor flows counter-currently to the liquid. The ethanol-water azeotrope is not broken by a MDP, however it was demonstrated that the two-phase membrane feed improves the mass and energy transfer in the entire operation. On the other hand, Fontalvo and Keurentjes (2015) presented a DPSU system with a membrane packing section inside the distillation column for two ternary mixtures: methanol-C4-MTBE and methanol-ethyl

acetate-water. For the second mixture, using a water-selective membrane, the distillation boundary was crossed by a continuous composition profile inside the column, allowing a feasible operation with product compositions in different regions, that are split by a distillation boundary of the topology diagram.

In this work, a simplified model is presented to study the DPSU behavior under specific thermodynamic conditions. In this way, it is possible to identify the impacts that an internal membrane section generates on the separation trajectory and topology of multicomponent azeotropic mixtures. Two ternary homogenous mixtures are studied with different Serafimov's topological classification: acetone (A)-isopropanol (I)-water (W) (1.0-2) and ethyl acetate (EA)-ethanol (E)-methanol (M) (2.0-2b).

2. Methodology

The model presented has similar characteristics of a previous simplified model for reactive distillation (Barbosa & Doherty, 1988). The separation inside the column is due to distillation and pervaporation mechanisms. Vapor permeation and Constant Molar Overflow (CMO) are not assumed in the model. Hypothetical selective membranes are considered and also the only necessary parameter to describe the pervaporation is the membrane selectivity. An Equilibrium model (EQ) is applied to describe the mass transfer between the liquid and vapor phases. Additionally, transformed compositions are used to reduce the degrees of freedom generated by introducing pervaporation equations in the mass balances. The resulting equations are shown below.

2.1 Hybrid rectifying section for a partial condenser

The mass balance in a membrane section (MS) located in a rectifying section:

$$\frac{dX_i}{dh_R} = X_i - \frac{\overline{R}_n+1}{\overline{R}_n}Y_i + \frac{1}{\overline{R}_n}Y_{i,T} \tag{1}$$

Where the internal transformed reflux ratio is:

$$\overline{R}_n+1 = \frac{1-x_{k,P}^{-1}y_k}{1-x_{k,P}^{-1}y_{k,T}}\left(\overline{R}_{Ex}+1\right) \tag{2}$$

And the external transformed reflux ratio is defined as:

$$\overline{R}_{Ex} = R_{Ex}\frac{1-x_{k,P}^{-1}x_{k,T}}{1-x_{k,P}^{-1}y_{k,T}} \tag{3}$$

Also, in eq. (1) the transformed composition in liquid and vapor phases are:

$$X_i = \frac{x_i - x_{i,P}x_k x_{k,P}^{-1}}{1-x_k x_{k,P}^{-1}}; Y_i = \frac{y_i - x_{i,P}y_k x_{k,P}^{-1}}{1-y_k x_{k,P}^{-1}} \tag{4}$$

Equation (4) was derived similarly to the transformed composition obtained by Ung & Doherty (1995) for i = 1…n-1 components. For a ternary mixture only 1 transformed composition is independent. The transformed composition for the dependent component j can be calculated as:

$$X_j = 1-X_i; Y_j = 1-Y_i \tag{5}$$

The transformed variables are function of the permeate composition x_P, which depends on membrane selectivity.

$$x_{i,P} = \frac{\alpha_{ij}f_i}{\sum_{\substack{i=1 \\ i \neq j}}^{n}\alpha_{ij}f_i} \tag{6}$$

The model presented in eqs.1-6 considers both, the mass transfer by distillation and pervaporation mechanisms.

2.2 Hybrid stripping section

The mass balance in a membrane section located in a stripping section is:

$$\frac{dX_i}{dh_S'} = \frac{\overline{S}_n}{\overline{S}_n + 1} Y_i - X_i + \frac{1}{\overline{S}_n + 1} X_{i,o} \tag{7}$$

Where the internal transformed boil-up ratio $\overline{S}_n$ is defined as:

$$\overline{S}_n = S_{ex} \frac{x_{k,P} - y_k}{x_{k,P} - x_{k,o}} \tag{8}$$

Composition profiles of the conventional rectifying and stripping section can be obtained by any simplified model based on EQ model (Thong & Jobson, 2001).

