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A Short Method To Calculate Residue Curve Maps in Multireactive and Multicomponent Systems

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ABSTRACT: Reactive residue curve maps (RRCMs) are useful for the design of reactive distillation columns as a tool to establish feasible zones of reaction−separation. However, the calculation of an 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 RRCMs is presented. This method is based on the application of reaction-invariant composition variables and assumes that the phase equilibrium constants (i.e., the relative volatilities) are independent of the temperature. Specifically, the phase equilibrium constants are calculated using a suitable estimation of the bubble temperature obtained from pure-component boiling temperatures and the reaction-invariant composition of liquid phase. These assumptions avoid iterative phase equilibrium calculations for obtaining a good approximation of RRCMs. Several reactive systems are used to identify the capabilities and limitations of the proposed method.

1. INTRODUCTION

Within the broad range of topics that are related to reactive distillation (RD), the design of these processes has received significant attention from many researchers due to the technological and economical advantages obtained from the simultaneous occurrence of distillation and reaction. Specifically, this technology offers significant benefits over conventional processes such as the elimination of a reaction vessel, fewer separation units, high conversion of reactants, the improvement of product selectivity, the effective separation of complex mixtures (e.g., azeotropic mixtures), and reduced reboiler duty in the case of exothermic reactions, among others.[1]

The RD process has been long known in the chemical industry. However, it is only during the past decade that there has been a significant interest and an increase in the number of publications on this subject.[1] Recently, this process has become very important in the production of fuel additives such as methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), and *tert*-amyl methyl ether (TAME), and also in the production of many other chemicals such as esters and alcohols.[2]

Because most of these reactive systems may contain azeotropes, the reactive residue curve maps (RRCMs) are an important tool in the initial stage of the process design for identifying, in a fast form, the infeasible sequences. A residual curve represents the change of the liquid composition with respect to time during a simple distillation.[3] Thus, RRCMs provide the possibility of determining the existence of distillation boundaries and, as a consequence, determining different potential zones of operation.[4] Once the zone of feasible operation is established, depending on the feed composition, it is possible to predict the different components obtained as distillate and bottom products. However, it is important to note that several numerical difficulties are involved in the modeling and design of RD systems. These difficulties have their origin mainly in the multicomponent nature of the reactive systems, the nonlinearity of the thermodynamic models caused by the presence of simultaneous chemical and physical equilibria, and also by the type of variables involved in defining the problem, which are generally composition variables in molar units and extents of reaction.[5] In particular, the use of composition variables in molar units is not suitable for modeling reactive systems because these variables do not have the same dimensionality as the number of degrees of freedom given by the Gibbs phase rule for reactive systems.[6] Based on this fact, some approaches for the transformation of composition variables have been introduced in the literature[5,6] and their aim is to provide a simpler thermodynamic framework for treating systems subject to chemical reactions. These approaches are generally based on transformation of the physical compositions, and the principal benefit is that the chemical and physical equilibrium model in the reactive mixture is very similar to a strictly physical equilibrium model. In this context, the premise of using the concept of transformed composition variables for obtaining RRCMs is that the equations that characterize a RD system are expressed mathematically in the same form as those reported for nonreactive distillation systems.[3,5] In particular, the reaction-invariant composition variables proposed by Ung and Doherty[6] are attractive for the simulation of separation process and favor the study of complex multireactive and multicomponent systems. Using this approach,

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the reaction-invariant composition variables depend only on the initial composition of each independent chemical species (i.e., they are independent of the amount of reaction), the solution space is restricted to compositions that are already at chemical equilibrium, and the problem dimension is also reduced.[3,6] These advantages allow study of 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 (i.e., $C - R = 3$). Therefore, the analysis of RRCMs can be performed in the same form as in simple distillation without chemical reactions. Until now, only a few methods have used transformed composition variables for the calculation of RRCMs. However, these methods may show significant computer time for the calculation of RRCMs due to the iterative calculations involved in the modeling of reactive phase equilibrium.[3,5,6]

In this study, we take advantage of the characteristics of reaction-invariant composition variables to develop a short method for calculating RRCMs. Specifically, we propose a simplified approach for determining RRCMs by discarding the effect of temperature on the phase equilibrium constants, but preserving the composition effect. Although this assumption has been used for nonreactive mixtures,[7] it has not been applied to the study of reactive mixtures. Our results indicate that the use of reaction-invariant composition variables and the application of simplified phase equilibrium constants (i.e., not dependent on temperature) avoid the iterative calculation of the reactive bubble temperature, resulting in an effective and faster strategy for estimating RRCMs. Finally, the performance of our short method is compared with those reported using a rigorous method in several reactive systems.

2. DESCRIPTION OF REACTIVE RESIDUE CURVE CALCULATION USING REACTION-INVARIANT COMPOSITION VARIABLES

In a reactive system, the thermodynamic property functions behave as in a nonreactive system if reaction-invariant composition variables are used instead of the conventional composition variables. With this approach, the solution space is restricted to compositions that are already at chemical equilibrium, and as a consequence, the problem dimension is also reduced.[6] Thus, the reactive phase diagrams look similar to the nonreactive ones and the nonreactive ash algorithms can be easily modified to account for the equilibrium reactions. For a system of C components that undergoes R independent chemical reactions, the reaction-invariant mole fractions (X) are defined by selecting R reference components

$$X_i = \frac{x_i - \nu_i N^{-1} x_{\text{ref}}}{1 - \nu_{\text{TOT}} N^{-1} x_{\text{ref}}} \qquad i = 1, \ldots, C - R \tag{1}$$

where x_i is the mole fraction of component i, x_{ref} is the column vector of R reference component mole fractions, ν_i is the row vector of stoichiometric number of component i for each reaction, ν_{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 reactions.[6] The reaction-invariant mole fractions (X) in reactive systems are similar to the mole fractions (x) in nonreactive mixtures, and the sum of all reaction-invariant mole fractions must equal unity: $\sum_{i=1}^{C-R} X_i = 1$. For the transformation procedure $X \rightarrow x$, which is necessary to evaluate thermodynamic properties, the reference mole fractions are calculated using eq 1 and the equilibrium constants for each reaction $K_{\text{eq},r}$ by solving a system of R nonlinear equations given by

$$K_{\text{eq},r} = \prod_{i=1}^{C} a_i^{\nu_i^r} \qquad r = 1, \ldots, R \tag{2}$$

where a_i is the activity of component i and ν_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 eq 1.

