

## Batch Heteroazeotropic Distillation in a New Generalised Double-Column System

Ferenc Denes<sup>1,2</sup>, Peter Lang<sup>1\*</sup>, Xavier Joulia<sup>2</sup>

<sup>1</sup>BME Department of Building Services and Process Engineering, Muegyetem rkp. 3-5, H-1521 Budapest, Hungary; lang@mail.bme.hu

<sup>2</sup>University of Toulouse, INP-ENSIACET-LGC, 4, allée Emile Monso, 31432 Toulouse Cedex 4, France

We study the separation of the minimum homoazeotrope isopropanol – water by applying cyclohexane and n-hexane as entrainer in a new Generalised Double-Column batch heteroazeotropic distillation System (GDACS). First its feasibility is studied by a simplified method then we do sensitivity analysis by rigorous simulation. The minimum duration is determined for the GDACS and for the original DCS, and their performances are compared. Due to its higher number of degrees of freedom the GDACS provides a more flexible operation than the DCS. In each case we obtained shorter process durations and lower energy demands by the GDACS than by the DCS.

### 1. Introduction

In the pharmaceutical and fine chemical industries the Batch Heteroazeotropic Distillation (BHD) is widely applied. So far the BHD was performed in the industry only in Batch Rectifiers (BR) equipped with a decanter (in open mode, with continuous distillate withdrawal). The BR was investigated with variable decanter holdup by Rodriguez-Donis et al. (2002) and with continuous entrainer feeding by Modla et al. (2003) and Rodriguez-Donis et al. (2003), respectively. The BHD in BR and also in multivessel columns was extensively studied by Skouras et al. (2005). For the BHD we suggested a new Double-Column System (DCS, Fig. 1, Denes et al., 2009) which was experimentally verified for the mixture water – 1-butanol (Denes et al, 2010). In the DCS the two products are accumulated in the reboilers (closed operation mode).

The goals of our paper are

- to extend the DCS and suggest a new Generalised DCS (GDACS),
- to study the feasibility of the separation of a homoazeotropic mixture in the GDACS,
- to study the effect of the new operational parameters on the energy demand of the process,
- to compare the performance of the new GDACS with that of the original DCS by rigorous simulation by using the dynamic simulator of ChemCAD (CC-DColumn).

The separation of the mixture isopropanol (IPA, *A*) – water (*B*) is studied. The entrainers applied (*E*) are cyclohexane and n-hexane, respectively.

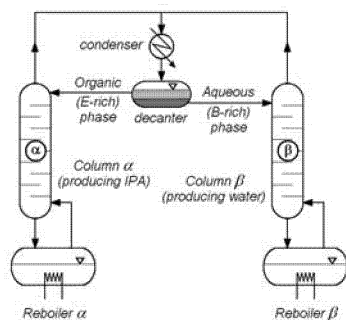


Fig. 1: Scheme of the original DCS

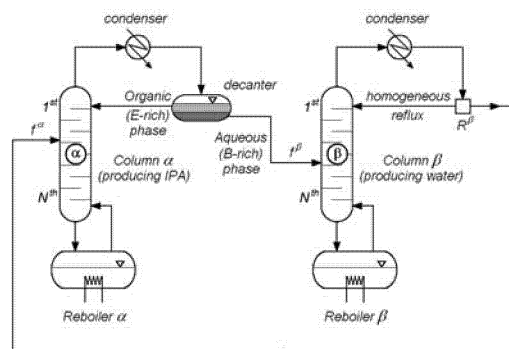


Fig. 2: Scheme of the GDCS

## 2. Feasibility studies

### 2.1 Description of the new configuration

We extended the original DCS. In the new generalised configuration (Fig. 2):

- the distillate of Column  $\beta$  can be fed into any ( $f^\alpha$ ) tray (or the decanter) of Column  $\alpha$  (not only into the decanter as by the DCS),
- the aqueous phase of the decanter can be fed into any ( $f^\beta$ ) tray of Column  $\beta$  (not only into the top of the column),
- Column  $\beta$  can be operated with homogeneous reflux (reflux ratio:  $R^\beta$ ).

By the GDCS the decanter is fed only by the ternary heteroazeotrope (TAZ) and not by a mixture with the binary  $A$ - $B$  homoazeotrope (BAZ). Hence sharper liquid-liquid separation can be reached (longer tie line). The condensate of Column  $\beta$  whose  $A$ -content is higher than that of the  $B$ -rich phase coming from the decanter, is partially refluxed. Consequently the  $A$ -content of the top vapour  $\beta$  can be higher than by the original DCS.

### 2.2 Method of the feasibility study

We apply a simplified model for the description of the distillation of the mixture  $A$ - $B$ : the integral and differential total and partial (for  $A$ ) material balances are solved. Simplifying assumptions: maximal separation, negligible holdup (except for the reboilers), constant molar overflow and no entrainer loss.

