

## NEW METHOD FOR THE DETERMINATION OF BATCH HETEROAZEOTROPIC DISTILLATION REGIONS

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A new, general method for the determination of batch distillation regions of heteroazeotropic distillation is suggested. The method proposed, which means the extension of the method of Pham and Doherty, takes into consideration the possibility of the withdrawal of any fraction of either liquid phase from the decanter as distillate. The simplified and rigorous simulation calculations were carried out for the mixtures 1,4-dioxanewater + benzene and isopropanol-water + benzene. The new method gives the right sequence of the cuts for all operation modes and strategies of heterogeneous batch distillation.

**KEYWORDS:** batch distillation, heterogeneous entrainer, separation of azeotropes, residue curves

### INTRODUCTION

Batch heteroazeotropic distillation is an efficient method for the separation of azeotropic and low relative volatility (low  $\alpha$ ) mixtures. A third component (entrainer,  $E$ ) is added to the binary  $A$ - $B$  mixture which makes the separation of  $A$  and  $B$  possible. The entrainer forms a heteroazeotrope with at least one (and preferably with only one (selective entrainer)) of the original components.

To our best knowledge so far the process was exclusively applied in the industry in batch rectifiers (equipped with a decanter) in open operation mode (continuous top product withdrawal), though recently the closed operation mode for batch rectifiers and also for multivessel columns was extensively studied by the team of Skogestad (Skouras et al. 2005a,b).

Design and synthesis tools of batch distillation involve the analysis of residue curve maps (e.g. Doherty and Perkins (1978), Doherty and Caldarola (1985), Kiva et al. (2003)). The residue curve is equivalent to the still path of simple (differential) distillation.

Bernot et al. (1990) used the batch distillation (BD) regions to determine the sequence of the fractions. Ewell and Welch (1945) defined a BD region as a region, which gives the same fractions upon rectification of any mixture lying within it. Bernot et al. investigated the still and distillate paths for the determination of the region boundaries under high number of stages and high reflux ratio ("maximal separation").

Pham and Doherty (1990) described the structure and properties of residue curve maps for ternary heterogeneous azeotropic mixtures. The residue curve map analysis and the subsequent determination of distillation regions consider only the phase equilibrium (VLLE) characteristics of the mixture. The singular points of the residue curve

maps determined by this method were used for assigning heterogeneous batch distillation regions by Rodriguez-Donis et al. (2002, 2003) and Skouras et al. (2005b).

Modla et al. (2003) pointed out that this method may give misleading results for the minimal amount of entrainer in the case where the distillate is withdrawn from the *E*-weak phase only and the *E*-rich phase is refluxed. This operation mode – which is very frequently applied, since the amount of the entrainer (*E*) can be reduced in this way – requires the simultaneous realisation of the two separation methods (distillation and liquid-liquid phase split) of the hybrid process. This operation mode is named Mode II by Skouras et al. (2005a,b). By Mode I the two separation methods are realised in sequence.

The aim of the paper is to suggest a new, general method for the determination of batch distillation regions of the heteroazeotropic distillation. The method considers, in addition to the VLLE, operating parameters of the column, such as withdrawal of the entrainer-lean or the entrainer-rich phase or any combination of them as distillate. In other words, the method presented combines both VLLE information and material balances in the still path map, which is used instead of (the open distillation) residue curve map.

The method proposed takes into consideration the possibility of refluxing any fraction of either liquid phase to the still pot (differential distillation) or to the column (rectification), that is, it is suitable for all operation modes and separation strategies.

The calculations were carried out for the mixtures

1. 1,4-dioxane – water + benzene (heavy, selective, heterogeneous entrainer) and
2. isopropanol-water (minimum azeotrope) + benzene (light, non-selective, heterogeneous entrainer).

For the feasibility (residue curve, still path etc.) calculations we developed a simple computer program (in Borland Pascal) based on the generalized model. For the VLLE calculations the algorithm of Brill et al. (1974) was applied.

The rigorous simulation calculations for the verification of batch distillation regions were made with the CHEMCAD 5.5 professional flow-sheet simulator.

## GENERALIZED MODEL

The model takes into consideration the possibility of refluxing any fraction of either liquid phase to the still pot (differential distillation) or to the column (rectification).

