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New Contributions to Modelling and Simulation of TAME Synthesis by Catalytic Distillation

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The residue curve map is a basic tool for distillation processes to get insights on the process behaviour and feasibility and represents the basis for any analysis. For instance, the infinite/infinite analysis recently applied to kinetically controlled reactive distillation systems is based only on the information provided by the residue curve maps. The shape of the residue curves depends on two essential parameters of the model, the Damköhler number (Da) and the operating pressure. This study presents a software tool developed in MATLAB® used to provide a set of residue curve maps for TAME synthesis, computed at various values of pressure and Da number covering the industrial operating conditions.

1. Introduction

Residue curve represents the change over the time of the residue composition in the still of a Rayleigh distillation. The usefulness of the residue curves in distillation analysis derives from matching a residue curve segment with the composition profile of a packed distillation column at infinite reflux. This property made the residue curve maps (RCM) a useful tool to determine the separation feasibility of various multi-component systems, ideal and non-ideal azeotropic mixtures with or without reactions, in chemical equilibrium or kinetically controlled. For example, when the distillate and the residual (bottom) composition of a distillation column lie on the same residue curve, the mixture separation is feasible if a big enough number of stages and reflux are used. RCM technique has been considered useful for the flow-sheet development and preliminary analysis of multi-component separation processes. The residue curves are the only data required for this evaluation, by existing methods such as the infinite/infinite analysis.
RCM have shown to provide valuable insights and design assistance for non-ideal systems, particularly for reactive distillation. Furthermore, RCM is also suitable to kinetically controlled processes, which are common in industrial practice. The

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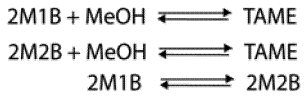
integration of reaction and distillation into a single unit (reactive distillation) may bring potential advantages such as reducing energy and capital cost, enhancing yield and selectivity, breaking thermodynamic restrictions, etc. Most of these processes are short of feasibility analysis methodologies due to process complexity. The analysis of the location and stability of the singular points in RCMs yield valuable information on the attainable products of an RD process. Reactive distillation provides a feasible and advantageous process for the TAME synthesis (Plesu et al 2008).

TAME (tert-amyl-methyl-ether) is commonly produced by liquid-phase etherification between methanol (MeOH) and isoamylene (IA), in the presence of an acidic catalyst. The process involves strongly non-ideal mixtures and is kinetically controlled. Among the three isoamylenes, only 2-methyl-l-butene (2M1B) and 2-methyl-2-butene (2M2B) are reactive, whereas 3-methyl-1-butene (3M1B) is non-reactive. Besides the main reactions of methanol addition to 2M1B and 2M2B, various side reactions are possible, among which the most important is isomerisation of the reactive isoamylenes. Therefore, the reactive mixture to be considered in the TAME synthesis consists of four components: MeOH, 2M1B, 2M2B and TAME. The reaction scheme can be described as follows:



2. Method

For illustration purposes, the RCM representation is performed for TAME synthesis, using as calculation basis the mathematical model proposed by Thiel et. al, 1997. The reactive batch distillation process in a heated still model, used to obtain the residue curves, is based on the mass balance equations:

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

$$y_i = P_{i,sat}(T)\ x_i\ \gamma_i(T,x_i), \qquad i = 1,2..N \qquad Da = \frac{c_L \cdot k_f(T^*) \cdot V_{cat}^0}{\dot{V}^0}$$

where: $P_{i,sat}$- vapour pressure; y_i, x_i – vapour and liquid molar fractions; γ_i - activity coefficient in liquid phase;

In the reactive distillation, the simple distillation is carried out simultaneously with the reaction. The liquid phase is at boiling point so that the reaction temperature in the still corresponds to the boiling temperature of the liquid at the given operating pressure. It is assumed that the heating produces a time constant ratio between the hold up and the vapour flow rate. To describe the non-ideal mixture behaviour, liquid-phase activities are introduced. The experimental vapour-liquid equilibrium data is not currently available for all the binary mixtures of the system, therefore the liquid-phase activities are predicted by the UNIFAC method.

