Pergamon

*Int. Comm. Heat Mass Transfer*, Vol. 28, No. 3, pp. 347–356, 2001
Copyright © 2001 Elsevier Science Ltd
Printed in the USA. All rights reserved
0735-1933/01/$–see front matter

**PII: S0735-1933(01)00240-8**

# CROSSING OF BOUNDARIES IN TERNARY AZEOTROPIC DISTILLATION: INFLUENCE OF INTERPHASE MASS TRANSFER

P.A.M. Springer and R. Krishna
Department of Chemical Engineering, University of Amsterdam
Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands
(Fax: +31 20 5255604; email: krishna@its.chem.uva.nl)

(Communicated by J.W. Rose and A. Briggs)

## ABSTRACT

This paper examines the influence of mass transfer on the composition trajectories in multicomponent azeotropic distillation. Simulations were carried out for five different ternary systems: methanol – *iso*propanol – water, water – ethanol – acetone, acetone – chloroform – methanol, acetone – chloroform – ethanol, and water – cyclohexane – ethanol. Two different models were used to calculate the composition trajectories in a tray column: an equilibrium (EQ) stage model and a rigorous nonequilibrium (NEQ) stage model based on the Maxwell-Stefan diffusion equations. The simulations show that the EQ and NEQ model trajectories could follow different composition paths and could end up in completely different corners of the composition triangular space. Furthermore, in some of the case studies the NEQ model trajectory was found to cross the distillation boundary even with the feed on the convex side or when the boundary is a straight line. The study has implications for the development of improved separation possibilities. © 2001 Elsevier Science Ltd

## Introduction

There is considerable industrial interest in the design and optimization of homogeneous and heterogeneous azeotropic distillation. This interest stems from the large number of industrial columns in operation and the potential of developing improved separation schemes so as to minimise energy consumption. Residue curve maps are commonly used in developing separation flow schemes [1 - 3]. The existence, location and curvature of distillation boundaries are very important in the synthesis of azeotropic distillation sequences. The curvature of the boundary has a significant impact on whether or not it is possible to cross it during distillation. In the literature [3 - 18] it is remarked that boundary crossing is only possible if the feed is located on the *concave* side of the distillation boundary. It is also stated in the literature that straight-line distillation boundaries cannot be crossed [11]. Consider, for example, the system methanol – *iso*propanol – water, for which the residue curves are shown in Fig. 1 (a).

This system has one binary azeotrope, that divides the composition space into two regions; these two regions are separated by a distillation boundary that is practically straight. For the feed located in the upper region, it should not be possible to cross the straight-line boundary during distillation. On the other hand, for the system acetone – chloroform –methanol, for a feed located on the concave side, as shown in Fig. 1 (b), the distillation trajectories during column operation can cross the boundary.

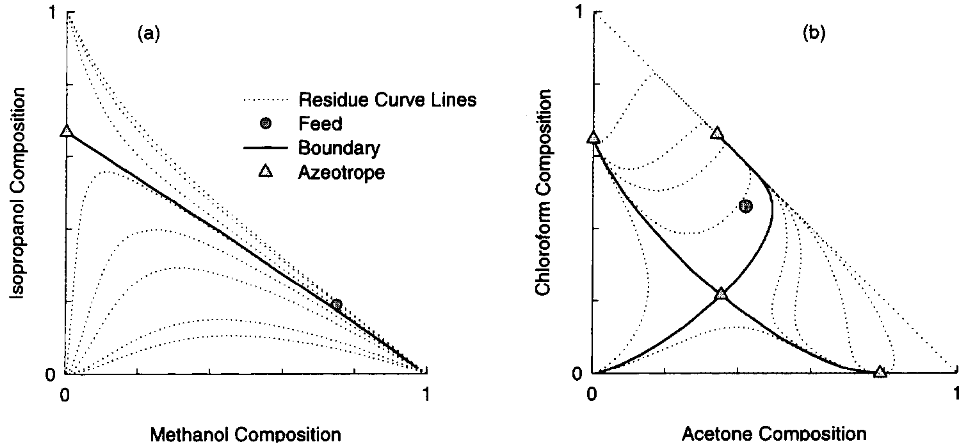

FIG. 1
(a) Residue curves for system methanol (1) – *iso*propanol (2) – water (3). (b) Residue curves for system acetone (1) – chloroform (2) – methanol (3).