Mass balance on components yields

$$\frac{dL^o \mathbf{x}^o}{dt} = -\dot{D}^o \mathbf{x}_D^o \quad (1)$$

where  $\mathbf{x}_D^o$  is the instantaneous (overall) distillate composition

$$\mathbf{x}_D^o = \frac{\alpha \eta \mathbf{y}' + \beta (1 - \eta) \mathbf{y}''}{\alpha \eta + \beta (1 - \eta)} \quad 0 \leq \alpha \leq 1, 0 \leq \beta \leq 1 \text{ and } \alpha + \beta > 0 \quad (2)$$

and where  $\alpha = (\dot{D}'/\dot{V})$ ,  $\beta = (\dot{D}''/\dot{V})$  and  $\eta$  is the ratio of the  $E$ -rich phase within the heterogeneous condensate

$$\eta = \frac{\dot{L}'_R + \dot{D}'}{\dot{V}} = \frac{y'' - y^o}{y'' - y'} \quad (3)$$

Applying the well-known transformations (e.g. Doherty and Perkins, 1978) we can derive for the variation of the (overall) still composition ( $\mathbf{x}^o$ )

$$\frac{d\mathbf{x}^o}{d\tau} = -(\mathbf{x}_D^o - \mathbf{x}^o) \quad (4)$$

where  $\tau$  is the dimensionless time variable ranging from 0 to  $+\infty$ .

(Eq. 4 is in harmony with those published for (heterogeneous batch) rectification by Rodriguez-Donis et al., 2002 and Skouras et al., 2005b.)

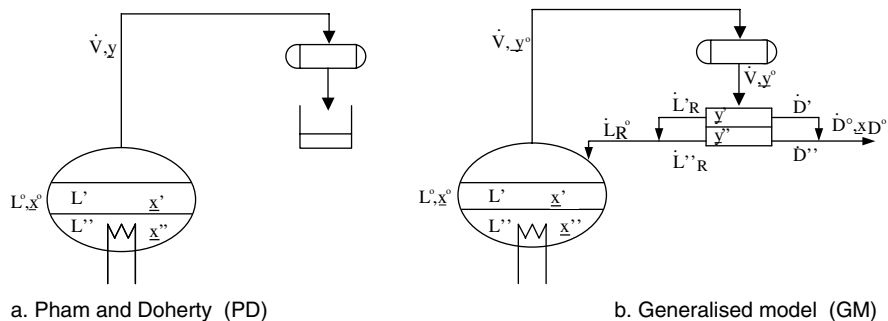
If the condensate is homogeneous ( $\eta = 0$  or 1) or  $\alpha = \beta$  then our model is reduced to that of Pham and Doherty.

For the sake of the simplicity we suppose that the condensate is boiling point liquid.

## CALCULATION RESULTS

On the sketch of the residue curve maps (Figures 1 and 2) the heterogeneous liquid boiling envelope (hlbe, 'isobaric boiling point solubility curve') and the vapour line are also shown.

For Mixture 1 (Figure 1) the unstable node (o) is the heteroazeotrope A–E ( $AZ_{AE}$ ), the stable ones (●) are vertices A and B. The heteroazeotrope splits into two (an  $E$ -rich ( $AZ'_{AE}$ ) and an  $E$ -lean ( $AZ''_{AE}$ ) liquid phases. Saddle points (▽) are the  $AZ_{AB}$  azeotrope and the vertex E. There is an unstable separatrix between  $AZ_{AE}$  and  $AZ_{AB}$ .



