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Short-Cut Method for the Design of Reactive Distillation Columns

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ABSTRACT: The design of reactive distillation (RD) has received significant attention because of the technological and economic advantages obtained from the simultaneous occurrence of reaction and separation. Although the advantages of RD are well-documented in the literature, the commercial applications of RD are still limited because of the control and operation complexity of these separation systems and the need for improved software tools to reliably model and design RD columns. In this study, a robust short-cut method for the design of multicomponent reactive distillation is presented. This method is based on distillation lines and tray-by-tray calculations defined in terms of reaction-invariant composition variables. Our method provides the number of theoretical stages, the operating reflux ratio, the feed tray location, and the top or bottom flow. We use three case studies to demonstrate the effectiveness of the proposed strategy, namely, the reactive systems for the syntheses of ETBE and MTBE in the presence of inert components and of TAME without inert components. The results obtained with our strategy show good agreement with those obtained using the rigorous model of the commercial simulator AspenONE Aspen Plus.

1. INTRODUCTION

With respect to the broad range of topics related to reactive distillation (RD), the complex design of these separation processes has received significant attention from many researchers because of the simultaneous occurrence of distillation and reaction, in addition to the high thermodynamic nonideality of the behavior of mixtures involved in these separation schemes. In some applications, particularly in cases where thermodynamic reaction equilibrium prevents high conversions, the use of distillation to remove the reaction products from the reaction zone can significantly improve the overall conversion and selectivity at pressures and temperatures that are compatible with the distillation conditions. In other applications, the presence of reactions is used to overcome the separation problems caused by the presence of azeotropes. Therefore, this combination of reaction and distillation often results in simpler and intensified processes with smaller recycle streams and reduced waste handling, thus leading to lower investment and operating costs.[1]

The applicability of RD depends on the thermodynamic properties of the chemical system at hand. In particular, the production of esters such as methyl acetate, ethyl acetate, and butyl acetate has long been an interesting RD application. However, during the past decade, the interest in and number of publications about this separation scheme have increased. For example, methyl *tert*-butyl ether (MTBE) is no longer used as a fuel additive in the United States, and its production by reactive distillation has almost completely vanished, but this reactive system is still used as a typical case study in the reactive distillation literature.[1,2] Other potential applications include the production of ethyl *tert*-butyl ether (ETBE) and *tert*-amyl methyl ether (TAME), which are widely used in modern gasoline. Because most of these reactive systems can contain reactive and nonreactive azeotropes, reactive residue curve maps are an important tool in the initial stage of process design for rapidly identifying infeasible sequences. Once the separation region has been established, it is possible to predict the different components obtained as distillate and bottom products for a given feed composition. 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 equilibrium; and the type of variables involved in defining the design problem, which are generally composition variables in molar units and extents of reaction.[2] 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.[3,4] Based on this fact, some approaches for the transformation of composition variables have been introduced in the literature,[2,4] with the aim of providing a simpler thermodynamic framework for treating systems subject to chemical reactions. These approaches are generally based on transformation of the physical compositions, and their principal benefit is that the simultaneous chemical and physical equilibrium model in reactive mixtures is very similar to a strictly physical equilibrium model. In this context, the premise of using transformed mole fraction variables is that the models used to characterize an RD system are expressed mathematically in the same form as those reported for nonreactive distillation systems.[2,5] Therefore, these variable transformation approaches are attractive for the simulation of RD separation

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processes and favor the study of complex multicomponent reactive systems.

To date, some methods for the design of RD have been developed.[6−12] For example, Barbosa and Doherty[6] extended the boundary-value method (BVM) for the design of distillation columns with reactions at equilibrium. This method uses residue curves and is based on material balances in the form of differential equations to calculate the number of stages in each section of the column. The differential equations are solved from the outside to the inside of the column, finding the feed stage for which the liquid compositions of the two sections are equal. The BVM is simple to use, but the intersection of the operating profiles does not necessarily provide the optimal feed tray location because the intersection of the operating profiles is not always close to the feed composition.[7] As consequence, in several circumstances, the composition of the feed tray can be quite different from the feed composition. This design method assumes constant molar flows, ideal stages, and a saturated liquid feed. On the other hand, there have been studies based on graphical methods such as the McCabe−Thiele and Ponchon−Savarit approaches that assume equilibrium conditions for the design of RD schemes. Design methods for reactive systems under kinetic control have been also proposed, which enable a more detailed analysis and design of the RD process.[8] These methods are generally based on a variable transformation approach using the concept of elements,[8] which has the main disadvantage that the number of systems that can be studied is limited. Recently, Dragomir and Jobson[9] extended a graphical design methodology developed for nonhybrid columns[10] to hybrid systems, using mass and energy balances and optimizing the system based on the equipment costs for the configurations obtained. This methodology also uses the BVM and is restricted to systems with two degrees of freedom (i.e., isobaric systems according to the Gibbs phase rule). Finally, formal optimization approaches have been applied for the optimal design of RD columns, including strategies such as disjunctive programming and stochastic optimization.[11,12] Despite the many advances in this area, alternative reliable methods for the design of RD are still needed.

In this study, we propose a short-cut method for the reliable design of RD processes for multicomponent reactive mixtures. This method is based on distillation lines, which constitutes a more appropriate tool than residue curve lines for the modeling of staged columns.[13] Our method is based on tray-by-tray calculations, and a strategy is suggested that uses the reflux ratio and the feed tray location to minimize the total number of stages. The material balances are solved from the outside (i.e., top and bottom) to the inside of the distillation column (i.e., feed tray) to ensure that the product compositions are met. In addition, to reduce the numerical difficulties related to the modeling of reactive phase equilibrium, the method is based on the application of reaction-invariant composition variables.[4] This approach allows for the study of a variety of real and complex multicomponent reactive systems that can be analyzed in ternary transformed mole fraction diagrams. Finally, the performance of our short-cut method is compared with those obtained with the commercial simulator AspenONE Aspen Plus for several reactive systems.

2. DESCRIPTION OF A SHORT-CUT METHOD FOR THE DESIGN OF REACTIVE DISTILLATION COLUMNS

To design a reactive distillation column, the operating minimum reflux ratio, number of theoretical stages, and feed stage should be calculated. As stated, these operating parameters can be determined using reactive distillation lines, which constitute a more appropriate tool than residue curve lines for the modeling of staged columns.[13] The use of distillation lines allows the material balances to be written in algebraic form.

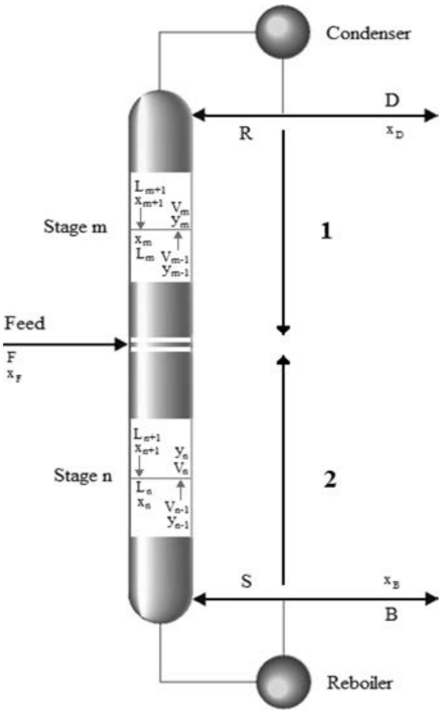

Figure 1. Depiction of the (1) rectifying section and (2) stripping section for the application of the design method proposed in this study.

