

# INFLUENCE OF MASS TRANSFER IN DISTILLATION OF MIXTURES WITH A DISTILLATION BOUNDARY

R. BAUR\*†, R. TAYLOR†, R. KRISHNA (FELLOW)\* and J. A. COPATI\*

\*Department of Chemical Engineering, University of Amsterdam, The Netherlands  
 †Department of Chemical Engineering, Clarkson University, Potsdam, New York, USA

This paper examines the influence of mass transfer on the composition trajectories during distillation of mixtures that exhibit distillation boundaries. Simulations for total reflux distillation of the systems methanol-*iso*-propanol-water and benzene-*iso*-propanol-*n*-propanol show that composition trajectories originating along the distillation boundary could end up in completely different corners of the composition triangle depending on whether or not diffusional interactions are taken into account. Using published experimental data it is concluded that for reliable design and simulation it is necessary to use a rigorous model for mass transfer based on the Maxwell-Stefan diffusion equations.

*Keywords:* distillation; residue curves; distillation boundaries; Maxwell-Stefan theory; Murphree efficiencies; diffusional interactions

## INTRODUCTION

Most commercially available simulation programs for distillation columns (Seader and Henley<sup>1</sup>) cater for 'real' or non-equilibrium trays. The departure of these real trays from equilibrium behaviour is allowed for in either of two ways. In the first procedure, the user is allowed to specify the individual component Murphree efficiencies for each stage. These component efficiencies can be estimated 'off-line' by using the various mass transfer correlations (AIChE method<sup>2</sup>; Chan and Fair<sup>3</sup>; Zuiderweg<sup>4</sup>) as discussed in the book of Lockett<sup>5</sup>. The second approach, which is gaining currency, is to use a fully rate-based approach. In this approach, the interphase mass and heat transfer equations are solved simultaneously along with the interphase equilibrium relations for each stage (Krishnamurthy and Taylor<sup>6</sup>; Taylor and Krishna<sup>7</sup>). In the rate-based approaches, the interphase mass transfer relations are invariably based on the Maxwell-Stefan diffusion equations in either fluid phase (Taylor and Krishna<sup>7</sup>; Krishna and Wesselingh<sup>8</sup>).

There is some evidence in the published literature that experimentally measured composition profiles in distillation columns are better simulated with models based on the rigorous Maxwell-Stefan diffusion equations than with simpler models that assume equal component efficiencies (Taylor and Krishna<sup>7</sup>; Krishna and Wesselingh<sup>8</sup>; Górak<sup>9</sup>; Ronje<sup>10</sup>).

Castillo and Towler<sup>11</sup> computed nonequilibrium distillation lines for a sieve tray column and demonstrated that modest differences between the efficiencies of different components in a ternary mixture could lead to significant differences in curvature between equilibrium and nonequilibrium distillation lines. They go 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 nonequilibrium distillation lines. In particular, it is shown that these lines can be extremely sensitive to the choice of model, particularly near to distillation boundaries. Specifically, it will be demonstrated that methods that ignore differences between binary pair (Maxwell-Stefan) diffusion coefficients (for example, the method of Zuiderweg<sup>4</sup>) can lead to erroneous predictions of column performance.

## SIMULATIONS OF TOTAL REFLUX OPERATIONS IN SIEVE TRAY COLUMNS

The influence of mass transfer on column composition profiles are examined and attention focused on two non-ideal mixtures which exhibit a distillation boundary: methanol-*iso*-propanol-water and benzene-*iso*-propanol-*n*-propanol. Shown in Figure 1 are the residue curve maps (described for example in Seader and Henley<sup>1</sup>) for these systems, calculated using the NRTL model (parameters listed in Table 1). The calculations of the residue curves were performed using Maple V Release 4 with BESIRK, a differential-algebraic equation solver. The distillation

Table 1. NRTL parameters for the mixtures methanol-*iso*-propanol-water and benzene-*iso*-propanol-*n*-propanol