3. Results and discussion

Hypothetical infinite selective membranes ($\alpha_k \to \infty$) to component k, which it is also the reference component, are used to identify the impacts of a DPSU column on the mixture topology. Results for the two explored mixtures are presented below.

3.1 Acetone (A)-isopropanol (I)-water (W) mixture

Figure 1a shows the operation leaves of the rectifying and stripping sections for a conventional distillation, since D (region 1) and B (region 2) are located in different regions, a feasible separation cannot be achieved. Both regions share the Unstable Node (UN), which is close to pure acetone vertex (A-W azeotrope, $x_A \approx 0.98$. Pure isopropanol vertex ($x_I = 1$) and pure water vertex ($x_W = 1$) are SN of region 1 and region 2, respectively. The ascendant volatility order for region 1 is I > W > A, on the other hand for region 2 the ascendant volatility order is W > I > A. Therefore, two sets of products can be obtained in a conventional distillation depending on feed composition, for instance: (1) a distillate rich in acetone and bottoms rich in isopropanol, or (2) a distillate rich in acetone and bottoms rich in water.

An operation leaf for a hybrid DPSU rectifying section with D located in region 1 using an isopropanol-selective membrane is shown in Figure 1b. The SN in region 1 is shifted to pure water vertex, this means that the distillation boundary is crossed. The removal of the heaviest component (isopropanol) in region 1 forces the water (component with intermediate volatility) to act as the heaviest component in this region. The trajectories of the hybrid rectifying section tend to achieve the SN of region 2. Pervaporation enhances the separation by distillation of the lightest component (acetone) and the component with intermediate volatility (water) of the region where D is located. This disturbance (Isopropanol removal) of the mass transfer between the liquid and vapor phases allows to overcome the distillation boundary because the thermodynamic equilibrium inside the MS is continuously modified by the isopropanol permeation. Additionally, in this topology the DPSU is not limited by the liquid-vapor equilibrium. The DPSU trajectories can go through the entire composition space of the Mass Balance Triangle (MBT) for a finite MS dimensionless height.

A high reflux ratio allows an extended trajectory in a conventional rectifying section, this same behavior is presented in a DPSU column (Figure 1b). The membrane capability to overcome the distillation boundary depends on the separation mechanism by distillation. A high reflux ratio promotes distant pinch points from D, stimulating the perturbation of the composition in the vapor and liquid phases from the phase equilibrium due to the pervaporation mechanism. Although, pervaporation makes possible to cross the distillation boundary, the mixture separation mainly depends on the distillation mechanism.

