DOUBLE COLUMN BATCH RECTIFIER IN CLOSED MODE FOR PRESSURE SWING BATCH DISTILLATION

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Abstract
The double column batch rectifier in closed mode is presented for pressure swing batch distillation and it is investigated by feasibility studies and rigorous simulation using a professional dynamic simulator moreover it is compared with double column batch stripper in open mode. The calculations are performed for a binary minimum (acetone - methanol) azeotropic mixture. Results show that by the application of the closed mode energy saving can be realised.

Keywords: Pressure Swing Batch Distillation, Separation of Azeotropes, Dynamic Simulation, Closed mode, Double Column System

1. Introduction

Pressure swing distillation is an efficient method for the separation of pressure sensitive azeotropic mixtures. Many mixtures form an azeotrope, whose position can be shifted substantially by changing system pressure, that is, a pressure sensitive azeotrope. (At some pressure the azeotrope may even disappear.) This effect can be exploited to separate azeotropic mixtures without the application of a separating agent by the so-called pressure swing distillation. Pressure swing distillation in continuous system was studied by several authors[1-6].

Batch distillation (BD) has always been an important part of seasonal, uncertain or low capacity and high-purity chemicals' production. It is a process of key importance in the pharmaceutical and several other industries and in the regeneration of waste solvent mixtures. Phimister and Seider[7] were the first who studied the batch application of binary pressure swing distillation (PSD) by simulation. They investigated the separation of a minimum azeotrope (THF-water) by semi-continuous PSD and reverse-batch operation (batch stripping). They also investigated the control and other practical aspects of these configurations, and their performance was compared with that of a continuous system, as well. To our knowledge Repke et al.[8] were the first, who investigated experimentally the application the pressure swing distillation in batch which was operated in open mode. They studied the separation of a minimum boiling, homoazeotropic mixture (acetonitrile-water) by pressure swing distillation in a batch rectifier and in a stripper with pilot-plant experiments and rigorous simulations. Modla and Lang[9] studied the feasibility of pressure swing batch distillation (PSBD) of binary mixtures (forming minimum or maximum azeotrope) in different column configurations assuming maximal separation. They suggested two novel configurations containing two rectifying (double column batch rectifier, DCBR) or two stripping sections (double column batch stripper, DCBS) operating in open mode. They made rigorous simulation calculations for the different column configurations, as well. For separating minimum azeotropes they suggested the application of double column batch stripper or batch stripper and for maximum azeotropes double column batch rectifier or batch rectifier, respectively. Modla et al.[10] studied the feasibility of the pressure swing batch distillation separation of ternary homoazeotropic mixtures in different single and double column configurations. In that paper the separation of the most frequent types of ternary mixtures were investigated. Kopasz et al.[11] presented a simple scheme for the control of product compositions (temperatures of bottoms product are controlled and their flow rates are manipulated) for double column batch stripper in open mode separating a minimum boiling point azeotropic mixture by pressure swing batch distillation. Denes et al.[12] suggested a new double column system operated in closed mode for the separation of binary heteroazeotropic mixtures.

The goal of this paper is to investigate the double column batch rectifier in closed mode by feasibility study and by rigorous simulation and to compare it with double column batch stripper in open mode for separating a binary minimum (acetone - methanol) azeotropic mixture. For the simulation we used the dynamic simulator of CHEMCAD 6.0 (module CC-DCOLUMN, Chemstations[13]).

2. The double column batch rectifier in closed mode

The pressure swing is performed in different column sections. The double column batch rectifier operated in closed mode (without continuous product withdrawal) is presented (DCBR-Closed, Fig. 1a.). Two components are simultaneously produced as vessel residues.The double column batch rectifier in closed mode is suitable for the separation of minimum boiling point pressure sensitive binary azeotropic mixtures (Modla and Lang[9]). At the beginning of the process the charge (U_{ch}) is divided into two parts (U^α_b, U^β_b) which are filled into two reboilers. The charge composition (x_{ch}) is located between the two azeotropic compositions (x^α_{AZ}, x^β_{AZ}). The distillate of Column α (D) is fed into Column β and that of of Column β (D^β) is fed into Column α, respectively. The compositions of both distillates are azeotropes (x^α_{AZ} and x^β_{AZ}). During the process the compositions of reboilers are changing. At the end of the process we obtain products (of prescribed purity x^α_{spec} and x^β_{spec}) in reboilers which can be theoretically pure components (A and B).
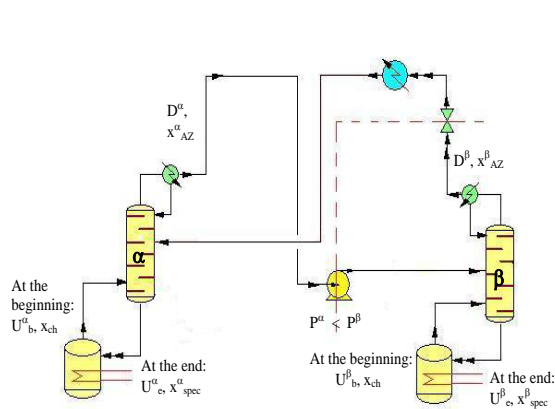