Consider the reactive distillation column presented in Figure 1.[6] As stated, the component and overall material balances are solved from the outside to the inside of the distillation column, to ensure that the product compositions are satisfied. In the literature, a short-cut method (i.e., a method that is easy to implement and that provides a quick predesign for a rigorous design method) used for the design of nonreactive and reactive distillation columns assumes constant molar overflows because the total and component mass balances are used to provide a predesign of the distillation column.[6−8] If variable molar overflows are assumed, the internal liquid and vapor flows along the column must be calculated. To account for these conditions, the mass and energy balances must be used to model each stage (i.e., as a rigorous model), which causes the complexity of the numerical problem to increase. Therefore, in our method, we assume constant molar overflows and distillation columns with only ideal reactive stages. In the following sections, we briefly describe the short-cut method proposed for the design of RD columns and its implementation with a commercial simulator.

2.1. Determination of Separation Region Using Reaction-Invariant Composition Variables. The first step of the design procedure is to check the feasibility of the system split. Reactive residue curve maps (RRCMs) are useful for the design of RD columns as a tool to establish regions of reaction and separation.[3] A residual curve represents the change of the liquid composition as a function of time during a simple distillation. Thus, RRCMs provide the possibility of determining the existence of distillation boundaries and, as a consequence, determining different potential separation regions.[3,14] Note that the region of the bottom and

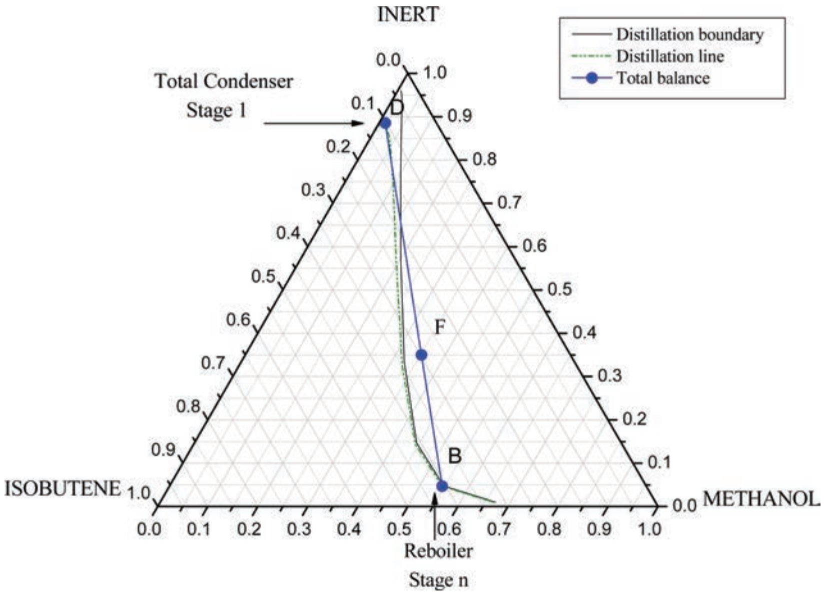

Figure 2. Separation region products for a given feed (F) in the synthesis of MTBE. Note that D denotes the distillate product, and B is the bottoms product.

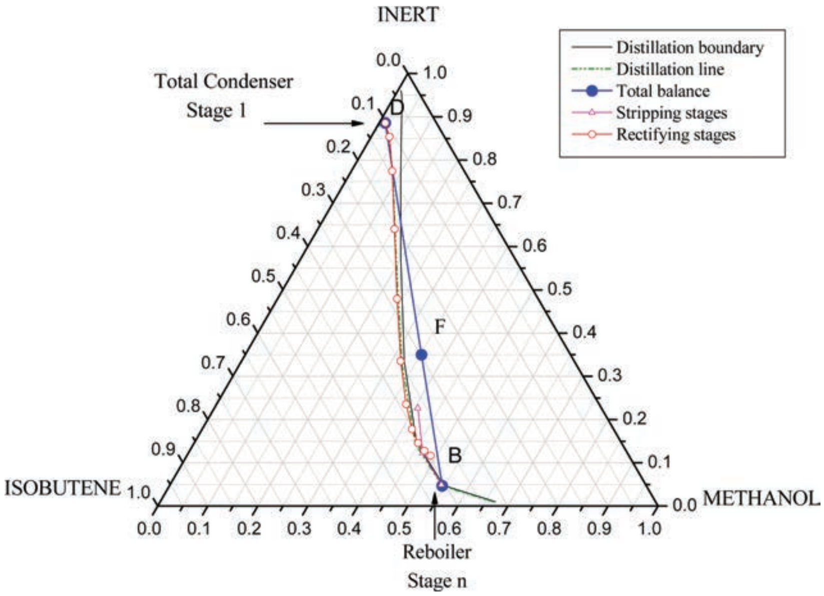

Figure 3. Operating profiles for the synthesis of MTBE using our short-cut design method.

top products for a given feed is delimited by the composition space, the distillation boundary, and the distillation line that contains the desired products. Specifically, Figure 2 illustrates how the feasible region can be identified in a ternary composition diagram using transformed mole fraction variables.[5] In this figure, line D—F—B represents the overall mass balance for the RD column in terms of transformed mole fraction variables. Points D and B refer to the desired products to be obtained at the top and bottom, respectively, of the RD column, whereas point F represents the feed composition also given in transformed mole fraction space. It is important to take into account that the bottom and top products must be collinear with respect to the feed to satisfy the overall material balance. If the desired split is not feasible, a new feasible split can easily be specified using this type of ternary composition diagram.

In our method, we have used reaction-invariant composition variables instead of the conventional composition variables because the analysis of RD can be performed in the same form as in simple distillation columns without chemical reactions. This result is because the solution space is restricted to compositions that are already at chemical equilibrium, and as a consequence, the problem dimension is also reduced. Specifically, 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[4]

$$X_i = \frac{x_i - \mathbf{v}_i^{\mathrm{T}}\mathbf{N}^{-1}\mathbf{x}_{\mathrm{ref}}}{1 - \mathbf{v}_{\mathrm{TOT}}^{\mathrm{T}}\mathbf{N}^{-1}\mathbf{x}_{\mathrm{ref}}} \qquad i = 1, ..., c - r \tag{1}$$

where X_i is the transformed mole fraction of component i, $\mathbf{x}_{\mathrm{ref}}$ is the column vector of r reference component mole fractions, $\mathbf{v}_i^{\mathrm{T}}$ is

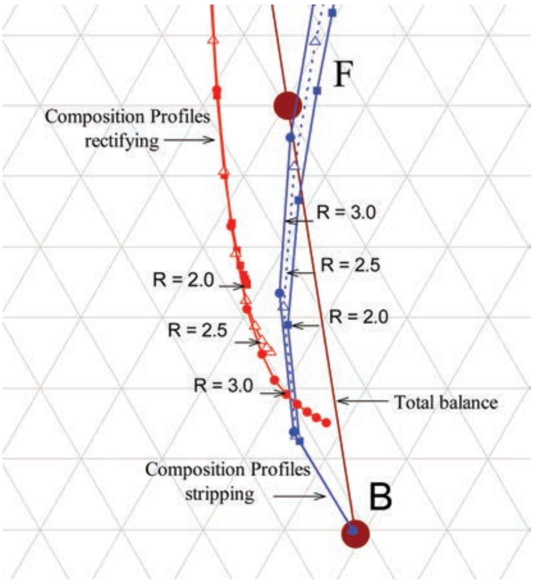

Figure 4. Operating profiles for different reflux ratios using a graphical approach to verify the intersection for MTBE synthesis.

the row vector of stoichiometric coefficients of component *i* for all reactions, $\mathbf{v}_{TOT}^T$ is a row vector of the sum of the stoichiometric coefficients for each reaction, and **N** is a square matrix formed from the stoichiometric coefficients of the reference components in the *r* reactions. Note that, to obtain physical consistency using these transformed mole fraction variables, the criteria for selecting a feasible set of reference components include the requirements that matrix **N** be invertible and that the product $\mathbf{v}_{TOT}^T\mathbf{N}^{-1}$ be a row vector containing negative or zero entries.[3] For all case studies considered in this work, the principal products (MTBE, TAME, and ETBE) were chosen as reference components because these components are able to obtain physical consistency in reaction-invariant composition space. To evaluate thermodynamic properties during the design of RD columns, the transformation procedure $X \rightarrow x$ is necessary, and the reference mole fractions can be calculated using eq 1 and the equilibrium constants for each reaction, $K_{eq,l}$, by solving a system of *r* nonlinear equations given by

$$K_{eq,l} = \prod_{i=1}^{c} a_i^{\nu_i^l} \qquad l = 1, ..., r \tag{2}$$

where a_i is the activity of component *i* and ν_i^l is the stoichiometric coefficient of component *i* in reaction *l*. When the reference mole fractions are known, the remaining mole fractions are calculated using eq 1. In summary, our analysis for the design of RD columns is based on these reaction-invariant composition variables.

