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Choosing the Right Model for Distillation Processes in Packed Columns: Theory and Experiments

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Packed distillation columns are usually designed on the basis of a sequential approach, in which first the Equilibrium Stage (EQ) model is used to quantify the separation effort before the required packing height is determined by HETP values. This approach is often sufficient for process design and proper sizing of the column. However, in certain cases the combination of the EQ model and HETP values results in an inappropriate column design. The design accuracy can be improved using a rate-based (RB) approach. Unfortunately, there is no reliable heuristic available to decide which modeling approach should be chosen. Therefore, the current study investigates the need for rate-based modeling in distillation processes by systematically evaluating the differences between EQ and RB composition trajectories. A criterion based on the Euclidean distance is proposed to evaluate the differences between the EQ and RB trajectories. Then, by means of a selectivity analysis basic criteria for model discrimination are derived and validated experimentally. Generally, for wide boiling mixtures the differences between the EQ and RB trajectories are the most distinct. The differences in the trajectories can be further increased or decreased by component specific mass transfer.

1. Introduction

Distillation is the most widely used fluid separation process in the chemical industry. For detailed design of distillation columns different mathematical models can be used. The common approach for the design of packed columns is a sequential procedure, consisting of the determination of the necessary separation effort through the use of the EQ model and a subsequent column sizing by means of specific HETP values. While being computationally efficient, sizing distillation columns on this basis can result in inappropriate designs for certain separation tasks. Alternatively, so called rate-based models can be used, which directly account for the characteristic dimensions of the column. These models are based on differential mass and energy balances for the liquid and vapor phase and account for the heat and mass transfer between the phases (Serwinski and Górak, 1983; Krishnamurthy and Taylor, 1985). While rate-based models are more complex and require additional component specific transport property data, they can be more accurate and hence, enable the proper sizing of the column (Taylor et al., 2003; Kenig, 2008).
Unfortunately, there are no general rules or guidelines for the selection of the rate-based approach instead of the EQ model. Similarly, it is not obvious under which circumstances the EQ model will suffice for sizing a column for a specified separation task. Some authors argue that the rate-based models should always be preferred to circumvent the selection of an inadequate model (Taylor et al., 2003). However, the general superiority of the rate-based model, which requires much more parameters in comparison to the EQ model, has not been proven yet. In order to support the decision-making process, a systematic evaluation of the major differences resulting from EQ and RB modeling of distillation processes in packed columns is presented in this paper. For the separation of binary mixtures the only reason for significant differences in the results of the EQ and RB models are inappropriate HETP values, since the composition trajectory is linear. By means of an adaption of the HETP value the resulting composition profiles can be aligned. However, the adapted HETP values might not be constant requiring variation along the column height (cf. Figure 1, left).

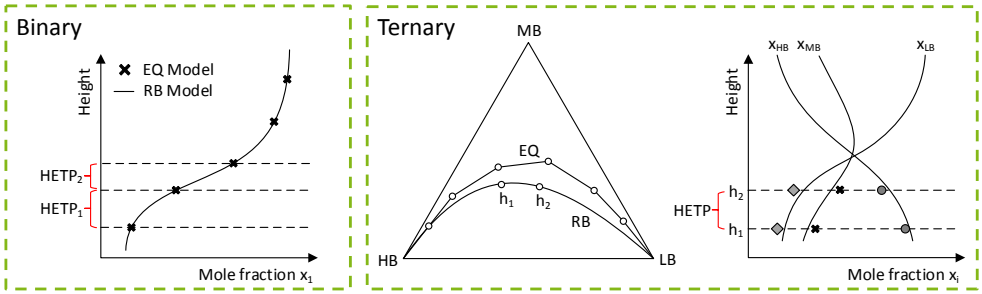

Figure 1: Possible differences between EQ and RB modelling results

For multicomponent mixtures, such an alignment of the concentration profiles is not always possible, as also the trajectory of the resulting composition profiles may differ. For example for ternary mixtures the composition simplex corresponds to the Gibbs triangle and the composition trajectories traverse a two dimensional plane. Thus, the composition trajectories (cf. Figure 1, middle) and the corresponding composition profiles (cf. Figure 1, right) can differ despite an optional adaption of the HETP value. In such cases the EQ model may not be sufficient to design a distillation column properly and RB models need to be used. On the other hand, for similar composition trajectories of the EQ and RB model an inappropriate design obtained by the EQ model may be just related to the use of inappropriate HETP values. In order to identify conditions that lead to significant differences in the composition trajectories of the EQ and RB models, a systematic investigation is performed. This investigation starts with a theoretical study for ideal systems at total reflux and is then extended to a specific multi-component mixture, for which the theoretical results are validated by dedicated experiments.