On the other hand, in a simple distillation process with or without chemical reactions, a liquid is vaporized and the vapor is removed from contact with the liquid as it is formed (see Figure 1). Each differential mass of vapor is in equilibrium with the remaining liquid. The composition of the liquid will change with time, since in general the vapor formed is richer in the more volatile components. Therefore, the locus of the liquid compositions remaining from a simple distillation process defines a residue curve.[8] For homogeneous mixtures with multiple chemical reactions, the calculation of a reactive residual curve (RRC) is based on a modification of the Rayleigh expression.[3,5,8] For a system of C components subject to R independent chemical reactions and using reaction-invariant composition variables, the following set of ordinary differential equations is used to describe the dynamics of simple distillation processes[3,5,8,9]

$$\frac{dX_i}{d\tau} = X_i - Y_i \qquad i = 1, \ldots, C - R - 1 \tag{3}$$

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 3 is obtained from a mass balance applied to a distillation unit and by introducing a dimensionless time variable.[3,5,8,9] To obtain physical consistency using these transformed composition variables, the reference components must be chosen such that the time τ increases with increasing the real time t.[9,10] Therefore, the criteria for selecting a feasible set of reference components includes the invertibility of matrix N and that the product $\nu_{\text{TOT}} N^{-1}$ is a row vector containing negative or zero entries.[10]

An RRCM is obtained from the forward and backward integration of eq 3 with respect to the dimensionless time starting from an initial composition, which is also defined in terms of transformed variables. Specifically, each residue curve in the map is characterized by defining an initial value for transformed liquid composition X and, in this study, eq 3 is solved using the Runge−Kutta fourth-order method. Note that 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 temperature and vapor-phase composition in the traditional approach. In the reaction-invariant composition space, the reactive bubble point calculations is based on the following function:[11]

$$f_{\text{Bubble}} = 1 - \sum_{i=1}^{C-R} (K_i \theta X_i + \delta_i) = 0 \tag{4}$$

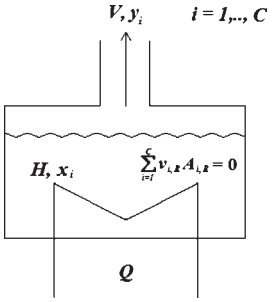

Figure 1. Schematic representation of a simple distillation process with chemical reactions.

where the reactive phase equilibrium condition is defined as

$$Y_i = X_i K_i \theta + \delta_i \qquad i = 1, \ldots, C - R \tag{5}$$

$$\theta = \frac{1 - \nu_{TOT} N^{-1} x_{ref}}{1 - \nu_{TOT} N^{-1} y_{ref}} \tag{6}$$

$$\delta_i = \frac{\nu_{TOT} N^{-1} (K_i x_{ref} - y_{ref})}{1 - \nu_{TOT} N^{-1} y_{ref}} \qquad i = 1, \ldots, C - R \tag{7}$$

where K_i is the phase equilibrium constant of component i. For reactive vapor−liquid equilibrium at low to moderate pressures, these equilibrium constants can be defined as

$$K_i = \frac{\gamma_i P_i^{sat}}{P} \qquad i = 1, \ldots, C \tag{8}$$

where γ_i is the liquid activity coefficient of component i, P_i^{sat} is the vapor pressure of pure component i, and P is the total pressure of the system. It is convenient to remark that γ_i is determined using the results of the transformation procedure $X \rightarrow x$ (i.e., we use mole fractions that satisfy the chemical equilibrium to evaluate the thermodynamic properties). Equation 4 is a nonlinear function with respect to temperature, pressure, and $C - R$ reaction-invariant mole fractions of the vapor phase (Y). Different numerical strategies can be used for performing bubble point calculations in reactive systems, and they include, for example, simultaneous equation-solving methods, equation-decoupling approaches, and global optimization techniques.[8] Therefore, the generation of RRCMs 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.[5,6]

In this study, we report the use of the reaction-invariant composition variables to reduce the problem dimension and the application of simplified phase equilibrium constants, which are independent of temperature, to significantly decrease the numerical effort for obtaining RRCMs. When the effect of temperature over K_i is neglected, we have found that a suitable estimation of the bubble temperature (T_B) is sufficient to obtain a good description of the reactive vapor-phase equilibrium composition. In our approach, a weighted sum of the pure-component boiling temperatures ($T_{b,i}$) and reaction-invariant liquid composition (X) is used for estimation of T_B:

$$T_B = \sum_{i=1}^{C-R} T_{b,i} X_i \tag{9}$$

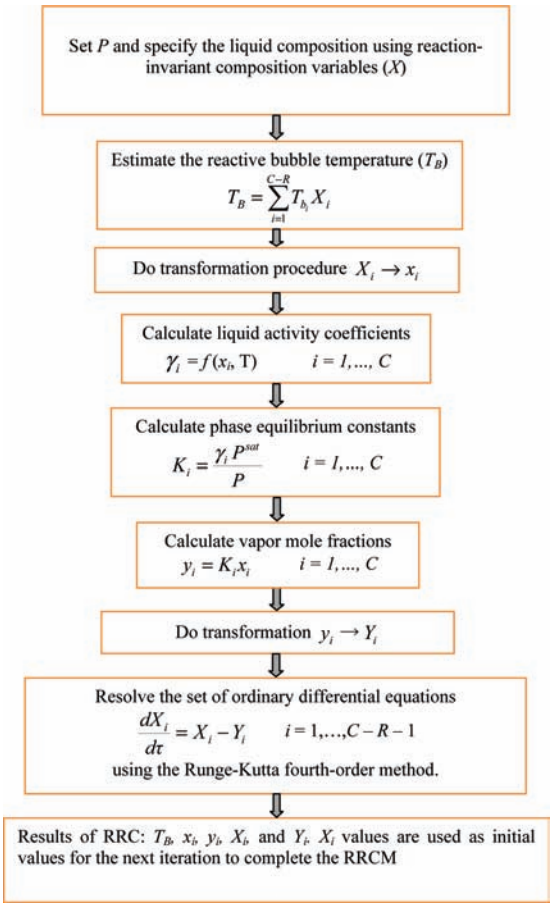

Figure 2. Flowchart for estimating reactive residue curve maps using reaction-invariant composition variables.

Using eq 9, the calculation of vapor-phase composition is straightforward. Specifically, based on the fact that the system is at equilibrium, the phase equilibrium relations are used for determining the molar vapor-phase composition (y):

$$y_i = K_i x_i \qquad i = 1, \ldots, C \tag{10}$$

where x_i is obtained from the transformation procedure $X \rightarrow x$ using the estimation for T_B. Note that a significant reduction in computer time should be observed because the bubble point temperature and vapor-phase composition are not calculated using an iterative procedure where γ_i, P_i^{sat}, and x (i.e., K_i) are obtained from X and T_B. For illustrative purposes, Figure 2 shows the ow diagram of this short method. In summary, this strategy is a simplified and efficient approach for estimating residue curve maps in multicomponent and multireactive systems. In section 3, we show the effectiveness of this simplified method and our results are compared to those obtained with the traditional method based on iterative reactive bubble-point calculations.

3. RESULTS AND DISCUSSION

RRCMs were calculated for four reactive mixtures: a multireactive ideal system at 1.013 bar and three systems that involve the synthesis of ethyl *tert*-butyl ether (ETBE) with inert at 10.13 bar, 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. Note that these

Table 1. Reactive Mixtures Selected To Calculate Reactive Residue Curve Maps

system	thermodynamic models and chemical equilibrium constants
hypothetical system of three reactions with inert A_1 and A_2: $A_3 \leftrightarrows A_4$ $A_5 \leftrightarrows A_4$ $A_4 \leftrightarrows A_6$	ideal liquid and ideal gas: $K_{eq,1} = 1.5, K_{eq,2} = 0.15,$ and $K_{eq,3} = 0.35$
isobutene + ethanol⇆ETBE with 1-butene as an inert	UNIQUAC model and ideal gas: $\Delta G^{\circ}_{rxs}/R = 4060.59 + 10.387T - 2.89055T \ln T - 0.0191544T^2 + (5.28586 \times 10^{-5})T^3 - (5.32977 \times 10^{-8})T^3$ where T is in K
isobutene + methanol⇆MTBE with *n*-butane as an inert	Wilson model and ideal gas: $\Delta G^{\circ}_{rxs}/R = -4205.05 + 10.0982T - 0.2667T \ln T$ where T is in K
2-methyl-1-butene (2M1B) + 2-methyl-2-butene (2M2B) + methanol⇆TAME	Wilson model and ideal gas: $K_{eq} = (1.057 \times 10^{-4})e^{4273.5/T}$ where T is in K

Table 2. Thermodynamic Data for a Hypothetical Multireactive System

component	A_i	B_i	C_i	γ_i
1	7.6313	1566.69	273.419	1.0
2	7.11714	1210.595	229.664	1.0
3	7.44777	1488.99	264.915	1.0
4	8.1122	1592.864	226.184	1.0
5	7.9701	1521.23	233.97	1.0
6	6.8664	1188.05	226.276	1.0

$\log P_i^{sat} = A_i - [B_i/(T + C_i)]$, where P_i^{sat} is in mmHg and T is in °C

Table 3. Thermodynamic Data for ETBE System

				u_{ij} in UNIQUAC model (K)			
component [a]	Q	Q'	R_u	1	2	3	4
1	2.68	2.68	2.92	*0*	−46.937	−21.484	24.245
2	1.97	0.92	2.11	436.034	*0*	424.521	404.721
3	4.94	4.94	5.86	39.215	−102.322	*0*	−42.130
4	2.56	2.56	2.92	−23.894	−26.93	−20.041	*0*

$\tau_{ij} = \exp(-u_{ij}/T)$

[a] 1, Isobutene; 2, ethanol; 3, ETBE; 4, 1-butene.

operating pressures are commonly used in industry for these reactive mixtures. Details of reactive systems and thermodynamic models are provided in Tables 1−5. We assume that all reactions are reversible and in thermodynamic equilibrium. In our calculations, all reference components have been selected for satisfying the conditions reported by Gadewar et al.[10] for the proper determination of RRCMs.