2.2. New Design Method for RD Columns. First, we define the total mass balance for an RD column using reaction-invariant composition variables. These balances for the rectifying and stripping sections are given by

$$X_{i,m} = \frac{R+1}{R} Y_{i,m-1} - \frac{1}{R} X_{i,D} \qquad i = 1, ..., c-r \tag{3}$$

$$X_{i,n+1} = \frac{S}{S+1} Y_{i,n} + \frac{1}{S+1} X_{i,B} \qquad i = 1, ..., c-r \tag{4}$$

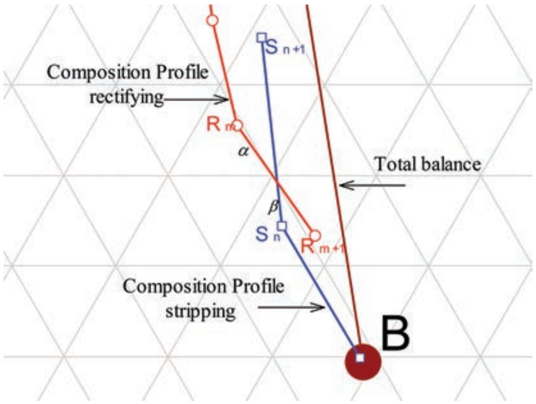

Figure 5. Illustration of the feasibility test for the design of reactive distillation columns.

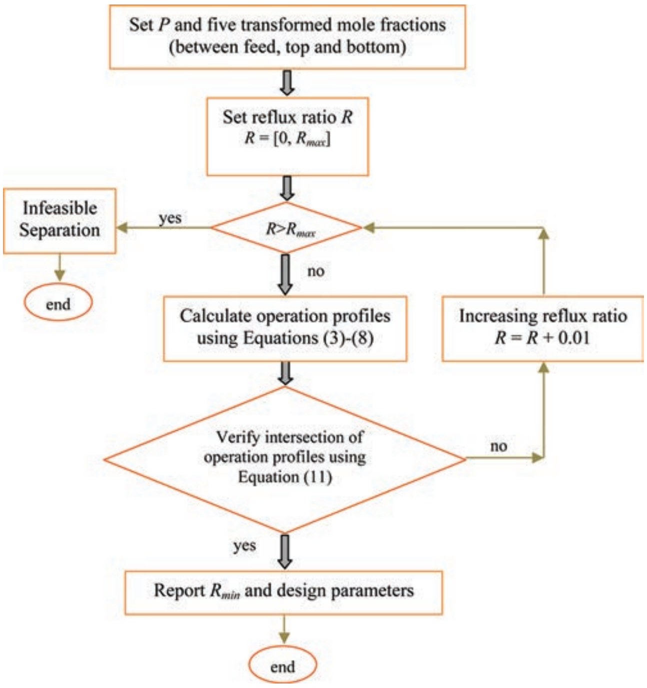

Figure 6. Algorithm to calculate the minimum reflux ratio for the design of RD columns.

where $X_{i,j}$ is the transformed mole fraction in the liquid phase of component *i* in stage *j*, $Y_{i,j}$ is the transformed mole fraction in the vapor phase of component *i* in stage *j*, *R* is the reflux ratio of liquid that returns to the column with respect to the distilled product (D), *S* is the reboil ratio of vapor *V* that returns to the column with respect to the bottom product (B), $X_{i,B}$ is the transformed mole fraction of component *i* at the bottom, and $X_{i,D}$ is the transformed mole fraction of component *i* at the column top. These component mass balance equations must be used with a proper thermodynamic model for the vapor—liquid equilibrium conditions.

In this study, the reactive systems for the production of MTBE, ETBE, and TAME are considered where $c = 4$ and $r = 1$. For these systems, an analysis of the number of degrees of freedom indicates that $2c - 1$ design variables must be specified.[6] The specification of these variables depends on the designer's interest,

Table 1. Reactive Mixtures Selected As Case Studies

system	thermodynamic model and chemical equilibrium constant
isobutene + ethanol ⟺ ETBE with 1-butene as an inert	UNIQUAC model and ideal gas $\Delta G^{\circ}_{\text{rxn}}/R = 4060.59 + 10.387T - 2.89055T \ln T - 0.0191544T^2 + 5.28586 \times 10^{-5}T^3 - 5.32977 \times 10^{-8}T^3$ for T in K
isobutene + methanol ⟺ MTBE with *n*-butane as an inert	Wilson model and ideal gas $\Delta G^{\circ}_{\text{rxn}}/R = -4205.05 + 10.0982T - 0.2667T \ln T$ for T in K
2-methyl-1-butene (2M1B) + 2-methyl-2-butene (2M2B) + methanol ⟺ TAME	Wilson model and ideal gas $K_{\text{eq}} = 1.057 \times 10^{-4}\text{e}^{(4273.5/T)}$ for T in K

Table 2. Design Specifications Using Transformed Molar Fractions and Molar Fractions of Feed (F), Distillate Product (D), and Bottom Product (B)

component	X_F	X_D	X_B	x_F	x_D	x_B
MTBE Feed I						
isobutene	0.29806	0.10192	0.40807	0.29806	0.09113	0.07650
methanol	0.35194	0.01212	0.54538	0.35194	0.00024	0.28630
n-butane	0.35000	0.88596	0.04655	0.35000	0.89660	0.07706
MTBE	–	–	–	0	0.01203	0.56014
MTBE Feed II						
isobutene	0.24258	0.10192	0.40807	0.24258	0.09113	0.07650
methanol	0.25713	0.01212	0.54538	0.25713	0.00024	0.28630
n-butane	0.50029	0.88596	0.04655	0.50029	0.89660	0.07706
MTBE	–	–	–	0	0.01203	0.56014
TAME						
2M1B	0.40000	0.90838	0.25458	0.40000	0.90968	0.14767
2M2B	0.25600	0.08832	0.30409	0.25600	0.08701	0.21874
methanol	0.34400	0.00330	0.44133	0.34400	0.00012	0.19794
TAME	–	–	–	0	0.00319	0.43565
ETBE						
isobutene	0.70000	0.94621	0.57842	0.70000	0.94621	0.41341
ethanol	0.26390	0.00002	0.39463	0.26390	0.00001	0.15768
1-butene	0.03610	0.05377	0.02695	0.03610	0.05377	0.03749
ETBE	–	–	–	0	0.00001	0.39142

so one can select the operating pressure or temperature, the condenser or reboiler reflux ratio, and transformed mole fractions (between feed, top, and bottom compositions). To complement the number of degrees of freedom, the summation constraints and the total mass balances are used. In particular, seven parameters must be specified for our case studies. For instance, we can specify the operating pressure, the reflux ratio (R), two feed compositions (Z_1, Z_2), and three product compositions ($X_{1,D}$, $X_{2,D}$, $X_{1,B}$); in that case, $X_{2,B}$ can be calculated from the total mass balances using the equation

