Heterogeneous batch distillation with variable decanter hold-up

László Hégely[a,b], Vincent Gerbaud[b,c], Péter Láng[a]

[a]*Budapest University of Technology and Economics, Dept. of Building Services and Process Engineering, Muegyetem rkp. 3-5, H-1521 Budapest, Hungary*
[b]*Université de Toulouse, INP, UPS, LGC (Laboratoire de Génie Chimique), 4 allée Emile Monso, F-31432 Toulouse Cedex 04, France*
[c]*CNRS, LGC (Laboratoire de Génie Chimique), F-31432 Toulouse Cedex 04, France*

Abstract

A general model of batch heteroazeotropic distillation is proposed, in which both liquid phases present in the decanter can be refluxed or withdrawn as distillate, their hold-up can be increased, decreased or kept constant, as well. A feasibility study is performed with the assumption of maximal separation, that is, that the composition of the condensate always equals to that of the heteroazeotrope. The still path directions are determined for all the 16 possible operation policies, and the results are validated by rigorous simulations for three cases not published yet. The still path can be steered in any direction by changing the operational parameters, allowing the recovery of a pure component in the still.

Keywords: heteroazeotropic distillation, operational policies, rigorous simulation.

1. Introduction

The separation of azeotropic and close-boiling mixtures requires the application of special distillation methods. Batch heteroazeotropic distillation is one of the possible methods: a third component (entrainer, E) is added to the mixture, leading to the formation of two liquid phases, which can be separated by decantation.

Decantation is performed in a decanter placed after the condenser. In the model of Pham and Doherty (1990) both liquid phases are refluxed. The model of Rodríguez-Donis et al. (2002) allows the reflux of any fraction of either phase; distillate is withdrawn from the E-lean phase, and the hold-up of the E-rich phase in the decanter is variable. Skouras et al. (2005) distinguished two modes of batch heteroazeotropic distillation. By Mode I, decantation and distillation are performed sequentially, and the reflux is heterogeneous. By Mode II, the phase separation and distillation are simultaneous. Mode II has two versions: Strategy A, where the E-rich phase is refluxed entirely, and Strategy B, where it is refluxed partially. In the model of Lang and Modla (2006) any fraction of either liquid phase can be refluxed, while the hold-up of both phases are constant. Distillate can be withdrawn from both phases.

2. Model description

Figure 1 shows the scheme of the heterogeneous distillation column of our generalised model. The condensate of the top vapour, which has a molar flow rate of V and molar composition of y_2, gives rise to two-phase liquid stream with a flow rate of L_0, composition of x_0, and a split ratio of ω (ratio of the E-rich phase and total flow rate).
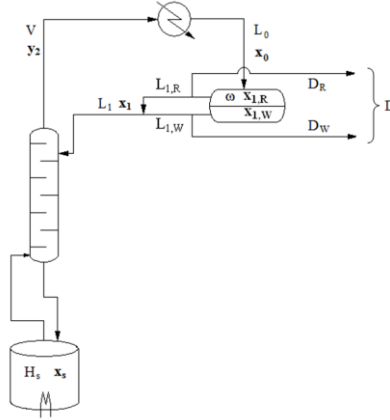
Figure 1. Heteroazeotropic distillation column scheme for the generalised model.

Both liquid phases can be refluxed or withdrawn as distillate. Besides, the hold-up of both phases can be increased, decreased or kept constant in the decanter. The change in the hold-up of the E-rich (resp. E-lean) phase is characterised by the variables θ_H (resp. φ_H), which are defined as the ratio of the amount of E-rich (resp. E-lean) phase removed from and entering the decanter:

$$\theta_H = \frac{L_{1,R} + D_R}{L_{0,R}} \qquad (1) \qquad\qquad \varphi_H = \frac{L_{1,W} + D_W}{L_{0,W}} \qquad (2)$$

where $L_{0,R}$ and $L_{0,W}$ are the flow rates of the E-rich and E-lean phase in the condensate, D_R and D_W are the flow rates of E-rich and E-lean phases withdrawn as distillate, $L_{1,R}$ and $L_{1,W}$ are those refluxed, respectively. If the value of θ_H is lower than one, the hold-up of the E-rich phase increases, if it is higher, the hold-up decreases.