3.1. Reactive System: $A_3 \leftrightarrows A_4$, $A_5 \leftrightarrows A_4$, $A_4 \leftrightarrows A_6$, with Inert A_1 and A_2. We have considered a hypothetical system[12,13] consisting of six components, where four of them are involved in three independent chemical reactions and the remaining two are inert. This reactive system was analyzed at atmospheric pressure and the presence of vapor−liquid equilibrium was assumed, where both phases were considered ideal.[12,13] Although the liquid phase is considered ideal, reactive systems may exhibit reactive azeotropes.[5,6,14] The saturation pressure of the pure compounds was calculated with the Antoine equation using the 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

$$X_1 = x_1 \tag{11}$$

$$X_2 = x_2 \tag{12}$$

$$X_6 = x_6 + x_3 + x_4 + x_5 = 1 - X_1 - X_2 \tag{13}$$

These reaction-invariant mole fractions present values in the interval (0, 1). In this reactive system, we use an algebraic approach for performing the transformation $X \rightarrow x$. Figure 3 shows the RRCMs using both our short method and the traditional approach. An excellent agreement of RRCMs is obtained using both strategies, and as a consequence, the reactive residue curves obtained from the simplified approach can be used in process design. Note that a reduction of 25% in integration steps is achieved using our short method (see results reported in Table 6). However, the CPU time required for the calculation of the RRCMs with our method is only 1.6% of the time with the rigorous method. In this system, the presence of distillation boundaries or azeotropes is not observed. With this example we show that our approach can be applied for estimating RRCMs in multireactive mixtures with and without inert components.

3.2. Reactive System: Isobutene + Ethanol ⇔ ETBE, with 1-Butene as an Inert. The second example is the synthesis of ETBE, which is an ether used as an oxygenate additive for enhancing the octane number of gasoline fuel. Recently, several studies have focused on ETBE production because of its interesting physicochemical properties for enhancing octane and lesser fuel vaporization loss.[15,16] The thermodynamic properties for the liquid phase are calculated using the UNIQUAC activity

Table 4. Thermodynamic Data for MTBE Reactive System

	parameters of pure component				u_{ij} in Wilson model (cal/mol)			
component [a]	A_i	B_i	C_i	V_i	1	2	3	4
1	6.841 32	923.201	239.99	93.33	–	169.9953	−60.1022	–
2	8.073 72	1578.23	239.382	44.44	2576.8532	–	1483.2478	2283.8726
3	6.872 01	1116.825	224.744	118.8	271.5669	−406.3902	–	–
4	6.808 96	935.86	238.73	100.39	–	382.3429	–	–

$\log P_i^{sat} = A_i - [B_i/(T + C_i)]$, where P_i^{sat} is in mmHg and T is in °C

$\Lambda_{ij} = (V_j/V_i) \exp(-u_{ij}/RT)$

[a] 1, Isobutene; 2, methanol; 3, MTBE; 4, butane.

Table 5. Thermodynamic Data for TAME Reactive System

	parameters of pure component					u_{ij} in Wilson model (J/mol)				
component[a]	A_i	B_i	C_i	D_i	V_i	1	2	3	4	5
1	74.527	−5232.2	−8.1482	8.474×10^{-6}	0.108 68	–	478.8	1376.5	−611.75	326.74
2	82.614	−5586.1	−9.4429	1.0858×10^{-5}	0.106 71	−477.94	–	968.81	−386.04	362.28
3	23.5347	−3661.468	−32.77		0.040 69	9772.3	10147	–	4826.3	11749
4	20.9441	−2936.223	−47.70385		0.133 45	951.33	712.33	−177	–	1143.9

$\ln P_i^{sat} = A_i + (B_i/T) + C_i \ln T + D_i T^2$ for $i = 1, 2$

$\ln P_i^{sat} = A_i + [B_i/(T + C_i)]$ for $i = 3, 4$

where P_i^{sat} is in Pa and T is in K

$\Lambda_{ij} = (V_j/V_i) \exp(-u_{ij}/RT)$

[a] 1, 2-Methyl-1-butene; 2, 2-methyl-2-butene; 3, methanol; 4, TAME.

model, and the Antoine equation is employed to determine the saturation pressures of pure components. Model parameters are given in Table 3. The reaction equilibrium constant is dependent on temperature and ETBE is selected as the reference component (x_3) for variable transformation, so

$$X_1 = \frac{x_1 + x_3}{1 + x_3} \tag{14}$$

$$X_2 = \frac{x_2 + x_3}{1 + x_3} \tag{15}$$

$$X_4 = \frac{x_4}{1 + x_3} = 1 - X_1 - X_2 \tag{16}$$

For all transformed mole fractions, the feasible domain is (0, 1) and the bisection method is used for variable transformation $X \rightarrow x$ in this reactive system. In the rigorous method, we use X_1, X_2, X_4, and $T = T_B$ as unknowns for reactive bubble calculations, while in the short method T is defined by eq 9 and the vapor-phase composition is obtained from eq 10. The calculated RRCMs for the synthesis of ETBE at 10.13 bar are shown in Figure 4. Reactive residue curves indicate that this reactive mixture presents no formation of any azeotrope. In this case of study, pure ethanol provides a stable node and 1-butene and isobutene are saddle nodes. In general, a satisfactory agreement between the RRCMs calculated by both simplified and rigorous methods is observed. The CPU time and integration steps for calculating RRCMs are given in Table 6. Using our simplified method, RRCMs are obtained with fewer integration steps and a significantly lower CPU time than those reported for the rigorous method without compromising the quality of their representation.

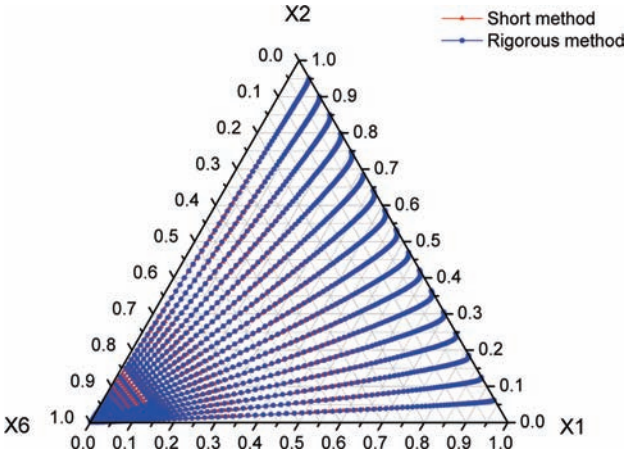

Figure 3. Reactive residue curve maps for a hypothetical multireactive system of three reactions with two inert components.

