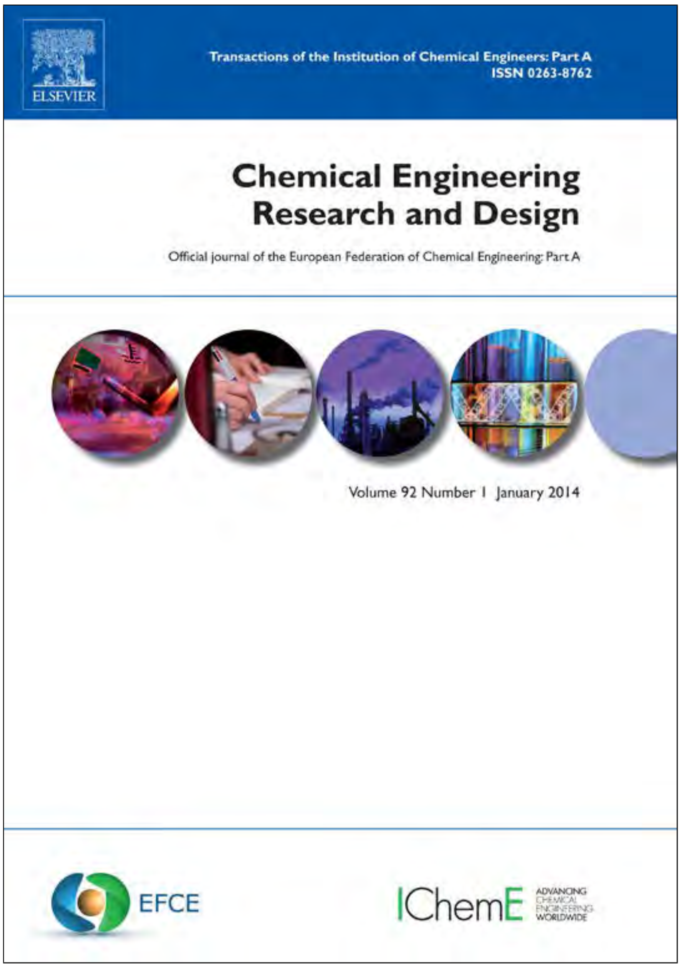

Transactions of the Institution of Chemical Engineers: Part A
ISSN 0263-8762

Chemical Engineering Research and Design

Official journal of the European Federation of Chemical Engineering: Part A

Volume 92 Number 1 January 2014

CHEMICAL ENGINEERING RESEARCH AND DESIGN 92 (2014) 1–12

Contents lists available at ScienceDirect

Chemical Engineering Research and Design

journal homepage: www.elsevier.com/locate/cherd

Short communication

A note on an extended short-cut method for the design of multicomponent reactive distillation columns

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ABSTRACT

Until now, few studies have proposed analytical short-cut methods for reliably designing multicomponent reactive distillation columns. Therefore, in this study we have improved and extended a design methodology for the design of RD columns of multicomponent systems. We have developed a graphical design method, based on distillation lines and tray-by-tray calculations defined in terms of reaction-invariant composition variables, to determine RD design parameters such as the number of theoretical stages, operating reflux ratio, the feed tray location and the top or bottom flow. In this note, we report our extended and improved method, which is analytical and useful for reliably determining the design parameters of multicomponent RD systems. We study the synthesis of TAME with inert components (with different feed thermal conditions) as case of study to show the effectiveness of the proposed strategy. Results obtained with our strategy show a significant agreement with those obtained using a rigorous model of commercial simulator AspenONE Aspen Plus®.

Keywords: Multicomponent reactive distillation; Distillation lines maps; Design short-cut method; TAME synthesis; Transformed composition variables; Rouche-Frobenius theorem

1. Introduction

The development of methodologies for the design and optimization of reactive distillation (RD) has received significant attention due to the economical and operational advantages obtained from the application of these separation schemes. In particular, the simultaneous occurrence of reaction and separation in a single unit often results into simpler and intensified processes with less recycle streams, reduced waste handling and, as a consequence, lowers investment and operating costs (Taylor and Krishna, 2000). Also, RD offers substantial operational advantages for process performance such as higher reaction rate and selectivity, the prevention of azeotropes, and reduced energy consumption as well as solvent usage. Although these advantages of RD are well documented in literature, the commercial applications of RD are still limited because of the partial knowledge about the control performance and operation complexity of these separation systems. Many of the current design strategies are often tedious from the point of view of their implementation and imply iterative procedures, which do not necessarily guarantee an optimal design of distillation system (Kraemer et al., 2011). As a consequence, an increasing interest in the development of effective and robust methods and simulation tools for the determination of optimum column configuration has been turned into a great design challenge. Until now, robust short-cut methods have been reported especially for the modeling of non-reactive separation systems involving homogeneous and heterogeneous azeotropic multicomponent mixtures. These methods are based on tray-to-tray calculations, pinch