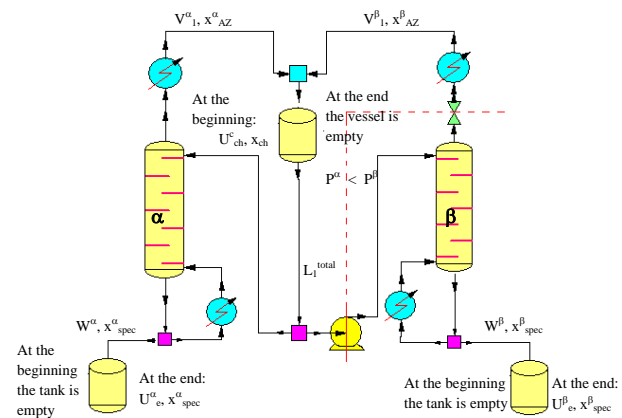**Figure 1a.**   **Figure 1b.**

a. Double column batch rectifier in closed mode
b. Double column batch stripper in open mode

3. VLE data of mixture acetone-methanol

The mixture acetone (A) -methanol (B) forming minimum azeotrope is a frequent waste in the pharmaceutical industry. This mixture cannot be separated into pure components by conventional rectification so a special distillation method (e.g. pressure swing distillation) must be applied. For the two different pressures (1.01 and 10 bar) the calculated azeotropic data of the mixture are presented in Table 1. The large shift in the azeotropic composition (x_{AZ}) from 78 to 37 mol % acetone indicates that a pressure swing separation should be feasible.

Table 1. Calculated data of the azeotropes

P [bar]	x_{AZ} [%]	T_{AZ} [°C]	$T_{BP,A}$ [°C]	$T_{BP,B}$ [°C]
1.01	78	55.2	56.0	64.4
10	37	142.9	142.9	136.7

4. Feasibility studies

The model equations are presented for double column batch rectifier in closed mode. Our aim is to estimate the duration of the process, the amount of the products. A simplified model was applied based on the following assumptions: 1) infinite plate number, 2) negligible hold-up on the trays, 3) constant molar overflow, 4) the flow rates do not vary with time. The total (TMB) and component material (CMB) balance equations are analytically solved. We assume that both products reach the prescribed purity at the same time, that is, the duration of the process (τ) is process minimal. Integral material balances for the whole system (for the whole process):

TMB: $U^\alpha_b + U^\beta_b = U_{ch}$, $U^\alpha_e + U^\beta_e = U_{ch}$ (1.ab)

CMB: $U^\alpha_b \cdot x_{ch,A} + U^\beta_b \cdot x_{ch,A} = U_{ch} \cdot x_{ch,A}$, $U^\alpha_e \cdot x^\alpha_{spec,A} + U^\beta_e \cdot (1 - x^\beta_{spec,B}) = U_{ch} \cdot x_{ch,A}$ (2.ab)

Differential material balances for Column α: $\dfrac{dU^\alpha}{dt} = D^\beta - D^\alpha$, $\dfrac{dU^\alpha}{dt} = -\dfrac{dU^\beta}{dt}$ (3.ab)

Boundary conditions: $U^\alpha(0) = U^\alpha_b$, $U^\alpha(\tau) = U^\alpha_e$ (4.ab)

Hence $U^\alpha_e = U^\alpha_b + (D^\beta - D^\alpha) \cdot \tau$ (5.)

DCMB: $\dfrac{d(U^\alpha \cdot x^\alpha_A)}{dt} = D^\beta x^\beta_{AZ,A} - D^\alpha x^\alpha_{AZ,A}$ (6.)