Most of the published literature simulation studies on the possibilities of crossing of distillation boundaries use the equilibrium (EQ) stage model. There is evidence in the published literature that experimentally measured composition profiles in distillation columns are better simulated with nonequilibrium (NEQ) stage models, in which proper account is taken of mass transfer in either fluid phase by use of the rigorous Maxwell-Stefan diffusion equations [19 - 25]. The Maxwell-Stefan formulation, based on the thermodynamics of irreversible processes, takes proper account of diffusional "coupling" between the species transfers i.e. the flux of any species depends on the driving forces of all the species present in the mixture. In a distillation column, the influence of species coupling manifests itself in significant differences in the component mass transfer efficiencies. Castillo and Towler [26] computed nonequilibrium distillation lines for a sieve tray column and demonstrated that modest differences between the efficiencies of different components, caused by mass transfer effects, could lead to significant differences in curvature between EQ and NEQ distillation lines. They went on to show that, in some cases, differences in curvature could be exploited by the engineer in order to obtain process designs that could not be contemplated if mass transfer effects were ignored, and that some designs based solely on equilibrium models can become infeasible when mass transfer is considered.

It is the purpose of this paper to contribute further to this emerging discussion of NEQ distillation lines. In particular, we show that whether or not a distillation boundary can be crossed depends on whether or not interphase mass transfer is accounted for.

TABLE 1
NRTL parameters for the mixtures

| $G_{ij} = \exp(-\alpha_{ij}\tau_{ij})$ with $\tau_{ij} = B_{ij}/T$ | | | |
|---|---|---|---|
| | $B_{ij}$/[K] | $B_{ji}$/[K] | $\alpha_{ij}$/[-] |
| Water - Ethanol | 624.8723 | -29.16687 | 0.2937 |
| Water - Acetone | 666.7592 | 409.696 | 0.5663 |
| Ethanol - Acetone | 188.8847 | 22.83154 | 0.3006 |
| Acetone - Methanol | 59.42076 | 149.0765 | 0.3003 |
| Acetone - Chloroform | -327.6945 | 151.8924 | 0.3054 |
| Methanol - Chloroform | -53.0728 | 671.975 | 0.2873 |
| Ethanol - Chloroform | -143.6139 | 648.7655 | 0.2909 |
| Water - Methanol | 594.629 | -182.605 | 0.297 |
| Water - *Iso*propanol | 729.2208 | 70.6619 | 0.288 |
| Methanol – *Iso*propanol | 65.711 | -89.7427 | 0.304 |
| Water - Cyclohexane | 4422.3 | 1688.273 | 0.21159 |
| Ethanol - Cyclohexane | 440.6134 | 717.6762 | 0.46261 |

## Simulation Results for Bubble Cap Tray Distillation Column

The equilibrium data (NRTL parameters) for the systems studied are specified in Table 1. All simulations were carried out a 101.3 kPa pressure, and the ideal gas law was applied. The vapour pressures were calculated using the Antoine equation. The feed was in the liquid state and fed to the column at 0.01 mol/s; a total condenser was used at the top producing a liquid product. A total reboiler was used producing a vapour product in the bottom. The column hardware details are as follows: column of diameter = 0.05 m; 1 bubble cap per tray; active area = 97.3% of total; tray spacing = 0.0462 m; number of flow passes = 1; downcomer area = 1.35% of total; Total hole area = 8.27% of active area; Liquid flow path length = 0.0308 m; weir type = circular; downcomer clearance = 0.0039 m; weir length = 0.0182 m; deck thickness = 0.003 m; Weir height = 0.0092 m; hole diameter = 0.0142 m; weir diameter =0.0058 m; hole pitch = 0.0142 m; cap diameter = 0.0281 m; slot area = 0.000221 m$^2$; skirt clearance= 0.003 m; riser area = 0.000158 m$^2$; slot height = 0.005 m; annular area = 0.000462 m$^2$.

