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# OPTIMIZATION OF THE OPERATING CONDITIONS OF AZEOTROPIC DISTILLATION COLUMNS WITH PERVAPORATION MEMBRANES

P.M. HOCH, M.C. DAVIOU, A.M. ELICECHE

*Planta Piloto de Ingenieria Quimica - PLAPIQUI (UNS-CONICET)*
*Camino La Carrindanga km 7 - 8000 Bahía Blanca - Argentina*
*e-mail: phoch@plapiqui.edu.ar*

***Abstract*— The main objective of this work is the optimization of the operating conditions of azeotropic distillation columns in hybrid distillation/pervaporation systems. In the configuration analyzed, a liquid side stream extracted from the azeotropic distillation column with the distributing non-key component is treated in a pervaporation membrane while the retentate is recycled to the column. The pervaporation membrane separates the pure distributing non-key component from the mixture, thus helping to improve the purity in the top and/or bottom products of the distillation column. The case study shows the hybrid process of a distillation column combined with pervaporation membranes, compared to the classical two-column process for Methyl tert-Butyl Ether production. In both cases, the operating conditions of the distillation columns such as reflux ratio, product and side draw flowrates are selected optimally. The numerical results show a significant reduction in operating cost obtained by using a pervaporation membrane instead of the second column in the original process.**

***Keywords*— Azeotropic distillation, Pervaporation, Optimization, MTBE**

## I. INTRODUCTION

Hybrid membrane systems can be successfully applied to debottlenecking and azeotrope breaking problems. Pervaporation is an interesting membrane separation alternative, because it is generally less energy consuming than distillation. It is not influenced by the equilibrium between components, making azeotrope breaking easier than using a sequence of distillation columns. The separation is based on a selective transport through a dense layer associated with the evaporation of the permeants. This phase changing is usually obtained by lowering the partial pressure of the permeants at the downstream side of the membranes to vacuum pressure.

Recent patents propose hybrid distillation/pervaporation technologies for azeotrope breaking processes involving the separation of alcohols and ethers (Chen *et al.*, 1988, Chen *et al.*, 1989) applied to the MTBE process, replacing the Hüls process. The pervaporation membrane used shows high flux and high selectivity to the permeation of methanol, effectively breaking the azeotrope methanol-MTBE. The process called "Total Recovery Improvement for MTBE" or TRIM™ is a combination of an organophilic pervaporation membrane and distillation, using two different layouts. The integration of the TRIM™ process to an existing one would be attractive if the production could be increased by 5%.

Lipnizki *et al.* (1999) presented an extensive review of pervaporation-based hybrid processes, focusing on industrial applications and pointing out the need of optimization of some of the processes analyzed. One of the fields where there is need of optimization is the distillation/pervaporation hybrid process.

Hömmerich and Rautenbach (1998) studied the integration of pervaporation and vapor permeation into the Hüls process, analyzing the influence of the operating conditions in a hybrid distillation-pervaporation-vapor permeation system for the Methyl tert-Butyl Ether (MTBE) production.

González and Ortiz (2001a) carried out experimental work to find the parameters for modeling the pervaporation membrane to separate methanol and MTBE, and an approach to define a hybrid process distillation/pervaporation based on the Hüls process. González and Ortiz (2001b) simulated the hybrid distillation/pervaporation process using gPROMS (PSEnterprises, 2000). Different operating conditions were explored by simulation performing a cost analysis.

However, the formal optimization of the debutanizer column with a pervaporation membrane to treat the side stream has not been attempted previously. In this work, the optimum operating conditions such as reflux ratio and product flow rates are calculated solving an optimization problem to minimize the operating cost.

## II. HYBRID DISTILLATION/PERVAPORATION PROCESS

This work was motivated by the possibility of revamping the Methyl tert-butyl ether (MTBE) sector of a refinery. The production process of Methyl tert-butyl ether (Figure 1), which is used as a high octane fuel additive, consists of a reaction sector where i-$C_4H_{10}$ is combined with methanol to form the ether, and a separation sector where all the MTBE must be separated from non-reacted methanol and $C_4$s. Non-reacted methanol forms azeotropic mixtures with MTBE and butanes. A sequence of azeotropic distillation columns is used to break the azeotropes, thus recovering MTBE as the final product and methanol to be recycled to the reactor. A hybrid distillation-pervaporation process, as shown in Figure 2, seems to be an attractive alternative, as it combines the advantages of both methods. The use of hybrid systems can improve the cost of the traditional Hüls separation sequence (Hömmerich and Rautenbach, 1998).