Boundary conditions: $(U^\alpha \cdot x^\alpha_A)(0) = U^\alpha_b \cdot x_{ch,A}$ $(U^\alpha \cdot x^\alpha_A)(\tau) = U^\alpha_e \cdot x^\alpha_{spec,A}$ (7.ab)

Hence $U^\alpha_e \cdot x^\alpha_{spec,A} = U^\alpha_b \cdot x_{ch,A} + (D^\beta x^\beta_{AZ,A} - D^\alpha x^\alpha_{AZ,A}) \cdot \tau$ (8.)

Known parameters: $U_{ch}, x^\alpha_{spec,A}, x^\beta_{spec,B}, x^\alpha_{AZ}, x^\beta_{AZ}, x_{ch,A}$, unknowns: $U^\alpha_b, U^\beta_b, U^\alpha_e, U^\beta_e, \tau, D^\alpha, D^\beta$, independent Equations: 1ab, 3b, 5, 8. The solution of the set of Eqs.:

Combination of Eqs. 1.b and 2.b: $U^\alpha_e = \dfrac{x_{ch,A} - (1 - x^\beta_{spec,B})}{x^\alpha_{spec,A} - (1 - x^\beta_{spec,B})} \cdot U_{ch}$ $U^\beta_e = \dfrac{x_{ch,A} - x^\alpha_{spec,A}}{(1 - x^\beta_{spec,B}) - x^\alpha_{spec,A}} \cdot U_{ch}$

Duration of the process from Eq. 5: $\tau = \dfrac{U^\alpha_e - U^\alpha_b}{D^\beta - D^\alpha}$

We define the division of the charge and the distillate flow ratio between the two columns:

$\phi_{ch} = \dfrac{U^\alpha_b}{U_{ch}}$, $\phi_D = \dfrac{D^\alpha}{D^\alpha + D^\beta}$. Hence the duration of the process: $\tau = \dfrac{U^\alpha_e - U_{ch} \cdot \phi_{ch}}{D^{tot}(1 - 2 \cdot \phi_D)}$

where the ϕ_D is (combination of Eqs. 5 and 8):

$$\phi_D = \frac{x^\beta_{AZ,A} - \dfrac{U^\alpha_e \cdot x^\alpha_{spec,A} - U_{ch} \cdot \phi_{ch} \cdot x_{ch,A}}{U^\alpha_e - U_{ch} \cdot \phi_{ch}}}{x^\beta_{AZ,A} + x^\alpha_{AZ,A} - 2 \cdot \dfrac{U^\alpha_e \cdot x^\alpha_{spec,A} - U_{ch} \cdot \phi_{ch} \cdot x_{ch,A}}{U^\alpha_e - U_{ch} \cdot \phi_{ch}}} \qquad (9.)$$

The amount of charge is 46.18 kmol (2.6 m^3) and it contains 50 mol% acetone. Column α produces methanol (product *B*) and Column β produces acetone (product *A*) hence: $x^\alpha_{spec,A}$=0.02 and $x^\beta_{spec,B}$=0.02. The total flow rate of distillates is: D^{total}=14 kmol/h. By the feasibility equations the amount of the products: U^α_e=23.09 kmol and U^β_e=23.09 kmol. We determine the duration of the process (τ) for different ratios of division of the charge (ϕ_{ch}) (Fig. 2). Figure 2 shows that there is a linear relation between the division of the charge (ϕ_{ch}) and the duration of the process.
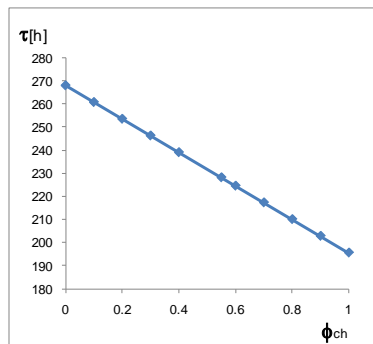

Figure 2. Duration of the process for different divisions of the charge

5. Rigorous simulation calculations

The aim of this section is to verify the results of feasibility study and to investigate the main operation parameter of DCBR-Close and to compare with double column batch stripper in open mode (DCBS-

Open, Fig. 1b.) for separation of acetone - methanol azeotropic mixture. For the simulation we used the dynamic simulator of CHEMCAD 6.0 (module CC-DCOLUMN, Chemstations[13]). The following simplifying assumptions are applied:

- theoretical trays,
- constant volumetric liquid hold-up on the trays,
- negligible vapour hold-up.