$$X_{2,B} = Z_2 + (Z_2 - X_{2,D})\left(\frac{S}{R+1}\right) \tag{5}$$

In particular, the boil-up ratio (S) is a key variable for the design of RD columns and can be determined using the total mass balance. Specifically, we have

$$S = (R+q)\left(\frac{X_{1,B} - Z_1}{Z_1 - X_{1,D}}\right) + (q-1) \tag{6}$$

where q is the thermal condition of the feed, with $q = 1$ for saturated liquid, $q = 0$ for saturated vapor, and $0 < q < 1$ for a liquid−vapor mixture. The remaining specifications $X_{3,D}$ and $X_{3,B}$ are obtained from summation constraints

$$\sum_{i=1}^{c-r} X_{i,D} = 1 \tag{7}$$

$$\sum_{i=1}^{c-r} X_{i,B} = 1 \tag{8}$$

Equations 3 and 4 can be solved using the vapor−liquid equilibrium model to obtain the composition profiles for a given reflux ratio R. The intersection of the composition profiles in composition space is a necessary and sufficient condition to establish the feasibility of the split (see Figure 3). Therefore, this intersection should be verified during our calculations.[15] This necessary and sufficient condition is employed to calculate the minimum reflux ratio in the proposed method.

Note that the calculations for RD design involve an iterative process in which a graphical approach can be used to verify the intersection of composition profiles for a given R (see Figure 4). However, such an approach implies a higher CPU time in addition to uncertainties and inaccuracies for defining the RD design parameters. Therefore, we propose an analytical strategy to perform these calculations. Specifically, to ensure the intersection of the composition profiles, we construct operating lines for two consecutive compositions of each profile that are calculated using eqs 3−8. For illustrative purposes, Figure 5 shows a graphical visualization of the feasibility test for the separation estimated by linear interpolation using eq 9 for the stripping section and eq 10 for the rectifying section. As result, we have a simple linear system with two unknown parameters (α and β should have values within the interval [0, 1]) and c - r equations (eq 11), one for each nonreference component. This gives

$$C^{R}_{i,m \to m+1} = C^{R}_{i,m} + \alpha(C^{R}_{i,m+1} - C^{R}_{i,m}) \qquad i = 1, ..., c - r \tag{9}$$

$$C^{S}_{i,n \to n+1} = C^{S}_{i,n} + \beta(C^{S}_{i,n+1} - C^{S}_{i,n}) \qquad i = 1, ..., c - r \tag{10}$$

$$C^{R}_{i,m} + \alpha(C^{R}_{i,m+1} - C^{R}_{i,m}) = C^{S}_{i,n} + \beta(C^{S}_{i,n+1} - C^{S}_{i,n}) \qquad i = 1, ..., c - r \tag{11}$$

where $C^{R}_{i,m\to m+1}$ is the rectifying section line that includes the composition points m and $m + 1$ and $C^{S}_{i,n\to n+1}$ is the stripping section line that includes the composition points n and $n + 1$.

The procedure to calculate the minimum reflux ratio is given in Figure 6 and can also be applied to verify the separation feasibility

Table 3. Design Specifications for the Synthesis of MTBE Using an RD Column. Example: Feed I

design specifications		component	molar fractions of products			
			proposed method		AspenONE Aspen Plus	
			top	bottom	top	bottom
			Saturated Liquid			
N_{TOT}	14	isobutene	0.09113	0.07650	0.01572	0.09998
N_F	8	methanol	0.00024	0.28630	0.02614	0.22332
R	2.97	*n*-butane	0.89660	0.07706	0.94858	0.06744
B (lbmol/h)	40.813	MTBE	0.01203	**0.56014**	0.00956	**0.60926**
			Liquid−Vapor Mixture			
			$q = 0.25$			
N_{TOT}	14	isobutene	0.09113	0.07650	0.08441	0.07875
N_F	12	methanol	0.00024	0.28630	0.01122	0.27461
R	3.08	*n*-butane	0.89660	0.07706	0.88439	0.08614
B (lbmol/h)	40.813	MTBE	0.01203	**0.56014**	0.01998	**0.56050**
			$q = 0.5$			
N_{TOT}	14	isobutene	0.09113	0.07650	0.03739	0.09112
N_F	8	methanol	0.00024	0.28630	0.02740	0.23156
R	3.19	*n*-butane	0.89660	0.07706	0.91375	0.08772
B (lbmol/h)	40.813	MTBE	0.01203	**0.56014**	0.02146	**0.58960**
			$q = 0.75$			
N_{TOT}	14	isobutene	0.09113	0.07650	0.06517	0.07891
N_F	7	methanol	0.00024	0.28630	0.03847	0.23375
R	3.267	*n*-butane	0.89660	0.07706	0.85225	0.12932
B (lbmol/h)	40.813	MTBE	0.01203	**0.56014**	0.04411	**0.55802**
			Saturated Vapor			
N_{TOT}	14	isobutene	0.09113	0.07650	0.11261	0.06452
N_F	7	methanol	0.00024	0.28630	0.05060	0.26617
R	3.3	*n*-butane	0.89660	0.07706	0.75809	0.15153
B (lbmol/h)	40.813	MTBE	0.01203	**0.56014**	0.07870	**0.51778**

in multicomponent mixtures, because, if the minimum reflux is not found, then the proposed separation is infeasible. For the design of distillation columns, $R > 5$ is consider as a high reflux ratio.[16] However, in this study, we have used $R_{max} = 10$ to favor the convergence of our method. It is convenient to remark here that the composition profile intersection does not necessarily provide a suitable criterion for the location of feed tray because it does not always locate the plate with the composition closest to that of the feed. In nonreactive distillation columns, Gutierrez-Antonio et al.[17] proposed a minimum difference criterion to determine the feed stage location whereby a search is performed for the tray location with the minimum difference between the composition of each stage in the column and the feed composition. This search procedure is performed for each column section, so that the numbers of stages in the stripping and the rectifying sections are obtained, along with the feed stage location. Based on this fact, we extended this approach for the design of RD columns. Specifically, the difference (i.e., distance) between the compositions is calculated using eqs 12 and 13, which were defined using transformed variables and were obtained by introducing small modifications of the model proposed by Gutierrez-Antonio et al.[17] to account for the presence of chemical reactions. These design equations are given by

$$d_R = \sqrt{\sum_{i=1}^{c-r}(Z_i - X_{i,NR})^2 + \sum_{i=1}^{c-r}(Z_i - Y_{i,NR})^2} \qquad (12)$$

$$d_S = \sqrt{\sum_{i=1}^{c-r}(Z_i - X_{i,NS})^2 + \sum_{i=1}^{c-r}(Z_i - Y_{i,NS})^2} \qquad (13)$$

where d_R is the distance between the equilibrium composition of a stage in the rectifying section and the feed composition, d_S is the distance between the equilibrium composition of a stage in the stripping section and the feed composition, $X_{i,NR}$ is the composition of component i in stage NR of the rectifying section, $X_{i,NS}$ is the composition of component i in stage NS of the stripping section, and Z_i is the feed composition of the reactive distillation column.