Different configurations for the hybrid distillation/pervaporation process can be used, locating the pervaporation membrane to treat the feed, products or side stream. In this work, the pervaporation membrane is located to treat the side stream and remove the distributing component as permeate, thus helping to improve the top and bottom purity.

### A. Pervaporation membrane modeling

A scheme of the pervaporation membrane is shown in Figure 3. It is assumed that only two components permeate through the membrane, while the rest of the components remain at the retentate side and do not permeate.

The equation system representing mass and energy transport for a binary mixture can be found in González and Ortiz (2001a). The system methanol-MTBE was used to test the model. The membrane used favored the permeation of methanol over MTBE. Experimental data were available for the system being studied.

It was assumed that the feed to the membrane is a pseudo-binary mixture of methanol-MTBE calculated as the composition of the multi-component mixture in $C_4$s-free basis. As it is assumed that $C_4$s do not permeate, a simple split of the $C_4$s is performed before entering the pervaporation unit and the $C_4$s are mixed with the retentate stream once it leaves the membrane module to be recycled to the column. This simplification allows to pose the differential algebraic system as if it was for a binary mixture, then the calculation of the compositions of the retentate and permeate streams is simpler than for a multi-component mixture. This assumption holds for the system being studied, as shown in Chen *et al.* (1988, 1989). Mass and energy transport equations are solved. A mathematical model based on the generalized Fick´s law and the assumption that transport through the membrane is the rate-limiting step was developed in order to describe the pervaporation flux of both components (González and Ortiz, 2001a). The prediction of the flux of methanol needed a concentration-dependent diffusion coefficient whereas a simple model with concentration-independent diffusivity was sufficient for the description of the MTBE flux.

The energy requirements to perform the pervaporation and condense the permeate are calculated as the interstage heating between modules and the cooling needed for condensation. The pervaporation membrane can be modeled in terms of a differential/algebraic system involving lumped and distributed parameters. This allows the discretization of the differential equations along the membrane thickness ($z_P$) and the use of a package to solve Initial Value Problems (IVPs) to integrate the equations along the membrane length $z_A$ (Fig. 3).

The rigorous model gives as a result the dimensions of the membrane needed to perform the separation. This is necessary in order to calculate the membrane replacement costs, as shown in Appendix A. The membrane has a lifetime of two years, and because of the short replacement cycle this cost was considered an operating cost.

## III. SELECTION OF THE OPERATING CONDITIONS IN THE SEPARATION OF MTBE FROM A MIXTURE OF BUTANES AND METHANOL.

The example deals with the separation of a mixture of i-butane, n-butane, i-butene, 1-butene, 2-butene trans and 2-butene cis, methanol and MTBE. The separation can be performed either using the two-column approach (Separation sector of Fig. 1) or replacing the second column (Methanol-MTBE separation) with a pervaporation membrane (Fig. 2).

The composition, temperature and pressure of the fresh feed are shown in Table 1, where $C_4$'s stands for a mixture of i-butane, n-butane, i-butene, 1-butene, 2-butene trans and 2-butene cis.

**Table 1**: Feed to the debutanizer column

| | |
|---|---|
| F1 [kgmol/h] | **513.8** |
| $C_4$'s [kgmol/h] | 325.8 |
| Methanol [kgmol/h] | 33.0 |
| MTBE [kgmol/h] | 155.0 |
| Temperature [K] | 334.3 |
| Pressure [bar] | 6.8 |

For the separation of MTBE, the classical two-column process and the hybrid process were studied, in order to be able to compare the operating costs of each one and to quantify the savings that can be obtained by replacing the second column of the conventional process with a pervaporation membrane.