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Received 21 May 2012; Received in revised form 4 June 2013; Accepted 18 June 2013

http://dx.doi.org/10.1016/j.cherd.2013.06.018

Notation

A	coefficient matrix
A^*	augmented matrix
a_i	activity of component *i*
B	bottom flow
c	number of components
d	minimum distance between line segments
D	top flow
F	feed flow
K_{eq}	chemical equilibrium constant
K_i	phase equilibrium constant of component *i*
N	square matrix of the stoichiometric coefficient of the reference components in *r* reactions
N_F	feed tray
N_{TOT}	total number of stages
p	pressure
P_n	point *n* on a line segment
q	thermal condition of the feed
r	independent chemical reactions
R	reflux ratio
R_{min}	minimum reflux ratio
Rn	matrix rank
S	reboil ratio
t	relative position of minimum distance
T	temperature
x_i	liquid mole fraction of component *i*
y_i	vapor mole fraction of component *i*
X_i	transformed mole fraction in the liquid phase of component *i*
Y_i	transformed mole fraction in the vapor phase of component *i*
Z_i	transformed mole fraction in the feed of component *i*
Greek letters	
ε	error
γ_i	liquid activity coefficient of component *i*

point analysis or hybrid approaches (e.g., Brüggermann and Marquardt, 2010; Prayoonyong and Jobson, 2011).

However, it is convenient to remark that several numerical difficulties are involved in the modeling, design and optimization of RD systems due to the presence of both separation and chemical reactions. As has been discussed by Carrera-Rodríguez et al. (2011) and other authors, 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. Based on this fact, some approaches for the transformation of composition variables have been used to simplify the modeling of reactive systems. These approaches are generally based on transformation of the physical compositions and its principal benefit is that the simultaneous chemical and physical equilibrium model in the reactive mixture is very similar to a strictly physical equilibrium model (Ung and Doherty, 1995; Seider and Widagdo, 1996; Wasylkiewicz and Ung, 2000).

Many researchers have paid attention on the development of robust and alternative approaches for the RD design especially for multicomponent systems. For example, Barbosa and Doherty (1988) extended the boundary value method (BVM) for the design of distillation columns with reactions at equilibrium. Also, design methods for reactive systems under kinetic control have been also proposed, which enables a more detailed analysis and design of RD process (Sánchez-Daza et al., 2003). On the other hand, Dragomir and Jobson (2005) extended the graphical design methodology developed for non-hybrid columns of Groemping et al. (2004) to hybrid systems, using mass and energy balances, that is optimized based on the equipment cost for the configurations obtained. For multicomponent mixtures, Jantharasuk et al. (2011) proposed the *element*-based approach coupled with a driving force diagram, which has been extended and applied to the design of reactive distillation column involving multi-element systems. This methodology is limited to systems that can be simplified to the equivalent binary element system.

To the best of our knowledge, reliable short-cut methods are not available yet for multicomponent reactive distillation. Therefore, in this study we introduce a new design methodology, based on an analytical approach, for designing RD columns of multicomponent systems. In a previous study (Carrera-Rodríguez et al., 2011), we have developed a graphical design method based on distillation lines and tray-by-tray calculations defined in terms of reaction-invariant composition variables. This method implies tray-by-tray calculations and a strategy has been suggested to locate the reflux ratio and the feed tray location that minimizes the total number of stages. 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. However, the method proposed in our previous study only is useful for reactive systems with three transformed composition variables (i.e., $c–r=3$). This fact limits its application for designing RD systems of more complex reactive systems involved in industrial applications. Therefore, this methodology has been modified and extended for performing the design of RD columns for multicomponent systems without any restriction with respect to the number of components or reactions. This preliminary design approach allows studying a variety of real and complex multicomponent reactive systems. Finally, the performance of our short cut method is compared with those obtained with the commercial simulator AspenONE Aspen Plus® using the synthesis of TAME with inert components as case of study. Results show the capabilities of this improved method for the design of multicomponent RD columns.

2. Description of the extended short cut method

To design a multicomponent reactive distillation column, the operating minimum reflux ratio, the 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 (Stichlmair and Fair, 1998). In particular, the use of distillation lines allows to the material balances to be written in algebraic form.

Consider the reactive distillation column represented in Fig. 1. 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 easy to implement, which provides a quick pre-design for a rigorous design