3.3. Reactive System: Isobutene + Methanol ⇔ MTBE, with *n*-Butane as an Inert. The production of MTBE from the reaction of isobutene with methanol in the presence of inert components (*n*-butane and/or 1-butene) is an important process because of the characteristics of MTBE as an antiknock agent.[17] MTBE is the most widely used compound to increase the octane level and to reduce atmospheric emissions of carbon monoxide and ozone. This system has been studied extensively by Ung and Doherty,[6] Barbosa and Doherty,[8] and Barbosa and Doherty,[18] among others. Transformed mole fractions for this mixture are given by eqs 14−16, where MTBE is selected as the reference

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Table 6. Computer Times and Integration Steps Required for Calculation of Reactive Residue Curve Maps in Selected Reactive Systems

	integration steps			
system	rigorous RRCM	short RRCM	computer time by integration step: short RRCM/rigorous RRCM, s	ΔT_{max}, °C
ideal	2651	1988	0.01/0.48	22.19
ETBE	750	677	0.02/15.2	97.52
MTBE	951	899	0.02/19.5	74.77
TAME	1820	1720	0.02/15.8	62.95

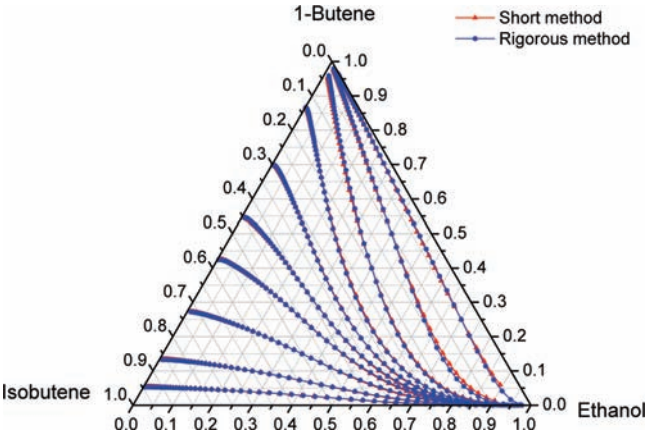

Figure 4. Reactive residue curve maps for the synthesis of ETBE in the presence of 1-butene as inert.

component (x_3). Wilson and Antoine models were used for the calculation of thermodynamic properties using the parameters reported by Maier et al.;[14] see Table 4. The calculation of reactive residue curves at 8.104 bar using both rigorous and simplified methods was performed as described in the second example, and results are shown in Figure 5. In this case, the presence of a reactive ternary azeotrope near the pure *n*-butane node and a nonreactive binary azeotrope (methanol−butane) is observed (see Table 7). This mixture shows a distillation boundary that divides the reaction-invariant composition diagram into two regions. In addition, pure methanol and isobutene provide a stable node, and the *n*-butane is a saddle node. Again, a good agreement is observed between the RRCM calculated by both the rigorous method and our short strategy including the proper prediction of both reactive and nonreactive azeotropes. In fact, the RRCM obtained with the short method is reliable for characterization of azeotropic behavior of this mixture but requires a reduced CPU time (see results reported in Table 6).

3.4. Reactive System: 2-Methyl-1-butene (2M1B) + 2-Methyl-2-butene (2M2B) + 2Methanol ⇔ 2TAME. TAME is an important chemical for gasoline and is commonly produced by liquid-phase etherification between methanol and isoamylenes, in the presence of an acidic catalyst. 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 nonreactive.[19] In this study, we have considered the lumped single reaction without inert, which can be written as 2M1B + 2M2B + 2Methanol ⇔ 2TAME. Wilson and ideal gas models have been used to calculate thermodynamic properties of this mixture. Model parameters are taken from Chen et al.[19] and

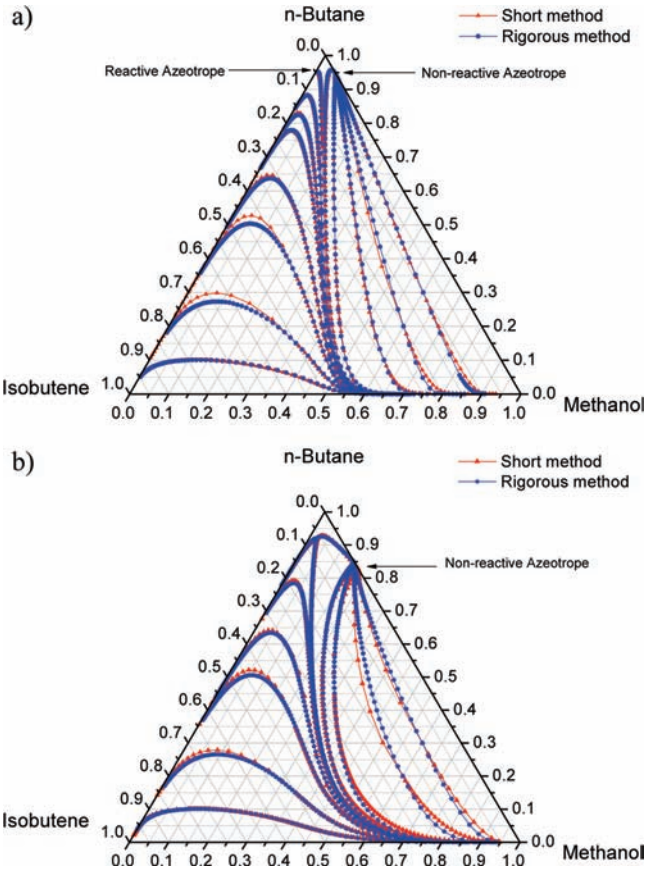

Figure 5. Reactive residue curve maps for the synthesis of MTBE in the presence of *n*-butane as inert: (a) 8.104 and (b) 30.39 bar.