The model equations to be solved are well-known: a) Non-linear differential equations (material balances, heat balances), b) Algebraic equations (VLE relationships, summation equations, hold-up and physical property models). For describing the phase equilibria the UNIQUAC model is applied.

The pressures of the columns are P^α=1.01 bar and P^β=10 bar for both modes (DCBR-Closed, DCBS-Open). The number of theoretical stages (N) for each column section is 40. (The total condenser and total reboiler do not provide a theoretical stage.) The liquid hold-up is 2 dm^3/plate. In each case the total quantity of the charge is 2.6 m^3. At the start the columns are filled with boiling point liquid (at the operation pressure of the column). The whole process is finished - at the open modes when the amount of liquid in the common vessel decreases to 2% of the charge, - at the closed mode when both product purities reach than the specified ($x_{spec,i}$=0.98). In all cases the specified purity ($x_{spec,i}$) is 98.0 mol% for both products.

In the rectifying columns the reflux ratios (R^α, R^β), and in the stripping columns the reboil ratios (R_s^α, R_s^β) are changed by PID controllers manipulating the distillate (D^α, D^β) and bottom flow rates (W^α, W^β), respectively. It must be still noted that in open modes the set points of the controllers are the specified purities and in closed modes they are near to the azeotropic composition at the given operation pressure (the azeotropic composition cannot be reached with finite reflux or reboil ratio). The tuning of the PID controllers is manually done by taking into consideration the usual criteria (maximal overshoot, control time, number of oscillations). The quality of control is determined by the evolution of the position of the two control valves (varying the flow rate). The following criteria of quality of control are given concerning the two control valves: a)maximal overshoot: 33 %, b) maximum number of oscillations during the settling time (within an error band of +-5 %): 3. The PID controller parameters are found in Appendix 2.

5.1 Double column batch rectifier in closed mode

First the process is presented and then the process duration is determined at different division ratios of the charge (ϕ_{ch}). Column α produces methanol (product *B*) and the column β produces acetone (product *A*). The total heat duty is 2400 MJ/h in each case. The division of the charge (ϕ_{ch}) is 0.50. The feed plates are N^α_f=10, N^β_f=10. The division of the total heat duty (ϕ_Q) is 0.6041. At the beginning of the process both purities (Fig. 4a) (methanol in reboiler α and acetone in reboiler β) increase in a monotone way. The concentration of acetone reaches the specified value (0.98) in a shorter time than that of methanol. At the beginning of the process the amount of the liquid (Fig. 4b) increases in the reboiler β while it decreases in the reboiler α. Afterwards the tendency changes due to fact that the compositions have changed in the reboilers which means that the heat of evaporation of the liquids has changed. When both products reach the prescribed purity at the same time then the duration is minimal at the given ϕ_{ch}.
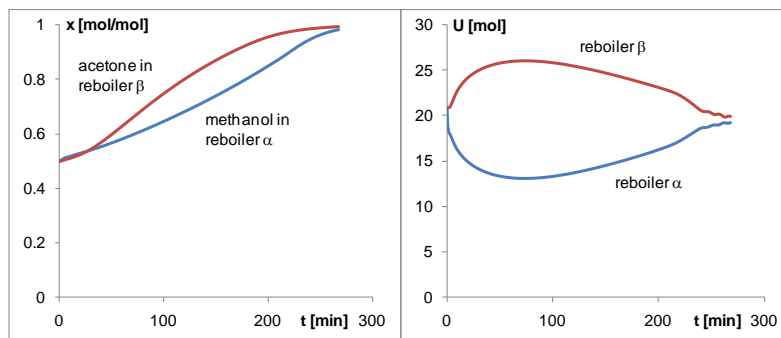

Figure 4a.   **Figure 4b.**
a. Evolution of the reboiler (bottom vessel) compositions
b. Evolution of the amount of the liquids in the reboilers (bottom vessels)