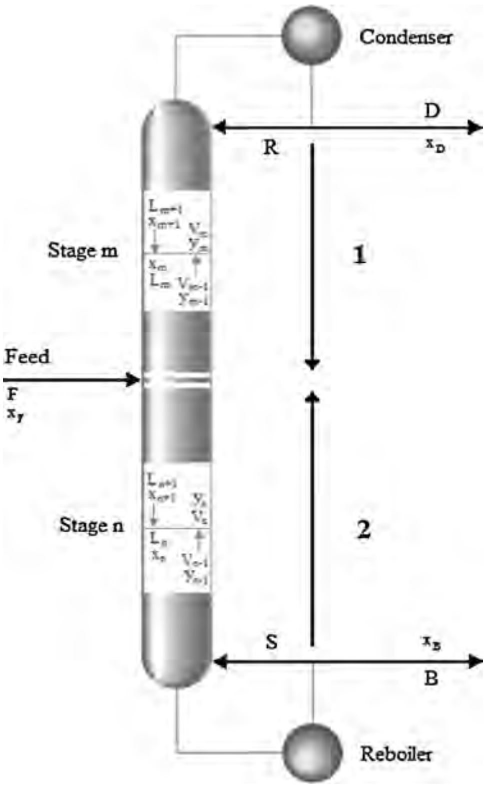


Fig. 1 – Description of rectifying section (1) and stripping section (2) for the application of the design method proposed in this study. This figure has been taken from Carrera-Rodríguez et al. (2011). Note that S and R are the boil up ratio and the reflux ratio, respectively.

method) used for the design of non-reactive and reactive distillation columns assumes constant molar overflows because of the total and component mass balances are used to provide a pre-design of the distillation column (Barbosa and Doherty, 1988). If we assume variable molar overflows, the internal liquid and vapor flows along the column must be calculated. To account for these conditions, the mass and energy balances should be used to model each stage (i.e., as a rigorous model), and the complexity of numerical problem increases. Therefore, in our method we assume constant molar overflows and distillation columns with only reactive ideal stages are used. In the following sections, we briefly describe the analytical short-cut method proposed for the design of RD columns and its comparison with results obtained by a rigorous method using the simulator AspenONE Aspen Plus®. In particular, the proposed methodology is described using the TAME reactive system, which has been selected as example for illustrating the capabilities of our approach. Note that some details of this design methodology have been reported in Carrera-Rodríguez et al. (2011) and an overview of this methodology is provided in this section with the intention of making the result and discussion easier to follow.

2.1. *Determination of feasible zone using reaction-invariant composition variables*

As stated in Carrera-Rodríguez et al. (2011), the first step of the design procedure is to check the feasibility of the system split. Reactive residue curve maps (RRCM) are useful for the design of RD columns as a tool to establish feasible zones of reaction-separation. Thus, RRCM provide the possibility of determining the existence of distillation boundaries and, as a consequence, determining different potential zones of operation (Kiva et al., 2003). Note that the region of the bottom and top products for a given feed is delimited by the composition space, the distillation boundary, and the distillation line that contains the desired products. As example, Fig. 2 illustrates how the feasible region can be identified for TAME synthesis in a quaternary composition diagram using transformed mole fraction variables. In this figure, line D–F–B represents the overall mass balance for the RD column in terms of transformed composition variables. Points D and B refer to the desired products to be obtained in the top and bottom of the RD column, respectively; while point F represents the feed composition also given in transformed composition space. It is important to take into account that the bottom products and the top products must be collinear with the feed for satisfying the overall material balance. If the desired split is not feasible, a new feasible split can be easily specified using this type of 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 dimensionality is also reduced.

2.2. *An extended design method for multicomponent RD columns*

First, we define the total mass balance for a multicomponent RD column using reaction-invariant composition variables. These balances for both the rectifying and stripping sections are given by Carrera-Rodríguez et al. (2011) and correspond to

$$X_{i,m} = \frac{R+1}{R} Y_{i,m-1} - \frac{1}{R} X_{i,D} \quad i = 1, \ldots, c - r \tag{1}$$

$$X_{i,n+1} = \frac{S}{S+1} Y_{i,n} + \frac{1}{S+1} X_{i,B} \quad i = 1, \ldots, c - r \tag{2}$$

where $X_{i,j}$ is the transformed composition in the liquid phase of component i in stage j, $Y_{i,j}$ is the transformed composition in the vapor phase of component i in stage j, R is the reflux ratio of liquid L that returns to the column with respect to the distilled D, S is the boil up ratio of vapor V that returns to the column with respect to the mass bottom B, $X_{i,B}$ is the transformed composition of component i at the bottom, and $X_{i,D}$ is the transformed composition of component i at the column top, respectively. These component mass balance equations must be used with a proper thermodynamic model that relates the vapor–liquid equilibrium conditions. For interested readers, the details of composition variable transformation and its application for the design of RD columns can be found in Carrera-Rodríguez et al. (2011).

As stated, in this study the reactive system for the production of TAME is considered as an example where $c = 5$ and $r = 1$. For this reactive system, an analysis of the number of degrees of freedom indicates that 2c–1 variables must be specified. The specification of these variables depends on the designer's interest, so we can select the operating pressure or temperature (which must be defined based on the requirements for the reactive separation system under study), the condenser reflux ratio or the reboiler reflux ratio, and transformed compositions (between feed, top and bottom compositions). To complement the number of degrees of