The optimization problem is formulated as:

$$\begin{aligned} &\min_{x} C_{oper}(x) \\ &\text{s.t. } g(x) \le 0 \qquad \text{(P1)} \\ &b^L \le x \le b^U \end{aligned}$$

where the optimization variables x are the reflux ratios (r) and product flow rates (B) of each column in the two-column scheme, or the reflux ratio (r), product flow rate (B) and the side draw flow rate (E) of the distillation column for the hybrid process. $b^L$ and $b^U$ are lower and upper bounds on the optimization variables x.

g(x) are constraints on required product compositions and recovery. The maximum rate of liquid sidedraw was considered an additional constraint for the hybrid process (Hömmerich and Rautenbach, 1998) to avoid column entrainment.

## IV. NUMERICAL RESULTS

### A. Two-column scheme:

The separation of pure MTBE as a bottom product of an azeotropic distillation column from a mixture of $C_4$s, methanol and MTBE is performed by means of two distillation columns.

The process being studied is shown in Figure 1.

The azeotrope formation of methanol with both MTBE and $C_4$ limits the purity of the products. The azeotrope $C_4$-Methanol is obtained as top product in the debutanizer column, while the bottom product consisting mainly of methanol and MTBE in azeotropic composition at 6 bar is fed to a second column in order to obtain high-purity MTBE. This second column must operate at a higher pressure (12 bar) in order to be able to obtain pure MTBE as the bottom product. The process requires a composition of MTBE of 98 %w and 95% recovery.

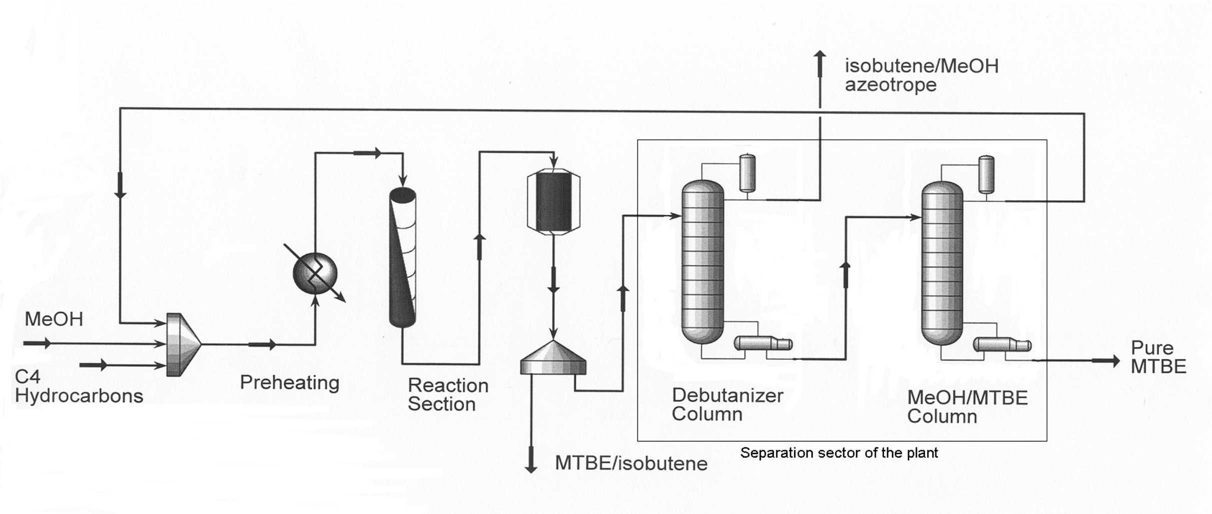

**Figure 1**: MTBE process with two-column configuration separation sector.

An optimization of this process was performed using Hysys. The "Mixed" optimization option was used, which begins the iterations with Box method with loose tolerance, and once the solution is conveniently bounded, uses an SQP method to find the solution within the desired tolerance.

Two rigorous distillation columns were used, using for both the azeotropic option in Hysys. Wilson equation with binary interaction coefficients taken from Espinosa *et al.* (1995) was used for the thermodynamic property prediction.