The component mass balances given by eqs 3 and 4 are determined by minimizing eqs 12 and 13. It is convenient to note that eqs 3 and 4 are solved from the top to the rectifying region and from the bottom to the stripping region, toward the column center. The operating minimum reflux ratio (R_{min}) is determined until a pinch point for the operating profiles is detected. After the operating minimum reflux ratio has been determined, an

Table 4. Design Specifications for the Synthesis of MTBE Using an RD Column. Example: Feed II

			molar fractions of products			
			proposed method		AspenONE Aspen Plus	
design specifications		component	top	bottom	top	bottom
			Saturated Liquid			
N_{TOT}	14	isobutene	0.09113	0.07650	0.07698	0.08967
N_F	6	methanol	0.00024	0.28630	0.00206	0.27395
R	2.75	*n*-butane	0.89660	0.07706	0.91713	0.04782
B (lbmol/h)	29.45	MTBE	0.01203	**0.56014**	0.00383	**0.58856**
			Liquid−Vapor Mixture			
			$q = 0.25$			
N_{TOT}	14	isobutene	0.09113	0.07650	0.06981	0.09292
N_F	6	methanol	0.00024	0.28630	0.00321	0.26151
R	2.805	*n*-butane	0.89660	0.07706	0.92163	0.04928
B (lbmol/h)	29.45	MTBE	0.01203	**0.56014**	0.00535	**0.59629**
			$q = 0.5$			
N_{TOT}	14	isobutene	0.09113	0.07650	0.05922	0.09768
N_F	6	methanol	0.00024	0.28630	0.00603	0.24148
R	2.838	*n*-butane	0.89660	0.07706	0.92650	0.05456
B (lbmol/h)	29.45	MTBE	0.01203	**0.56014**	0.00825	**0.60628**
			$q = 0.75$			
N_{TOT}	14	isobutene	0.09113	0.07650	0.04612	0.10382
N_F	6	methanol	0.00024	0.28630	0.01290	0.21157
R	2.882	*n*-butane	0.89660	0.07706	0.92777	0.06894
B (lbmol/h)	29.45	MTBE	0.01203	**0.56014**	0.01321	**0.61567**
			Saturated Vapor			
N_{TOT}	14	isobutene	0.09113	0.07650	0.04049	0.10461
N_F	6	methanol	0.00024	0.28630	0.03110	0.17042
R	2.915	*n*-butane	0.89660	0.07706	0.90282	0.12133
B (lbmol/h)	29.45	MTBE	0.01203	**0.56014**	0.02559	**0.60364**

operating reflux ratio can be fixed using a heuristic rule (e.g., $1.1R_{min}$ proposed by Douglas[18] or $1.5R_{min}$ proposed by Doherty and Malone[19]). Alternatively, this design parameter can be optimized using a suitable objective function related to energy savings or operating costs. The number of theoretical stages obtained involves a partial reboiler and considers the use of a total condenser. The most important feature of our methodology is that it considers just mass balances and simple analytical equations to obtain the design parameters of RD columns.

3. RESULTS AND DISCUSSION

To demonstrate the effectiveness of the proposed method, we consider three reactive systems: the synthesis of methyl *tert*-butyl ether (MTBE) in the presence of an inert component at 11.143 bar, the synthesis of *tert*-amyl methyl ether (TAME) without any inert components at 4.052 bar, and the synthesis of ethyl *tert*-butyl ether (ETBE) with an inert component at 10.13 bar. These operating conditions are commonly used in industry for these reactive mixtures. Details of the reactive systems are reported in Table 1, and all model parameters were obtained from Carrera-Rodríguez et al.[3] All reactions are assumed to be reversible and in thermodynamic equilibrium. In all the cases, the heuristic of $1.1R_{min}$ was used to fix the operating reflux ratio, and the column feed was assumed to be saturated liquid, saturated vapor, and liquid−vapor mixtures with $q = 0.25$, 0.5, and 0.75, respectively.

Our method provides an estimation of R, the top (D) or bottom (B) flow, the total number of stages (N_{TOT}) including the reboiler and total condenser, and the feed tray (N_F) when eqs 12 and 13 are minimized. The compositions obtained from our short-cut method have been compared with results obtained by a rigorous method, using AspenONE Aspen Plus simulator, to illustrate the capabilities of our strategy. To model these reactive systems using AspenONE Aspen Plus, it is necessary to use only the four design parameters obtained (R, B, N_{TOT}, N_F) without any other restrictions. In addition, the operating pressure, feed thermal condition of the column, and N_{TOT} are given. In the simulations performed, we assumed that all stages are reactive and that the column involves a partial reboiler and a total condenser. These design parameters are introduced in the RadFrac module of AspenONE Aspen Plus, which contains a rigorous model that assumes variable molar overflows. Therefore, the internal liquid and vapor flows along the column are calculated by material and energy balances in each stage. To obtain thermodynamic consistency, we used the same model parameters for the calculation of thermodynamic properties and the chemical equilibrium constants in our method and in Aspen

Table 5. Design Specifications for the Synthesis of TAME Using an RD Column

design specifications		component	molar fractions of products			
			proposed method		AspenONE Aspen Plus	
			top	bottom	top	bottom
			Saturated Liquid			
N_{TOT}	24	2M1B	0.90968	0.14767	0.89459	0.19057
N_F	16	2M2B	0.08701	0.21874	0.03238	0.22794
R	7.15	methanol	0.00012	0.19794	0.05344	0.16368
B (lbmol/h)	56.752	TAME	0.00319	**0.43565**	0.01959	**0.41781**
			Liquid—Vapor Mixture			
			$q = 0.25$			
N_{TOT}	23	2M1B	0.90968	0.14767	0.87696	0.19693
N_F	15	2M2B	0.08701	0.21874	0.04211	0.22416
R	7.48	methanol	0.00012	0.19794	0.05766	0.16123
B (lbmol/h)	56.752	TAME	0.00319	**0.43565**	0.02327	**0.41768**
			$q = 0.5$			
N_{TOT}	23	2M1B	0.90968	0.14767	0.87307	0.19838
N_F	15	2M2B	0.08701	0.21874	0.04903	0.22166
R	8.25	methanol	0.00012	0.19794	0.05445	0.16196
B (lbmol/h)	56.752	TAME	0.00319	**0.43565**	0.02345	**0.41800**
			$q = 0.75$			
N_{TOT}	23	2M1B	0.90968	0.14767	0.85634	0.20431
N_F	13	2M2B	0.08701	0.21874	0.05954	0.21775
R	8.69	methanol	0.00012	0.19794	0.05763	0.16008
B (lbmol/h)	56.752	TAME	0.00319	**0.43565**	0.02649	**0.41786**
			Saturated Vapor			
N_{TOT}	25	2M1B	0.90968	0.14767	0.84377	0.20873
N_F	13	2M2B	0.08701	0.21874	0.07244	0.21316
R	9.46	methanol	0.00012	0.19794	0.05603	0.16005
B (lbmol/h)	56.752	TAME	0.00319	**0.43565**	0.02776	**0.41806**

Plus. These parameters were introduced in this commercial process simulator and are also reported in Table 1. The results of all simulations are reported in Tables 2—6, and a detailed analysis of each case study is provided in the following subsections.

3.1. MTBE Synthesis. Our first case study is the synthesis of MTBE (x_3) from isobutene (x_1) and methanol (x_2) in the presence of n-butane (x_4) as an inert. The Wilson and Antoine models were used for the calculation of thermodynamic properties using the parameters reported by Maier et al.[20] This reactive system is a benchmark problem used in process design and has been studied extensively by Ung and Doherty[2] and Barbosa and Doherty,[6,21] among other authors. With MTBE as the reference component (x_3), the transformed mole fractions for this mixture are given by the equations

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

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

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

In this case, the presence of a reactive ternary azeotrope near the pure n-butane node and a nonreactive binary azeotrope (methanol—butane) divides the reaction-invariant composition diagram into two regions.[3] The feed composition and top and bottom products required for the design of the RD column are reported in Table 2. As stated in section 2 of this article, we must verify that both the distillate point and the bottom point fall into a separation region and are also collinear with respect to the feed composition. After the feasibility of the separation region has been verified, the calculation of the operating minimum reflux ratio is started. The target of this separation is to obtain the maximum amount of MTBE by the column bottom. In this system, two feed conditions were tested to achieve the same top and bottom products and to determine their effects on the RD design. In the case of feed I, $N_{TOT} = 14$ for all thermal conditions q (see Table 3). Note that N_F is located in stages 7 and 8, and the operating reflux ratio increases with the feed vapor fraction (i.e., R ranges from 2.97 to 3.30). This trend is commonly reported in the literature for nonreactive distillation[13,15], and therefore, it increases the amount of heat needed in the reboiler. Especially for the MTBE purity in the bottom stream, the best agreement between our method and AspenONE Aspen Plus is obtained for designs of feed I using a liquid—vapor feed because the relative