Figure 1c shows a feasible separation with D located in region 1, and B and F located in region 2. The DPSU is able to achieve outlet streams with product compositions located in different regions in a MBT overcoming the distillation boundary with a hybrid rectifying section. By changing the composition of B, it would be always possible to achieve a feasible separation, if the separation trajectories generated by a hybrid rectifying section in region 2 reaches region 1. Also, pervaporation in a DPSU generates a change of the temperature profile in the column (Figure 1d) as it is compared to a conventional distillation. Since isopropanol is removed (component with intermediate boiling point), the bubble temperature of the liquid is higher than in a conventional rectifying section. Due to the pervaporation section the liquid phase is enriched in water and, thus the bubble temperature of the liquid increases. On the contrary, if the component with the highest boiling point (e.g. water) is removed by pervaporation, the liquid temperature profile in the MS would be lower than in a convention rectifying section. This behavior is useful to separate multicomponent azeotropic mixtures with thermosensitive components.
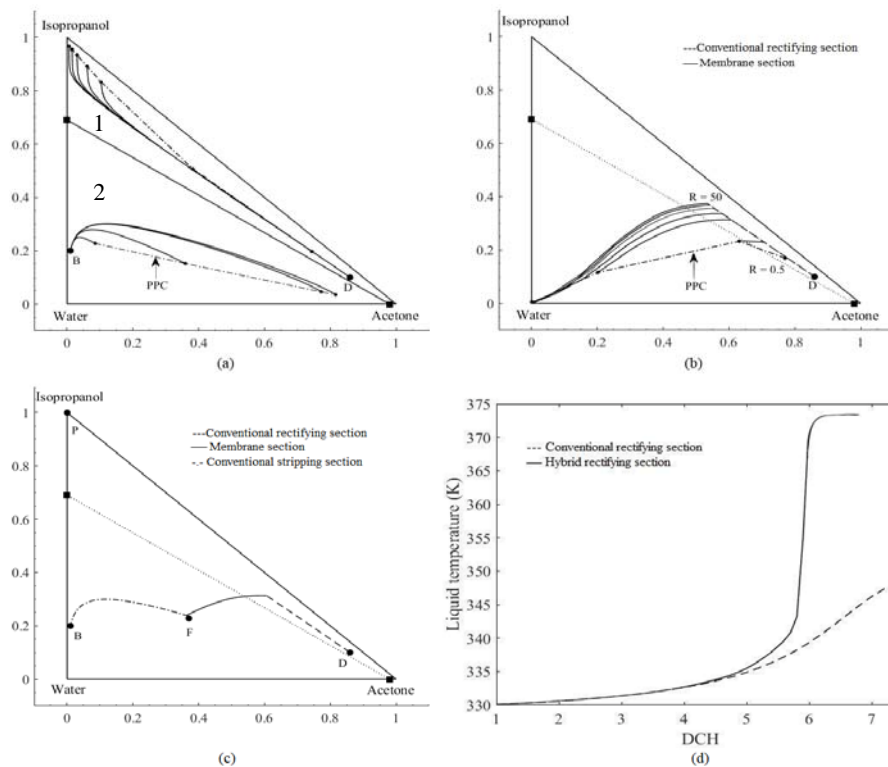
Figure 1: (a) Operation leaves (OLs) for a conventional distillation, (b) OL for a hybrid rectifying section, (c) Composition profile of a DPSU and (d) Temperature profile of liquid inside the hybrid rectifying section.

3.2 Ethyl acetate (EA)-ethanol (E)-methanol (M) mixture

In Figure 2a, the topological diagram for conventional rectifying and stripping sections is presented and two regions can be identified. A feasible separation by distillation cannot be achieved with D located in region 2 and B in region 1. Three (3) nodes can be observed, the binary ethyl acetate-methanol azeotrope is the UN for both regions, the pure ethanol vertex ($x_E = 1$) and the pure ethyl acetate vertex ($x_{EA} = 1$) are the SN for regions 1 and 2, respectively. The ascendant volatility order is E > EA > M for region 1 and EA > E >M for region 2. The maximum methanol composition at the top of the stripping section (region 1) correspond to the binary EA-M azeotrope. It is possible to produce a distillate with a higher ethanol composition if a rectifying section is located inside region 1, considering that for rectifying section the saddle point is located in $x_M = 1$ (not shown).

Figure 2b shows the operation leaves of two hybrid DPSU stripping sections with a methanol-selective membrane with two bottom compositions located in different regions. It is observed that the trajectories generated by the two hybrid stripping sections cannot reach a pure component vertex, no pinch point corresponds to any node identified in Fig.2a. Because methanol is removed by pervaporation the DPSU trajectories tend to move away from the methanol vertex, so the trajectories generated by a hybrid striping section in region 1 are able to overcome the distillation boundary. However, for region 2 these trajectories do not cross the boundary.

Unlike to the DPSU column for the separation of A-I-W mixture where an operation leaf covers an important area of the composition space (Fig. 1b), the corresponding operation leaf for a hybrid stripping section in the EA-E-M covers a smaller area and so the chances of having a feasible separation, with products in both regions, is reduced. In a conventional process the distillation trajectories move from point B increasing the EA concentration reaching a maximum after which the EA concentration decreases (region 1 in Fig. 2a). However, Figure 2b shows that, in a DPSU due to the methanol removal by pervaporation, the EA concentration is not reduced and thus, such a maximum in EA concentration is not reached for DPSU trajectories that move away from B in Region 1. This also means that the separation mechanisms of distillation and pervaporation are not complementary for a methanol selective membrane, in contrast with the A-I-W case study, and on the contrary they counteract each other.

