

## PRESSURE OPTIMISATION OF AN ORIGINAL SYSTEM OF PRESSURE SWING WITH A REACTIVE COLUMN

J Bonet<sup>1,2</sup>, MI Galan<sup>1</sup>, J Costa<sup>1</sup>, R Thery<sup>2</sup>, X Meyer<sup>2</sup>, M Meyer<sup>2</sup>, JM Reneaume<sup>3</sup>

<sup>1</sup>Univ. de Barcelona, Dep. d'Enginyeria Quimica i Metallurgia, Marti i Franques 1, E-08028 Barcelona, Spain, E-mail: galan@angel.qui.ub.es

<sup>2</sup>Laboratoire de Génie Chimique, UMR-CNRS 5503, INPT-ENSIACET, 5 rue Paulin Talabot, 31106 Toulouse Cedex 01, France, E-mail: xuan.meyer@ensiacet.fr, michel.meyer@ensiacet.fr

<sup>3</sup>UPPA/LATEP rue J Ferry 64000 PAU France, E-mail: jean-michel.reneaume@univ-pau.fr

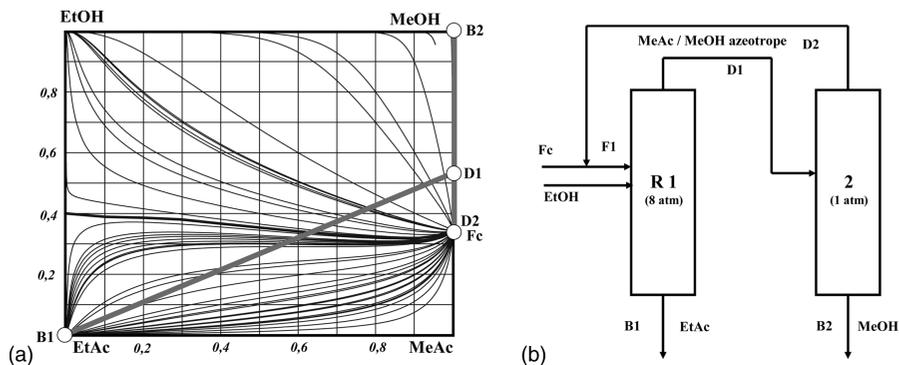
Different processes can be considered to separate multicomponent mixtures involving azeotropes. Among them, the pressure swing distillation is particularly interesting when the azeotropic composition is very pressure sensitive. The main advantage of this process is that the separation is performed without any extractive agent or entrainer. The main difficulty at the design step is to find reasonable pressures for both columns. The influence of these parameters on the minimal recirculation flow, the minimum number of stages, and the minimal reflux is presented here. The pressure is analysed from an economical point of view and an optimal pressure region is found. The transesterification of methyl acetate (MeAc) with ethanol (EtOH) to produce ethyl acetate (EtAc) and methanol (MeOH) is presented as an illustrative example.

**KEYWORDS:** reactive distillation, pressure sensitive distillation, methyl acetate transesterification

### INTRODUCTION

Pressure swing distillation is one way to perform the separation of multicomponent mixtures involving azeotropes. This process can be considered when the azeotropic composition vary at least of 5% (preferably 10% or more) over a moderate pressure range (not more than ten atmospheres between the two pressures) (Perry, 1997). In consequence, if the first column pressure of 10 atm and the second column pressure of 1 atm fulfil the 5% minimal variation, then these pressure values are used without further considerations until the final rigorous economical optimization. Now, reasonable pressures should be fixed at the design step, as it is done for the reflux, instead of choosing them arbitrarily and let them be optimised later on.