**Figure 1.**

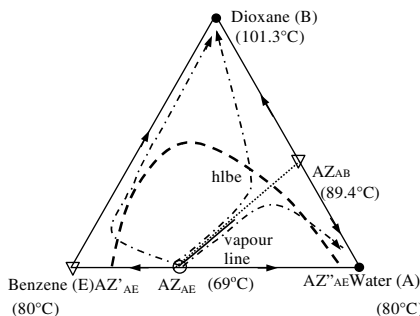


Fig. 2.1 Mixture 1

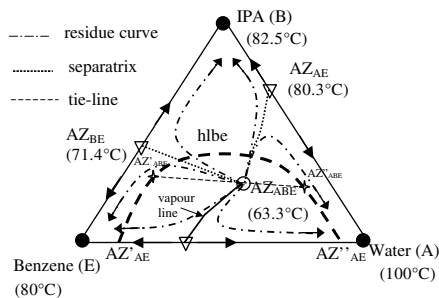


Fig. 2.2 Mixture 2

**Figure 2.** The sketch of the residue curve maps

For Mixture 2 (Figure 2) the unstable node is the ternary heteroazeotrope ( $AZ_{ABE}$ ). The stable nodes are the three pure component vertices. The heteroazeotrope splits into two liquid phases ( $AZ'_{ABE}$ ,  $AZ''_{ABE}$ ). The saddle points are the three binary minimum azeotropes (the homoazeotropes  $AZ_{AB}$ ,  $AZ_{BE}$  and the heteroazeotrope  $AZ_{AE}$ ); there are three unstable separatrices. (The separatrix between  $AZ_{ABE}$  and  $AZ_{AE}$  coincides with the vapour line.)

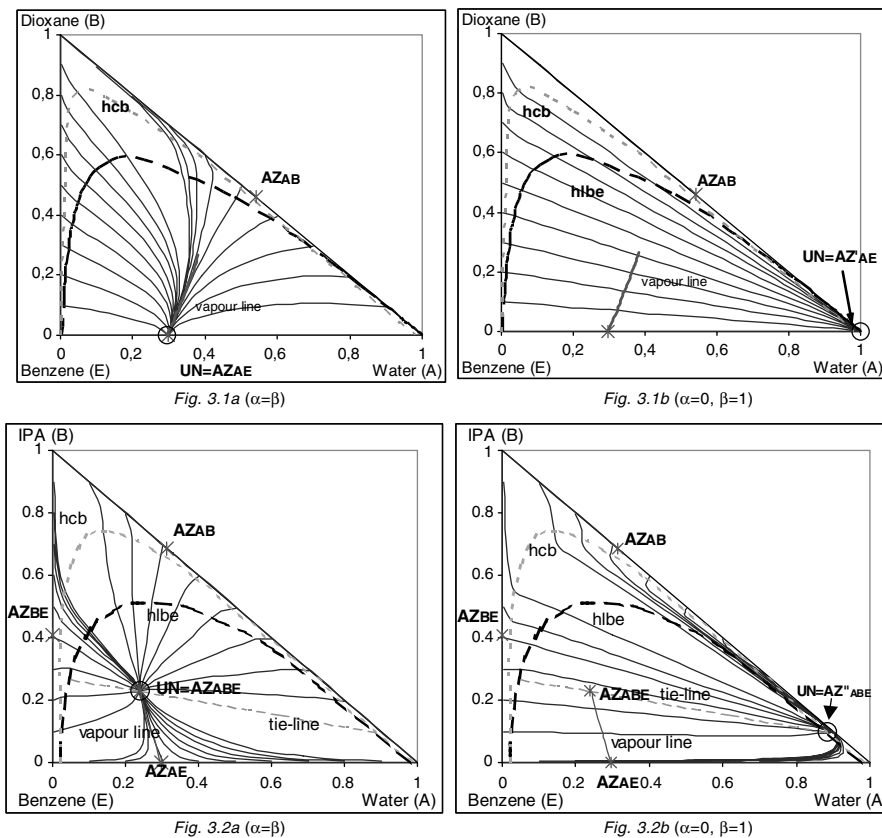
For both mixtures the still paths were calculated by the GM with Eq. 4 for two different cases.

- When  $\alpha = \beta$  the still paths are identical to the PD residue curves (Figures 1a, 2a).
- If  $\alpha \neq \beta$  (e.g.  $\alpha = 0$ ;  $\beta = 1$ ) the specification is valid only in the overall composition ( $\mathbf{x}^0$ ) region where the condensate ( $\mathbf{y}^0$ ) is heterogeneous. (This case can be performed only in the region where the condensate splits into two liquid phases.) The borders of the heterogeneous condensate area are the curved boundary hcb and the AE edge. Outside this area the curves were calculated by the PD method. When  $\alpha \neq \beta$ , the unstable node of the curves (UN) is not the heteroazeotropic point as it would be by the PD method.

In the case where the distillate is withdrawn from only the *E*-lean phase ( $\alpha = 0$ ,  $\beta > 0$ , Figures 1b, 2b) the unstable node is the *E*-lean phase of the heteroazeotrope ( $AZ''_{AE}$  for Mixture 1 and  $AZ''_{ABE}$  for Mixture 2, respectively).

On the increase of the ratio  $\alpha/\beta$  (in the practice its maximal value is 1.0) UN moves on the tie line from the *E*-lean phase towards the *E*-rich phase.