Because of the fact that there are three reactions taking place simultaneously, three coupled chemical equilibrium constants have to be considered. Rihko et al. (1994) proposed the following expressions (T in K):

- TAME synthesis from 2M1B: $K_{a,1} = 1.057 \cdot 10^{-4} \exp(4273.5/T)$

- TAME synthesis from 2M2B: $K_{a,2} = 1.629 \cdot 10^{-4} \exp(3374.5/T)$

- isoamylenes isomerisation: $K_{a,3} = K_{a,1}/K_{a,2}$

Generalized Langmuir-Hinshelwood rate expressions are applied to formulate the heterogeneously-catalyzed etherification. In order to simplify the description of the TAME-synthesis process, 2M1B and 2M2B will be lumped in a single pseudo-component (IA), so that the two methanol addition reactions will be represented as a single reaction (Thiel et. al, 1997):

$$\text{IA} + \text{MeOH} \rightleftharpoons \text{TAME}$$

The kinetic model of this global reaction, is formulated according to Oost and Hoffmann (1995):

$$r_{1,2} = r_1 + r_2 = k_{f,12} \cdot \left(\frac{a_{2M1B}}{a_{MeOH}} - \frac{1}{K_{a,1}} \frac{a_{TAME}}{a_{MeOH}^2} \right)$$

and the reaction rate constant is given by the following Arrhenius equation:

$$k_{f,12} = \left(1 + K_{a,3}(T)\right) \cdot 2.576 \cdot \exp\left[-10.764 \times 10^3 \left(\frac{1}{T} - \frac{1}{333.15} \right) \right]$$

The kinetics of isoamylenes isomerisation reaction is also neglected, the two isomers, 2M1B and 2M2B, being considered at chemical equilibrium. In this way, the two remaining independent concentrations allow its graphical representation in a Gibbs diagram. Otherwise, the relation between the two concentrations of isoamylenes (when calculated independently) lets a degree of freedom not fixed and when summated in a pseudo-component (IA), the residue curves cross each other.

A RCM computation tool was implemented in MATLAB®, being able to represent kinetically controlled processes. RCM's are constructed based upon physical properties of the system (vapour-liquid equilibrium) and reaction kinetics. This tool can be adapted to any system and provides an interactive interface that allows the free choice of the starting compositions (Figure 1).

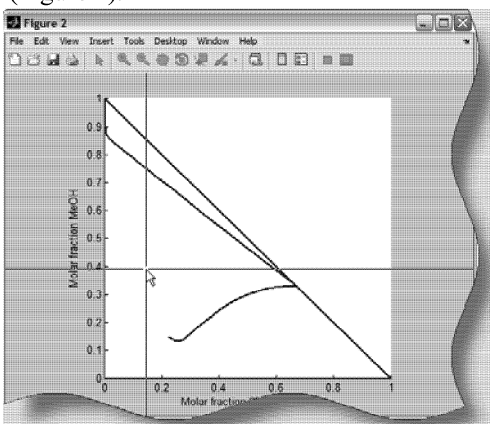


Figure 1. Screen snapshot for initial concentration selection

The residue curve trajectories are described by a system of non-linear differential algebraic equations. Therefore, the computation method is based on the built-in

command *ode15s,* integrating a system of differential and algebraic equations. This command uses a singular diagonal mass matrix, which multiplies the time derivatives. The residue curve trajectories are calculated by integration of mass balance equations in both senses, until they arrive at the stable and unstable node of the corresponding distillation region. The free choice of the residue curves location provides a map without gaps, improving the appearance of most of the available residue curve diagrams. All the nodes are calculated, even when they are outside of the physical meaning zone.

3. Results

The industrial interest for TAME synthesis is at pressures around 4 or 6 bar. Thiel et al (1997) provided the results at 1 and 10 bar. This paper is focused on the pressure values relevant to industrial application. The residue curve maps for several Da at 4 bar are shown in Figure 1 and at 6 bar in Figure 2.

