

Number of Transfer Units Information on Residue Curve Maps

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The feasibility of alternative distillation schemes for any process usually is evaluated using the information provided by the residue curve map (RCM). The RCM shows all the possible composition profiles along a packed column operating at infinite reflux flow rate. A residue curve from a distillate to a bottoms composition indicates that with an enough reflux and number of stages this separation is feasible. Nevertheless, the residue curves do not provide a quantification of the separation difficulty and a feasible separation according the RCM can become infeasible when the number of stages required is too large. The number of transfer units (NTU) is a parameter able to solve this gap of information in the RCM. The NTU are easily determined during the RCM calculation. The knowledge of the difficulty of separation in the RCM provides important insights in the separation strategy to follow. The originality of this paper is the study and quantification of the difficulty of separation as additional information provided by residue curve maps based on the NTU concept. The TAME synthesis is used as illustrative example.

1. Introduction

The RCMs are widely used because they provide fast insights into the distillation processes such as chemical affinity between components, distillation regions and the presence of azeotropes and boundary lines are easily identified. The RCMs are the basis for analysis calculations, e.g. infinite/infinite analysis. The inclusion of a quantification of the separation difficulty in the residue curve maps is proposed for first time in the present paper to contribute to the enhancement of the RCM tool.

A tool to plot kinetically controlled residue curve maps has been implemented in MATLAB. It can be adapted to any system and provides an interactive interface that allows the free choice of the starting compositions. For illustrative purposes, the RCM representation is performed for TAME synthesis in a reactive distillation column, using as calculation basis the mathematical model proposed by Thiel et. al, 1997. The

distillation process details, reactions and kinetic parameters are described by Bonet-Ruiz et al (2009). Obviously the study is also valid for non reactive distillations (when the reaction kinetic term is neglected from the presented equations, $Da=0$). The reactive batch distillation process in a heated still model, used to obtain the residue curves, is based on the mass balance equations:

$$\frac{dx_i}{d\tau} = \left[x_i - y_i^*(x, p) + \frac{Da}{k_f(T^*)} \sum_{j=1}^M [(v_{i,j} - x_i v_j) \cdot r_j(x, p)] \right] \quad i=1, \dots, N-1; j=1, \dots, M. \quad (1)$$

where

$$y_i = P_{i,sat}(T) x_i \gamma_i(T, x_i), \quad i=1, 2..N \quad (2)$$

$$Da = \frac{c_L \cdot k_f(T^*) \cdot V_{cat}^0}{V^0} \quad (3)$$

$P_{i,sat}$ - vapour pressure; y_i, x_i – vapour and liquid molar fractions; γ_i - activity coefficient in liquid phase, τ - is a monotonically increasing quantity related to real time.

2. Method

It is traditional for chemical engineers to model packed columns through the concept of transfer units (NTU) according to the dimensionless expression (Taylor and Krishna, 1993):

$$\frac{dy}{d\zeta} = NTU \cdot (y^* - y) \quad (4)$$

where y^* is the vapor composition in equilibrium with the bulk liquid (x) and y is the vapor composition in contact with the bulk liquid (x). The difference between y^* and y is the driving force for the components transfer from the liquid phase (x) to the vapor phase (y), $\zeta=z/H$ is a dimensionless height ratio where H represents the overall height of packing. When the reflux is infinite then:

$$x = y \quad (5)$$

And the expression (4) becomes, in the case of infinite reflux (5), the following equation:

$$\frac{dx}{d\zeta} = NTU \cdot (y^* - x) \quad (6)$$

The similitude of equation (6) with the residue curve map expression (7) is obvious:

$$\frac{dx}{d\tau} = (x - y^*) \quad (7)$$

The coincidence of the residue curve profile with the profile of a packed column with infinite reflux was demonstrated by several authors (Van Dongen and Doherty, 1985; Laroche et al, 1992). The value of τ is directly related to the height of the column. From the equations (6) and (7), the variable related with the time can be linked with the NTU. Integrating for the total height of a column, the NTUs are calculated from the next equation:

$$\int_{\tau}^{\tau=0} d\tau = NTU \cdot \int_{\zeta=0}^{\zeta=1} d\zeta = NTU = \int_{x_0}^x \frac{dx}{y^* - x} \quad (8)$$

The NTU depends only on the composition column profile and it does not depend on the characteristics and performance of the packing. The information provided by RCM is supplemented in the present paper with more details related to the number of transfer units to quantify the difficulty of separation in specified operating conditions.