DPSU separation can be limited by the change of the volatility order between regions close to the distillation boundary, based on the product location (B) of the hybrid section. Although in this case study some thermodynamic limitation remains for the DPSU system, it is possible to obtain a feasible separation with

product compositions located in different regions. For a feasible separation, D must be located close to EA-E azeotrope in region 2 and B located in region 1 as shown by Figure 2c. In case of B located in region 2, it is not possible to achieve a feasible separation with product composition located in different regions.

Also, in a hybrid stripping section, the liquid temperature is modified in comparison to the conventional stripping section in distillation with the corresponding profiles shown in Figure 2d. Since methanol is recovered by pervaporation, the ethyl acetate and ethanol compositions are higher than in a conventional stripping section and so the bubble temperatures. Besides, the liquid temperature along the MS is almost constant due to the main composition change is related to ethyl acetate and ethanol and their boiling temperatures are similar ($T_{b,EA}$ = 350. 1 K and $T_{b,E}$ = 351.3 K at 1.0325 bar). The results and analysis shown in this section only apply for a methanol selective membrane for this particular mixture using hybrid stripping sections in a DPSU and thus an important amount of possibilities arise.
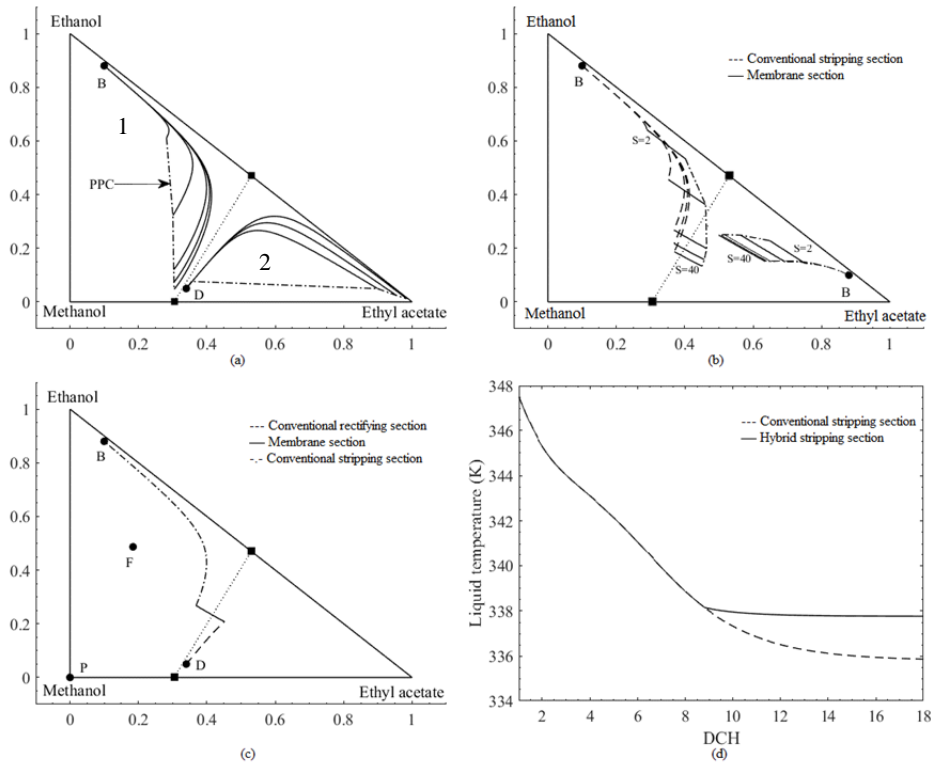

Figure 2: (a) OLs for a conventional distillation, (b) OL for a hybrid stripping section, (c) Composition profiles for a DPSU column and (d) Temperature profile of liquid inside the hybrid rectifying section.