**Table 2**: Optimization results for the two-column scheme.

| | *Initial Point* | *Optimal Point* | *Lower Bound* | *Upper Bound* |
|---|---|---|---|---|
| ***Debutanizer Column*** | | | | |
| Reflux Ratio | 1.20 | 0.9441 | 0.90 | 1.22 |
| Bottom flow rate [kgmol/h] | 188.0 | 178.9 | 160 | 195 |
| $x_{MTBE, D}$ | $1.8\ 10^{-6}$ | 0.00198 | | 0.002 |
| Cost [$/h] | 139.3 | **130.4** | | |
| ***MeOH-MTBE Column*** | | | | |
| Reflux Ratio | 4.0 | 3.604 | 2.5 | 4.5 |
| Bottom flow rate [kgmol/h] | 155.9 | 155.5 | 155. | 160. |
| $x_{MTBE, B}$ | 98.02 | 98.02 | | |
| Cost [$/h] | 60.36 | **43.3** | | |
| MTBE Recovery [%] | 95.325 | 95.043 | 95.00 | |
| **Total Operating Cost [$/h]** | 199.66 | **173.70** | | |

The objective is to minimize the operating cost of both columns. Cooling water is used to condense the distillate of the columns. Low pressure steam is used to heat the bottoms of the debutanizer column, and medium pressure steam is used to heat the bottoms of the methanol-MTBE column. Details of the cost function are given in Appendix A. The bottom flow rate and reflux ratio of each column were posed as optimization variables. The debutanizer column has 22 theoretical stages plus condenser and reboiler, and the feed is introduced at stage 10. The methanol-MTBE column has 30 stages plus condenser and reboiler, and the feed is introduced at stage 20. The optimization results are shown in Table 2. There is a cost reduction of 13% comparing the initial point with the optimum point given by Hysys.

### B. Hybrid distillation/pervaporation system:

The separation of pure MTBE as a bottom product of an azeotropic distillation column from a mixture of $C_4$s, methanol and MTBE is performed by means of a combined distillation column and pervaporation membrane process. The process being studied is shown in Figure 2.

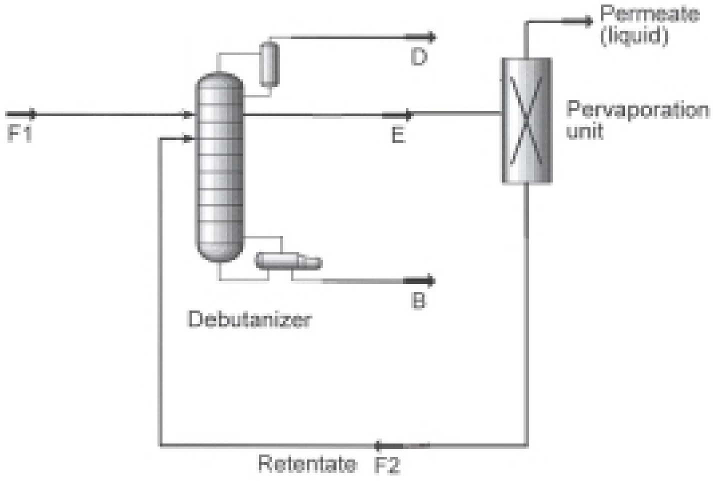

**Figure 2**: Schematic flowsheet for the distillation/pervaporation process.

The azeotrope formation of methanol with both MTBE and $C_4$ limits the purity of the products. A high purity of MTBE is required in the bottom product (B) of the column that separates a multicomponent mixture (F1) including MTBE, $C_4$'s and methanol. A sidestream (E) of the column, rich in methanol, is processed through the membrane. The membrane selectivity allows the methanol in the column sidestream to be permeated and then condensed and recycled to the reactor (Permeate liquid stream), thus helping to improve the MTBE bottom product purity. The retentate, consisting of a mixture of $C_4$ and MTBE with a lower composition of methanol, is then recycled to the column (F2).

The pervaporation takes place when a vacuum of 15 torr is maintained at the permeate side. For the start-up a vacuum pump is needed; but, when steady state is reached, vacuum is maintained by the permeate condensation as shown in Fig. 3.