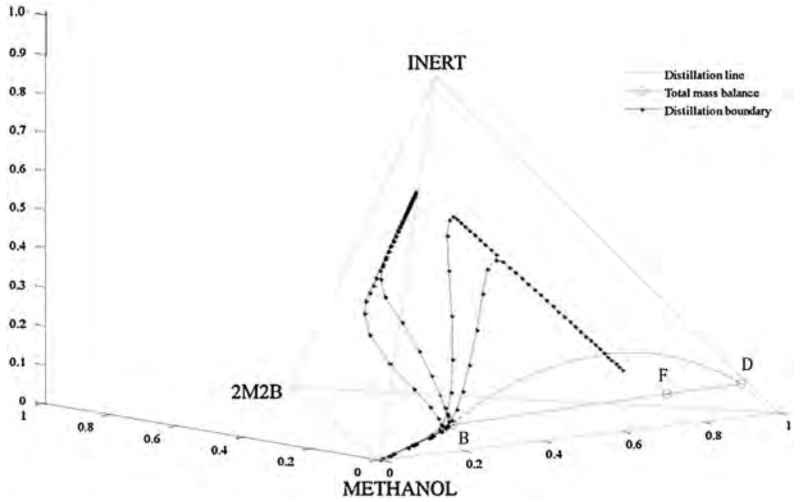


Fig. 2 – Separation region products for a given feed in the synthesis of TAME. Note that B, F and D represent the bottoms product, feed and distillate product, respectively.

freedom, the summation constraints and the total mass balances are used. In particular, we must specify nine parameters for our case of study. For instance, in TAME synthesis we can specify the operation pressure (p), the reflux ratio (R), three feed compositions (Z_1, Z_2, Z_3) and four product compositions ($X_{1,D}$, $X_{2,D}$, $X_{3,D}$, $X_{1,B}$); then $X_{2,B}$ and $X_{3,B}$ can be calculated from the total mass balances using the following equation

$$X_{i,B} = Z_i + (Z_i - X_{i,D})\left(\frac{S}{R+1}\right) \quad i = 2, \ldots, c-r-1 \tag{3}$$

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

$$S = (R+q)\left[\frac{X_{1,B} - Z_1}{Z_1 - X_{1,D}}\right] + (q-1) \tag{4}$$

where q is the thermal condition of the feed where $q = 1$ for saturated liquid, $q = 0$ for saturated vapor, and $0 < q < 1$ for a liquid–vapor mixture, respectively. The remaining specifications $X_{4,D}$ and $X_{4,B}$ are obtained from summation constraints

$$\sum_{i=1}^{c-r} X_{i,D} = 1 \tag{5}$$

$$\sum_{i=1}^{c-r} X_{i,B} = 1 \tag{6}$$

Eqs. (3) and (4) can be solved using the vapor–liquid equilibrium model to obtain the composition profiles for a given reflux ratio R. For multicomponent systems, the intersection of the composition profiles in the composition space is difficult to achieve. Therefore, the intersection and the minimum distance between the composition profiles are necessary and sufficient conditions, respectively, to establish the split feasibility. Fig. 3 illustrates these conditions using the TAME reactive system. These necessary and sufficient conditions are employed to calculate the minimum reflux ratio in the proposed method.

Note that the calculations for RD design involve an iterative process where a graphical approach can be used to verify the intersection of composition profiles for a given R. However, this approach implies a higher CPU time in addition to uncertainties and inaccuracies for defining the RD design parameters. For multicomponent mixtures, multidimensional profiles have to be checked for intersection, which can be a tedious and ineffective numerical procedure; moreover, the automation of the check procedure for intersection of composition profiles remains difficult. So, we propose an analytical strategy to perform these calculations. Specifically, to ensure the intersection of the composition

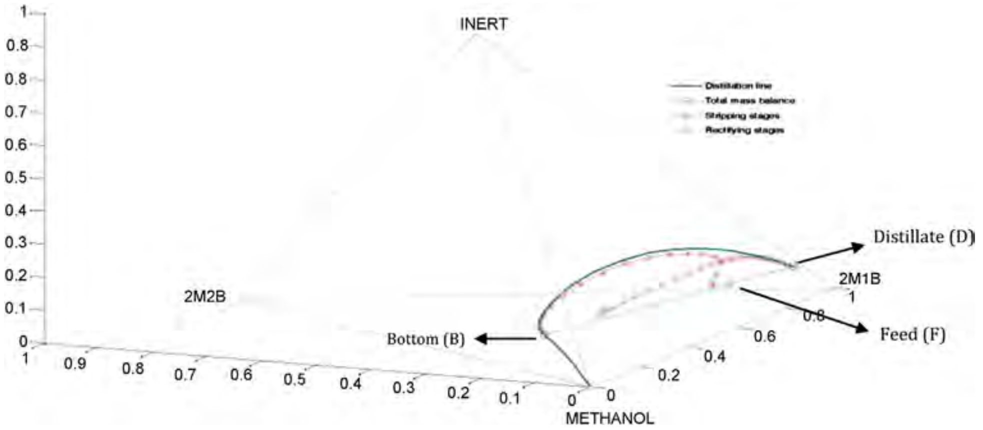


Fig. 3 – Operating profiles for the synthesis of TAME using our short-cut design method.