2. Methodology

The aforementioned differences in the composition trajectories, calculated using EQ and RB models, can be caused by different factors such as the vapor-liquid equilibrium (VLE) of the mixture, the operating conditions of the column and feed or product specifications as well as component specific mass transfer rates. In order to evaluate the influence of each of these factors on the differences in the composition trajectories, a sensitivity analysis with one at a time variations was performed.

2.1 Calculation of composition trajectories

For total reflux the EQ composition trajectory corresponds to the distillation line (DL) (Stichlmair and Herguijuela, 1992). Thus, the term DL is used in the following to denote the EQ model at total reflux.

$$\vec{x}^{n+1} = \vec{y}^{EQ}(\vec{x}^{n}) \tag{1}$$

For the evaluation of the rigorous RB model two different modes are considered, which both assume that the mass transfer resistance in the liquid phase is negligible compared to the resistance in the vapor phase. The first mode assumes equal mass transfer rates for all components. In this paper it is called equal mass transfer (RB-EMT) model (see equation (2)). The RB-EMT model corresponds to the well-known residue curve (RC) (Vogelpohl, 1964). In equation (2) η is a dimensionless height.

$$d\vec{x}/d\eta = \vec{y}^{EQ} - \vec{x} \tag{2}$$

The second mode is based on the Maxwell-Stefan diffusion (RB-MS). The effect of the component specific mass transfer rates is accounted for by the matrix $[D]$, which is calculated as described by Taylor and Krishna (1993). All other scalar coefficients are incorporated into the adapted integration variable η*.

$$d\vec{x}/d\eta^{*} = [D] \cdot (\overrightarrow{y^{EQ}} - \vec{x}) \tag{3}$$

By comparison of the EQ and RB-EMT model the influence of the VLE on the differences between the composition trajectories is evaluated. By including the RB-MS model in the comparison, the influence of component specific mass transfer on the composition trajectories can further be investigated. For the computation of the composition trajectories the ordinary differential equations in eq. (2) and (3) are solved numerically with MATLAB's ode45 solver utilizing the Dormand-Prince method. All composition trajectories are calculated starting at an initial point in the composition space and the integration is performed in both directions of the integration variable.

2.2 Visualization of differences between composition trajectories of the EQ and RB model

The composition trajectories calculated for one initial point based on the EQ and RB model can be easily compared by depiction in the Gibbs triangle. However, in order to investigate the influence of the initial composition on the differences between the EQ and RB trajectories systematically the trajectories should be calculated for a multitude of initial compositions. Therefore, an adequate form of representation is required to analyze the results. In this paper the differences between the DL and the corresponding RB-EMT and RB-MS trajectories, for the same initial point are described by the maximum of the shortest Euclidean distance between the two trajectories (cf. Figure 2, left). This value is used to characterize the maximum deviation of the two trajectories. In order to determine this value a spline interpolation of the DL is used. The resulting distances are then plotted in a ternary contour plot, which allows a direct identification of regions in which the differences between DL and RB-EMT, or DL and RB-MS trajectories are significant.

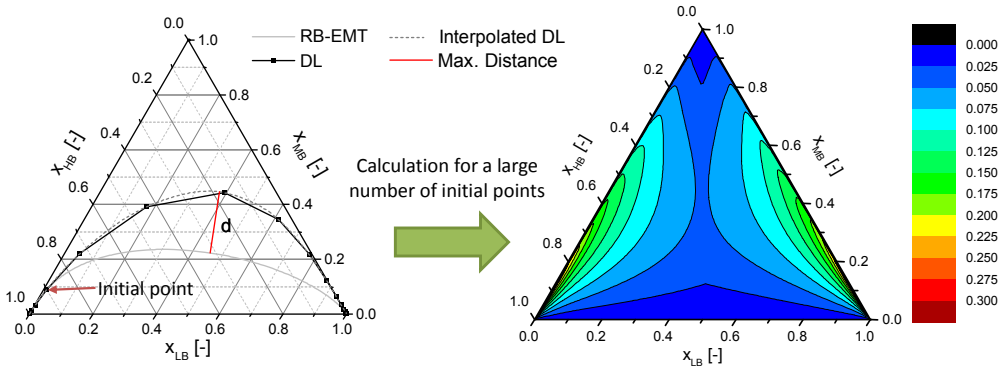

Figure 2: Calculation of contour plots to illustrate differences in DL and RB composition trajectories