### 2.3 Input data

Molar quantity of the charge:  $U_{\text{ch}} = 100$  kmol, composition of the charge [ $A$ ,  $B$ ,  $E$ ]:  $\bar{x}_{\text{ch}} = [0.662, 0.338, 0] = \bar{x}_{\text{BAZ}}$ , prescribed purities:  $x_{A/\text{prod}A} = x_{B/\text{prod}B} = 0.99$ , total vapour flow rate:  $V = 20$  kmol/h, division of the charge:  $u^\alpha = 0.6$ , reflux ratios:  $R^\alpha = 3.79$  (by applying cyclohexane as entrainer, determined by the liquid-liquid split),  $R^\beta = 1/2$ .

### 2.4 Results

Molar quantity of Product  $A$ :  $U_c^\alpha = 66.53$  kmol, division of the vapour flow rate:  $v^\alpha = 0.740$ , duration:  $t = 1052$  min. The separation proved to be feasible.

### 3. Rigorous simulation

The influence of the new operational parameters is studied and the two configurations are compared. The simplifying assumptions are: theoretical trays, constant molar liquid and negligible vapour tray holdups, constant volumetric liquid holdup in the decanter. The calculations are presented in details for the case when the entrainer is cyclohexane.

#### 3.1 Influence of the operational parameters

We studied the effect of the supplementary operational parameters ( $f^\alpha$ ,  $f^\beta$ ,  $R^\beta$ ) on the energy demand of the process which is proportional to the duration.

##### 1.1.1 Input data

Fixed parameters: molar quantity of the charge:  $U_{ch} = 100$  kmol, composition of the charge in mole fraction:  $\bar{x}_{ch} = \bar{x}_{BAZ} = [0.662, 0.338, 0]$ , division of the charge:  $u^\alpha = 0.6$ , initial molar quantity of  $E$  in Reboiler  $\alpha$ :  $U_{b,E}^\alpha = 0.5$  kmol, prescribed purity of the products:  $x_{A/prodA} = x_{B/prodB} = 0.99$ , number of trays:  $N^\alpha = N^\beta = 8$ , tray holdups:  $U_{HU}^\alpha = U_{HU}^\beta = 0.5$  kmol, decanter holdup:  $U_{HU}^{dec} = 0.106$  m<sup>3</sup>, total heat duty of the reboilers:  $Q = 200$  kW, division of the heat duty:  $q^\alpha = 0.792$ .

Basic values of the parameters varied: feed tray in Column  $\alpha$ :  $f^\alpha = 3$ , feed tray in Column  $\beta$ :  $f^\beta = 6$ , reflux ratio in Column  $\beta$ :  $R^\beta = 1/2$ .

##### 1.1.2 Results

*Feed tray location in Column  $\alpha$  (Fig. 3)*

This parameter  $f^\alpha$  has influence mainly on the duration of the production of  $A$  ( $t^\alpha$ ). We get the shortest  $t^\alpha$  when the distillate of Column  $\beta$  is fed into the decanter. When  $f^\alpha = 1$  (top tray) the composition of the top vapour of Column  $\alpha$  is out of the heterogeneous region therefore there is no liquid-liquid split in the decanter which makes the separation infeasible. From the 2<sup>nd</sup> tray the separation is feasible again but a further increase of  $f^\alpha$  results in the increase of  $t^\alpha$ . If  $f^\alpha > 4$ , the prescribed purity can not be reached.

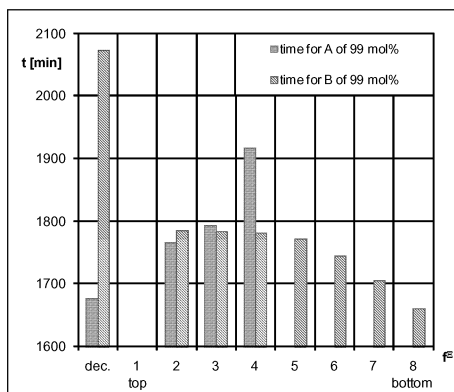


Fig. 3: Effect of  $f^\alpha$  on  $t^\alpha$  and  $t^\beta$

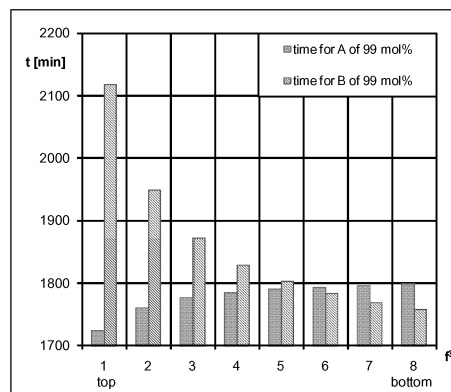


Fig. 4: Effect of  $f^\beta$  on  $t^\alpha$  and  $t^\beta$

If the distillate of Column  $\beta$  is fed into the decanter the duration of the production of  $B$  ( $t^\beta$ ) is much higher than in the cases when it is fed into Column  $\alpha$  because the distillate of Column  $\beta$  changes significantly the liquid composition in the decanter and the difference between the compositions of the two liquid phases is smaller (the tie line is shorter). The increase of  $t^\alpha$  results in the slight decrease of  $t^\beta$ .