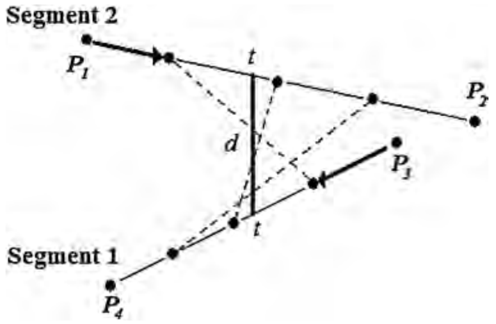
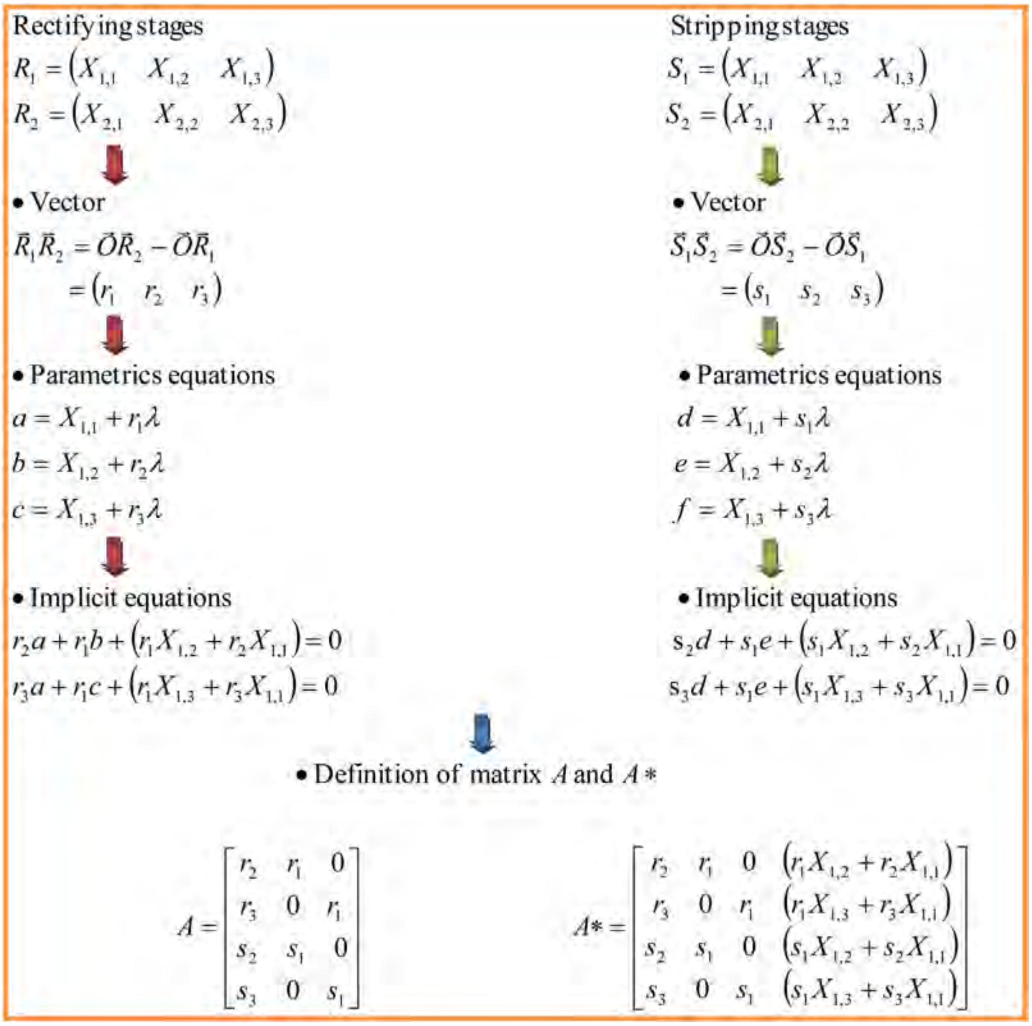


Fig. 4 – Illustration of the feasibility test for the design of reactive distillation column.

profiles, we construct operating lines for two consecutive compositions of each profile and the relative position of these lines in the space is determined using the Rouché-Fröbenius theorem. In the following sentences, we will provide more details of these procedures. With illustrative purposes, Fig. 4 shows an illustration of the feasibility test used for analyzing the separation. In particular, Rouché-Fröbenius is the theorem in linear algebra that allows computing the number of solutions in a system of linear equations given the ranks (*Rn*) of its augmented matrix (A^*) and coefficient matrix (*A*). In our design method, these matrixes are conformed by the implicit equations of the line segments constructed from the operating lines of the transformed composition in the liquid phase, see Fig. 5 for illustration of this procedure using our case of study, i.e., TAME reactive system. According to this theorem, the two line segments can take the following relative positions in the space:

- $Rn\ (A) = Rn\ (A^*) = 2$: The system of equations is compatible indefinite (i.e., it has infinite solutions). The lines have all their points in common and, as consequence, *they are coincident lines*.
- $Rn\ (A) = 2$ and $Rn\ (A^*) = 3$: The system is incompatible (i.e., there is no solution). The lines have no points in common, but as rank $(A) = 2$, the lines are coplanar (they are in the same plane) and, therefore, *they are parallel lines*.
- $Rn\ (A) = Rn\ (A^*) = 3$: The system of equations is compatible determined (i.e., it has a unique solution). The lines have one common point, which is the cutoff point for both lines. So, *they are secant lines*.
- $Rn\ (A) = 3$ and $Rn\ (A^*) = 4$: The system is inconsistent and there is no solution. The lines have no points in common, and as rank $(A) = 3$, the lines are not coplanar (i.e., they are not contained in the same plane). Thus, *they are lines that cross roads*.