Component <i>i</i>	Component <i>j</i>	$A_{ij}$ /[J/mol]	$A_{ji}$ /[J/mol]	$\alpha_{ij}$
methanol	<i>iso</i> -propanol	546.323	-746.121	0.3040
methanol	water	-1518.18	4943.753	0.2970
<i>iso</i> -propanol	methanol	587.483	6062.742	0.2880
<i>iso</i> -propanol	benzene	1386.688	3260.067	0.2913
<i>iso</i> -propanol	<i>n</i> -propanol	-2819.03	4150.621	0.2978
benzene	<i>n</i> -propanol	4236.07	659.124	0.2888

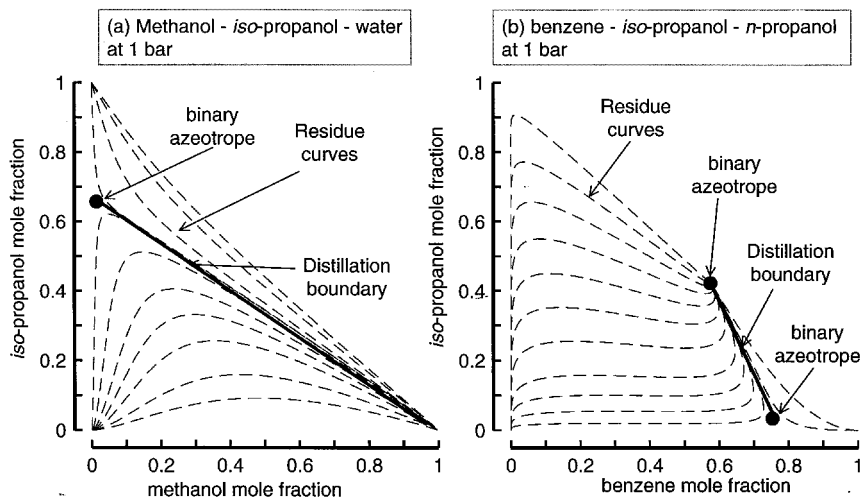


Figure 1. Residue curve maps for the systems (a) methanol-*iso*-propanol-water and (b) benzene-*iso*-propanol-*n*-propanol.

boundaries for the two systems are indicated by thick lines. The mixture methanol-*iso*-propanol-water has a binary minimum boiling azeotrope for *iso*-propanol-water. The distillation boundary splits the residue curve map into two regions. For the system benzene-*iso*-propanol-*n*-propanol there are two minimum boiling azeotropes: benzene-*iso*-propanol and benzene-*n*-propanol. The distillation boundary connects these two azeotropes and again distinguishes two regions. It can be seen that the residue curves, which originate along the distillation boundary, can choose two different paths ending up in different corners of the composition triangle. The residue curves coincide with the liquid composition trajectories during distillation at total reflux in a differential-contact column, such as a packed column, in which the liquid and vapour phases are in thermodynamic equilibrium.

Column simulations were carried out for the two systems

methanol-*iso*-propanol-water and benzene-*iso*-propanol-*n*-propanol at total reflux in a 40-stage sieve tray column with the hardware specifications in Table 2. The simulations were carried out using ChemSep, a steady-state equilibrium stage and non-equilibrium stage simulator described in earlier work (Taylor and Krishna<sup>7</sup>; Taylor *et al.*<sup>12</sup>).

Figure 2 (a) shows the liquid composition trajectories in the column, calculated using four different models for interphase mass transfer:

- (1) AIChE correlation<sup>2</sup>,
- (2) Chan and Fair correlation<sup>3</sup>,
- (3) Zuiderweg<sup>4</sup> correlation and
- (4) a model in which all component efficiencies are assumed to be equal to one another.

The detailed description of the mass transfer correlations are available elsewhere<sup>5,7</sup>. In addition, both vapour and