The simulations were carried out using ChemSep developed by R. Taylor [22 - 25]; details are available at: http://www.clarkson.edu/~chengweb/faculty/taylor/chemsep/chemsep.html and the technical manual can be downloaded from this site. This manual contains details of all thermodynamics, hydrodynamics and mass transfer models for tray columns that have been implemented into the software. The mass transfer coefficients were estimated using the AIChE correlation and including the liquid phase resistance [27]. The vapour was assumed to be in plug flow and the liquid to be well-mixed. No pressure drop or entrainment was considered.

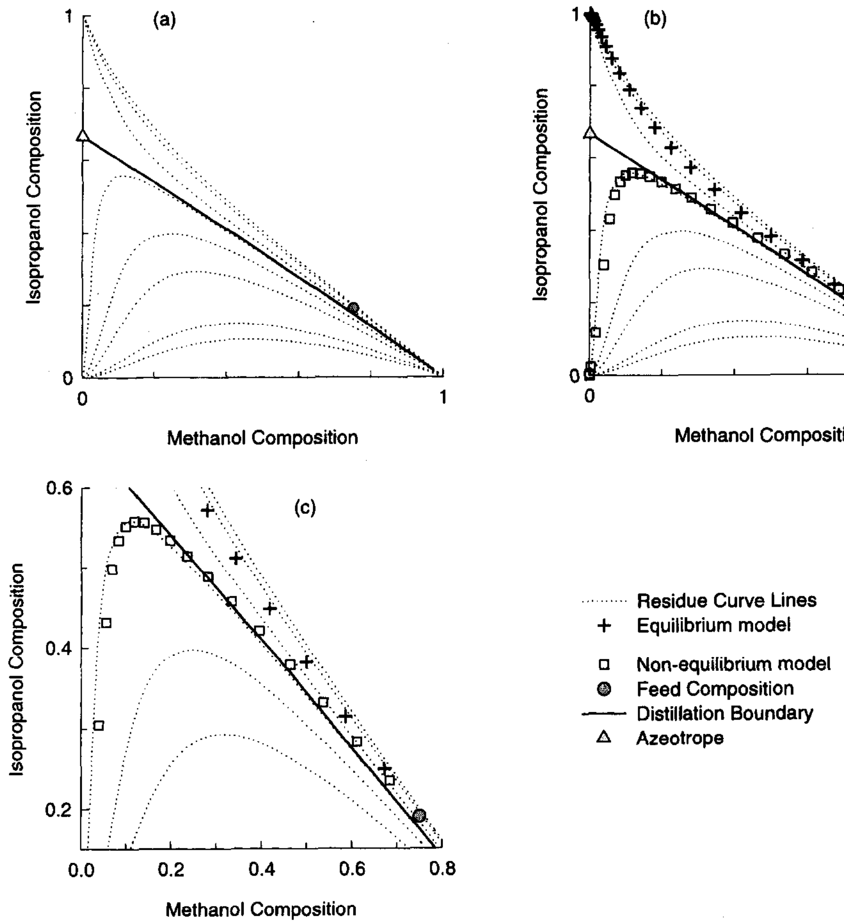

FIG. 2

(a) Residue curves for system methanol (1) – *iso*propanol (2) – water (3). (b) and (c) compare EQ and NEQ distillation trajectories, showing same simulation drawn to different scales. In this simulation the total number of stages, including condenser and reboiler is 32. The feed composition is $x_1$ = 0.75, $x_2$ = 0.19, the liquid feed is on the top tray, counting downwards with condenser = 1. The reflux ratio used is 6.

