

A SHORT METHOD TO CALCULATE REACTIVE RESIDUE CURVE MAPS

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Abstract

Reactive residue curve maps (RRCM) are useful for the design of reactive distillation columns as a tool to establish feasible zones of reaction-separation. The calculation of RRCM usually involves great computational effort due to the nonlinearity of the model equations and its iterative nature for the determination of reactive phase equilibrium. In this study, a simplified method for the generation of RRCM is presented. This method is based on the application of reaction-invariant composition variables and assumes that the phase equilibrium constants and the relative volatilities are independent of the temperature. These assumptions allow avoiding iterative calculations for obtaining a good approximation of RRCM. Several case studies are used to show the effectiveness of the proposed method.

Keywords: reactive residue curve maps, reactive phase equilibrium, separation boundaries, reaction-invariant composition variables

1. Introduction

A residual curve represents the change in composition with respect to time of the phases during a simple distillation¹. The residue curve maps (RCM) are an important tool in the initial stage of the process design for identifying, in a fast form, the infeasible sequences. This is because RCM provide the possibility of determining the existence of distillation boundaries and, as a consequence, determining different potential zones of operation². Once established the zone of feasible operation and, depending on the feed composition, it is possible to predict the different components obtained as distillate and bottom products. It is important to note that several numerical difficulties are involved in the modeling and design of reactive distillation (RD) systems. These difficulties have their origin mainly in the multicomponent nature of the problems considered, the nonlinearity of the thermodynamic models caused by the presence of simultaneous chemical and physical equilibrium, and also by the type of variables involved in defining the problem, which are generally composition variables in molar units and extents of reaction³. In this context, the premise of using the concept of transformed composition variables for obtaining RCM is that the equations that characterize a RD system are expressed mathematically in the same form that those reported for non-reactive distillation system¹. Using a transformed variable approach, the solution space is restricted to compositions that are already at chemical equilibrium and the problem dimension is also reduced³. These advantages allow studying a variety of real and complex reactive systems, because there are several combinations between the number of reactions (R) and the number of components (C) that can be analyzed in ternary diagrams. Therefore, the analysis of RRCM can be performed in the same form as in simple distillation without chemical reactions. Until now, only few methods have used transformed composition variables for the calculation of RRCM. However, current methods may show a significant computer time for the calculation of RRCM^{3,4}.

In this study, we take advantage of the characteristics of reaction-invariant composition variables⁴ to develop a short method for calculating RRCM. Specifically, we propose a simplified approach for determining RRCM by discarding the effect of temperature on the reactive phase equilibrium constants, but preserving the composition effect. Although this assumption has been used for non-reactive mixtures⁵, it has not been applied for the study of reactive mixtures. Our results indicate that the use of transformed composition variables and the application of simplified phase equilibrium constants (i.e., not dependent of temperature) avoid the iterative calculation of the mixture bubble temperature, resulting in an effective and faster strategy for calculating RRCM. Finally, the performance of our short method is compared with those reported using a rigorous method.

2. Description of Reactive Residue Curve Calculation

For homogeneous mixtures with multiple chemical reactions, the calculation of a reactive residual curve (RRC) is based on a modification of the Rayleigh expression⁴. For a system of C components subject to R independent chemical reactions, the following set of equations is used¹:

$$\frac{dX_i}{d\tau} = X_i - Y_i \quad (1)$$

where X_i represents the transformed composition in the liquid phase of component i , Y_i is the transformed composition in the vapor phase of component i , and τ is the dimensionless time, respectively. Equation (1) is obtained from a mass balance applied to a distillation unit and by introducing a dimensionless time variable¹. RRCM is obtained from the forward and backward integration of Equation (1) with respect to time starting from an initial composition. For calculating the RRC, the integration step depends on the case study, however, a small integration step is usually recommended. It is convenient to note that each RRC requires a significant number of points to be constructed, each one involving the calculation of the vapor-phase composition in equilibrium with the liquid-phase composition. Therefore, bubble point calculations are needed to obtain the vapor-phase composition in the traditional approach. Because such calculations are iterative, the generation of RRCM requires a significant numerical effort and computer time due to the nonlinearity of the model equations and the use of numerical methods for calculating the reactive phase equilibrium^{3,4}. In this study, we propose the use of transformed composition variables to reduce the problem dimension and the application of simplified phase equilibrium constants, which are independent of temperature, to decrease the numerical effort for obtaining a RRCM.