The transesterification of methyl acetate (MeAc) with ethanol (EtOH) to produce ethyl acetate (EtAc) and methanol (MeOH) is presented for illustrative proposals (España, 1996). The pressure swing reactive distillation opens a way to revalorize the methanol/methyl acetate azeotropic mixture produced as a residual stream in the polyvinyl alcohol industry. The ethyl acetate (EtAc) is a high value product and the methanol is a raw material for the polyvinyl alcohol industry and can be recycled in the process. The residue curve map of the system presents a boundary line (Figure 1a). The reaction takes place in a first column under high pressure. Pure ethyl acetate (EtAc) is collected at the first



**Figure 1.** Studied transesterification system: (a) reactive residue curve map; (b) process flowsheet

column bottom. The methanol/methyl acetate azeotropic composition is collected at the distillates. The methanol/methyl acetate azeotropic composition is richer in methanol (MeOH) at high pressure than at low pressure. The methanol (MeOH) quantity corresponding to the difference between the high and the low pressure azeotrope composition is collected at the second column bottom (Figure 1b).

The reactive distillation is contributing to the on going process intensification involving cost reduction (Kaymak et al., 2004). The proposed innovating process consisting in combining a reactive distillation column inside a pressure swing distillation system will generate new opportunities of product synthesis by breaking reactive and non-reactive azeotropes at the same time.

## METHODOLOGY

A fast to rigorous calculation model is used (Thery, 2002). The infinite/infinite analysis is used at the analysis step (Ulrich, 2002). The stream flow rates are calculated from the azeotropic compositions given by each pressure. The assumptions are infinite number of stages, infinite reflux, pure products at the bottoms and azeotropic composition at the distillates. A modified boundary value method is used at the synthesis step with a stage by stage calculation from the feed plate location to the distillate and bottom. Some assumptions are used: constant flow rates, chemical equilibrium, fed at the stage with the same composition than the feed. The other input data come from the analysis step: distillate and bottom flow rates and compositions. The stage by stage calculation is stopped when the last calculated stage reaches a fixed desired purity. For each pressure, several reflux values are tested and the number of stages to get the desired purity is obtained for each reflux. The reflux ( $r$ ) and number of stages ( $N$ ) are related by the equation 1.

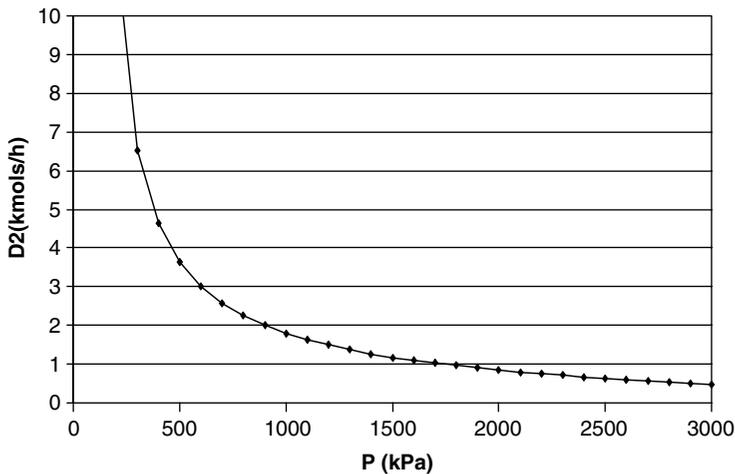
The adjustment of the equation 1 parameters gives the minimal reflux ( $r_{\min}$ ) and the minimal number of stages ( $N_{\min}$ ) at the stripping and rectifying sections for each pressure. The overall minimum reflux corresponds to the highest minimum reflux of both sections and the overall minimum number of stages corresponds to the sum of the minimum number of stages for each section.

$$N = N^s + N^r = N_{\min}^s \cdot \left( \frac{1}{r - r_{\min}^s} + 1 \right) + N_{\min}^r \cdot \left( \frac{1}{r - r_{\min}^r} + 1 \right) \quad (1)$$