Let us consider the system: methanol (1) – *iso*propanol (2) – water (3) that has a binary azeotrope, as indicated in Fig. 2 (a). We note that the boundary is very nearly a straight line. According to literature guidelines [11] it is not possible to cross a straight-line boundary. But these remarks regarding boundary crossing are based on the use of the EQ stage model. In order to see whether the introduction of mass transfer resistance has an influence on boundary crossing, we carried out simulations with both EQ and NEQ stage models for a 32-stage column. The feed composition was chosen to be $x_1$ =

0.75, $x_2$ = 0.19 which is located in the top region *above* the distillation boundary. The EQ and NEQ composition trajectories are seen to follow completely different composition trajectories; see Fig. 2 (b). The NEQ model predicts that the bottom product composition corresponds to pure water whereas the EQ model predicts the bottom product to consist of pure *iso*-propanol. There is experimental evidence, for total reflux in a packed distillation column [16] that the NEQ model predictions correspond to reality. Fig. 2 (c), drawn to a different scale, clearly shows that the NEQ model crosses the distillation boundary. This study underlines the important influence of interphase mass transfer on distillation trajectories. Apparently the commonly stated remark that straight-line distillation boundaries cannot be crossed, is not a general conclusion and restricted to the EQ model. The species methanol, *iso*propanol and water have different diffusivities in the vapour and liquid phases; this causes the component efficiencies to differ significantly from one another. These differences in component efficiencies cause the actual distillation trajectories in the column to deviate from those dictated by residue curves. Put another way, an additional curvature is introduced. This allows boundary crossing to occur.

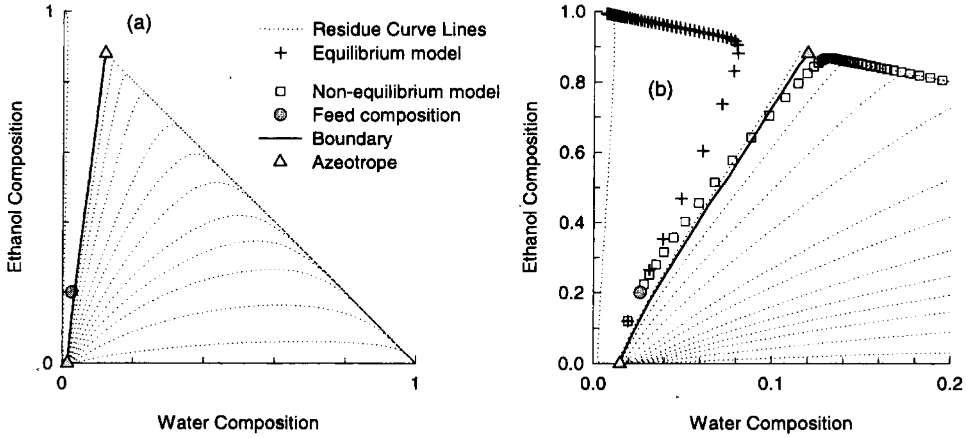

FIG. 3

(a) Residue curves for system water (1) – ethanol (2) – acetone (3). (b) Comparison of EQ and NEQ distillation trajectories. In this simulation the total number of stages is 50. The feed composition is $x_1$ = 0.0265, $x_2$ = 0.2, the liquid feed is on the stage 2, which is the top tray. The reflux ratio used is 12.

Now we analyse the system: water (1) – ethanol (2) – acetone (3) that has two binary azeotropes, as indicated in Fig. 3 (a). The boundary has only a slight curvature and divides the composition triangle into two regions. We carried out simulations of a 50-stage column with a feed composition is $x_1$ = 0.026, $x_2$ = 0.2. For the chosen feed composition, which is located to the left of distillation boundary on the *convex* side, the EQ and NEQ trajectories are seen to follow completely different composition trajectories; see Figs 2 (b) and (c). The top product in both cases consists of an acetone-rich product. The

EQ model predicts that the bottom product consists of virtually pure ethanol; see Fig. 3 (b). The NEQ model, on the other hand, predicts that the bottoms product composition corresponds to a ethanol-water mixture with a water content higher than that of the binary azeotrope. We note that the NEQ model crosses the distillation boundary with the feed placed on the *convex* side. This boundary crossing is forbidden according to literature guidelines.