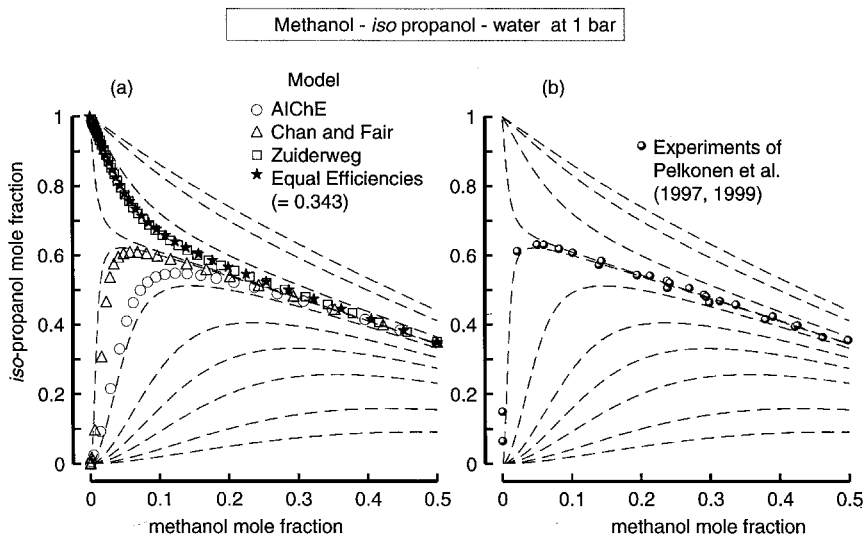


Figure 2. Composition trajectories for the system methanol-*iso*-propanol-water. (a) Liquid composition trajectories in a sieve tray column predicted with four different mass transfer models. In all calculations shown here the liquid and vapour phases were assumed to be well mixed on a tray. For the equal efficiency model all the component efficiencies were set equal to 0.343, which represents the average of the component efficiencies shown in Figure 3. (b) Liquid composition trajectories measured by Pelkonen *et al.*<sup>13,14</sup> in a 0.1 m diameter column packed with Sulzer BX packing and operating at total reflux. The broken lines in the figure represent the residue curves.

Table 2. Specification of sieve tray column used in the simulations.

Column internals	Sieve tray
Number of stages	40
Column diameter / [m]	0.8
Tray spacing / [m]	0.6
Number of flow passes	1
Weir length / [m]	0.74
Weir height / [m]	0.05
Hole diameter / [m]	0.005

liquid phases are assumed to be completely mixed on any tray. In all cases, excepting the fourth one, the generalized Maxwell-Stefan diffusion equations are used to predict the ternary mass transfer behaviour based on the information of the constituent binary pairs. For the fourth, equal efficiency model, the value of the component efficiencies of each of the components were forced to equal the average of the component efficiencies calculated using the Maxwell-Stefan formulation and the AIChE correlation. A detailed step-by-step calculation procedure for the estimation of the mass transfer fluxes, and component efficiencies in multi-component systems is to be found in Chapter 13 of the book by Taylor and Krishna<sup>7</sup>. Also shown with broken lines in Figure 2 (a) are the residue curves for this system. All four mass transfer models predict composition trajectories, which tend to follow the residue curves, albeit ending up in different corners of the composition triangle. The Zuiderweg and Equal-component-efficiency models predict almost identical column composition trajectories. More interestingly, it is noted that the AIChE and Chan-Fair correlations predict that the reboiler composition corresponds to pure water whereas the Zuiderweg and Equal-component-efficiency model predicts the reboiler to consist of pure *iso*-propanol. Put another way, the choice of the mass transfer model dictates which residue curve path is followed if the column compositions originate from a distillation boundary.

Though the rate based approach do not use Murphree component efficiencies in the material and energy balances, these can be calculated on each stage:

$$E_i^{MV} = \frac{\bar{y}_{iL} - y_{iE}}{y_i^* - y_{iE}}; \quad i = 1, 2, \dots, n \quad (1)$$

where  $\bar{y}_{iL}$  is the average composition of the vapour leaving the tray,  $y_{iE}$  is the composition of the vapour entering the tray and  $y_i^*$  is the composition of the vapour in equilibrium with the liquid leaving the tray. Since the mole fractions add to unity, only  $(n-1)$  of the Murphree component efficiencies are independent. For distillation of systems with three or more species, the component efficiencies are almost always unequal to one another and these can routinely assume values greater than unity or less than zero<sup>7,8</sup>. The component efficiencies, calculated with the AIChE model for the sieve tray, are shown in Figure 3. The component efficiency of *iso*-propanol is significantly lower than that of the other two components; this is the major reason why the trajectory followed by the AIChE model ends up with a reboiler with pure water (lower left corner). When all component efficiencies are forced to equal one another (as in model (4)), the column trajectory