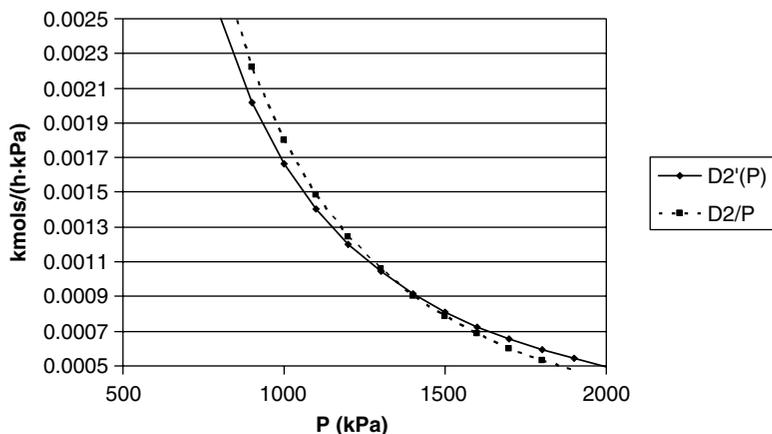
### INFINITE/INFINITE ANALYSIS

The pressure of the second column is fixed to atmospheric pressure because a diminution of the pressure leads to expensive condenser fluids. When the second column operates at ambient pressure, then the vacuum pump is avoided. The pressure studied in the next sections is the first column pressure. The column bottoms are fixed to pure components and the distillates at the azeotropic compositions. From one stream flow rate value, all the stream flow rates are calculated by mass balances. The distillate azeotropic composition depends on the pressure and for each pressure, the minimal second column distillate flow rate is represented on Figure 3 (calculations based on 1 kmol/h crude feed). A pressure increase reduces the recirculation flow rate from the second column distillate.

At low pressures, a small increase of pressure leads to great recirculation diminution but, at high pressures, the diminution is not significant. A marginal calculation indicates



**Figure 2.** First column pressure influence on the recirculation flow rate



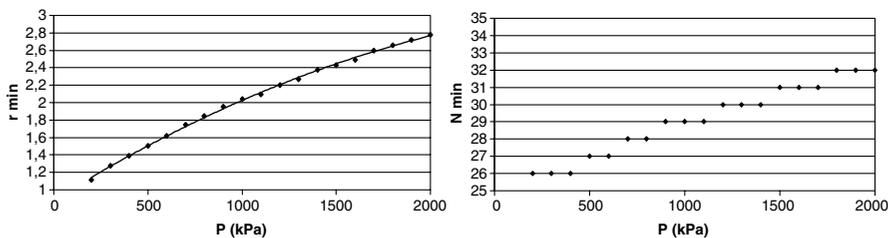
**Figure 3.** Marginal analyse for the recirculation flow rate

that pressures above 1300 kPa are not suitable to diminish the recirculation flow rate (Figure 3).

### BOUNDARY VALUE METHOD

A modified Boundary Value Method performing the calculation from the feed stage to the column distillate and bottom is used. The purities considered are: EtAc 99% and MeOH 99.9%. The minimum reflux and minimum number of stages for the first reactive column are determined for each pressure (Figure 4). The minimum number of stages is a discontinuous function which will introduce local minima to the cost function.

The second column recovers the MeOH from the first column distillate near the azeotropic composition. The second column can be approximated to a binary distillation of MeOH and MeAc and can be solved by the McCabe-Thiele method. The minimum



**Figure 4.** Boundary value method results for the first column

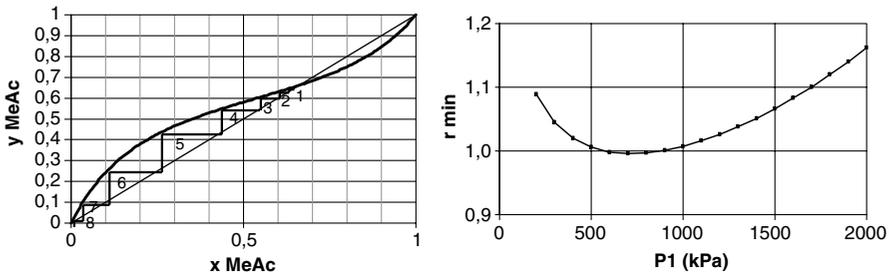


Figure 5. McCabe-Thiele method results for the second column

number of stages is eight at atmospheric pressure. The feed to the second column is the distillate of the first column and the minimum reflux of the second column changes accordingly (Figure 5).