The process was also simulated with the commercial package Hysys with the azeotropic distillation option. The distillation column has 22 theoretical stages plus a reboiler and a condenser. The objective function is the operating cost of the process. It is assumed that cooling water is used to condense the distillate of the column and low pressure steam is used to heat the bottoms of the column. A refrigerant is needed to maintain the vacuum at the permeate side by condensation.

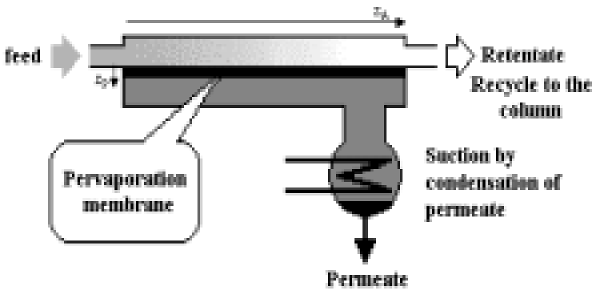

**Figure 3**: Scheme of the pervaporation membrane

The cost is a function of the heat withdrew from the condenser of the column, the heat added to the reboiler of the column, the interstage heating between pervaporation modules and the heat withdrew in the pervaporation unit to condense the methanol. Details of the cost functions are given in Appendix A.

For this configuration, the Hysys selected optimization option was also the Mixed method. The desired MTBE weight composition and MTBE recovery in the bottom product are the same as in the two-column process. The optimization results are shown in Table 3. A significant reduction in the operating cost of 19 % can be observed from the initial to the solution point, showing the importance of optimization with rigorous simulation in hybrid distillation/pervaporation processes.

**Table 3**: Optimization results for the hybrid process.

| | *Initial Point* | *Optimal Point* | *Lower Bound* | *Upper Bound* |
|---|---|---|---|---|
| ***Debutanizer Column*** | | | | |
| Reflux Ratio | 1.20 | 0.6746 | 0.65 | 1.40 |
| Side draw flow rate [kgmol/h] | 76.36 | 65.00 | 25.0 | 85.0 |
| Bottom flow rate [kgmol/h] | 162.33 | 155.4 | | |
| E/liq (%) | 26.27 | 41.00 | | 41.00 |
| $x_{MTBE, B}$ | 98.02 | 98.02 | | |
| Distillation Cost [$/h] | 144.0 | **121.4** | | |
| ***PV Modules*** | | | | |
| Number of modules (30 $m^2$ each) | 23 | 12 | | |
| PV Process Cost [$/h] | 18.4 | **10.2** | | |
| MTBE Recovery [%] | 99.22 | 95.00 | 95.00 | |
| **Total Operating Cost [$/h]** | 162.4 | **131.6** | | |

A significant cost reduction of 24 % is achieved by changing from the two-column scheme to the hybrid process, optimizing the operating variables of the debutanizer column. Side stream E is withdrew from the plate were the liquid composition of methanol reaches its maximum value.

For the hybrid distillation/pervaporation process, it was also possible to obtain a bottom product with an MTBE recovery of 98 %, which was not possible to obtain with the two-column scheme. The cost of the hybrid system with an MTBE recovery of 98% is 131.6 $/h, which is also cheaper than the operating cost of the two-column process.

There are important decisions to be made regarding the location of the fresh feed, side stream and recycle of the retentate stream. The systematic selection of the number of plates requires the incorporation of integer optimization variables. The procedure developed by Hoch and Eliceche (1991) treats the number of stages as continuous optimization variables, allowing the simultaneous selection of feed and side stream locations with the flowrates in a nonlinear programming problem formulation. The implementation of this option at the conceptual design stage is currently being studied.

## V. CONCLUSIONS

Optimization results are reported for the conventional process and the hybrid configuration for MTBE production. An important reduction in the operating cost of the separation process to obtain pure MTBE with the distillation/pervaporation process has been achieved. Significant improvements are obtained by optimizing the operating conditions of the debutanizer column, as shown in Table 3. Similar results can be expected in new applications of hybrid distillation/pervaporation systems. Future work on this process contemplates the inclusion of the number of stages of the column as optimization variables at the conceptual design stage, expecting even greater savings than considering the operating variables alone.