In a reactive system, the Gibbs free energy function behaves as in a non-reactive system if transformed composition variables (X) are used instead of the conventional composition variables⁴. Using these transformed variables, the solution space is restricted to compositions that are already at chemical equilibrium and, as a consequence, the problem dimension is also reduced³. So, the reactive phase diagrams look similar to the non-reactive ones and the non-reactive flash algorithms can be easily modified to account for the equilibrium reactions. Ung and Doherty⁴ showed that the chemical potential follows all the thermodynamic relationships of a non-reactive system as long as all the thermodynamic properties are functions of the transformed composition variables. Based on this fact, the equilibrium constant \hat{K}_i for phase equilibrium calculations can be defined as⁶

$$\hat{K}_i \{X_i, Y_i\} = \frac{\gamma_i^\alpha}{\gamma_i^\beta} \quad i = 1, \dots, C - R \quad (2)$$

where the transformed mole fractions X_i and Y_i are given by

$$X_i = \frac{x_i - \mathbf{v}_i N^{-1} x_{ref}}{1 - \mathbf{v}_{TOT} N^{-1} x_{ref}} \quad i = 1, \dots, C - R \quad (3)$$

$$Y_i = \frac{y_i - \mathbf{v}_i N^{-1} y_{ref}}{1 - \mathbf{v}_{TOT} N^{-1} y_{ref}} \quad i = 1, \dots, C - R \quad (4)$$

where x_i is the liquid mole fraction of component i , y_i is the vapor mole fraction of component i , γ_i^α is the liquid activity coefficient of component i , and γ_i^β is the vapor activity coefficient of component i . For transformed variables, x_{ref} is the column vector of R reference component mole fractions, \mathbf{v}_i is the row vector of stoichiometric number of component i for each reaction, \mathbf{v}_{TOT} is a row vector where each element corresponds to reaction R and it is the sum of the stoichiometric number for all components that participate in reaction R , and N is a square matrix formed from the stoichiometric number of the reference components in the R reactions⁴.

Then, the reactive phase equilibrium condition in terms of transformed variables, using Equations (2)-(4), is given by⁶

$$Y_i = X_i \hat{K}_i \theta + \delta_i \quad i = 1, \dots, C - R \quad (5)$$

and

$$\theta = \frac{1 - \mathbf{v}_{TOT} N^{-1} x_{ref}}{1 - \mathbf{v}_{TOT} N^{-1} y_{ref}} \quad (6)$$

$$\delta_i = \frac{\mathbf{v}_{TOT} N^{-1} (\hat{K}_i x_{ref} - y_{ref})}{1 - \mathbf{v}_{TOT} N^{-1} y_{ref}} \quad i = 1, \dots, C - R \quad (7)$$

For the transformation procedure $X \rightarrow x$, the references mole fractions are calculated using Equation (3) or (4) and from the equilibrium constants for each reaction K_{eq} by solving a system of R nonlinear equations given by

$$K_{eq} = \prod_{i=1}^n a_i^{v_i^r} \quad r = 1, \dots, R \quad (8)$$

where a_i is the activity of component i and v_i^r is the stoichiometric number of component i in reaction R , respectively. When we know the reference mole fractions, the remaining mole fractions are calculated using Equation (3) or (4) for liquid and vapor phase, respectively.

When the effect of temperature over \hat{K}_i is neglected, a suitable estimation of the bubble temperature (T_B) is sufficient to obtain a good description of the reactive vapor-phase equilibrium composition. In this study, a weighted sum of the pure-component boiling temperatures (T_{b_i}) is used for estimation T_B

$$T_B = \sum_{i=1}^{C-R} T_{b_i} x_i \quad (9)$$

Using Equation (9), the transformed composition in the vapor phase is calculated applying the Equations (2) and (5)-(7). Note that a significant reduction in computer time should be observed because the bubble point temperature is not calculated using an iterative procedure.

3. Results and Discussion

In this section, we show the effectiveness of the proposed short method for the calculation of RRCM and the results are compared to those obtained with the traditional method based on iterative bubble-point calculations. RRCM were calculated for three reactive mixtures: a multireactive ideal system at 1.013 bar and two real systems that involves the synthesis of methyl *tert*-butyl ether (MTBE) in the presence of inert at 8.104 bar, and the synthesis of *Tert*-amyl methyl ether (TAME) without inert at 4.052 bar. Details of reactive systems and thermodynamic models are provided in Table 1. For the sake of brevity, in this paper we report the RRCM for all reactive systems and detailed results are analyzed for one case of study.