3. Results

For kinetically controlled reactive distillation columns, the reaction is taken into account for the NTU calculation as it is also considered in the reactive residue curve maps. The TAME synthesis is used as illustrative example. Reactive distillation provides a feasible and advantageous process for the TAME synthesis (Plesu et al 2008). The expression for the NTU (8) according to the reactive residue curve map equation (1) for the example becomes:

$$NTU = \int \left[\frac{dx_i}{y_i^*(x, p) - \left(x_i + \frac{Da}{k_f(T^*)} \sum_{j=1}^M [(v_{i,j} - x_i v_j) \cdot r_j(x, p)] \right)} \right] \quad i=1, \dots, N-1; j=1, \dots, M. \quad (9)$$

For the case of reactive distillation, the driving force is represented by the difference between the vapor composition in equilibrium with the bulk liquid (y^*) and the bulk liquid composition (x_i) plus the reaction term. The driving force between the vapor (y^*) and the corresponding bulk liquid (x_i) can be increased or decreased by the reaction term. In some cases, the non reactive driving force (y^*-x) can be cancelled by the reaction, producing the so-called reactive azeotropes.

Figures 1 and 2 illustrate the residue curve maps for TAME synthesis at 4 and 6 bar, which are the pressures of industrial interest. The background represents a visual expression of the driving force. In this way, the pinch zones where the separation is more difficult are easily identified. It is important to notice that the presence and situation of the pinch zones follow the evolution of the nodes with the reaction. The chemical equilibrium curve, separatrix and nodes are indicated in the maps to provide complete information. A transfer unit is required to move from one circle to the next on the residue curves. The black circles indicate the points of the residue curves with

highest driving force. When a greater number of residue curves are plotted, it can be observed that the black circles approach each other defining a curve, the next whiter circles define a new curve and so on towards the stable and unstable nodes. Only a few curves are presented because they approach very much one to the other in some zones and the circles information is more difficult to be discerned. The pinch zones generated by the saddle points produce a minimum in the driving force. Therefore, if the saddle compound is not the product to be collected, the residue curves passing through the saddle points should be avoided and the more straightforward residue curves are preferable.

The reactive distillation for the TAME synthesis must contain a non reactive section at the lower part of the column to avoid decomposition of TAME to its reactants. The reactive residue curve map section at the right side of the equilibrium line contributes to the formation of TAME meanwhile the section at the left side decomposes TAME. For Da equal to 10^{-4} and 10^{-3} , the highest driving force is at the left side of the chemical equilibrium. For Da equal to 10^{-2} the maximum driving force is around the chemical equilibrium and therefore this Da is preferable to lower ones.

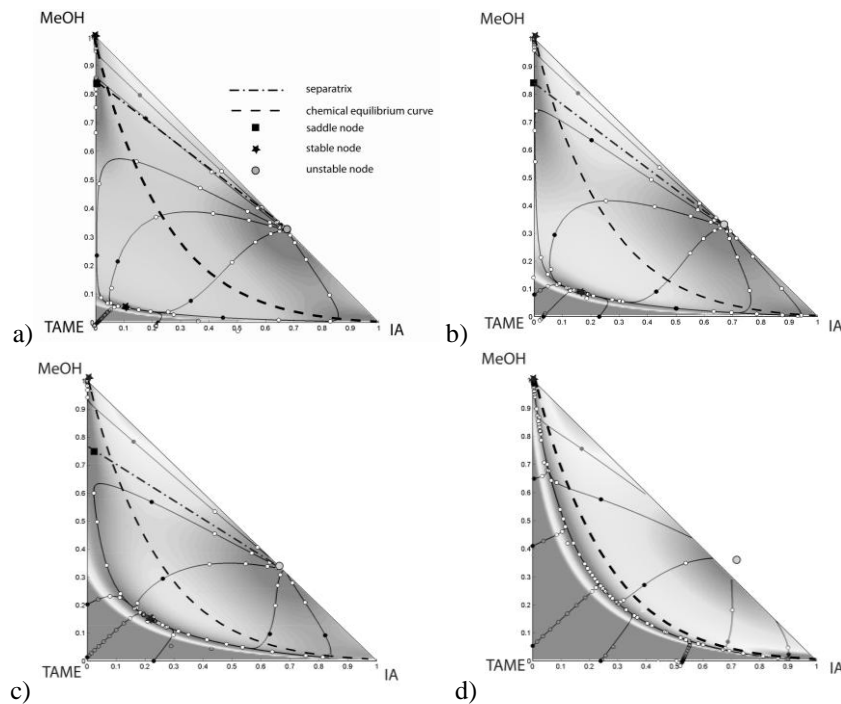


Figure 1: RCMs at $p = 4$ bar and Da equal to a) 10^{-4} , b) 10^{-3} , c) 10^{-2} , d) 10^{-1}

The pressure also influences the number of NTU and the position of the chemical equilibrium. As the increase of pressure from 4 to 6 bar is small, the increase in the NTU required is not appreciable (Figure 3). Due to the exothermic characteristic of the TAME synthesis, the chemical equilibrium curve is shifted towards the reactants MeOH

and IA when pressure increases. This fact is appreciable in the Figures 1 and 2 when the pressure changes from 4 to 6 bar. At 6 bar the number of reactive NTU is smaller than at 4 bar, but the number of non reactive NTU increases.