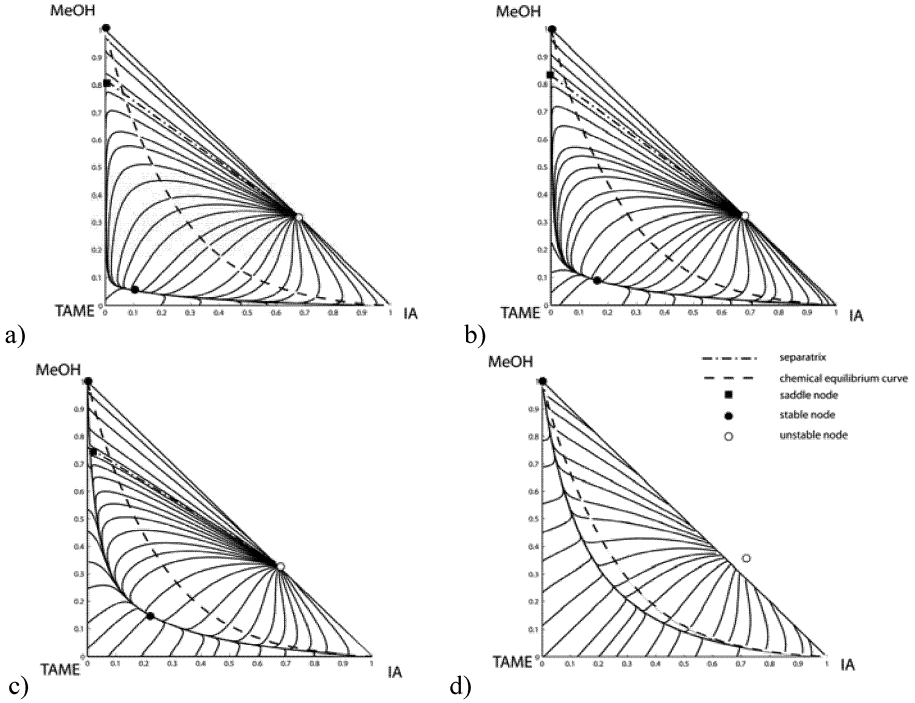


Figure 2. RCMs at p = 4 bar and Da equal to a) 10^{-4}, b) 10^{-3}, c) 10^{-2}, d) 10^{-1}

The presence of singular points in the obtained RCMs allows to divide the composition diagram into separate distillation regions by introducing distillation separatrices, which connect two singular points in the composition space.

In the diagrams presented in Figures 2 and 3 (except 2d), four singular points are depicted. The stable nodes are associated to pure MeOH vertex and to a ternary azeotropic mixture MeOH-TAME-IA. The unstable node is represented by the binary azeotrope MeOH-IA, which changes its location, leaving physical meaning range. The

saddle node is represented by the binary azeotrope TAME-MeOH at Da values of 10^{-4} and 10^{-3} and by the ternary azeotrope TAME-MeOH-IA at Da values of 10^{-2} and 10^{-1}. Additionally, another unstable node is expected far outside of the physical meaning range, suggested by the orientation of the residue curves near pure TAME vertex. A reactive residue curve may follow the map egdes only if both components defining the edge do not react and any of them doesn't decompose. In the present case, two of the edges include TAME which decomposes due to reaction reversibility. Therefore, TAME vertex doesn't act as a singular point and this situation supports the mathematical existence of the expected unstable node.