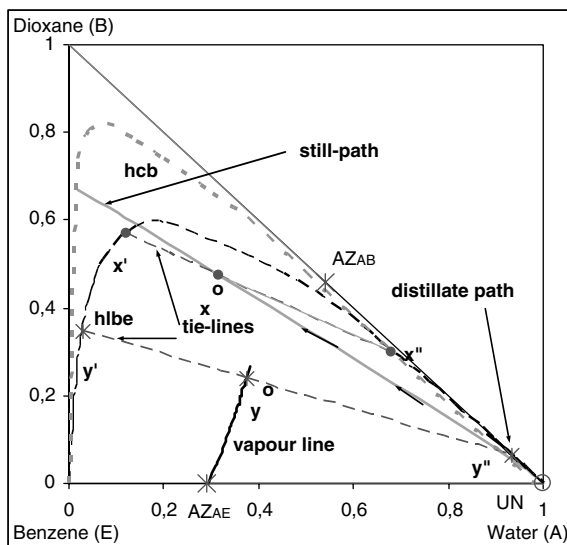
Refluxing one part of the *E*-lean phase (besides the *E*-rich phase) does not vary the distillate and still paths in the case of simple distillation (no column), only the distillation process will be slower. This is not valid at all for the rectification (in column) where the different reflux ratio results in different distillate composition and so in the variation of distillate and still paths.



**Figure 3.** The still path maps calculated by the GM

A still path and the distillate path belonging to it are presented for the case  $\alpha = 0$ ,  $\beta = 1$  (Figure 4). A heterogeneous point of the still path ( $x^0$ ) splits into two equilibrium liquid phases: an  $E$ -rich phase ( $x'$ ) and an  $E$ -lean phase ( $x''$ ). These liquid phases are in equilibrium with the vapour phase of overall composition  $y^0$ . The condensate of this vapour splits into two equilibrium liquid phases ( $y'$  and  $y''$ ).  $y''$  gives one point of the distillate path (in this case). Both distillate and still paths start from the unstable node (UN), which is the  $E$ -lean phase of the heteroazeotrope.

For the case  $\alpha = 0$ ,  $\beta > 0$  (Mode II, Strategy A) batch distillation regions were determined by the use of the singular points of Pham and Doherty and those of the GM (Figures 1a–2b). Since the unstable node UN is a common vertex of all BD regions due to the difference of unstable nodes all BD regions are different by the two methods.



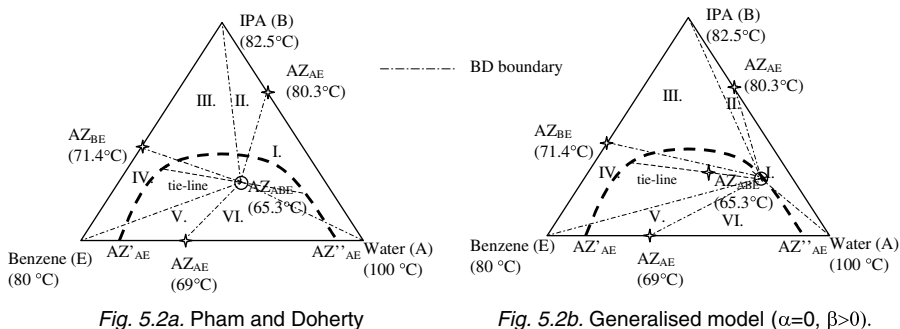
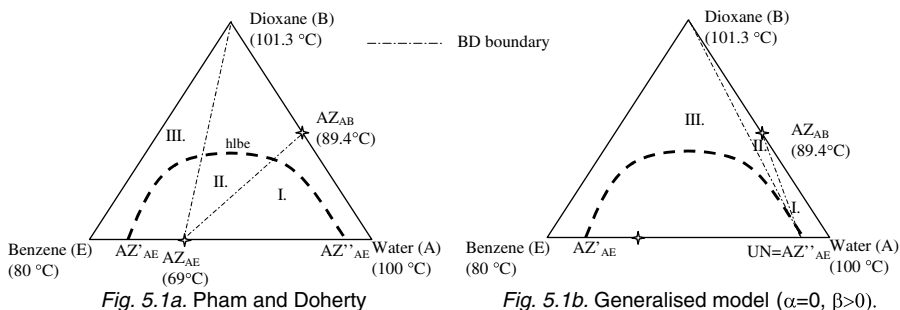
**Figure 4.** A still path and a distillate path for the case  $\alpha = 0$ ,  $\beta = 1$  (for Mixture 1)

The area of the BD regions whose one side is located on the AB edge, which contains the original, binary mixture  $A-B$  (Regions I and II), diminishes to the favour of the area of the BD regions whose one side is located on the BE edge (for Mixture 1 Region II, for Mixture 2 Regions III and IV, respectively).