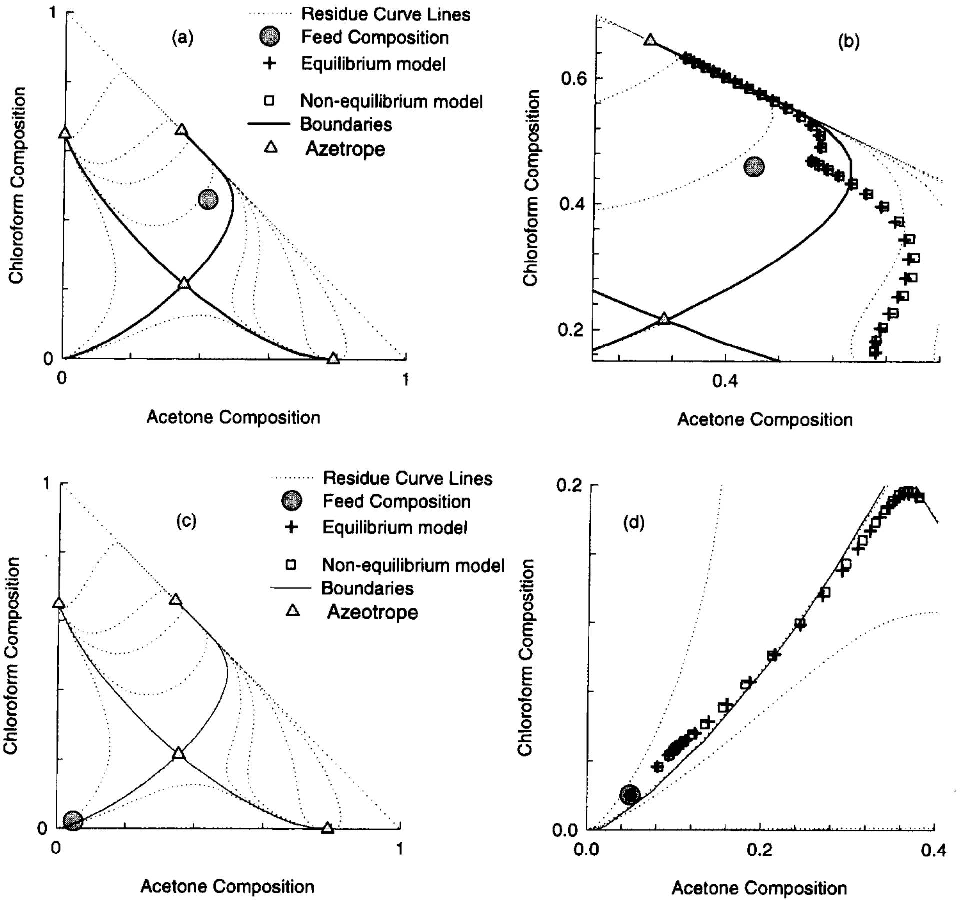

FIG. 4

(a) Residue curves for system acetone (1) – chloroform (2) – methanol (3). (b) Compares EQ and NEQ distillation trajectories for feed compositions $x_1 = 0.42$, $x_2 = 0.46$. The total number of stages is 32. The liquid feed is on stage 18. The reflux ratio used is 6. (c) Different feed location for this system. (d) For this simulation the feed composition is $x_1 = 0.05$, $x_2 = 0.02$. The total number of stages is 32. The liquid feed is on stage 20 and the reflux ratio used is 6.