The variables θ_{refl} and φ_{refl} determine the ratio of the amount refluxed and the total amount leaving the decanter for the E-rich and E-lean phases, respectively:

$$\theta_{refl} = \frac{L_{1,R}}{L_{1,R} + D_R} \qquad (3) \qquad\qquad \varphi_{refl} = \frac{L_{1,W}}{L_{1,W} + D_W} \qquad (4)$$

Multiplying θ_H and θ_{refl} (resp. φ_H and φ_{refl}), the ratio of the refluxed E-rich (resp. E-lean) phase is obtained, which value can be higher than one:

$$\theta = \theta_H \theta_{refl} = \frac{L_{1,R}}{L_{0,R}} \qquad (5) \qquad\qquad \varphi = \varphi_H \varphi_{refl} = \frac{L_{1,W}}{L_{0,W}} \qquad (6)$$

The following simplifying assumptions are applied in the feasibility analysis:
- the composition of the condensate is constant and equals to that of heteroazeotrope,
- the vapour and liquid hold-ups of the column and of the condenser are negligible,
- constant molar overflow.

The first assumption also means that ω, $x_{1,R}$ and $x_{1,W}$ are not changing in time, although they may change slightly during a real operation (Pommier et al., 2008).

The flow rate of the condensate (equal to that of the top vapour, V):

$$L_0 = L_{0,R} + L_{0,W} = \omega L_0 + (1-\omega)L_0 = V \qquad (7)$$

The total flow rate of reflux stream is the following:

$$L_1 = L_{1,R} + L_{1,W} = \theta L_{0,R} + \varphi L_{0,W} \qquad (8) \qquad\qquad L_1 = \theta \omega V + \varphi(1-\omega)V \qquad (9)$$

The component flow rates of the reflux flow:

$$L_1 x_1 = L_{1,R} x_{1R} + L_{1,W} x_{1,W} \qquad (10)$$

The evolution of the still composition is described by a differential equation, which can be derived from the total and component (differential) material balances of the still pot. The total material balance (assuming constant molar overflow):

$$\frac{dH_S}{dt} = L_1 - V = (\theta - 1)\omega V - (1 - \varphi)(1 - \omega)V \tag{11}$$

The component material balance:

$$\frac{d(H_S x_S)}{dt} = L_1 x_1 - V x_0 = (\theta - 1)\omega V x_{1,R} - (1 - \varphi)(1 - \omega)V x_{1,w} \tag{12}$$

By applying the product rule of differentiation, the equation of the still path:

$$H_S \frac{dx_S}{dt} = \frac{d(H_S x_S)}{dt} - x_S \frac{dH_S}{dt} \tag{13}$$

The final form of the equation describing the evolution of the still composition:

$$\frac{dx_S}{dt} = (1 - \theta)\omega \frac{V}{H_S}(x_S - x_{1,R}) + (1 - \varphi)(1 - \omega)\frac{V}{H_S}(x_S - x_{1,W}) \tag{14}$$

The two terms represent the removal of the E-rich and the E-lean phase from the system, respectively, by either withdrawal as distillate, or accumulating in the decanter.

3. Operational policies

Based on the values of two operational parameters θ and φ, 16 different cases can be distinguished, shown in Table 1. If θ (resp. φ) is 0, the E-rich (resp. E-lean) phase is not refluxed. If θ (resp. φ) is 1, the E-rich (resp. E-lean) phase is refluxed entirely. If θ (resp. φ) is greater than 1, the amount of the E-rich (resp. E-lean) phase refluxed to the column is greater than what is removed from it with the top vapour. To supply this difference in the flow rates, the hold-up of the respective phase must be decreased.