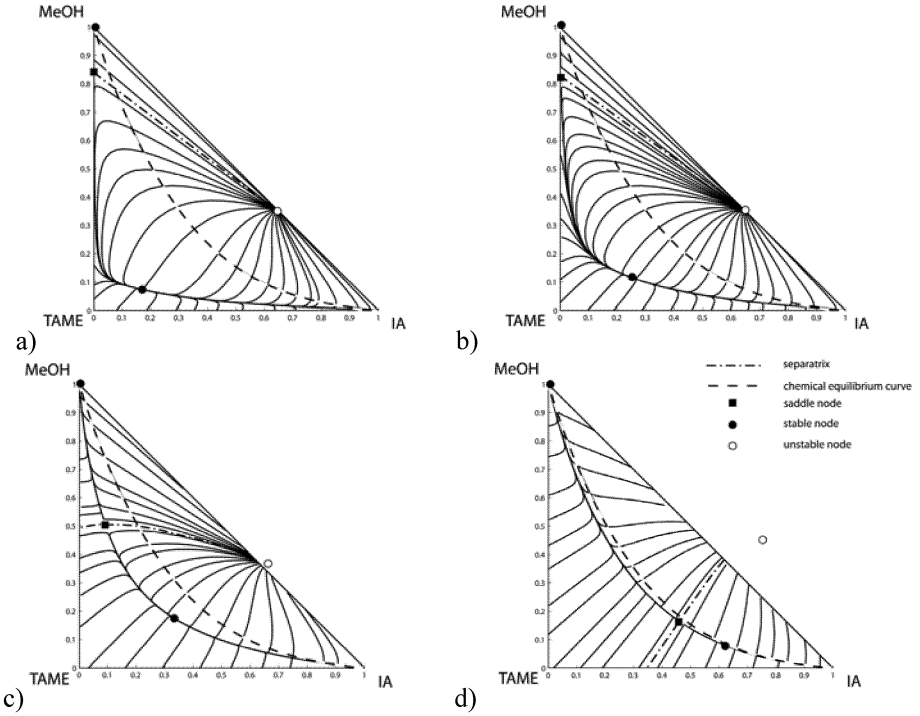


Figure 3. RCMs at p = 6 bar and Da equal to a) 10^{-4}, b) 10^{-3}, c) 10^{-2}, d) 10^{-1}

The singular points detected define several separatrices: from the unstable node to the saddle point, from the saddle point to the stable nodes, from the ternary stable node to the IA vertex and from the saddle point to the expected unstable node mentioned above. Therefore, the diagrams composition space is divided into several distillation regions.

The change of location and composition for all the singular points detected (except pure MeOH vertex) is due to the influence of operating conditions (pressure) and chemical reaction (Da number). The unstable node gets enriched in MeOH as the pressure increases. At low Da values (10^{-4} and 10^{-3}), it is represented by the binary azeotrope MeOH-IA. At higher Da values (10^{-1}), the unstable node moves out of the physically relevant composition space. This fact was also described by Thiel et al. (1997) although its position was not indicated. The saddle point gets richer in MeOH as the pressure

increases from 4 to 6 bar and Da = 10^{-4}. However, for Da = 10^{-2}, the saddle point gets poorer in MeOH.
For low Da value, the boundary lines departing from the ternary stable node are close to the pure TAME vertex and approach the chemical equilibrium curve when Da and pressure increase. TAME decomposes due to the reaction reversibility and it is noticed that this tendency increases with the increase of pressure and Da. The boiling point of the mixture and the reaction temperature and rate are related to pressure values as well. Due to the exothermic characteristic of the TAME-synthesis, the chemical equilibrium curve is shifted towards the reactants MeOH and IA when pressure increases from 4 to 6 bar.
The diagram at Da=10^{-1} and 4 bar presents a different topology (Figure 3d). In this case, the ternary stable node is not present. Consequently, the saddle point and the corresponding boundary lines are neither present. Thiel et al. (1997) reported the same behaviour for Da=1 and 1 bar, where the stable node disappears and every trajectory runs into the collecting trajectory which is the only remaining separatrix in the composition space. Other residue curve map topologies such as with three stable nodes are not detected in the operating conditions considered in the present study.

4. Conclusions

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 illustration purposes, it has been used to compute RCM for TAME synthesis based on the mathematical model provided in the reference paper (Thiel et al.,1997). In the present study, the reactive residue curve maps at 4 and 6 bar are provided, including the singular points location. The studied pressures are in the range of the industrially used values. A residue curve map with two distillation regions is obtained in the reference paper at Da=1 and pressure 1 bar; in the present paper, a similar diagram is obtained at Da=0.1 and pressure 4 bar. The results obtained are in agreement with the ones reported in the reference study. A further improvement of the tool developed will consider the joint use of Simulis Thermodynamics as database and for vapour-liquid equilibrium data computation.

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