3. Results

The investigation starts with a study of the resulting contour plots for ideal mixtures at total reflux. After the models are discriminated, a real mixture is analyzed and the obtained results are experimentally validated. The investigations in the following sections are carried out only for ternary systems, although the calculations can be extended to mixtures with more components without further modification. The component index 1-3 denote the low, medium and heavy boiling (LB, MB, HB) component, in order of the boiling temperature.

3.1 Influence of the VLE on the differences between the EQ and RB composition trajectories

First, the influence of the VLE on the differences between the EQ and RB composition trajectories shall be investigated. Thus, only the differences between the DL and RB-EMT trajectories are evaluated. At first, the trajectories are calculated under the assumption of constant relative volatilities (CRV). Then, the comparison of the contour plots for different sets of relative volatilities allows the analysis of the influence of the VLE on the differences between the DL and RB-EMT composition trajectories for the complete composition simplex.

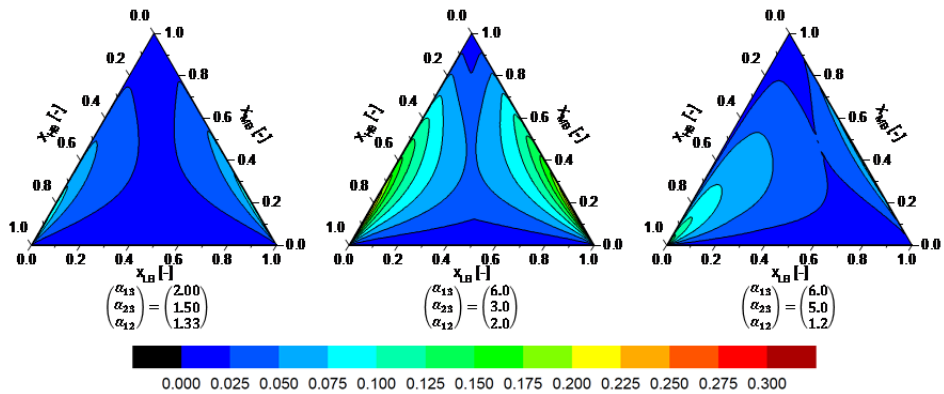

Figure 3: Differences between DL and RB-EMT trajectories for different sets of relative volatilities

Figure 3 depicts the contour plots of three exemplary mixtures with different combinations of relative volatilities. The left mixture is close boiling with the relative volatilities smaller than two. For this mixture the

distances between the DL and RB-EMT trajectories are small and for large parts of the composition simplex negligible. However, two regions with slightly higher differences between the DL and RB-EMT trajectories can be identified. These regions are close to the binary MB-HB-axis respectively close to the LB-HB-axis. The contour plot shown in the figure in the middle is calculated for a wider-boiling mixture with relative volatilities between two and six. The differences between DL and RB-EMT trajectories increase significantly compared to the close boiling mixture. However, the wide-boiling mixture exhibits similarly to the close boiling mixture two regions close to the binary MB-HB-axis respectively close to the LB-HB-axis with increased differences between DL and RB-EMT trajectories. The mixture on the right is a combination of wide- and close-boiling binary subsystems. While the LB-MB-subsystem is close boiling, the LB and MB are both significantly more volatile than the HB. This combination results in smaller differences between the DL and RB-EMT trajectories. However, the shape of the contour plot is different to the two other mixtures. Now, the region with the highest differences between DL and RB-EMT is shifted closer to pure HB.