We can state that the distillate of Column  $\beta$  must be fed into one of the upper trays.

#### Feed tray location in Column $\beta$ (Fig. 4)

This parameter  $f^\beta$  has influence mainly on  $t^\beta$ . The increase of  $f^\beta$  results in the decrease of  $t^\beta$  and in the slight increase of  $t^\alpha$ . We can state that the distillate of Column  $\beta$  must be fed into one of the lower trays.

#### Reflux ratio of Column $\beta$ (Fig. 5)

This parameter has strong influence on the duration of the production of both products, especially on  $t^\beta$ . The increase of  $R^\beta$  results in the increase of  $t^\beta$  and in the decrease of  $t^\alpha$ . The purification of  $B$  needs less energy therefore the heat duty of Column  $\beta$  can be much lower than that of Column  $\alpha$ . Hence the flow rate of the top vapour  $\beta$  is much lower than that of top vapour  $\alpha$  which results in a slighter effect of the flow rate of Distillate  $\beta$  (and  $R^\beta$ ) on  $t^\alpha$ . We can state that a low reflux ratio ( $R^\beta < 1$ ) must be applied.

We performed the above study also for two other charge compositions (20 and 40 mol% of  $A$ ) and obtained similar results.

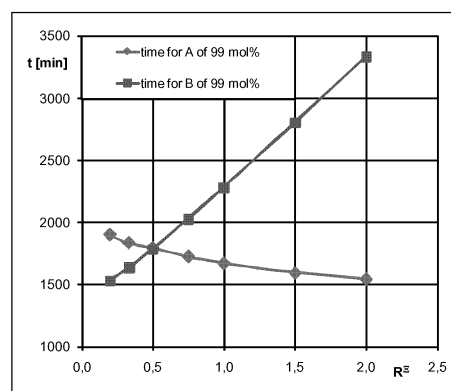


Fig. 5. Effect of  $R^\beta$  on  $t^\alpha$  and  $t^\beta$

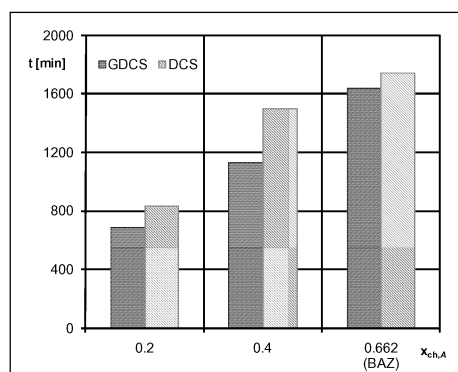


Fig. 6: Minimum duration for each configuration ( $E$ : cyclohexane)

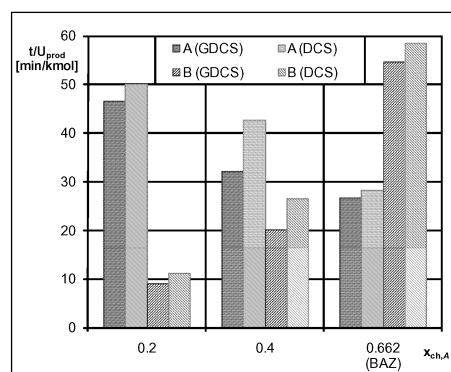


Fig. 7: Specific energy demand for each product and configuration (cyclohexane)

### 3.2 Comparison of the configurations

#### 1.1.3 Method of the study

We compare the GDCS with the original DCS having the same fixed parameters ( $U_{ch}, \bar{x}_{ch}, x_{A/prodA}, x_{B/prodB}, N^\alpha, N^\beta, U_{HU}^\alpha, U_{HU}^\beta, Q$ ) as in the study of the influence of the new operational parameters, except for  $u^\alpha, q^\alpha$  and  $U_{b,E}^\alpha$  which are variable like  $f^\alpha, f^\beta, R^\beta$ . Before the comparison the optimum values of the variable parameters are determined in each case. The objective function is the minimum duration.

#### 1.1.4 Results for the cyclohexane as entrainer

The optimum values of the operational parameters for both configurations are presented in Table 1. In the cases of the GDCS the feed tray location of Column  $\alpha$  is always one of the upper trays but not the first. The feed tray location of Column  $\beta$  is always the lowest tray and  $R^\beta$  is always low. The durations (Fig. 6) and the specific energy demands of the products (Fig. 7) are compared. In the cases studied the duration of the GDCS is always shorter and the specific energy demands of the products are also lower than by the original DCS.