3.1 System $A_3 \Leftrightarrow A_4$ $A_5 \Leftrightarrow A_4$ $A_4 \Leftrightarrow A_6$ with inert A_1, A_2

We considered a hypothetical system consisting of six components where four of them are involved in three independent chemical reactions and the remaining two are inert. This system was analyzed at atmospheric pressure. The presence of liquid-vapor equilibrium was assumed, where both phases were considered ideal. The saturation pressure of the pure compounds was calculated with the Antoine equation, see parameters reported in Table 2. The components A_3 , A_4 and A_5 were used as reference substances to calculate the transformed mole fractions, which are defined as

$$X_1 = x_1 \tag{10}$$

$$X_2 = x_2 \tag{11}$$

$$X_6 = x_6 + x_3 + x_4 + x_5 = 1 - X_1 - X_2 \tag{12}$$

These transformed mole fractions present values in the interval (0, 1). Figure 1 displays the RRCM for the multireactive system using both our short method and the traditional approach. An excellent agreement of RRCM is obtained with both methods and both reactive residue curves can be considered for process design. In this reactive system, the presence of distillation boundaries or azeotropes are not observed.

In Figure 2, the RRCM for the synthesis of MTBE is shown. In this case, the presence of a reactive ternary azeotrope near the pure n-Butane node and a nonreactive binary azeotrope (Methanol-Butane) are observed. This mixture shows a distillation boundary that divides the composition diagram in two regions. In addition, pure Methanol and Isobutene provides a stable node, and the n-Butane is a saddle node. Again, an excellent agreement is again observed between the RRCM calculated by both the rigorous method and our short strategy.

The RRCM for the reactive mixture related to the synthesis of TAME is shown in Figure 3. Two unstable binary azeotropes (2M1B-Methanol and 2M2B-Methanol) were found and there are two distillation boundaries that divide the composition diagram in three regions. The distillation boundaries have a pronounced curvature. In addition, pure Methanol provides a stable node, and the 2M1B and 2M2B are saddle nodes. The complex nature of this reactive mixture is reflected in the shape of its RRCM. Although our short method does not match the results of the rigorous method as well as it does for others reactive systems, it may consider as a proper reference point for preliminary applications, because a good description of the composition space is observed.

Table 1. Reactive mixtures selected to calculate RRCM using the short method

System	Thermodynamics Model	Chemical equilibrium constant
Hypothetic system of three reactions with inert A_1, A_2 $A_3 \Leftrightarrow A_4$ $A_5 \Leftrightarrow A_4$ $A_4 \Leftrightarrow A_6$	Ideal liquid and Ideal gas	$K_{eq}^1 = 1.5, K_{eq}^2 = 0.15$ and $K_{eq}^3 = 0.35$
Isobutene + Methanol \Leftrightarrow MTBE with n-Butane as an inert	Wilson model and Ideal gas ⁷	$\Delta G_{rxs}^o / R = -4205.05 + 10.0982T - 0.2667T \ln T$ $K_{eq} = e^{-(G/T)}$ $T [=] K$
2-methyl-1-butene (2M1B) + 2-methyl-2-butene (2M2B) + Methanol \Leftrightarrow TAME	Wilson model and Ideal gas ⁸	$K_{eq} = 1.057 \cdot 10^{-4} e^{(4273.5/T)}$ $T [=] K$

Table 2. Parameters of the Antoine equation for modeling a hypothetical multireactive system

Component	A	B	C
A ₁	7.63130	1566.690	273.419
A ₂	7.11714	1210.595	229.664
A ₃	7.44777	1488.990	264.915
A ₄	8.11220	1592.864	226.184
A ₅	7.97010	1521.230	233.970
A ₆	6.86640	1188.050	226.276

$$\log_{10} P_i^{sat} = A - \frac{B}{T + C} \quad P_i^{sat} [=] \text{ mmHg } T [=] \text{ } ^\circ\text{C}, \quad {}^5 P_i^{sat} [=] \text{ Pa}, T [=] \text{ K}$$

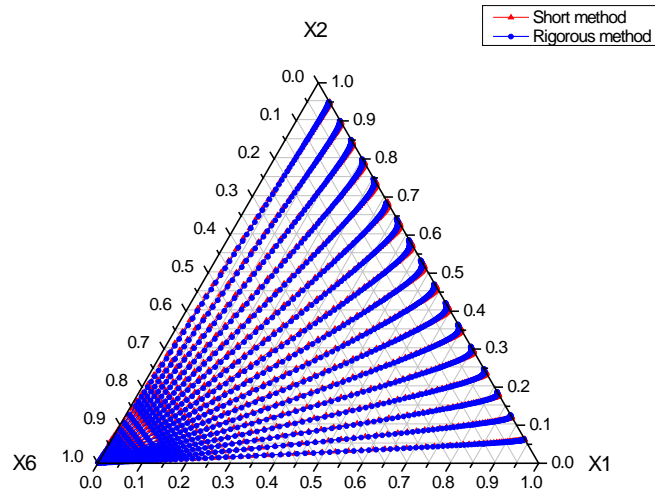


Figure 1. The RRCM for a hypothetical multireactive system of three reactions with two inert