Table 6. Design Specifications for the Synthesis of ETBE Using an RD Column

design specifications		component	molar fractions of products			
			proposed method		AspenONE Aspen Plus	
			top	bottom	top	bottom
			Saturated Liquid			
N_{TOT}	8	isobutene	0.94621	0.41341	0.89826	0.44459
N_F	8	ethanol	0.00001	0.15768	0.00468	0.14230
R	0.44	1-butene	0.05377	0.03749	0.06431	0.03157
B (lbmol/h)	48.05	ETBE	0.00001	**0.39142**	0.03275	**0.38154**
			Liquid–Vapor Mixture			
			$q = 0.25$			
N_{TOT}	9	isobutene	0.94621	0.41341	0.91628	0.43303
N_F	9	ethanol	0.00001	0.15768	0.00161	0.15212
R	0.572	1-butene	0.05377	0.03749	0.06510	0.03053
B (lbmol/h)	48.05	ETBE	0.00001	**0.39142**	0.01701	**0.38432**
			$q = 0.5$			
N_{TOT}	8	isobutene	0.94621	0.41341	0.93366	0.42174
N_F	8	ethanol	0.00001	0.15768	0.00001	0.16252
R	1.32	1-butene	0.05377	0.03749	0.06632	0.02907
B (lbmol/h)	48.05	ETBE	0.00001	**0.39142**	0.00001	**0.38667**
			$q = 0.75$			
N_{TOT}	7	isobutene	0.94621	0.41341	0.93356	0.42181
N_F	7	ethanol	0.00001	0.15768	0.00001	0.16250
R	1.98	1-butene	0.05377	0.03749	0.06642	0.02901
B (lbmol/h)	48.05	ETBE	0.00001	**0.39142**	0.00001	**0.38668**
			Saturated Vapor			
N_{TOT}	7	isobutene	0.94621	0.41341	0.93356	0.42179
N_F	7	ethanol	0.00001	0.15768	0.00001	0.16253
R	2.86	1-butene	0.05377	0.03749	0.06642	0.02300
B (lbmol/h)	48.05	ETBE	0.00001	**0.39142**	0.00001	**0.38668**

difference in composition is minimal (i.e., 0.064% for $q = 0.25$). On the other hand, Table 4 lists the results for feed II used as an example. Again, the total number of stages for all feed thermal conditions is 14, but the feed is located in stage 6. R increases with the vapor fraction in the feed (i.e., R ranges from 2.75 to 2.915) as occurs in nonreactive distillation.[18] In all cases analyzed for feed II, our results show that the design methodology proposed here provides good agreement with the results obtained by a rigorous method using the commercial simulator AspenONE Aspen Plus. In particular, the MTBE purities obtained at the bottom of the column using the two approaches are very similar, with a relative difference of 4.83%. Therefore, it is clear that the thermodynamic condition and feed composition do not limit the application of the design method proposed in this study.

3.2. TAME Synthesis. 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. Of the three isoamylenes, only 2-methyl-1-butene (2M1B) and 2-methyl-2-butene (2M2B) are reactive, whereas 3-methyl-1-butene (3M1B) is nonreactive.[22] In this study, we considered a lumped single reaction without an inert for this system, which can be written as: 2M1B (x_1) + 2M2B (x_2) + 2methanol (x_3) ⇔ 2TAME (x_4). The Wilson and ideal gas models were used to calculate the thermodynamic properties of this mixture, using model parameters taken from Chen et al.[22] The reaction-invariant mole fractions, considering TAME as the reference component, are defined as

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

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

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

The target of this reactive separation is to obtain the maximum flow of TAME at the column bottom. The feed composition and top and bottom product compositions established for the column design are reported in Table 2. Our results show that the thermodynamic behavior of this reactive mixture is complex. In particular, this system forms two binary nonreactive azeotropes (2M1B–methanol and 2M2B–methanol), and there are two distillation boundaries that divide the composition diagram into three regions.[3] Therefore, it is very important to verify that

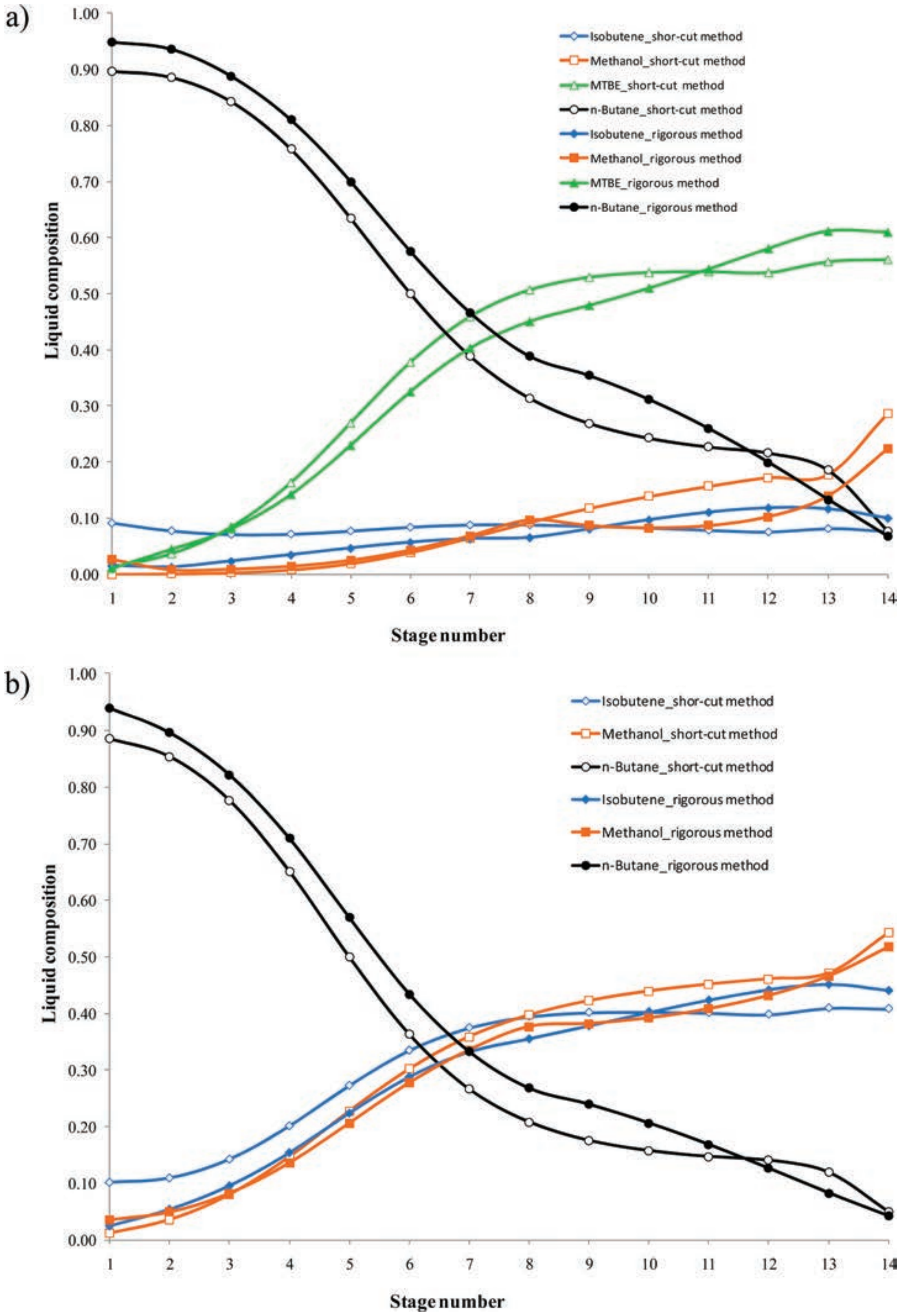

Figure 7. Composition profiles in the RD column for MTBE synthesis (feed I) using a saturated liquid as the column feed: (a) mole fraction and (b) transformed mole fraction.