4. Conclusions

In this work, a simplified model developed as an analytical tool to predict the behavior of a DPSU column is presented. This analytical tool is able to identify operating conditions where a DPSU column can overcome distillation boundaries or azeotropic limitations. But also, it is able to predict new limitations that arise of the DPSU process due to the simultaneous interaction between pervaporation and distillation.

For a topology type 1.0-2, the volatility order between the regions do not affect the DPSU trajectory to achieve a stable node. For a more complex topology (2.0-2b), the distillation and pervaporation mechanisms counteract and to find feasible separation with products in both regions is more elusive.

For a topology type 1.0-2 is recommended to remove the heaviest component in the region to overcome the distillation boundary, using a hybrid rectifying section. In a topology type 2.0-2b is recommended to consider the thermodynamic influence, such the volatility order between regions. The lightest component must be removed using a hybrid stripping section in the region with a stable node with the highest temperature, otherwise the distillation boundary cannot be overcome.

In a DPSU, pervaporation modifies the temperature profile inside the hybrid section, which it could be used to separate thermosensitive components. However, the effect of this temperature profiles on the energy requirements of a DPSU is not well known.

Nomenclature

f	Fugacity [bar]	S_{Ex}	External boil-up ratio
h'	Dimensionless height	x	Molar fraction of liquid
p	Pressure [bar]	x_P	Molar fraction of permeate
$\overline{R}_n$	Internal transformed reflux ratio	X	Transformed molar fraction of liquid
$\overline{R}_{Ex}$	External transformed reflux ratio	y	Molar fraction of vapor
R_{Ex}	External reflux ratio	Y	Transformed molar fraction of vapor
$\overline{S}_n$	Internal transformed boil-up ratio		

Greek symbols

α	Selectivity

Subscript

i	Independent component i	R	Rectifying section
k	Reference component	S	Stripping section
o	Initial point in the membrane section located in a stripping section	T	Initial point in the membrane section located in a rectifying section

Superscript

P	Permeate side

Abbreviation

DCH	Dimensionless column height	MBT	Mass balance triangle
DPHS	Distillation-pervaporation hybrid system	MS	Membrane section
DPSU	Distillation-pervaporation in a single unit	PPC	Pinch Point Curve

References

Baker, R. W. (3rd), 2012, Membrane Technology and Applications, Wiley, Hoboken, USA.

Barbosa, D., Doherty, M. F., 1988, Design and minimum-reflux calculations for single-feed multicomponent reactive distillation columns, Chemical Engineering Science, 43(7), 1523-1537.

Fontalvo, J., Keurentjes, J., 2015, A hybrid distillation-pervaporation system in a single unit for breaking distillation boundaries in multicomponent mixtures, Chemical Engineering Research and Design, Issue 99, 158-164.

Fontalvo, J., Keurentjes, J. T. F., Wijers, J. G., Vorstman, M. A. G., 2007, Pervaporation process and apparatus for carrying out same, Patente nº EP1762295A1, Netherlands.

Fontalvo, J., Vortsman, M. A., Wijers, J. G., Keurentjes, J. T., 2006, Separation of organic-water mixtures by co-current vapor liquid pervaporation with transverse hollow-fiber membranes, Industrial & Engineering Chemistry Research, 6(45), 2002-2007.

Haelssig, J. B., Tremblay, A. Y., Thibault, J., 2012, A new hybrid membrane separation process for enhanced ethanol recovery: Process description and numerical studies, Chemical Engineering Science, 1(68), 492-505.

Nagy, E., 2010, Coupled effect of the membrane properties and concentration polarization in pervaporation: Unified mass transport model, Separation and Purification Technology, 2(73), 194-210.

Skiborowski, M., Harwardt, A., Marquardt, W., 2013, Conceptual design of distillation-based hybrid separation process, Annual Review of Chemical and Biomolecular Engineering, 1(4), 45-68.

Thong, D. Y., Jobson, M., 2001, Multicomponent homogenous azeotropic distillation 1: Assesing product feasibilty, Chemical Engineering Science, 14(56), 4369-4391.

Ung, S., Doherty, M. F., 1995, Vapor-liquid phase equilibrium in systems with multiple chemical reactions. Chemical Engineering Science, Issue 50, 23-48.