For our purposes it is desirable to satisfy this last statement because it implies the intersection of composition profiles.


Rectifying stages

$R_1 = (X_{1,1} \quad X_{1,2} \quad X_{1,3})$

$R_2 = (X_{2,1} \quad X_{2,2} \quad X_{2,3})$

- Vector

$$\vec{R_1}\vec{R_2} = \vec{O}\vec{R_2} - \vec{O}\vec{R_1} = (r_1 \quad r_2 \quad r_3)$$

- Parametrics equations

$a = X_{1,1} + r_1\lambda$

$b = X_{1,2} + r_2\lambda$

$c = X_{1,3} + r_3\lambda$

- Implicit equations

$r_2a + r_1b + (r_1X_{1,2} + r_2X_{1,1}) = 0$

$r_3a + r_1c + (r_1X_{1,3} + r_3X_{1,1}) = 0$

Stripping stages

$S_1 = (X_{1,1} \quad X_{1,2} \quad X_{1,3})$

$S_2 = (X_{2,1} \quad X_{2,2} \quad X_{2,3})$

- Vector

$$\vec{S_1}\vec{S_2} = \vec{O}\vec{S_2} - \vec{O}\vec{S_1} = (s_1 \quad s_2 \quad s_3)$$

- Parametrics equations

$d = X_{1,1} + s_1\lambda$

$e = X_{1,2} + s_2\lambda$

$f = X_{1,3} + s_3\lambda$

- Implicit equations

$s_2d + s_1e + (s_1X_{1,2} + s_2X_{1,1}) = 0$

$s_3d + s_1e + (s_1X_{1,3} + s_3X_{1,1}) = 0$

- Definition of matrix *A* and *A**

$$A = \begin{bmatrix} r_2 & r_1 & 0 \\ r_3 & 0 & r_1 \\ s_2 & s_1 & 0 \\ s_3 & 0 & s_1 \end{bmatrix} \qquad A* = \begin{bmatrix} r_2 & r_1 & 0 & (r_1X_{1,2} + r_2X_{1,1}) \\ r_3 & 0 & r_1 & (r_1X_{1,3} + r_3X_{1,1}) \\ s_2 & s_1 & 0 & (s_1X_{1,2} + s_2X_{1,1}) \\ s_3 & 0 & s_1 & (s_1X_{1,3} + s_3X_{1,1}) \end{bmatrix}$$

Fig. 5 – Illustration of the algorithm to calculate the matrix A and A* for the design of reactive distillation column for TAME synthesis.

The next methodology is used to compute the minimum distance between two line segments in 3D, see Fig. 4. Note that this approach can be easily extended to *n*-Dimension for the analysis of multicomponent and multireactive systems. Consider that a line segment is the finite portion of a line that lies between two points. Then, the first step is to find the points on a line segment 2 for the stripping section (defined by P_1 and P_2) nearest to endpoints of the line segment 1 for the rectifying section (defined by P_3 and P_4). The parametric equation of the line segment 1 is given by

$$P = P_1 + t(P_2 - P_1) \tag{7}$$

The point P_3 is closest to the line at the tangent to the line which passes through P_3. Therefore, the dot product of tangent and line is 0, so

$$(P_3 - P) \cdot (P_2 - P_1) = 0 \tag{8}$$

Substituting Eq. (7) of the line segment and solving this expression, we obtain the value of *t* (which is the variable in the procedure required to estimate the point of intersection of tangents) that should has value within the interval [0, 1]

$$t = \frac{(P_3 - P_1) \cdot (P_2 - P_1)}{||P_2 - P_1||^2} \tag{9}$$

Substituting this result into Eq. (9) of the line segment gives the point of intersection of the tangent as follows

$$X_{i,n} = X_{i,P1} + t(X_{i,P2} - X_{i,P1}) \quad i = 1, \ldots, c - r \tag{10}$$

$$Y_{i,n} = Y_{i,P1} + t(Y_{i,P2} - Y_{i,P1}) \quad i = 1, \ldots, c - r \tag{11}$$

$$Z_{i,n} = Z_{i,P1} + t(Z_{i,P2} - Z_{i,P1}) \quad i = 1, \ldots, c - r \tag{12}$$

Therefore, the distance between the point P_3 and the line is the distance between $(X_{i,n1}, Y_{i,n1}, Z_{i,n1})$ and P_3. This method is used to find the intersection point $(X_{i,n2}, Y_{i,n2}, Z_{i,n2})$ and distance for P_4.