are reported in Table 5. Reaction-invariant mole fractions, considering TAME as reference component (x_4), are defined as

$$X_1 = \frac{x_1 + 0.5x_4}{1 + x_4} \tag{17}$$

$$X_2 = \frac{x_2 + 0.5x_4}{1 + x_4} \tag{18}$$

$$X_3 = \frac{x_3 + x_4}{1 + x_4} = 1 - X_1 - X_2 \tag{19}$$

where $X_i \in (0, 1)$. In this system, the bisection method is also used for variable transformation $X \rightarrow x$. RRCMs for this reactive mixture at 4.052 bar are shown in Figure 6. Our results show that

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Table 7. Results of Azeotrope Calculations in MTBE Reactive System Using Reactive Residue Curve Maps at Different Operating Pressures

pressure, bar	azeotrope	short method	rigorous method
2.026	nonreactive	x (0.0000, 0.0105, 0.0000, 0.9895)	x (0.0000, 0.0114, 0.0000, 0.9886)
		T = 20.017 °C	T = 20.595 °C
	reactive	X (0.0108, 0.0010, 0.9882)	X (0.0111, 0.0016, 0.9873)
		T = 19.205 °C	T = 20.594 °C
8.104	nonreactive	x (0.0000, 0.0583, 0.0000, 0.9417)	x (0.0000, 0.0555, 0.0000, 0.9445)
		T = 74.187 °C	T = 70.694 °C
	reactive	X (0.0465, 0.0048, 0.9487)	X (0.0454, 0.0035, 0.9511)
		T = 69.994 °C	T = 70.343 °C
14.182	nonreactive	x (0.0000, 0.0965, 0.0000, 0.9035)	x (0.0000, 0.0842, 0.0000, 0.9158)
		T = 102.877 °C	T = 96.172 °C
	reactive	—	—
20.26	nonreactive	x (0.0000, 0.1291, 0.0000, 0.8709)	x (0.0000, 0.1149, 0.0000, 0.8851)
		T = 123.560 °C	T = 114.253 °C
	reactive	—	—
30.39	nonreactive	x (0.0000, 0.1737, 0.0000, 0.8263)	x (0.0000, 0.1516, 0.0000, 0.8484)
		T = 149.407 °C	T = 137.058 °C
	reactive	—	—

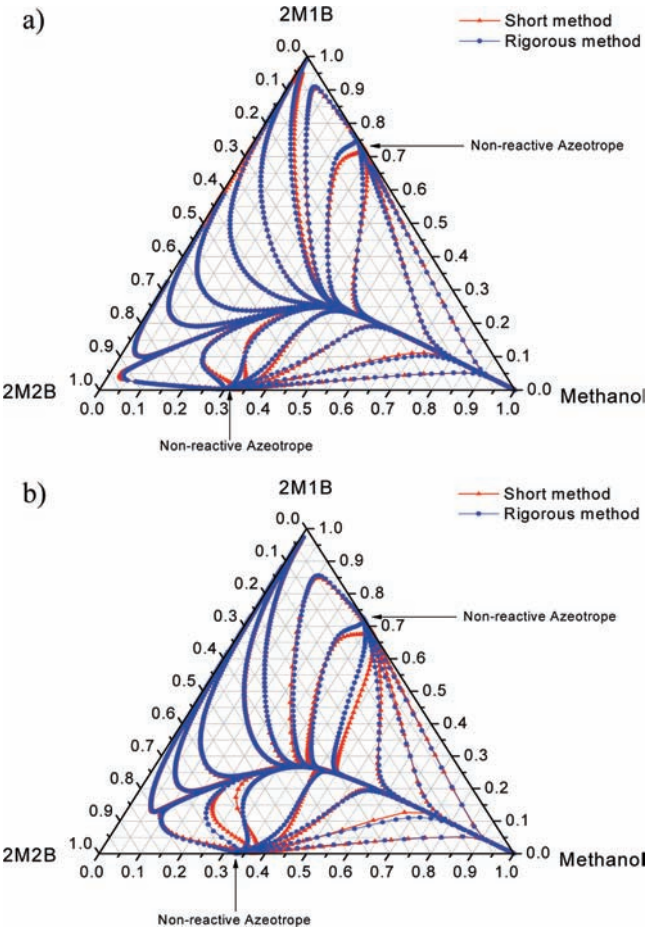

Figure 6. Reactive residue curve maps for the synthesis of TAME: (a) 4.052 and (b) 6.078 bar.

this reactive mixture forms to binary nonreactive azeotropes (2M1B−methanol and 2M2B−methanol) and there are two distillation boundaries that divide the composition diagram into three regions. The azeotropic conditions calculated by both rigorous and simplified approaches are reported in Table 8. In addition, pure methanol provides a stable node, and 2M1B and 2M2B are saddle nodes. Note that the distillation boundaries have a pronounced curvature where the shape of the RRCM reflects the complex nature of this reactive mixture. However, a satisfactory agreement is observed between the rigorous RRCM and short RRCM. Although our method does not match the results of the rigorous method as well as it does for other reactive systems, the calculated RRCM may be considered a proper reference point for preliminary design applications because a suitable description (qualitatively and quantitatively) of the reaction-invariant composition space is obtained including the prediction of azeotropic conditions.