In Eq. 14, the terms related to the refluxing of a phase (θ_{refl} and φ_{refl}) and to the change in its hold-up (θ_H and φ_H) are only present with their products (θ and φ). That is, the same effect can be achieved either by accumulating one of the phases, or by withdrawal as distillate. The practical implementation of withdrawal is easier. Accumulating one of the phases in the decanter may be useful, e.g. in order to ensure the existence of two liquid phases. However θ or φ can only be greater than 1, if the hold-up is reduced. In Table 1 examples are given for some operational policies.

The still path can be characterised by the direction of the derivative vector of the still composition. This can be written (Eq. 14) as the sum of two other vectors, whose magnitude depends on θ and φ, respectively. Their direction can even be reversed, if θ or φ is greater than 1. Therefore, the direction of the resultant vector depends on the operation policy and the value of the operational parameters θ and φ. The results are illustrated with a mixture of A, B and E. A and the entrainer E form a binary heteroazeotrope, which is the only unstable node of the system.

The two vectors influencing the still path are presented in Fig. 2a. The vector corresponding to the E-lean phase points away from $x_{1,W}$, if $\varphi<1$, and towards it, if $\varphi>1$. The other vector, corresponding to the E-rich phase points away from $x_{1,R}$, if $\theta<1$, and towards it, if $\theta>1$. If θ or φ equals 1, the respective vector does not exist.

Fig. 2b shows the possible directions of the derivative vector, that is, the instantaneous direction of the still path for every possible operational policy shown in Table 1. By directing the still path appropriately, through choosing the right values of θ and φ, B can be recovered in the still, thus eliminating the need of a further separation step.

Table 1. The possible operational policies (reintr.: reintroduction - a greater amount of liquid is refluxed than what leaves the column as distillate).

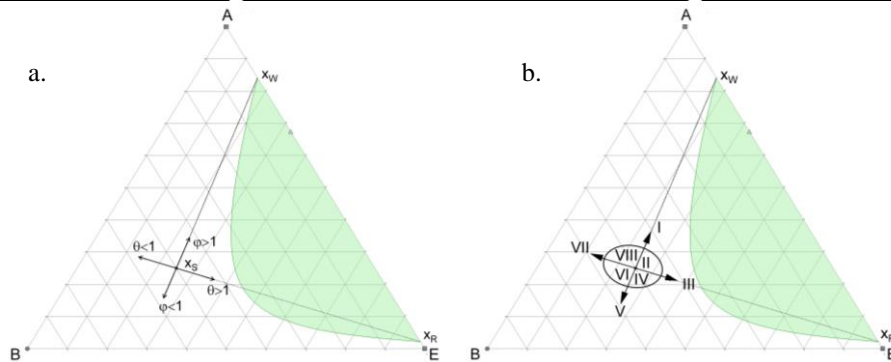|	θ	φ	Reflux	Example
1	0	0	No reflux	
2		<1	E-lean phase (partial)	
3		1	E-lean phase (total)	
4		>1	E-lean phase (reintr.)	
5	<1	0	E-rich phase (partial)	Mode II, Strategy B (Skouras et al., 2005); Mode II, Strategies 2' and 2" (Gerbaud and Rodríguez-Donis, 2010)
6		<1	E-rich (partial) and E-lean phase (partial)	
7		1	E-rich (partial) and E-lean phase (total)	
8		>1	E-rich (partial) and E-lean phase (reintr.)	
9	1	0	E-rich phase (total)	Mode II, Strategy A (Skouras et al, 2005); Mode II, Strategy 1 (Gerbaud and Rodríguez-Donis, 2010)
10		<1	E-rich (total) and E-lean phase (partial)	Operation with reflux from E-lean phase, as well
11		1	E-rich (total) and E-lean phase (total)	Total reflux operation
12		>1	E-rich (total) and E-lean phase (reintr.)	
13	>1	0	E-rich phase (reintr.)	Mode II, Strategy 3 (Gerbaud and Rodríguez-Donis, 2010)
14		<1	E-rich (reintr.) and E-lean phase (partial)	
15		1	E-rich (reintr.) and E-lean phase (total)	
16		>1	E-rich (reintr.) and E-lean phase (reintr.)	

Figure 2 a. The possible directions of the vectors influencing the still path. b. The direction of the still path for the different operational policies.