As mentioned before the RB-EMT trajectory corresponds to the well-known RC. For the analysis of split feasibility it is often assumed that the differences between the DL and RC can be neglected (Fidkowski et al., 1993) and therefore, RC and DL can be used equivalently. However, the preceding results demonstrate that this is not valid for the design of distillation columns. Similar differences between RC and DL were reported by other authors, e.g. Wahnschafft et al. (1992) and Kiva et al. (2003), and can be contributed to the curvature of the trajectories as well as the length of the equilibrium vector (Kiva et al., 2003). By means of the contour plots the differences between DL and RB-EMT trajectories can be assessed easily for a given VLE and the comparison of the trajectories for different VLE's becomes possible. The results show that differences between the models are more distinct for mixtures in which all binary subsystems are relatively wide-boiling, i.e. have a relative volatility of at least two. Moreover, the differences are the most significant in regions close to the binary LB-MB-axis respectively close to the MB-HB-axis. On the other hand, for close boiling mixtures with relative volatilities less than two the differences between DL and RB-EMT trajectories are found to be rather small. Although these criteria are derived based on ideal mixtures with constant relative volatilities, the results apply to real mixtures as long as the order of relative volatilities remains constant (Vogelpohl, 2002).

3.2 Influence of component specific mass transfer rates on the differences between EQ and RB composition trajectories

In this section the differences between the EQ and RB trajectories that are related to component specific mass transfer rates are investigated exemplarily, for the ideal mixture with (α_{13} α_{23} α_{12}) = (6 3 2). While other authors, e.g. Baur et al. (2005), have already investigated the influence of component specific mass transfer on the path of the RB model trajectories, a systematic investigation of how different combinations of diffusion coefficients affect the differences of the RB compared to the EQ composition trajectories has not been conducted, to the best of our knowledge. The trajectories of the DL and RB-MS model are further compared for different sets of the three binary diffusion coefficients D_{ij} of the ternary mixture. Only the ratios of these diffusion coefficients determine the path of the RB-MS trajectory in the composition simplex. Thus, the diffusion coefficients are set to any of the following values $D_{ij} \in \{0.5, 1, 1.5\}$.

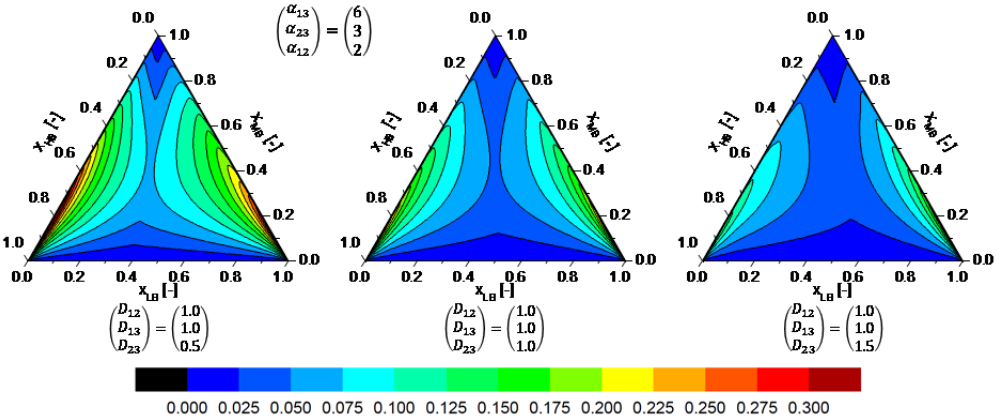

Figure 4: Influence of the binary vapor diffusion coefficient D_{23} on the differences between DL and RB-MS composition trajectories for an ideal mixture with CRV

Figure 4 depicts the three contours plots with different values for the binary diffusion coefficient D_{23} between MB and HB. The contour plot in the middle corresponds to the differences between DL and RB-EMT. Thus, the effect of the binary diffusion coefficient D_{23} on the differences between the EQ and RB trajectories can be

evaluated directly. While a decrease of D_{23} results in a significant increase in the differences between DL and RB-MS trajectories, the increase of D_{23} leads to the contrary effect and decreases the differences between the EQ and RB-MS trajectories. However, the general shape of the contour plot does not change in this case. Generally, component specific mass transfer rates can either increase or decrease the differences between the DL and the RB-MS trajectories. However, as noted by Baur et al. (2005), mass transfer does not affect the general topology of the mixture, which is determined by the VLE alone.