In the case of Mixture 2 BD regions V and VI have no side on either the AB or the BE edge of the triangle ABE. The variation of the areas of these regions depends on the distribution of  $B$  between the  $E$ -lean and  $E$ -rich phases. Since  $B$  is less soluble in the  $E$ -lean phase than in the  $E$ -rich one and therefore its concentration is lower in the  $E$ -lean phase than in the ternary heteroazeotrope, the unstable node vertex of these BD regions triangles is found nearer to the AE edge. Hence the area of these regions decreases.

From point of view of industrial practice the most important conclusion is that by the GM in the case of a binary feed (located on the AB edge) by the addition of a much smaller amount of entrainer we can reach a BD region where none of the borders is found on the AB edge (e.g. in the case of Mixture 1 the Region III starting from the azeotropic feed  $AZ_{AB}$ , see Figure 1).

For the verification of BD regions *rigorous simulation calculations* were made with the CHEMCAD 5.5 professional flow-sheet simulator (Chemstations, 2005). For both mixtures Mode II and Strategy A (with  $\alpha = 0$ ,  $\beta = 1$ ) were applied. In both cases the



**Figure 5.** Batch distillation regions determined by the use of the singular points of the two different methods

still path starting from the feed composition (F) crosses the BD region boundary between Regions II and III determined by the PD method (Figures 1–2). However in each case the still path remains in the BD region (Region III) determined by the GM.

The sequence of the cuts determined by the two different methods for the above feed compositions are shown in Table 1.

We can conclude that the rigorous simulation verified that in each case it is the GM, which gives the right sequence of the cuts. Since the PD method gives the right sequence of the cuts (only) for Mode I, considering the above sequence of the cuts we can state that none of the mixtures can be successfully separated by Mode I because the original A–B separation problem would arise again after the first, heteroazeotropic cut (the still path would arrive to the AB edge in each case). However we can separate each mixture without any problem by Mode II Strategy A.

It can be also seen in Figure 1 that the still path leaves the heterogeneous condensate area. In spite of this the still path remains straight indicating that the distillate composition does not change significantly even outside the heterogeneous condensate area. This can be

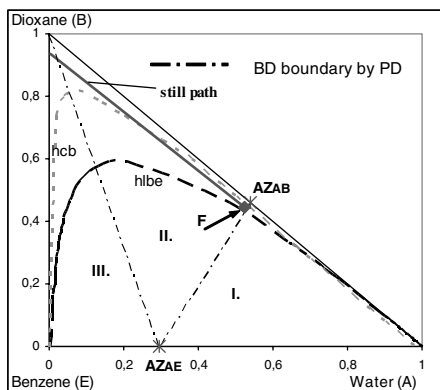


Fig. 6.1. Water-Dioxane + Benzene

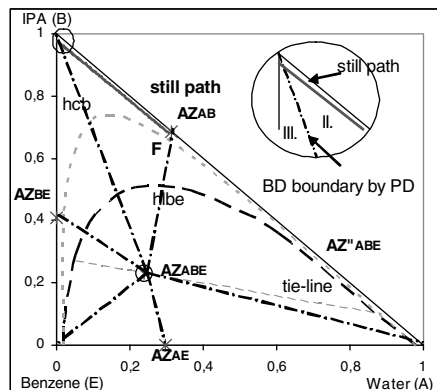


Fig. 6.2. IPA-Water + Benzene

Figure 6. Still paths calculated by rigorous simulation ( $\alpha = 0$ ,  $\beta = 1$ )

Table 1. The sequence of the cuts by the PD and GM methods

	Mixture 1		Mixture 2	
	PD	GM	PD	GM
1 <sup>st</sup> cut	AZ <sub>AE</sub>	AZ'' <sub>AE</sub>	AZ <sub>ABE</sub>	AZ'' <sub>ABE</sub>
2 <sup>nd</sup> cut	AZ <sub>AB</sub>	E	AZ <sub>AB</sub>	AZ <sub>BE</sub>
3 <sup>rd</sup> cut	B	B	A	B

explained by the fact that the heterogeneous condensate area of rectification is obviously greater than that of the simple distillation. In the case of rectification the separation is performed on several theoretical stages and the composition of only the top stage liquid must be located within heterogeneous condensate area.