In this context, it is important to remark that the maximum differences in boiling temperatures (ΔT_{max}) of the pure components may affect the agreement between both rigorous and simplified approaches. As a reference, the minimum and maximum differences are 22.19 °C for the ideal system and 97.52 °C for the ETBE system. Neither system presents distillation boundaries or azeotropes, but the ideal system shows better agreement between RRCMs calculated by both methods. These results suggest that, for reactive systems that do not present distillation boundaries or azeotropes, the calculation of RRCMs using an approximate T_B value is very reliable and efficient.

On the other hand, the high pressures and the presence of azeotropes may affect the agreement between both strategies. For example, the MTBE and TAME systems are more complex because they show azeotropes and distillation boundaries. The biggest differences between the RRCM results of the short method and the rigorous method are present around these points. In general, our results indicate that the differences in the quantitative description of the azeotropes are more significant when the pressure is increased. To illustrate this performance, we have examined the sensitivity of RRCM results, using MTBE and TAME reactive systems, with respect to changes in pressure. It is convenient to note that, by increasing or decreasing

Table 8. Results of Azeotrope Calculations in TAME Reactive System Using Reactive Residue Curve Maps at Different Operating Pressures

pressure, bar	azeotrope	short method	rigorous method
1.013	nonreactive	x (0.0000, 0.7782, 0.2218, 0.0000)	x (0.0000, 0.7990, 0.2010, 0.0000)
		T = 44.272 °C	T = 33.408 °C
	nonreactive	x (0.8296, 0.0000, 0.1704, 0.0000)	x (0.8443, 0.0000, 0.1557, 0.0000)
		T = 36.837 °C	T = 27.665 °C
2.026	nonreactive	x (0.0000, 0.7261, 0.2739, 0.0000)	x (0.0000, 0.7537, 0.2463, 0.0000)
		T = 66.725 °C	T = 53.168 °C
	nonreactive	x (0.7811, 0.0000, 0.2189, 0.0000)	x (0.8036, 0.0000, 0.1964, 0.0000)
		T = 59.317 °C	T = 47.373 °C
4.052	nonreactive	x (0.0000, 0.6669, 0.3331, 0.0000)	x (0.0000, 0.7003, 0.2997, 0.0000)
		T = 92.334 °C	T = 75.633 °C
	nonreactive	x (0.7223, 0.0000, 0.2777, 0.0000)	x (0.7533, 0.0000, 0.2467, 0.0000)
		T = 85.224 °C	T = 69.946 °C
6.078	nonreactive	x (0.0000, 0.6305, 0.3695, 0.0000)	x (0.0000, 0.6707, 0.3293, 0.0000)
		T = 108.909 °C	T = 90.211 °C
	nonreactive	x (0.6842, 0.0000, 0.3158, 0.0000)	x (0.7220, 0.0000, 0.2780, 0.0000)
		T = 102.149 °C	T = 84.656 °C
8.104	nonreactive	x (0.0000, 0.6033, 0.3967, 0.0000)	x (0.0000, 0.6468, 0.3532, 0.0000)
		T = 121.439 °C	T = 101.294 °C
	nonreactive	x (0.6559, 0.0000, 0.3441, 0.0000)	x (0.6979, 0.0000, 0.3021, 0.0000)
		T = 115.018 °C	T = 95.841 °C

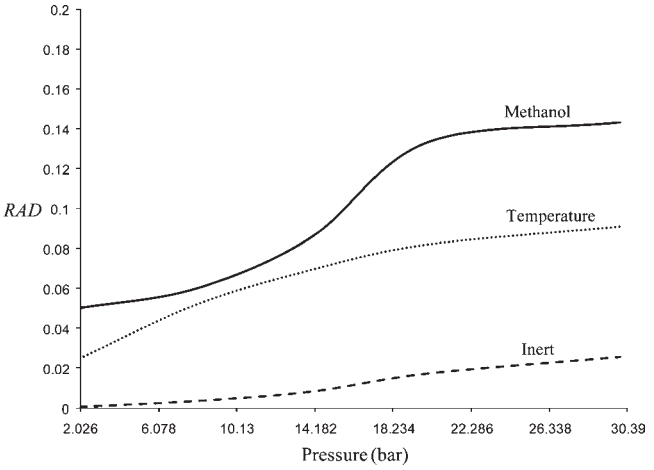

Figure 7. Relative absolute deviation (RAD) for the prediction of nonreactive azeotrope (methanol + butane) in MTBE synthesis using the rigorous and simplified methods for calculation of RRCMs.

the operating pressure, the distillation boundaries are modified and the azeotropes may appear or disappear. Therefore, these calculations are useful to identify some capabilities and limitations of our short method for estimating RRCMs. In this sensitivity analysis, the relative absolute deviation (RAD) for the azeotrope prediction using both methods is determined with the following equation:

$$\mathrm{RAD} = \left| \frac{x_{i,\,\mathrm{azeo}}^{\mathrm{rigorous}} - x_{i,\,\mathrm{azeo}}^{\mathrm{short}}}{x_{i,\,\mathrm{azeo}}^{\mathrm{rigorous}}} \right| \qquad (20)$$

where $x_{i,\mathrm{azeo}}^{\mathrm{rigorous}}$ is the composition of component i in azeotrope calculated using the rigorous method and $x_{i,\mathrm{azeo}}^{\mathrm{short}}$ is the composition of component i in azeotrope calculated using the short method, respectively.