3.3 Transfer to real mixtures and experimental validation

Based on the derived criteria for model discrimination the real mixture methanol (LB), 2-butanol (MB) and DMF (HB) is selected. For this mixture all binary subsystems are wide boiling and the binary diffusion coefficient D_{23} of 2-butanol and DMF is lower than the other binary diffusion coefficients (averaged and normalized (D_{12} D_{13} D_{23}) = (1.00 1.02 0.59)). The VLE of this mixture is described by the UNIQUAC g^E-model in combination with the extended Antoine equation and parameters from the Aspen Plus® databanks NISTV88 NIST-IG and PURE32, while the binary vapor diffusion coefficients are calculated by the correlation of Wilke et al. (1955). The differences between the EQ and RB trajectories illustrated in Figure 5 demonstrate the applicability of the guidelines, derived for ideal mixtures, to a real zeotropic mixture. The left contour plot shows high differences between the DL and RB-EMT trajectories. The right contour plot displays the differences between DL and RB-MS trajectories. For the chosen mixture the consideration of component specific mass transfer rates increases the differences between EQ and RB trajectories further.

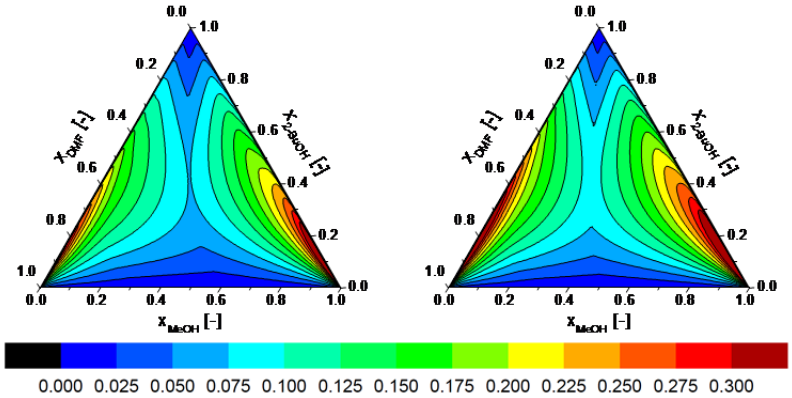

Figure 5: Differences between DL and RB-EMT (left) and DL and RB-MS trajectories (right) for the wide-boiling mixture methanol / 2-butanol / DMF

In order to validate the results of the theoretical investigation a special laboratory column, designed to measure concentration profiles, was constructed by BASF. The column is equipped with Montz A3-500 structured packing. After initial calibration by measurements with a standard binary test mixture, total reflux experiments were performed for the methanol, 2-butanol and DMF mixture, for which exemplary results are shown in Figure 6.

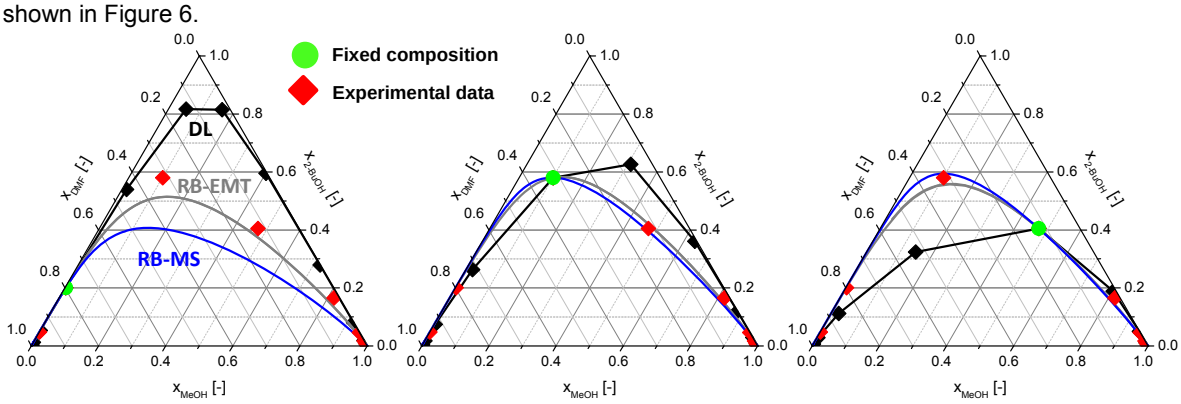

Figure 6: Comparison of experimental points with DL, RB-EMT and RB-MS trajectories for the mixture methanol, 2-butanol, DMF