both the distillate point and the bottom point fall into the feasible separation region, as well as the colinearity of these points with respect to the feed composition. The results for this system are reported in Table 5. In this case, the total number of stages varies by only two stages for all feed thermal conditions (i.e., N_{TOT} ranged from 23 to 25). The feed stage is located closer to the reboiler as the feed vapor fraction decreases (i.e., N_F = 13 for saturated vapor and N_F = 16 for saturated liquid). R increases with the feed vapor fraction (i.e., R = 7.15 for saturated liquid and R = 9.46 for saturated vapor), and as a consequence, the amount of heat needed in the reboiler increases. Another result to illustrate the reliability of our design method is the comparison between the TAME composition of the bottom stream obtained from AspenONE Aspen Plus and that obtained from the proposed design methodology (see Table 5). In general, a satisfactory agreement is observed between the TAME compositions calculated by the two modeling approaches. Therefore, the most suitable design corresponds to that one with the fewest stages and the lowest R value (in this case, feeding as saturated liquid), resulting in lower operating costs.

3.3. ETBE Synthesis. Our last example is the synthesis of ETBE [isobutene (x_1) + ethanol (x_2) ⟺ ETBE (x_3), with 1-butene (x_4) as

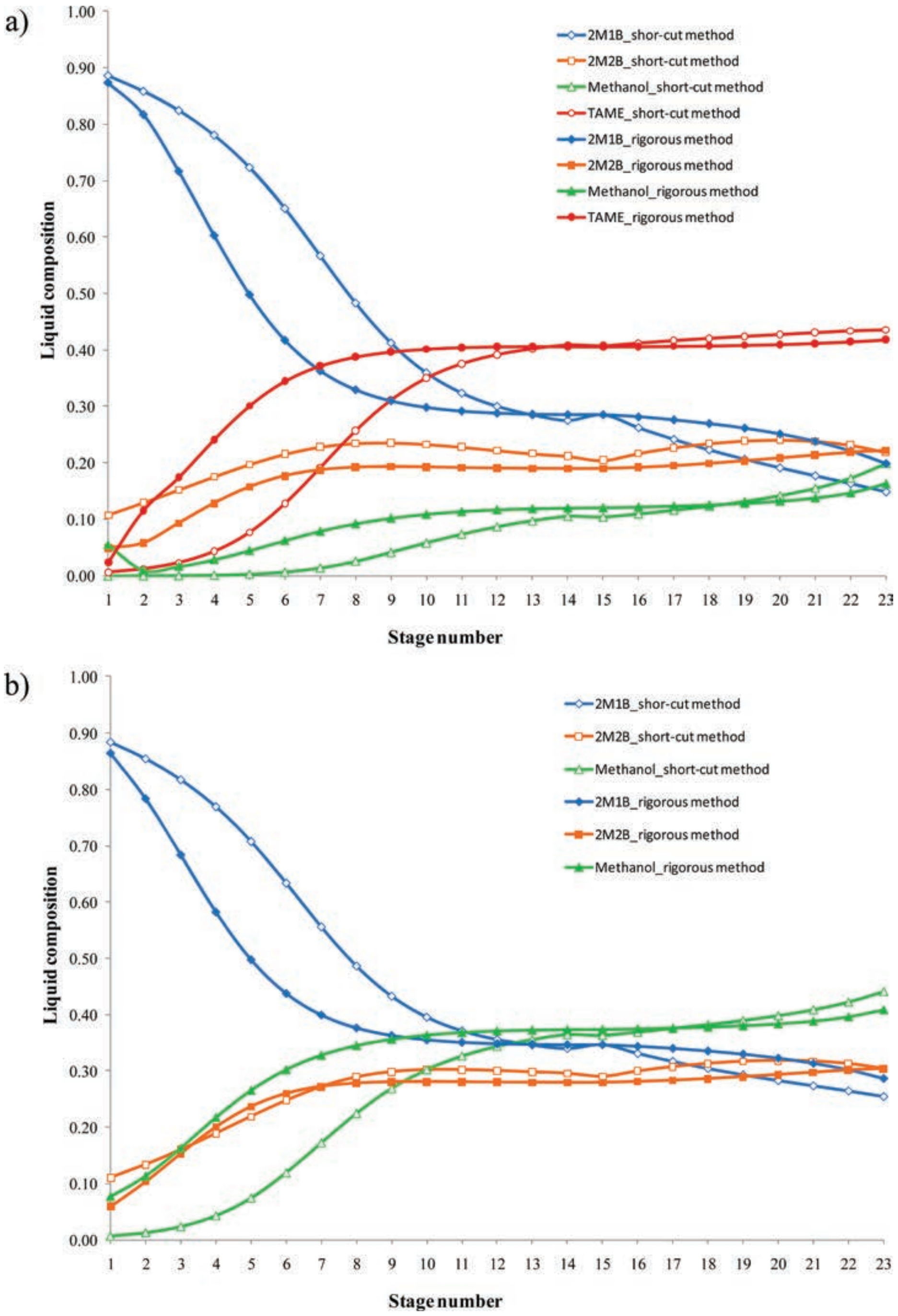

Figure 8. Composition profiles in the RD column for TAME synthesis using $q = 0.5$ as the column feed: (a) mole fraction and (b) transformed mole fraction.

an inert], which is an ether used as an oxygenate additive for enhancing the octane number of gasoline fuel. Recently, several studies have been focused on the production of ETBE because of its interesting physicochemical properties for enhancing octane and decreasing fuel vaporization losses.[23,24] The thermodynamic properties for the liquid phase were calculated using the UNIQUAC activity model, and the Antoine equation was employed to determine the saturation pressures of the pure components.[3,23,24] The transformed mole fractions for this mixture are given by eqs 14−16, with ETBE as the reference component (x_3). The operating conditions required for the design of RD column are reported in Table 2. The reactive residue curves indicate that this reactive mixture does not form azeotropes.[3] Therefore, the separation region is easier to locate, and the calculation of the operating parameters and minimum reflux ratio is started using our approach. The objective of this reactive separation is to obtain the maximum flow of ETBE at the column bottom. In this case, the total number of stages is low and varies by only three stages for all of the considered feed thermal conditions (i.e., N_{TOT} ranges from 7 to 9); see the results reported in Table 6. The feed stage is located in the last stage for all of the designs obtaine,d and R increases with