In general, the magnitude of the pressure effect on RRCMs using both the rigorous and simplified methods depends on the reactive mixture. In the MTBE system, both reactive and nonreactive azeotropes are pressure-sensitive and, in particular, the reactive azeotrope eventually disappears as the pressure increases (see Figure 5 and Table 7). In fact, these azeotropes have an azeotropic temperature within the interval of the boiling temperatures of the pure components. Overall, our method provides good results for estimating RRCMs up to 14 bar. For example, RAD is less than 9% for the nonreactive azeotrope (see Figure 7). However, at higher operating pressure, RAD increases and the quantitative prediction of azeotrope becomes inadequate using our simplified method.

On the other hand, the results of pressure-sensitivity analysis for TAME synthesis are reported in Table 8 and Figure 8. In this reactive system, the two binary nonreactive azeotropes are also pressure sensitive and are present in the whole range of investigated pressures (see Figure 6 and Table 8). Figure 8 shows that RAD also increases with the operating pressure, but the deviations are more significant due to the presence of two azeotropes of minimum boiling point. Note that the boiling points of both azeotropes fall outside and below the boiling points of the pure components. Based on the fact that eq 9 is defined using the boiling points of pure components, it is expected that our approach may fail to predict properly this type of azeotrope. In summary, it is expected that, for reactive systems at high operating pressure and containing several azeotropes, the prediction of RRCM may be inadequate using our simplified approach especially in the vicinity of azeotropic conditions and distillation boundaries.

Finally, the main advantage of the proposed short method is the significant reduction of computer time. Table 6 shows the

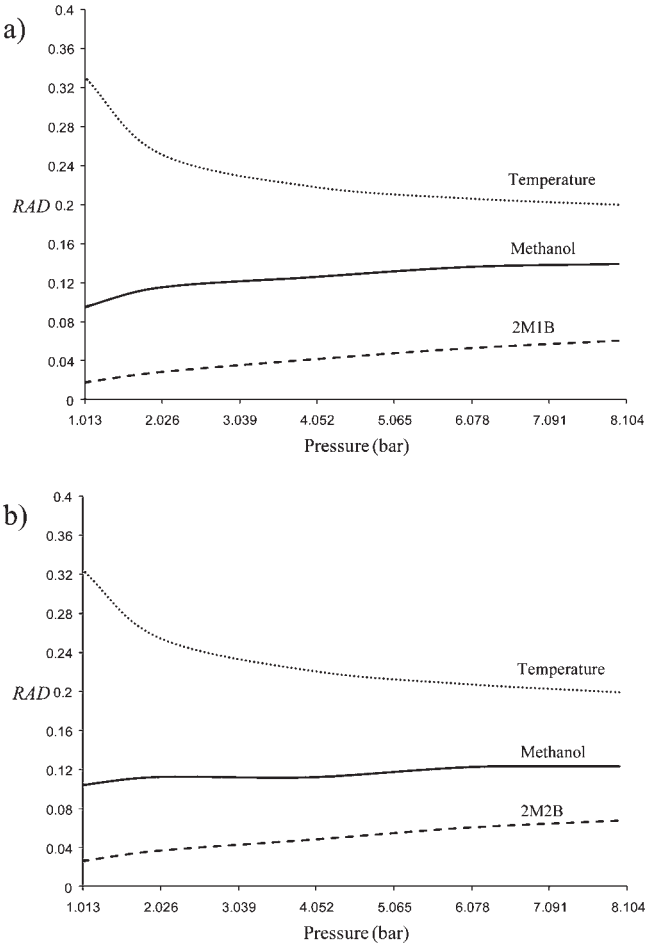

Figure 8. Relative absolute deviation (RAD) for the prediction of nonreactive azeotropes (a) 2M1B + methanol and (b) 2M2B + methanol in TAME synthesis using the rigorous and simplified methods for calculation of RRCM.

number of integration steps, the computer time required for the calculation of RRCMs, and ΔT_{max} for all reactive systems used in this study. Overall, the calculation time for the short method is only 0.1−1.6% of the time required for the rigorous method whereas there is a reduction from 5.0 to 25.0% in the number of integration steps. Therefore, these results indicate that our approach is an alternative and effective strategy for obtaining a suitable estimation of RRCMs in multicomponent and multireactive systems.

4. CONCLUSIONS

Reactive residue curve maps (RRCMs) 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. These simplified phase equilibrium constants are obtained using a suitable estimation of the bubble temperature from pure-component boiling temperatures and the reaction-invariant liquid composition. Our results indicate that a good approximation of the RRCM is obtained with this simplified method for reactive systems specially operating at low to moderate pressures. The biggest differences between the short method and the rigorous method are present around the azeotropes and distillation boundaries. However, this discrepancy does not represent a significant problem because these RRCMs 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 can be calculated with the short method. Using this approach, a significant reduction in computation time for the calculation of RRCM is assured without compromising the representation of composition space. Finally, our results not only show potential advantages of this simplified method for determining RRCMs, but also provide an alternative tool for the design and synthesis of reactive separation processes.

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NOTATION

a_i = activity of component i
C = number of components
K_{eq} = chemical equilibrium constant
K_i = phase equilibrium constant of component i
N = square matrix of the stoichiometric number of the reference components in R reactions
R = independent chemical reactions
T = temperature, °C or K
T_B = bubble temperature, °C or K
$T_{b,i}$ = pure-component boiling temperature, °C or K
ΔT_{max} = maximum difference in boiling temperatures, °C or K
v_i = row vector of stoichiometric number of component i for each reaction
v_{TOT} = row vector of the sum of the stoichiometric number for all components
v_i^r = stoichiometric number of component i in reaction r
x_i = liquid mole fraction of component i
x_{ref} = column vector of R reference component liquid mole fractions
y_i = vapor mole fraction of component i
y_{ref} = column vector of R reference component vapor mole fractions
X_i = transformed composition in the liquid phase of component i
Y_i = transformed composition in the vapor phase of component i

Greek Symbols

τ = dimensionless time
γ_i = liquid activity coefficient of component i

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