Consider the system: acetone (1) – chloroform (2) – methanol (3) for which the residue curve maps are shown in Fig. 4 (a). This system has three binary azeotropes, one ternary azeotrope and there are four distillation boundaries, all curved, which divide the composition triangle into four regions. Figure 4 (b) compares EQ and NEQ distillation trajectories in a 32-stage column for feed composition $x_1$ = 0.42, $x_2$ = 0.46. The feed is located on the concave side of the boundary. According to the literature [11], boundary crossing is allowed for this case. We find that both EQ and NEQ column trajectories are able to cross the distillation boundary and the two trajectories almost coincide with each other. The component efficiencies for this system do not differ significantly from one another and therefore there is little difference between EQ and NEQ column trajectories. For this system we carried out another simulation with the NEQ model with a feed composition $x_1$ = 0.05, $x_2$ = 0.02, close to another distillation boundary and also placed on the concave side; see Fig. 4 (c). Again we note the boundary crossing effect; see Fig. 4 (d). The column trajectories with the EQ stage model is virtually coincidental with that of the NEQ stage model. Our study emphasises that boundary crossing effects are not necessarily related to the influence of mass transfer. Even the EQ trajectory can cross the boundary, provided the curvature is high enough and the feed is on the concave side [11].

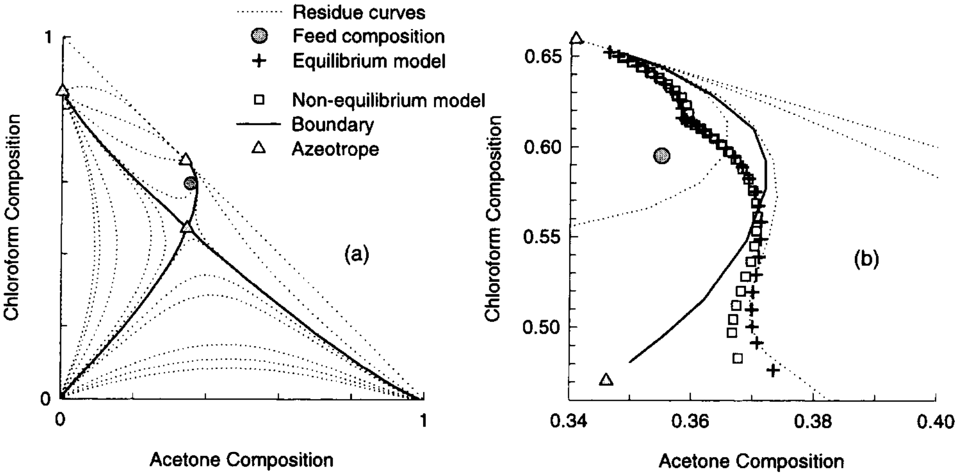

FIG. 5
(a) Residue curves for system acetone (1) – chloroform (2) – ethanol (3). (b) Compares EQ and NEQ distillation trajectories for feed compositions $x_1$ = 0.35, $x_2$ = 0.595. The total number of stages is 32. The liquid feed is on stage 18. The reflux ratio used is 6.

Consider the system: acetone (1) – chloroform (2) – ethanol (3) for which the residue curve maps are shown in Fig. 5 (a). This system has two binary azeotropes, one ternary azeotrope and there are four distillation boundaries, all curved, which divide the composition triangle into four regions. Figure 5 (b) compares EQ and NEQ distillation trajectories in a 32-stage column for feed composition $x_1$ = 0.35, $x_2$ = 0.595. The feed is located on the concave side of the boundary. According to the literature [11], boundary crossing is allowed for this case. We find that both EQ and NEQ column trajectories are able to cross the distillation boundary and the two trajectories almost coincide with each other. Similar to the foregoing system, the component efficiencies for this system do not differ significantly from one another and therefore there is little difference between EQ and NEQ column trajectories.