### COST FUNCTION

The cost function ( $C$ ) is considered as the sum of the operating cost ( $C_0$ ) and the investment cost ( $C_i$ ) (equation 2).

$$C = C_0 + C_i \quad (2)$$

The operating cost ( $C_0$ ) for a distillation column is related mainly to the energy consumption. The reboiler heat duty cost and the condenser heat duty cost depend on the available kind and quality of the services, but as a first approximation both costs are considered constants (equation 3). With the McCabe-the assumptions that the vapour flow rate is constant along the column,  $C_0$  is obtained by equation 3.

$$C_0 = K_1 \cdot D \cdot (r + 1) \quad (3)$$

The investment cost ( $C_i$ ) involves the cost of the columns, piping and all the items around it. A detailed calculation is very time consuming and a lot of information is necessary that changes with the place and the time. A rough estimation is performed using graphics of cost versus type and dimensions of the main apparatuses. The result is increased by a first factor to take into account the piping and other secondary items, a second factor is used to take into account the unexpected costs and a third factor is necessary to actualize the cost from the calculation year to nowadays. The investment cost calculations can be invalidated by any change, as it had happened the December 2003 by an unexpected increase of the steel cost. To avoid the variability of the investment cost, a simplifying hypothesis is introduced, considering that the investment cost is

proportional to the weight of the distillation column. Under these assumptions, it can be proved that  $C_i$  can be expressed by equation 4

$$C_i = K_5 \cdot P \cdot N \cdot D \cdot (r + 1) \quad (4)$$

The overall cost ( $C$ ) is composed by the operating cost ( $C_0$ ), which are proportional to the energy consumption, and by the investment cost ( $C_i$ ), which are proportional to the material consumption (equation 5).

$$C = C_0 + C_i = (K_1 \cdot D \cdot (r + 1))(K_5 \cdot P \cdot N \cdot D \cdot (r + 1)) \quad (5)$$

The constants ( $K_1$  and  $K_5$ ) are unknown and the overall cost value becomes unknown, but a cost function ( $C_f$ ) proportional to the cost ( $C$ ) can be obtained (equation 6).

$$C_f = C/K_1 = (D \cdot (r + 1)) + \left( \frac{K_5}{K_1} \cdot P \cdot N \cdot D \cdot (r + 1) \right) \quad (6)$$

The distillate flow rate ( $D$ ) is calculated by the infinite/infinite analysis for each pressure. The reflux ( $r$ ) and number of stages ( $N$ ) are substituted by their minimal values ( $r_{\min}$  and  $N_{\min}$ ) obtained by the adjustment of the boundary value method results for each pressure. So, all the cost function variables become defined for each working pressure except the constant ratio ( $K_5/K_1$ ). This ratio ( $K_5/K_1$ ) produces the optimal overall cost ( $C$ ) when the operational cost ( $C_0$ ) is of the same order than the investment cost ( $C_i$ ) (equation 7).

$$C_f(\min) \Rightarrow D \cdot (r_{\min} + 1) = (K_5/K_1 \cdot P \cdot N_{\min} \cdot D \cdot (r + 1)) \quad (7)$$

As the system consists of two columns, both columns must be taken into account to determine the cost. An optimal pressure can be found fulfilling the relation of constants  $K_5/K_1$  calculated (equation 8) and verifying a minimum cost for this optimal pressure on the cost function (equation 9).