## CONCLUSIONS

By the extension of the method of Pham and Doherty a new, general method for the determination of heterogeneous batch distillation regions is suggested. The new method allows the withdrawal of any fraction of either liquid phase from the decanter as distillate, that is, it is suitable not only for operation Mode I (sequential distillation and liquid-liquid phase split) but also for operation Mode II (simultaneous distillation and liquid-liquid phase split). Instead of the residue curve map (of open distillation) we suggested the use of the still path map combining both VLE information and material balances. The new



method was presented for the separation of mixtures 1,4-dioxane-water and isopropanol-water using benzene as entrainer with simplified and rigorous simulation calculations. The results of rigorous simulation calculations verified that the new method gives the right sequence of the cuts even in operation Mode II.

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### REFERENCES

1. Bernot C., M. Doherty, M. and M. F. Malone, (1990). Patterns of composition change in multicomponent batch distillation, *Chemical Engineering Science*, **45**, 1207.
2. Bril Zs. A., Mozzsuhin, A. C., Petljuk and F. B., Serafimov, L. A., (1974). Mathematical modelling of the rectification of multicomponent mixtures with liquid phase splitting on the plates of the column, *Teor. Osn. Chim. Technol.*, **8**, 351.
3. Chemstations, (2005). "CHEMCAD User Guide".
4. Doherty, M. F. and J. D. Perkins, (1978). On the Dynamics of Distillation Processes I. The Simple Distillation of Multicomponent Nonreacting, Homogeneous Liquid Mixtures, *Chemical Engineering Science*, **33**, 281.
5. Doherty M. F., and G. A. Calderola, (1985). Design and Synthesis of Homogeneous Azeotropic Distillations. 3. The Sequencing of Columns for Azeotropic and Extractive Distillation," *Industrial Engineering Chemistry Fundamentals* **24**, 474.
6. Ewell, R. H. and L. M. Welch, (1945). Rectification in Ternary Systems Containing Binary Azeotropes, *Industrial Engineering Chemistry*, **37**, 1224.
7. Kiva V., E. Hilmen and S. Skogestad, (2003). Azeotropic Phase Equilibrium Diagrams: a Survey, *Chemical Engineering Science*, **58**, 1903–1953.
8. Koehler, J., H. Haverkamp, and N. Schadler, (1995). Zur Diskontinuierlichen Rektifikation Azeotroper Gemische mit Hilfsstoffeinsatz, *Chemie Ingenieur Technik*, **67** (8), 967.
9. Modla G., P. Lang, B. Kotai and K. Molnar, (2003). Batch Heteroazeotropic Rectification of a Low Relative Volatility Mixture under Continuous Entrainer Feeding, *AIChE Journal*, **49** (10), 2533.
10. Pham, H. N. and M. F. Doherty, (1990). Design and synthesis of heterogeneous azeotropic distillations II. Residue curve maps, *Chemical Engineering Science*, **45** (7), 1837.
11. Rodriguez-Donis I, V. Gerbaud and X. Joulia, (2002). Feasibility of Heterogeneous Batch Distillation Processes, *AIChE Journal*, **48** (6), 1168.
12. Rodriguez-Donis Y., J. A. Equijarosa, V. Gerbaud and X. Joulia, (2003). Heterogeneous Batch-extractive Distillation of Minimum Boiling Azeotropic Mixtures, *AIChE Journal*, **49** (12), 3074.
13. Serafimov, L.A. (1970). The Azeotropic Rule and the Classification of Multicomponent Mixtures. VII. Diagrams for Ternary Mixtures. *Russian Journal of Physical Chemistry* **44** (4), 567.

14. Skouras S., V. Kiva and S. Skogestad, (2005a). Feasible separations and entrainer selection rules for heteroazeotropic batch distillation, *Chemical Engineering Science*, **60**, 2895.
15. Skouras S., S. Skogestad and V. Kiva, (2005b). Analysis and Control of Heteroazeotropic Batch Distillation, *AIChE Journal*, **51** (4), 1144–1157.