Three of the experimental data points are fixed for the calculation of the DL, RB-EMT and RB-MS trajectories. As indicated by the contour plots the calculated composition trajectories differ in dependence of the initial composition. While the DL matches the experimental compositions to a more or less reasonable degree in the middle diagram, the agreement between DL and experimental points is significantly worse for the left and right diagram. On the contrary, the RB-EMT model matches the experimental points to an excellent degree regardless of the fixed composition. The agreement of the RB-MS trajectory with the experimental data is also excellent for the middle and right diagram, while the differences to the experimental points are slightly larger for the left diagram.

4. Conclusion

The current paper proposed a method to characterize the differences between EQ and RB composition trajectories for total reflux operation, by an analysis of the maximum distance between the corresponding trajectories. The proposed contour plots allow for an easy assessment of these differences. By using this form of representation the influence of the VLE as well as component specific mass transfer rates on the differences between EQ and RB composition trajectories were investigated. It was shown that for generally wide-boiling mixtures, the differences between the EQ and RB trajectories are the most distinct. Moreover, component specific mass transfer rates can either increase or decrease the differences between the EQ and RB trajectories. Based on the determined criteria a real mixture was chosen and used for validation of the theoretical results. In future work the model discrimination between EQ and RB models will be extended to finite reflux operation.

Acknowledgments

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References

Baur, R., Krishna, R., & Taylor, R., 2005. Influence of mass transfer in distillation: feasibility and design. AIChE journal, 51(3), 854-866.

Fidkowski, Z. T., Doherty, M. F., & Malone, M. F., 1993. Feasibility of separations for distillation of nonideal ternary mixtures. AIChE journal, 39(8), 1303-1321.

Kenig, E. Y., 2008. Complementary modelling of fluid separation processes. Chemical Engineering Research and Design, 86(9), 1059-1072.

Kiva, V. N., Hilmen, E. K., & Skogestad, S., 2003. Azeotropic phase equilibrium diagrams: a survey. Chemical Engineering Science, 58(10), 1903-1953.

Krishnamurthy, R., & Taylor, R., 1985. A nonequilibrium stage model of multicomponent separation processes. Part I: model description and method of solution. AIChE Journal, 31(3), 449-456.

Serwinski, M., Górak, A., 1983. Eine neue Berechnungsmethode für den axialen Konzentrationsverlauf bei der Mehrstoffrektification in Füllkörperkolonnen. Teil I: Theoretische Grundlagen. VT. Verfahrenstechnik, 17(8), 469-473.

Stichlmair, J. G., Herguijuela, J. R., 1992. Separation regions and processes of zeotropic and azeotropic ternary distillation. AIChE journal, 38(10), 1523-1535.

Taylor, R., & Krishna, R. (1993). Multicomponent mass transfer (Vol. 2). John Wiley & Sons.

Taylor, R., Krishna, R., & Kooijman, H., 2003. Real-world modeling of distillation. Chemical Engineering Progress, 98(7), 28-39.

Taylor, R., Baur, R., & Krishna, R., 2004. Influence of mass transfer in distillation: Residue curves and total reflux. AIChE journal, 50(12), 3134-3148.

Vogelpohl, A., 1964. Rektifikation von Dreistoffgemischen. Teil 1: Rektifikation als Stoffaustauschvorgang und Rektifikationslinien idealer Gemische. Chemie Ingenieur Technik, 36(9), 907-915.

Vogelpohl, A., 2002. On the relation between ideal and real mixtures in multicomponent distillation. Chemical engineering & technology, 25(9), 869-872.

Wahnschafft, O. M., Koehler, J. W., Blass, E., Westerberg, A. W., 1992. The product composition regions of single-feed azeotropic distillation columns. Industrial & engineering chemistry research, 31(10), 2345-2362.

Wilke, C. R. and C. Y. Lee, 1955. Estimation of diffusion coefficients for gases and vapors. Industrial & Engineering Chemistry, 47(6), 1253–1257.