$$\frac{K_5}{K_1} = \frac{\sum_{j=1}^2 (D_j \cdot (r_{j,\min} + 1))}{\sum_{j=1}^2 (P_j^{opt} \cdot N_{j,\min} \cdot D_j \cdot (r_{j,\min} + 1))} \quad (8)$$

$$C_f = \sum_{j=1}^2 (D_j \cdot (r_{j,\min} + 1)) + \frac{K_5}{K_1} \cdot \sum_{j=1}^2 (P_j \cdot N_{j,\min} \cdot D_j \cdot (r_{j,\min} + 1)) \quad (9)$$

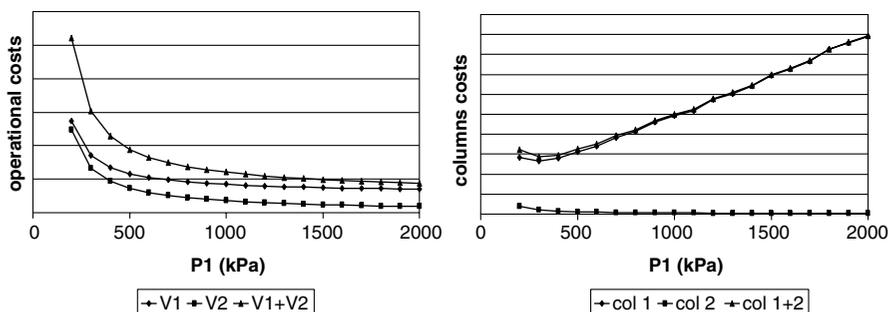
Once the constant ratio ( $K_5/K_1$ ) is determined, it can be used at the cost function (equation 9) to determine the influence of the pressure on the cost.

### OPTIMAL PRESSURE DETERMINATION

The operational cost at each pressure is considered proportional to the minimum vapour flow rate in the condenser and the capital cost is considered proportional to the column weight. Feasible pressures and temperatures ranges are considered. The pressure optimization is limited by the heating and cooling services available at the plant (Hamad et al., 2002). A marginal analysis on the distillate flow rate versus the pressure can be used to set the upper limit for the optimal pressure. The pressure influences the minimum reflux flow rate and its purity (Horwitz, 1997). The minimum vapour flow rate decreases with the pressure while the minimum number of stages cost increases (Figure 6). The cost comes mainly from the first column although the energy cost of the second column is also appreciable. The sum of the operating and investment costs presents a minimum at 800 kPa (Figure 7) ( $K_1/K_5 = 6.52 \cdot 10^{-5}$ ).

The total cost graph can be divided into three regions. The first region corresponds to pressures near the second column pressure (from 100 to 600 kPa), the cost increases drastically for a small pressure decrease. The operating cost is predominant on the first region. The second region corresponds to a flat zone of almost constant cost (from 600 to 1100 kPa) where the decrease of the operating cost is balanced by the increase on the investment cost. The optimal pressure will be anywhere on the plate region depending on energy and steel prices. A rigorous economic analysis is necessary to determine exactly where the optimal pressure is. The third region is for high pressures (higher than 1100 kPa). The cost for the third region comes mainly from the inversion cost. The cost increase produced by an increase of pressure in this third region is lower than the cost variation produced by the same pressure variation on the first region. Then it is preferable to use a pressure a bit higher than the optimal.

The same cost function is used to calculate the optimal reflux at each pressure. The results show that the heuristic with an optimal reflux of 1.2 to 1.5 times the minimum reflux is fulfilled (Figure 8). When the pressure is lower, it is better to use a higher multiplication factor.