5.2 Influence of the division of the charge

For each division of ratio the minimum of process duration is determined by varying the division of the total heat duty (ϕ_Q). The optimum values of ϕ_Q for different ϕ_{ch} are shown in Fig. 5a. The influence of the division of the charge (ϕ_{ch}) on process duration is shown in Fig. 5b, which presents that there is nearly linear relation between the division of the charge (ϕ_{ch}) and the duration of the process. Hence we can state that the results are similar to those of feasibility studies. The minimum value of the process duration is at ϕ_{ch} =1.0 the results are shown for ϕ_{ch}=0.96 because of problems of convergence. The minimal overall specific energy consumption is 225 MJ/kmol.
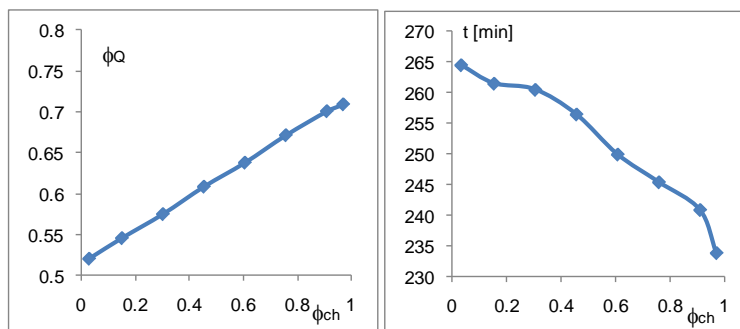

Fig. 5a. The optimum values of ϕ_Q at difference ϕ_{ch} **Fig. 5b.** The influence of ϕ_{ch} on process duration

5.3 Double column batch stripper in open mode

The double column batch stripper in open mode (DCBR-Open Fig. 1b,) is suitable for the separation of minimum boiling point pressure sensitive binary azeotropic mixture (Modla and Lang 2008). The influence of liquid division ratio (ϕ_L) as operational parameter on the performance of the process is studied, and the optimum value yielding the minimal overall specific energy consumption is determined (Fig. 6, 284 MJ/kmol).
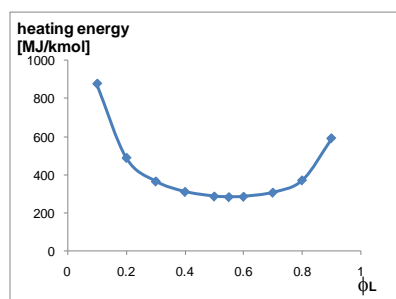

Fig. 6. Influence of liquid division ratio on overall specific energy consumption (DCBS-open)

5.4 Comparison of the DCBR-closed and DCBS-open modes

It must be noted that in the case of open mode the optimum of separation was determined by the investigation of the only one main operational parameter. However for the closed mode the global optimum of separation was not determined since some operation parameters (e.g. feed plate locations) are not investigated. In this case only local optimum was determined. Comparing the two different modes we can conclude that the closed mode is significantly more economical (the minimal overall specific energy consumption is 225 MJ/kmol contra 284 MJ/kmol) than the open one due to its higher flexibility (more operational parameters).

6. Conclusion

The double column batch rectifier in closed mode was presented for pressure swing batch distillation and it was investigated by feasibility studies and rigorous simulation by using a professional dynamic simulator. Moreover it was compared with double column batch stripper in open mode. The calculations were performed for a binary minimum azeotropic mixture (acetone - methanol).

We verified the result of feasibility study (there is a nearly linear relation between the division of the charge and the process duration and the minimum process duration is at $\phi_{ch}=1$) by rigorous simulation. Based on the rigorous calculations we conclude that the separation of a minimum azeotrope by the double column batch rectifier in closed mode was found to be more economical than in open mode (20% overall energy saving).

Acknowledgements

Appendices

Appendix 1 The value of the parameters used for the phase equilibrium calculations

a. Antoine parameters: $\ln(p) = A - \dfrac{B}{T+C}$, where p vapour pressure (mmHg), T temperature (K)

component	A	B	C
Acetone	16.732	2975.9	-34.523
Methanol	18.5100	3593.4	-35.225

b. UNIQUAC parameters for Acetone (A) – Methanol (B) mixture:

i	j	u_{ij}-u_{jj} [cal/mol]	u_{ji}-u_{ii} [cal/mol]
A	B	434.944	-101.228

Appendix 2 The value of the PID parameters used for rigorous calculations

DCBR-Close	PB [%]	TI [min]	TD [min]	Set point [mol/mol]
Column α	200	4	0	0.75 acetone
Column β	400	4	0	0.58 methanol

DCBS-Open	PB [%]	TI [min]	TD [min]	Set point [mol/mol]
Column α	80	2.5	0	0.98 methanol
Column β	50	10	1	0.98 acetone

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