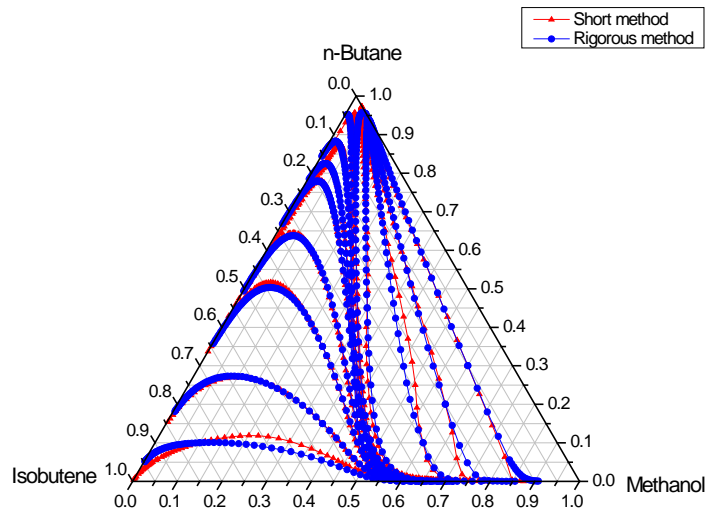


Figure 2. RRCM for the synthesis of MTBE in presence of n-butane as inert

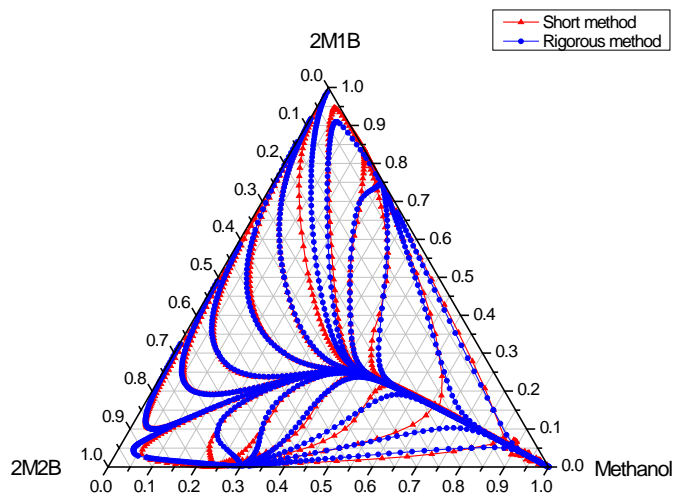


Figure 3. RRCM for the synthesis of TAME

It is convenient to remark that the main advantage of the proposed short method is the reduction of computer time. Table 3 shows the number of integration steps and the computer time required for the calculation of 20 reactive residue curves. The calculation time for the short method is 10% – 16% of the time required for the rigorous method.

Table 3. Computer times and integration steps required for RRCM calculations in selected reactive systems

System	Integration steps		Ratio of computer time: short RRCM/rigorous RRCM
	Rigorous RRCM	Short RRCM	
Ideal	2651	1670	0.107
MTBE	951	781	0.159
TAME	1820	1494	0.151

Our results suggest that, for ideal multireactive systems that not present distillation boundaries or azeotropes, the calculation of RRCM using an approximate T_B value produced excellent results. However, the MTBE and TAME systems are more complex because they show azeotropes and distillation boundaries. The biggest differences between the results of the short method and the rigorous method are present around these points. For MTBE, the azeotrope has a temperature value within the interval of the boiling temperatures for the pure components. The proposed method provides good results for RRCM in this case. In the case of TAME, which shows the major deviations, there is an azeotrope with temperature outside the range given by the bubble points of the pure components. Even under these conditions, the short method provides reactive residue curves that satisfactorily match those obtained by rigorous calculations. These results suggest that the proposed method is an alternative for obtaining a suitable estimation of RRCM efficiently.

4. Conclusions

Reactive residue curve maps (RRCM) are important tools to analyze the feasibility of a proposed split for the design of reactive distillation columns in an easy, fast, and qualitative format. In this study, the use of simplified phase equilibrium constants based on reaction-invariant composition variables has been proposed to calculate these reactive residue curves. Our results indicate that a good approximation of the RRCM is obtained with this simplified method, even for reactive azeotropic mixtures with more than one separatrix. The biggest differences between the short method and the rigorous method are present around of the azeotropes and distillation boundaries. However, this discrepancy does not represent a significant problem because these RRCM are used in the initial stages of process design. However, if a better representation in the neighborhood of the distillation boundaries is required, a hybrid method can be used: the boundary and the closer curves can be calculated with the rigorous method and the rest of the composition space with the short method. Using this approach, a significant reduction in computation time for the calculation of RRCM is assured.

Acknowledgements

We acknowledge the financial support provided by Universidad de Guanajuato, Instituto Tecnológico de Aguascalientes, CONACyT and CONCyTEG (Mexico).

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