4. Rigorous simulation results

In order to validate the model, rigorous simulations are performed with the professional flowsheet simulator CHEMCAD. Operational policies 8, 12 and 16 are applied in order to demonstrate that the still path can be turned into directions previously not reported, that is, towards the E-lean phase. The column has 50 theoretical plates; the mixture to be separated is water (A) – formic acid (B) – propyl formate (E). The vapour-liquid-liquid equilibria are described with the NRTL model. The mixture A – B exhibits a minimum boiling-point homoazeotrope, while A and E form a heteroazeotrope, enabling the separation of the A – B mixture.

The hold-up of the decanter is 0.5 dm^3; that of the column is 0.01 dm^3/plate. The charge has a molar amount of 160 mol and a composition of 52.5 mol% A, 40.5 mol% B and 7% E. The heat duty applied is 2 kW. The column is operated for 40 minutes under total reflux, after which one of the policies previously mentioned is applied. At the end of the total reflux period, the volumes of liquid phases in the decanter are equal. The values of the operational parameters are: $\varphi = 1.21$, $\theta = 0.986$ (Policy 8), 1.0 (Policy 12), and 1.014 (Policy 16), respectively. The respective still paths are shown in Fig. 3. Each path starts from the composition at the end the total reflux period ($x_{s,\infty}$). For Policy 12, the still composition moves towards that of the entrainer-lean phase, while for Policies 8 and 16, the path deviates from this direction as predicted: towards the edge A-B (Policy 8) or vertex E (Policy 16). That is, the still path directions are in accordance with the results of the feasibility analysis.
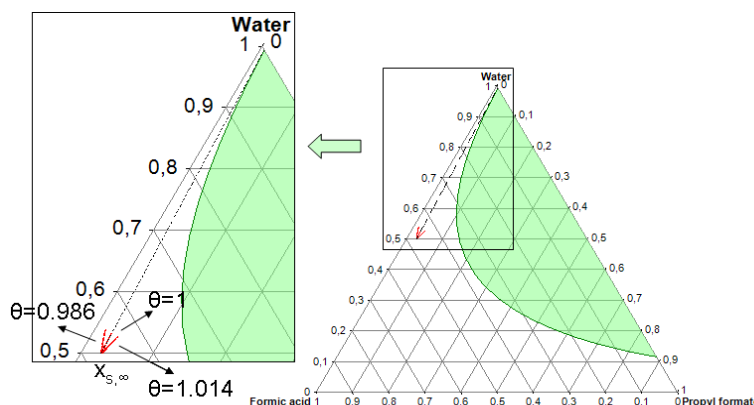

Figure 3. The calculated evolution of still composition (operational policies 8, 12, 16)

5. Conclusions

A general model of batch heteroazeotropic distillation was proposed. Both liquid phases present in the decanter can be refluxed or withdrawn as distillate, their hold-up can be increased, decreased or kept constant, as well. By assuming maximal separation, that is, that the condensate is always the heteroazeotrope, the still path equation was derived and the vectors determining the evolution of still composition were identified. The still path directions were determined for all the 16 possible operation policies. The results were validated by rigorous simulations for three cases not published yet. By using appropriate operational policies, it is possible to steer the still path in any desired direction, making possible to recover a pure component in the still.

Acknowledgement

References

Gerbaud, V. and Rodríguez-Donis, I., 2010, Techniques de l'ingénieur, J2 612, Tissot, Paris.
Lang P. and Modla G., 2006, Chemical Engineering Science, 61, 426.
Rodríguez-Donis, I., Gerbaud, V., Joulia, X., 2002, AIChe Journal, 48, 1168
Pham, H.N., Doherty, M.F., 1990, Chemical Engineering Science, 45 (7), 1837.
Pommier, S., Massebeuf, S., Kotai B., Lang, P., Baudouin, O., Floquet, P., Gerbaud, V., 2008, Chem. Eng. Proc., 47(3), 408.
Skouras, S., Kiva, V., Skogestad, S., 2005, Chemical Engineering Science 60, 2895.