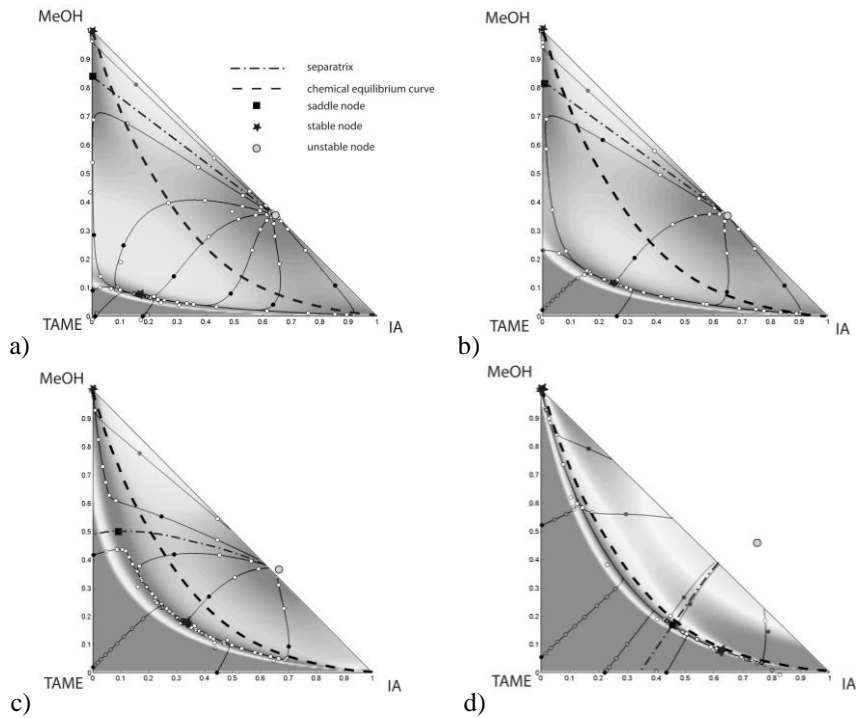


Figure 2: RCMs at $p = 6$ bar and Da equal to a) 10^{-4} , b) 10^{-3} , c) 10^{-2} , d) 10^{-1}

From the obtained results, it would be possible to propose a feasible column profile: (a) At 4 bar Figure 1-c, following the reactive residue curve from the IA/MeOH azeotrope until the black circle near the chemical equilibrium line and near the composition 0.3 MeOH and 0.3 IA (NTU=4). (b) At 4 bar Figure 3-a, following the residue curve from a white circle near the composition 0.3 MeOH and 0.3 IA until pure TAME is reached (NTU=3). Therefore the process is feasible with a reasonable NTU at 4 bar, a non reactive section at the bottom and a reactive section with a $Da=10^{-2}$.

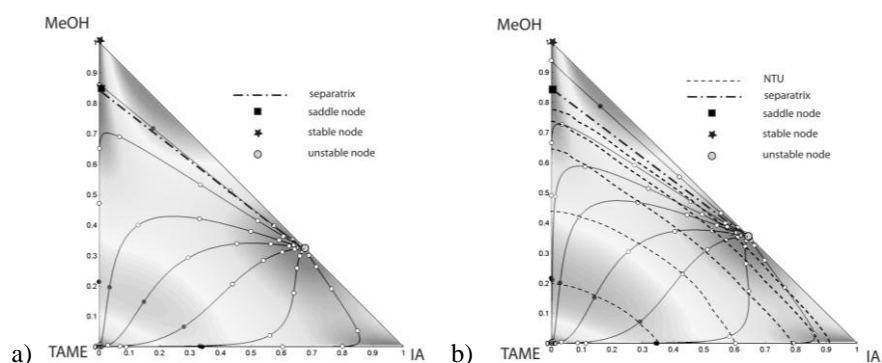


Figure 3: RCMs at $Da=0$ and P equal to a) 4, b) 6 bar

4. Conclusions

An original tool to plot kinetically controlled residue curve maps has been implemented in MATLAB, providing an interactive interface that allows the free choice of the starting compositions. Additionally, the information provided by RCM is supplemented with more details related to the number of transfer units (NTU) to quantify the difficulty of separation. NTU depends only on the column profile and it does not depend on the characteristics and performance of the packing. As the composition profile of a packed column at infinite reflux corresponds to a residue curve map, the NTU can be calculated according to the residue curve map (RCM) results. The TAME synthesis is used as illustrative example. From the RCM results, it can be concluded that the Da is recommendable to be higher than 0.01 for this particular system.

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