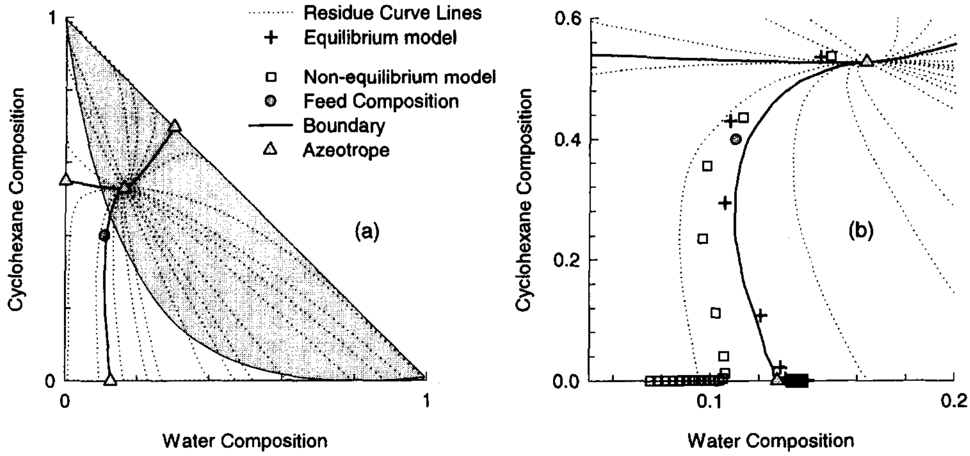

FIG. 6
(a) Residue curves for system water (1) – cyclohexane (2) – ethanol (3). (b) Compares EQ and NEQ distillation trajectories for feed compositions $x_1 = 0.11$, $x_2 = 0.4$. The total number of stages is 20. The liquid feed is on stage 2 (top tray). The reflux ratio used is 6. The shaded region has two-liquid phases.

Finally we consider the system: water (1) — cyclohexane (2) - ethanol (3) which exhibits a liquid phase demixing region, shown shaded in Fig. 6 (a). This system has three binary azeotropes and a ternary (heterogeneous) azeotrope. The composition triangle is divided into three regions. We carried out simulations of a 20-stage distillation column with the feed composition $x_1 = 0.11$, $x_2 = 0.4$. For the chosen feed composition and column configuration the top product is the heterogeneous azeotrope but all the trays are homogeneous (single liquid phase) in character; see Fig. 6 (b). Also noteworthy is the fact that the feed is located on the convex side of the boundary. Therefore the calculations can be performed with ChemSep, without incorporation of liquid phase splitting algorithms. We note that the EQ and NEQ model predict trajectories that are different in character. The NEQ model produces a bottoms product which is almost pure in ethanol. The EQ model, on other hand follows the residue curve, as it should because of the assumption of vapour-liquid equilibrium, and produces a bottoms product which is a water-ethanol mixture with considerably more water than predicted by the NEQ model. Neither EQ nor the NEQ model is able to cross the distillation boundary because of the location of the feed on the convex side. Boundary crossing is therefore not always possible; it is system dependent.

## Conclusions

The following major observations and conclusions can be drawn.

- The EQ and NEQ models *may* predict completely different composition trajectories in ternary azeotropic distillation.
- For the methanol – *iso*propanol – water system, the NEQ model has been shown to be capable of crossing distillation boundaries, even when these have no curvature. In the literature it is remarked that straight-line distillation boundaries cannot be crossed; this conclusion is restricted in its applicability to EQ models.
- For the system water – ethanol - acetone, our simulations with the NEQ model show that the boundary can be crossed even when the feed is located on the *convex* side of the boundary.
- For the system water - cyclohexane - ethanol, with the feed located on the convex side, we have observe that neither the EQ or NEQ model is capable of crossing the distillation boundary. However, the EQ and NEQ models do follow completely different composition trajectories.
- For the systems acetone – chloroform – methanol and acetone – chloroform – ethanol, with the feed located on the *concave* side of a distillation boundary, both EQ and NEQ model trajectories are seen to be capable of crossing the boundary. However, for this case EQ and NEQ model trajectories practically coincide. The boundary crossing effects for this system have also been demonstrated experimentally by Li *et al.* [28].

Our simulations demonstrate that the literature guidelines regarding boundary crossing do not have general validity. Boundary crossing phenomenon could also be influenced by interphase mass transfer. A straight-line boundary can be crossed. A boundary can be crossed even if the feed is located on the convex side. However, boundary crossing is not always possible; it depends on the system, and on the operating conditions. Separation strategies in practice are influenced by boundary crossing effects.