On line segment 2, over the interval between the points nearest to line segment 1, the square of the distance of any point to line segment 1 is a quadratic function. So, we have to evaluate it at three points, and seek its minimum distance using the following procedure:

- *First point*: Calculate the coordinates, the relative position (t_l) and distance (d_l) of the nearest point to the defined line segment 1 and $(X_{i,n1}, Y_{i,n1}, Z_{i,n1})$.
- *Second point*: Calculate the coordinates, the relative position (t_m) and distance (d_m) of the nearest point to the defined line segment 1 and $[0.5(X_{i,n1} + X_{i,n2}), 0.5(Y_{i,n1} + Y_{i,n2}), 0.5(Z_{i,n1} + Z_{i,n2})]$.
- *Third point*: Calculate the coordinates, the relative position (t_r) and distance (d_r) of the nearest point to the defined line segment 1 and $(X_{i,n2}, Y_{i,n2}, Z_{i,n2})$.

These calculations are performed using Eqs. (7)–(12). We now proceed to find the minimum distance. The square of the distance function between a point and a line segment has the form of $f(h) = ah^2 + bh + cte$. Hence, we can seek the line on the second segment which minimizes the square of the distance to the other line segment. The next strategy finds the point of concavity of the parabola defined by three points. For these calculations, the inputs are: t_l, d_l, t_m, d_m, t_r, d_r and the coordinates of three points on the parabola; while the outputs are *t* and *d*: the *t* coordinate of the point of concavity of the parabola, and the value of the parabola at that point. Using these variables, the function for distance can be defined as

$$d = at^2 + bt + cte \tag{13}$$

where the relative position is given by

$$t = -\frac{b}{2a} \tag{14}$$

By substituting the three points in Eq. (13), we obtain a system of three equations with three unknown variables:

$$d_l = a{t_l}^2 + bt_l + cte \tag{15}$$

$$d_m = a{t_m}^2 + bt_m + cte \tag{16}$$

$$d_r = a{t_r}^2 + bt_r + cte \tag{17}$$

Solving this system of equations, the three variables (*a*, *b*, *cte*) are given by

$$a = \frac{-d_l(t_m - t_r) + d_m(t_l - t_r) - d_r(t_l - t_m)}{{t_r}^2(t_m - t_l) - {t_m}^2(t_r - t_l) - {t_l}^2(t_m - t_r)} \tag{18}$$

$$b = \frac{{t_l}^2(d_r - d_m) + {t_m}^2(d_l - d_r) + {t_r}^2(d_m - d_l)}{{t_r}^2(t_m - t_l) - {t_m}^2(t_r - t_l) - {t_l}^2(t_m - t_r)} \tag{19}$$

$$cte = \frac{{t_r}^2(d_l t_m - d_m t_l) - {t_m}^2(d_l t_r - d_r t_l) + {t_l}^2(d_m t_r - d_r t_m)}{{t_r}^2(t_m - t_l) - {t_m}^2(t_r - t_l) - {t_l}^2(t_m - t_r)} \tag{20}$$

Substituting these variables in Eqs. (13) and (14), the relative position and the minimum distance are defined as

$$t = \frac{0.5[{t_l}^2(d_r - d_m) + {t_m}^2(d_l - d_r) + {t_r}^2(d_m - d_l)]}{d_l(t_m - t_r) - d_m(t_l - t_r) + d_r(t_l - t_m)} \tag{21}$$

$$d = \frac{[(t - t_m)(t - t_r)(t_m - t_r)d_l - (t - t_l)(t - t_r)(t_l - t_r)d_m + (t - t_l)(t - t_m)(t_l - t_m)d_r]}{(t_l - t_m)(t_m - t_r)(t_l - t_r)} \tag{22}$$

According to the numerical experience gained in this study, the intersection and an error ($\varepsilon < 1 \times 10^{-1}$) in the minimum distance between two line segments of the composition profiles are necessary and sufficient conditions to generate a suitable design of multicomponent RD columns.

For illustration, the procedure proposed to calculate the minimum reflux ratio in TAME reactive system is given in Fig. 6; while the general procedure for any multicomponent reactive system is given in Fig. 7 where an analysis of the number of degrees of freedom is necessary to define the number of design variables for the system under study. Note that if the minimum reflux is not found, then the proposed separation is infeasible. For the design of distillation columns, $R > 5$ is considered as a high reflux ratio (Luyben, 1992). However, in this study we have used $R_{max} = 10$ to favor the convergence of our method. It is convenient to remark that the composition profile intersection does not necessarily provide a suitable criterion for the location of feed tray because it does not always