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## APPENDIX A: OPERATING COST EVALUATION

### Distillation column cost

The operating cost of the column *i* is calculated as the sum of the operating costs for the condenser and reboiler:

$$C_{oper,column,i} = C_{c,i} + C_{r,i} \qquad (A.1)$$

where

$$C_{c,i} = C_{o,c}.Q_{cond,i} \qquad (A.2)$$

is the operating cost of the condenser, and

$$C_{r,i} = C_{o,r}.Q_{reb,i} \qquad (A.3)$$

is the operating cost of the reboiler.

Low pressure steam is used to heat the bottoms of the debutanizer column for both the conventional and hybrid process; while medium pressure steam is required to heat the bottoms of the second column. Cooling water is used for the condensers of both columns.

**Pervaporation cost:**

The operating cost of the pervaporation process can be expressed as a sum of the interstage heating cost, the condensing cost and the membrane replacement cost:

$$C_{oper,PV} = C_{heat} + C_{refrig} + C_{memb} \qquad (A.4)$$

where

$$C_{ref} = C_{o,ref} Q_{ref} \qquad (A.\ 5)$$

$$C_{heat} = \sum_{k=1}^{n} C_{o,k} Q_k \qquad (A.\ 6)$$

$$C_m = n\ C_{m,r}\ a/8000 \qquad (A.\ 7)$$

(A.5) represents the cost of condensing to maintain vacuum at the permeate side. A refrigerant is needed because of the low temperature required.

(A.6) is used to find the interstage heating cost.

(A.7) allows to calculate the membrane replacement cost. n represents the number of pervaporation modules; $C_{m,r}$, the replacement cost of each module and a the annuity, calculated considering a lifetime of two years and an inflation rate of 10% a year. It was considered that the process operates 8000 h/year.

Cost coefficients for both processes can be found in Seider *et al.* (1999).

**Objective function:**

For the conventional two-column scheme, the operating cost is obtained as

$$C_{oper} = C_{oper,column,1} + C_{oper,column,2} \qquad (A.8)$$

For the hybrid process,

$$C_{oper} = C_{oper,column,1} + C_{oper,PV} \qquad (A.9)$$

## LIST OF SYMBOLS

| | |
|---|---|
| a | Annuity (1/year) |
| B | Bottom flow rate, [kgmol/h] |
| $C_{c,i}$ | Operating cost of the condenser of column i[$/h] |
| $C_{heat}$ | Membrane interstage heating cost [$/h] |
| $C_{m,r}$ | Cost of each membrane for replacement [$] |
| $C_{memb}$ | Membrane replacement cost [$/h] |
| $C_{o,c}$ | Condenser cost coefficient [$/kJ] |
| $C_{o,i}$ | Interstage heating cost coefficient [$/kJ] |
| $C_{o,r}$ | Reboiler cost coefficient [$/kJ] |
| $C_{o,ref}$ | Membrane condensing cost coefficient [$/kJ] |
| $C_{oper}$ | Operating cost [$/h] |
| $C_{oper,\ column\ i}$ | Operating cost of column i [$/h] |
| $C_{oper,PV}$ | Operating cost of the pervaporation process [$/h] |
| $C_{r,i}$ | Operating cost of the reboiler of column i [$/h] |
| $C_{ref}$ | Membrane condensing cost [$/h] |
| D | Distillate flow rate [kgmol/h] |
| E | Sidestream [kgmol/h] |
| $F_1$ | Fresh feed flow rate [kgmol/h] |
| $F_2$ | Retentate flow rate [kgmol/h] |
| n | Number of pervaporation modules |
| $Q_{cond}$ | Condenser cooling requirement [kJ/h] |
| $Q_k$ | Membrane interstage heating requirement [kJ/h] |
| $Q_{reb}$ | Reboiler heating requirement [kJ/h] |
| $Q_{ref}$ | Refrigerantr cooling requirement [kJ/h] |
| $x_{MTBE,B}$ | Liquid mass composition of MTBE in the bottom product |
| $x_{MTBE,D}$ | Liquid mass composition of MTBE in the distillate |

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