**Figure 6.** Influence of the first and the second columns on the overall cost

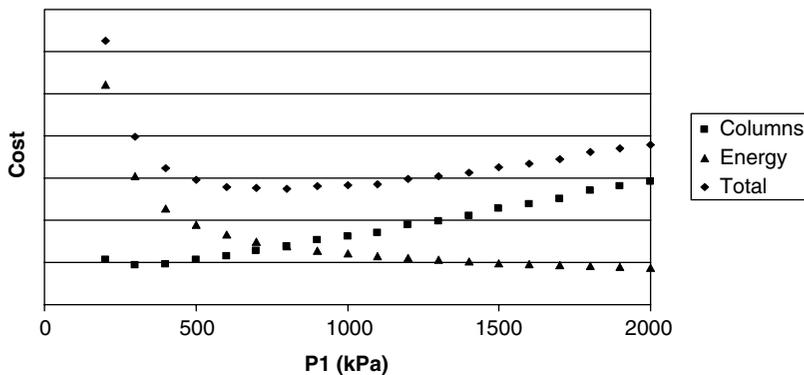


Figure 7. Cost function

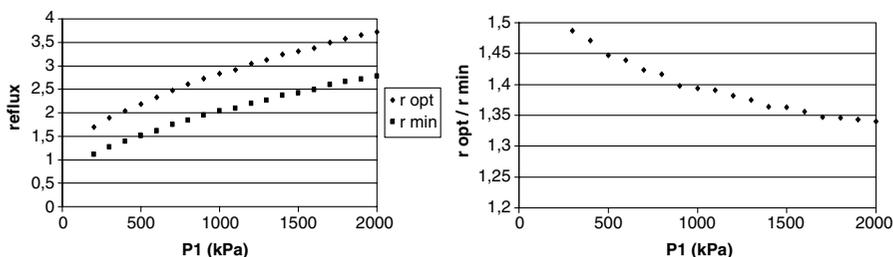


Figure 8. Optimal reflux

## CONCLUSION

The introduction of a reactive column in a pressure swing distillation system can successfully break reactive and non reactive azeotropes at the same time. It is demonstrated by the methyl acetate transesterification by ethanol.

The optimal pressure for pressure swing distillation is determined at an early design step using only thermodynamic data and the flowsheet scheme as inputs. An optimal pressure of 800 kPa has been obtained. The cost function is divided in three regions: (1) an energy cost controlled region, (2) a region where the energy and investment costs balance each other and (3) an investment cost controlled region. The energy cost controlled region must be avoided because the cost becomes very pressure sensitive. The proposed methodology a near optimal pressure, reflux and number of theoretical stages and in a near future these results will be used as initialisation in a MINLP optimisation in order to obtain more precise values of these parameters. This more rigorous economic optimisation must be undertaken in the second zone.

**NOMENCLATURE**

r	Reflux ratio
N	Number of stages
C	Cost function (€)
D	Distillate flow rate (kmol/h)
P	Pressure (kPa)

**SUBSCRIPT**

0	Operation
i	Investment
min	Minimum
r	reboiler
c	Condenser
j	Number of column

**SUPERSCRIPIT**

s	Stripping
r	Rectifying

**REFERENCES**

- España, F.J. (1996) Contribución al estudio de la transesterificación de acetato de metilo con etanol mediante rectificación extractiva reactiva catalítica heterogénea. PhD Thesis, Barcelona University, Spain.
- Hamad, A. and Dunn, R.F. (2002) Energy Optimization of Pressure-Swing Azeotropic Distillation Systems. *Industrial & Engineering Chemistry Research*, 41(24), 6082–6093.
- Horwitz, B. A. (1997) Optimize pressure-sensitive distillation. *Chemical Engineering Progress*, 93(4), 47–51.
- Kaymak, D. B. and Luyben, W. L. (2004) Quantitative comparison of reactive distillation with conventional multiunit reactor/column/recycle systems for different chemical equilibrium constants. *Industrial & Engineering Chemistry Research*, 43(10), 2493–2507.
- Perry, R.H. (1997) *Perry's chemical engineers' handbook*. 7th edition, McGraw-Hill.
- Thery, R. (2002) Analyse de faisabilité, synthèse et conception de procédés de distillation réactive. PhD Thesis, génie des procédés de l'INP Toulouse, France.
- Ulrich, J. (2002) Operation and control of azeotropic distillation column sequences. PhD Thesis, ETH No. 14890 Zurich, Switzerland.