Table 1: Optimum values of the variable operational parameters (E: cyclohexane)

Mole fraction of A in the charge	Column config.	Variable parameters					
		$f^\alpha$	$f^\beta$	$R^\beta$	$u^\alpha$	$U_{b,E}^\alpha$	$Q^\alpha$
		-	-	mol/mol	%	kmol	%
0.2	GDCS	3	8	0.3	5	0.5	70.9
	DCS	decanter	1	0	5	0.5	65.0
0.4	GDCS	3	8	0.3	5	0.5	66.6
	DCS	decanter	1	0	28	0.5	72.7
0.662 (BAZ)	GDCS	2	8	0.45	10	0.5	62.3
	DCS	decanter	1	0	40	0.5	69.8

Table .: Optimum values of the variable operational parameters (E: n-hexane)

Mole fraction of A in the charge	Column config.	Variable parameters					
		$f^\alpha$	$f^\beta$	$R^\beta$	$u^\alpha$	$U_{b,E}^\alpha$	$q^\alpha$
		-	-	mol/mol	%	kmol	%
0.2	GDCS	1	8	0.75	5	3.6	64.3
	DCS	decanter	1	0	5	3.0	73.1
0.4	GDCS	1	8	0.55	5	3.6	66.8
	DCS	decanter	1	0	5	4.0	68.2
0.662 (BAZ)	GDCS	1	8	0.5	20	4.0	69.8
	DCS	decanter	1	0	35	3.1	75.8

### 1.1.5 Results for the n-hexane as entrainer

The comparison of the GDCS and the DCS is repeated by applying another entrainer (n-hexane). On the basis of the VLLE conditions the n-hexane seems to be more favourable than the cyclohexane:

*i.* The IPA content of the TAZ is lower. *ii.* The tie line passing through the TAZ is longer. *iii.* The distribution of IPA between the organic and aqueous phases is more favourable. *iv.* Higher  $R^\alpha$  can be ensured by refluxing the organic phase only.

*v.* In the case of the DCS the condensate remains in the heterogeneous region at higher BAZ/TAZ ratio. *vi.* The difference of the densities of the two liquid phases is much higher.

The optimum values of the operational parameters are shown in Table 2. The results are similar to those obtained for the cyclohexane. (The feed tray location of Column  $\beta$  is always the lowest tray and  $R^\beta$  is always low.) However, for the GDCS the optimum feed tray of Column  $\alpha$  is always Tray 1.

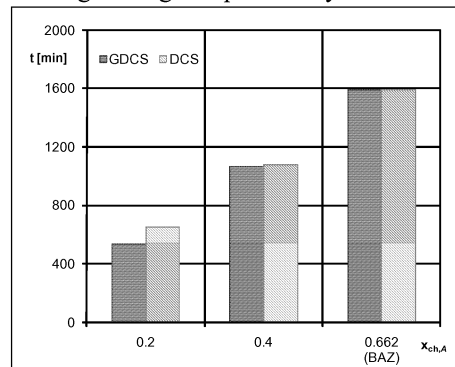


Fig. .: Minimum durations for n-hexane

The duration of the GDCS is always shorter (Fig. 8) therefore its energy demand is always lower than those of the DCS.

### Acknowledgement

This project is supported by the Hungarian Research Funds (OTKA, No.: K-82070), by the New Hungary Development Plan (Project ID: TÁMOP-4.2.1/B-09/1/KMR-2010-0002) and by the Embassy of France in Hungary.

### References

- Denes F., Lang P., Modla G. and Joulia X., 2009, New double column system for heteroazeotropic batch distillation, *Comp. Chem. Eng.*, 33, 1631-1643.
- Denes F., Lang P., Joulia X., 2010, Experimental validation of a new double-column system for heteroazeo. batch distillation, *Distillation & Absorption 2010*, 289-294.
- Modla G., Lang P., Kotai B. and Molnar K., 2003, Batch Heteroazeotropic Rectification of a Low Relative Volatility Mixture, *AIChE Journal*, 49, 2533-2552.
- Rodriguez-Donis I., Gerbaud V. and Joulia X., 2002, Feasibility of Heterogenous Batch Distillation, *AIChE Journal*, 48, 1168-1178.
- Rodriguez-Donis I., Equijarosa J. A., Gerbaud V. and Joulia X., 2003, Separation of minimum boiling azeotropic mixtures by extractive batch distillation processes with heterogenous entrainers, *AIChE Journal*, 49, 3074-3083.
- Skouras S., Kiva V. and Skogestad S., 2005, Feasible separations and entrainer selection rules for heteroazeo. batch distillation, *Chem. Eng. Sci.*, 60, 2895-2909.