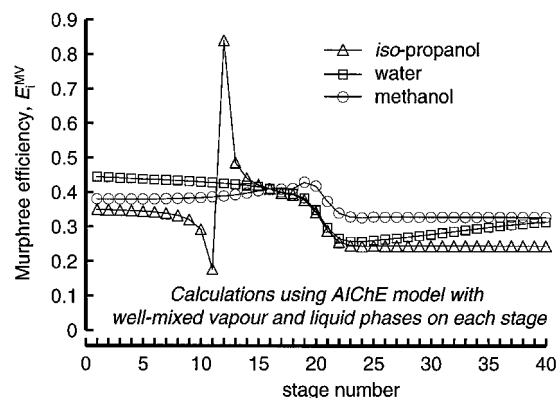


Figure 3. Component vapour phase Murphree tray efficiencies for the system methanol-*iso*-propanol-water. Calculations using the AIChE model and assuming liquid and vapour phases to be well mixed.

ends up in the upper left corner with pure *iso*-propanol in the reboiler.

The correlations developed by Zuiderweg<sup>4</sup> for the vapour and liquid phase mass transfer coefficients on sieve trays are summarized below

$$k_G = 0.13/\rho_G - 0.065/\rho_G^2 \quad (1 < \rho_G < 80) \quad (2)$$

$$k_L = 0.024D_L^{0.25} \quad (3)$$

It is important to note that the gas phase diffusivity does not appear in the correlation for the gas phase mass transfer coefficient. Therefore, the component efficiencies, for systems dominated by vapour phase mass transfer, will be equal for all components. This explains why the Zuiderweg and Equal-component-efficiency models predict almost identical composition trajectories. Lockett<sup>5</sup> has also underlined the special feature of the Zuiderweg correlation (2) for the gas phase mass transfer coefficient and its independence on the gas phase diffusivity. He has suggested a hybrid approach in which the gas phase mass transfer coefficient is calculated using the AIChE method while the liquid phase mass transfer coefficient is estimated from the Zuiderweg correlation.

Analogous calculations have been carried out for columns with other types of internals (bubble cap trays, dumped and structured packings), and with other assumptions regarding the mixing characteristics of the vapour and liquid phases (plug flow in either or both phase) with essentially the same results as discussed above.

Experiment data points reported by Pelkonen *et al.*<sup>13,14</sup> for total reflux operation of methanol-*iso*-propanol - water in a 0.1 m diameter column packed with Sulzer BX packing are plotted in Figure 2 (b) as black circles. Also shown with broken lines in Figure 2 (b) are the residue curves for this system. The experimental composition trajectories, which lie along a residue curve, start at a composition  $x_{\text{methanol}} = 0.5$ ,  $x_{\text{isopropanol}} = 0.35$  at the top of the column and end up with virtually pure water in the reboiler. Model calculations carried out by Pelkonen *et al.*<sup>13</sup>, also using ChemSep, assuming equal HETPs for each individual component predicted that the reboiler would consist of pure *iso*-propanol, i.e. follow the residue curve emanating from  $x_{\text{methanol}} = 0.5$ ,  $x_{\text{isopropanol}} = 0.35$  but going in the opposite direction to the experiments towards the pure *iso*-propanol vertex. The experiments and simulation results of Pelkonen

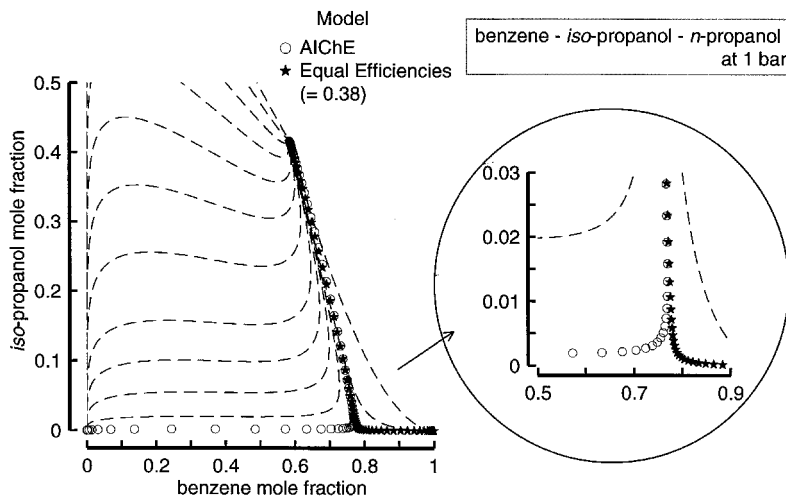


Figure 4. Composition trajectories for the system benzene-*iso*-propanol-*n*-propanol in a 40-stage sieve tray column. For the equal efficiency model all the component efficiencies were set equal to 0.38, which represents the average of the component efficiencies shown in Figure 5.