## Acknowledgment

RK acknowledges a grant *Programmasubsidie* from the Netherlands Organisation for Scientific Research (NWO) for development of novel concepts in reactive separations technology.

## References

1. J.G. Stichlmair and J.R. Fair, *Distillation principles and practice*, Wiley-VCH, New York (1998)
2. M.F. Doherty and M.F. Malone, *Conceptual design of distillation systems*, McGraw-Hill, New York (2001)
3. S. Widagdo and W.D. Sieder, *A.I.Ch.E. J.*, **42**, 96 (1996).
4. J.P. Knapp and M.F. Doherty, *Ind. Eng. Chem. Research*, **31**, 346 (1992).

5. E.R. Foucher, M.F. Doherty and M.F. Malone, *Ind. Eng. Chem. Research*, **30**, 760 (1991).

6. J.P. Knapp and M.F. Doherty, *A.I.Ch.E. J.*, 36, 969 (1990).

7. H.N. Pham and M.F. Doherty, *Chem.Eng.Sci.*, **45**, 1837 (1990).

8. V. Julka and M.F. Doherty, *Chem.Eng.Sci.*, **45**, 1801 (1990).

9. D. Barbosa and M.F. Doherty, *Chem.Eng.Sci.*, **43**, 541 (1988).

10. Z. T. Fidkowski, M. F. Doherty and M. F. Malone, *A.I.Ch.E. J.*, **39**, 1303 (1993).

11. S.G. Levy, D.B. Van Dongen and M.F. Doherty, *Ind. Eng. Chem. Fundamentals*, **24**, 463 (1985).

12. O. M. Wahnschafft, J. W. Koehler and A. W. Westerberg, *Comput. Chem. Eng.*, **18**, S31 (1993).

13. O. M. Wahnschafft, J. W. Koehler, E. Blass and A. W. Westerberg, *A.I.Ch.E. J.*, **31**, 2345 (1992).

14. B.S. Bossen, S.B. Joergensen and R. Gani, *Ind. Eng. Chem. Research* **32**, 620 (1993).

15. L. Laroche, N. Bekiaris, H. W. Andersen and M. Morari, *A.I.Ch.E. J.*, 38, 1309 (1992).

16. S. Pelkonen, R. Kaesemann, and A. Gorak, *Ind. Eng. Chem. Research*, **36**, 5302 (1997).

17. F.J.L. Castillo, D.Y.C. Thong and G. P. Towler, *Ind. Eng. Chem. Research*, **37**, 998 (1998).

18. E. Rev, *Ind. Eng. Chem. Research*, **31**, 893 (1992).

19. Ronge, G., *Überprüfung unterschiedelicher Modelle für den Stoffaustausch bei der Rektifikation in Packungskolonnen*. Fortschritt-Berichte VDI Verfahrenstechnik No. 390, Düsseldorf (1995).

20. R. Krishna and J.A. Wesselingh, *Chem. Eng. Sci.*, **52**, 861 (1997).

21. J.A. Wesselingh and R. Krishna, *Mass transfer in multicomponent mixtures*, Delft University Press, Delft, ISBN 90-407-2071-1 (2000).

22. R. Baur, A.P. Higler, R. Taylor and R. Krishna, *Chem.Eng. Journal*, **76**, 33 (2000).

23. R. Krishnamurthy and R. Taylor, *A.I.Ch.E.J.*, **32**, 449 (1985).

24. R. Taylor, H.A. Kooijman and J.S. Hung, *Comput. Chem. Engng.* **18**, 205 (1994)

25. R. Baur, R. Taylor, R. Krishna and J. A. Copati, *Chem. Eng. Research & Design, Trans.I.Chem.E.*, **77**, 561 (1999)

26. F.J.L. Castillo and G.P. Towler, *Chem.Eng.Sci.*, **53**, 963 (1998).

27. A.I.Ch.E. Bubble Tray Design Manual, A.I.Ch.E., New York (1958).

28. Y. Li, H. Chen and J. Liu, *Ind. Eng. Chem. Research*, **38**, 2482 (1999).

*Received January 7, 2001*