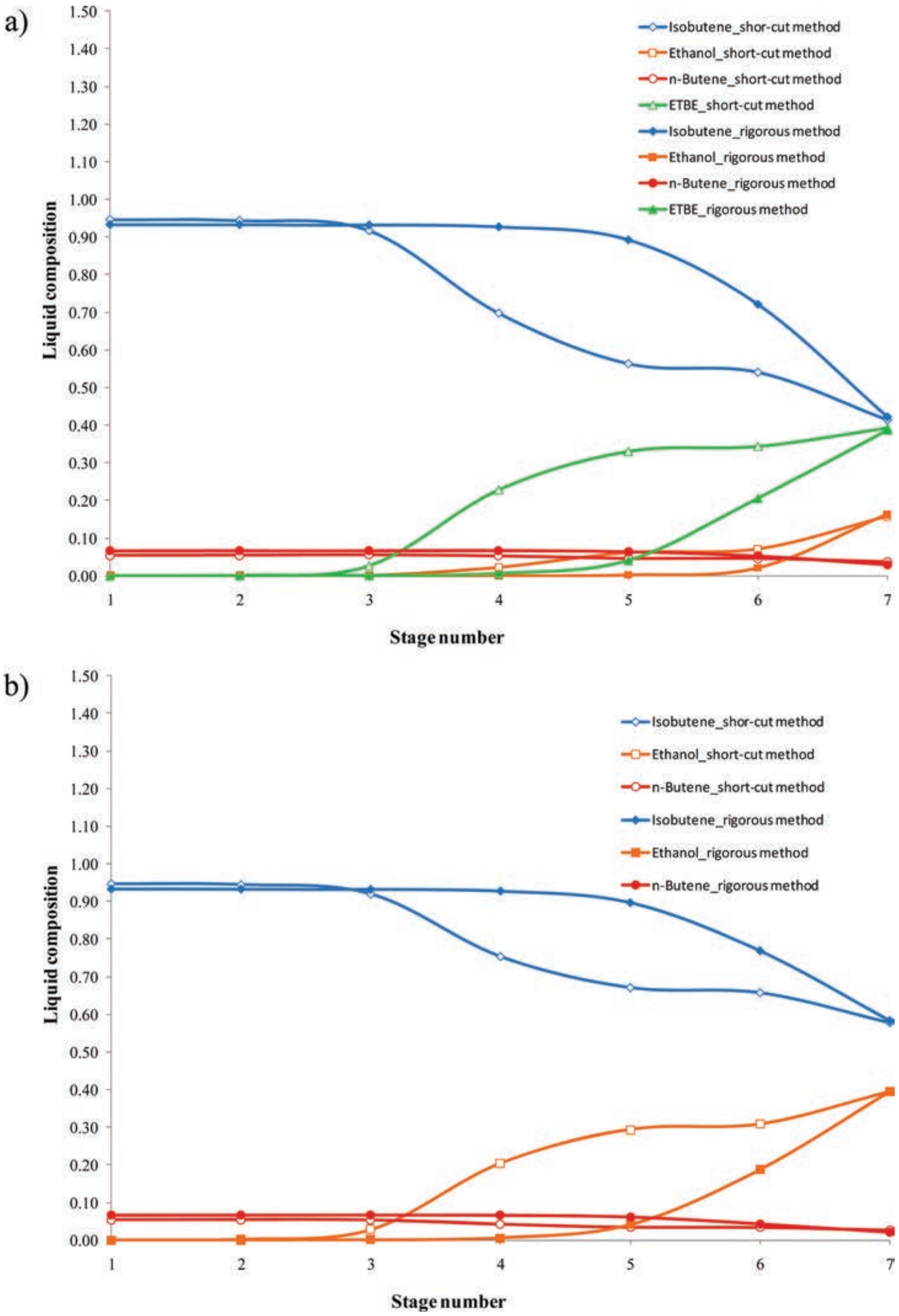

Figure 9. Composition profiles in the RD column for ETBE synthesis using a saturated vapor as the column feed: (a) mole fraction and (b) transformed mole fraction.

increasing feed vapor fraction: $R = 0.44$ for saturated liquid and $R = 2.86$ for saturated vapor. As stated, similar trends have been reported in the literature for conventional distillation.[13,15] The results reported in Table 6 show that the design methodology proposed here provides good agreement with the composition calculated by the commercial simulator AspenONE Aspen Plus. In this case study, the relative difference in purity of the main component is around 2.52% for all feed conditions. Based on the fact that all of the designs obtained have few stages, we prefer the design that has lower energy requirements, which is related to R. Therefore, the design with saturated liquid as the feed appears to be the best for this reactive separation.

For illustration, Figures 7−9 show some cases of the composition profiles along of the column for MTBE, TAME, and ETBE syntheses. In general, our results indicate that the key purities in the top and bottom of the column from MTBE, TAME, and ETBE obtained from AspenONE Aspen Plus and those obtained from the proposed design methodology are in good agreement. However, this agreement between the two approaches might be less along of the column because our method assumes constant molar flows along the RD column and uses only total and component mass balances. On the other hand, the rigorous model used in AspenONE Aspen Plus considers that the numbers of moles of the reaction are not conserved because of the reaction heat. As a consequence, the vapor and liquid flow rates change along the column, and to take these changes into account, mass and energy balances are always used for modeling each stage.

Finally, the obtained purities using only reactive stages are low but they can be improved using additional physical stages (i.e., a hybrid model that combines reactive stages and nonreactive stages can be used for this purpose). Therefore, the results obtained using our approach are useful for providing a quick predesign that can be further optimized to reach the designer targets.

4. CONCLUSIONS

A new short-cut method for the design of reactive distillation columns has been introduced. This method is easy to implement and provides a quick predesign (providing operating parameters as a starting point) for a rigorous design method. Our method uses distillation lines in combination with algebraic component mass balances, defined in terms of reaction-invariant composition variables, for each section of the column and solves the equations from the outside of the column to the inside of the column to meet the overall material balance. Contrary to the concept of the intersection of the two operating profiles, our method optimizes the feed location by searching for the minimum difference in composition between any given tray and the feed point. This strategy avoids situations in which a designer begins a rigorous design without information and employs more time in trial-and-error calculations to find the main operating parameters in search of the expected results. From our results, it is clear that the design methodology proposed here provides good agreement with the results obtained with the commercial simulator AspenONE Aspen Plus, principally for the target purities (MTBE, TAME, and ETBE) in the top or bottom of column. On the other hand, we have also illustrated the effect of the feed thermal conditions and composition on the designs obtained. Analyzing the obtained operating conditions, one can improve RD designs by reducing the total number of stages and the reflux ratio *R* because it is directly related to the amount of material that is heated in the reboiler and, therefore, affects the overall energy requirements.

With respect to the case studies, because of the highly nonideal thermodynamic behavior of the systems considered, the main products (MTBE, TAME, and ETBE) cannot be obtained with high purity using distillation columns with only reactive stages. However, the purification targets can be achieved through the addition of nonreactive stages to the column, resulting in a hybrid design. In summary, our method is reliable for performing the design of multicomponent reactive distillation using any feed conditions (i.e., saturated liquid, saturated vapor, or liquid—vapor mixture).

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NOTATION

a_i = activity of component *i*
B = bottom flow
c = number of components
$C^{R}_{i,m}$ = line in the rectifying section that includes the composition points *m*
$C^{S}_{i,n}$ = line in the stripping section that includes the composition points *n*
D = top flow
K_{eq} = chemical equilibrium constant
K_i = phase equilibrium constant of component *i*
$\mathbf{N}$ = square matrix of the stoichiometric coefficient of the reference components in *r* reactions
N_F = number of feed trays
N_{TOT} = total number of stages
q = thermal condition of the feed
r = independent chemical reaction
R = reflux ratio
S = reboil ratio
$\mathbf{v}_i{}^{T}$ = row vector of stoichiometric coefficients of component *i* for each reaction
$\mathbf{v}_{TOT}{}^{T}$ = row vector of the sum of the stoichiometric coefficients for all components
v_i^r = stoichiometric coefficient of component *i* in reaction *r*
X_i = transformed mole fraction in the liquid phase of component *i*
x_i = liquid mole fraction of component *i*
$\mathbf{x}_{ref}$ = column vector of *R* reference-component liquid mole fractions
Y_i = transformed mole fraction in the vapor phase of component *i*
y_i = vapor mole fraction of component *i*
$\mathbf{y}_{ref}$ = column vector of *R* reference-component vapor mole fractions
Z_i = transformed mole fraction in the feed of component *i*

Greek Letters

α = scalar parameter
β = scalar parameter
γ_i = liquid activity coefficient of component *i*
τ = dimensionless time

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