*et al.*<sup>13,14</sup> could be used to conclude that the Zuiderweg and Equal Component Efficiency (=0.343) model calculations in Figure 2 (a) follow the *wrong* residue curve originating from the distillation boundary.

Results analogous to the foregoing are obtained for the system benzene-*iso*-propanol-*n*-propanol. Simulation results for the AICHe and equal-component-efficiency models are shown in Figure 4. Again, it is noted that the two composition trajectories end up in two different composition corners, pure *n*-propanol and pure benzene, respectively. The component efficiency for benzene is significantly lower than that of the other two components (see Figure 5). This is the reason that the composition trajectory predicted by the rigorous Maxwell-Stefan model (taking differences in component efficiencies into consideration) predicts a reboiler composition which consists of pure *n*-propanol. Forcing the component efficiencies to equal one another results in a trajectory with pure benzene in the reboiler. Using the evidence of the Pelkonen experiments for the system methanol-*iso*-propanol – water, the reboiler is expected to consist of pure *n*-propanol. It would be interesting to obtain experimental verification of this.

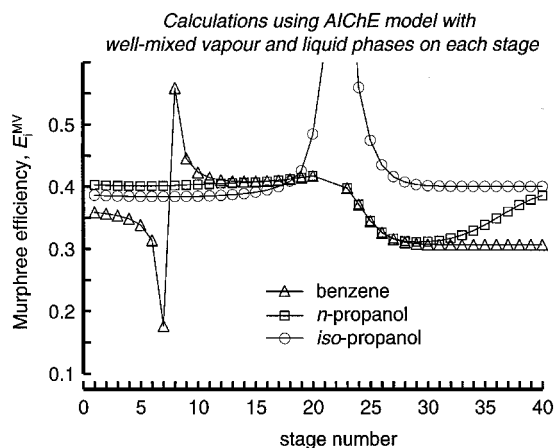


Figure 5. Component vapour phase Murphree tray efficiencies for the system benzene-*iso*-propanol-*n*-propanol. Calculations using the AICHe model and assuming liquid and vapour phases to be well mixed.

## CONCLUDING REMARKS

It has been demonstrated that the column composition trajectories in sieve tray operations can follow different residue curve paths originating from a distillation boundary. A model, in which the component efficiencies are all forced to equal one another, predicts a column composition profile ending up in the ‘wrong’ corner. In the context of sieve tray design for non-ideal mixtures, the Zuiderweg<sup>4</sup> correlation is not to be recommended. This correlation is perhaps adequate for thermodynamically ideal hydrocarbon mixtures.

## NOMENCLATURE

$A_{ij}$	NRTL parameters, $\text{J mol}^{-1}$
$D_L$	Fick diffusivity for binary liquid phase mixture, $\text{m}^2 \text{s}^{-1}$
$E_i^{MV}$	overall Murphree tray efficiency, dimensionless
HETP	Height equivalent to a theoretical plate, m
$k_G$	vapour phase mass transfer coefficient, $\text{m s}^{-1}$
$k_L$	liquid phase mass transfer coefficient, $\text{m s}^{-1}$
$n$	the number of components in the mixture, dimensionless
$y_{iL}$	average composition of the vapour leaving the tray, dimensionless
$y_{iE}$	composition of the vapour entering the tray, dimensionless
$y_i^*$	composition of the vapour in equilibrium with the liquid leaving the tray, dimensionless

### Greek letters

$\alpha$	non-randomness parameter in NRTL equation, dimensionless
$\rho_G$	density of gas mixture, $\text{kg m}^{-3}$

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### ADDRESS

Correspondence concerning this paper should be addressed to Professor R. Krishna, Department of Chemical Engineering, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands (E-mail: krishna@chemeng.chem.uva.nl).

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