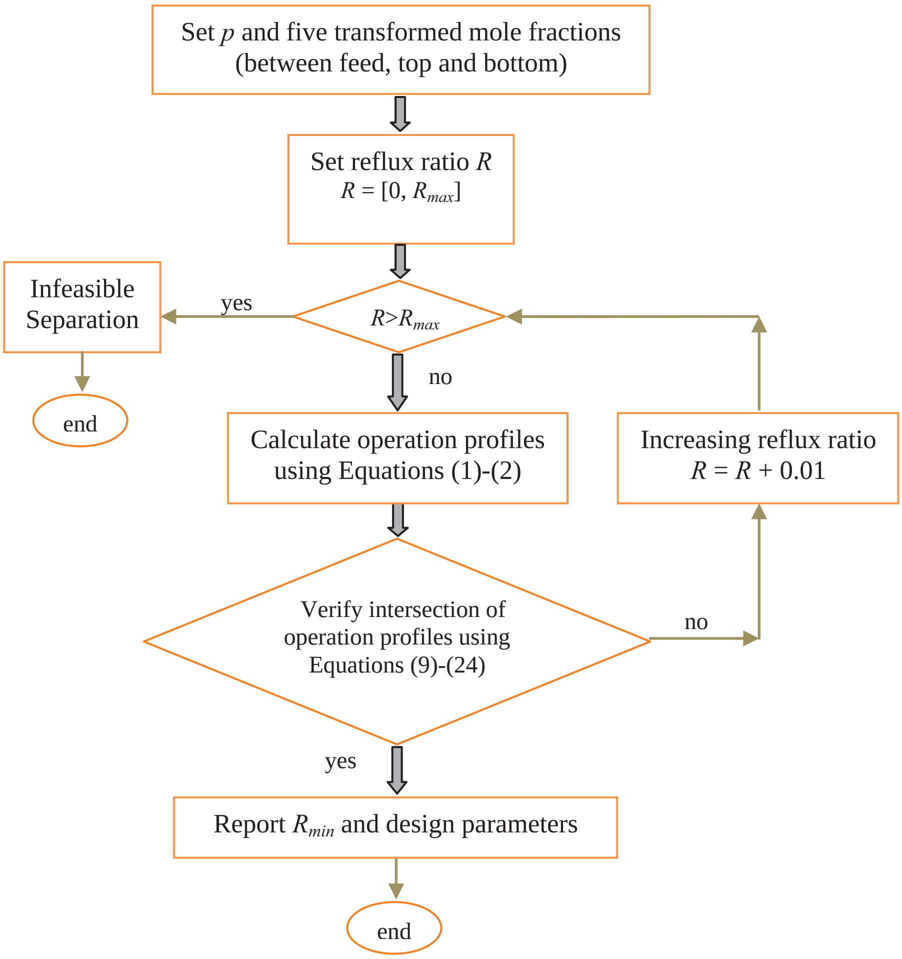


Fig. 6 – Algorithm to calculate the minimum reflux ratio for the design of RD columns for TAME synthesis.
***Source*: This figure has been taken from Carrera-Rodríguez et al. (2011).**

locate the plate with the composition closest to the feed. In non-reactive distillation columns, Gutiérrez-Antonio and Jiménez-Gutiérrez (2007) proposed a minimum difference criterion to determine the feed stage location where 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 number of stages in the stripping and the rectifying sections are obtained along with the feed stage location. Based on this fact, we have extended this approach for the design of RD columns. Specifically, the difference (i.e., distance) between the compositions is calculated using Eqs. (23) and (24), which are also defined using transformed variables and have been obtained by introducing small modifications of the model proposed by Gutiérrez-Antonio and Jiménez-Gutiérrez (2007) due to the presence of chemical reactions. So, these design equations are defined as

$$d_R = \sqrt{\left(\sum_{i=1}^{c-r}(Z_i - X_{i,NR})\right)^2 + \left(\sum_{i=1}^{c-r}(Z_i - Y_{i,NR})\right)^2} \tag{23}$$

$$d_S = \sqrt{\left(\sum_{i=1}^{c-r}(Z_i - X_{i,NS})\right)^2 + \left(\sum_{i=1}^{c-r}(Z_i - Y_{i,NS})\right)^2} \tag{24}$$

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, respectively.

Component mass balances given by Eqs. (1) and (2) are determined by minimizing Eqs. (23) and (24). It is convenient to note that Eqs. (1) and (2) are solved from the top to the rectifying zone and from the bottom to the stripping zone toward the column center, respectively. The operating minimum reflux ratio (R_{min}) is determined until a point of intersection for the operating profiles is detected. After determining the operating minimum reflux ratio, an operating reflux ratio can be fixed using a heuristic rule [e.g., $1.1R_{min}$ proposed by Douglas (1988) or $1.5R_{min}$ proposed by Doherty and Malone (2001) can be applied]. Alternatively, this design parameter can be optimized using a suitable objective function related to energy savings or operation costs. The number of theoretical stages obtained involves a partial reboiler and considers the use of a total condenser.

With respect to the iterative method given in Figs. 6 and 7, the bubble and dew point calculations are crucial for the design of reactive distillation columns. These calculations are a special case of equilibrium problems and, robust and efficient methods for these calculations are required. Based on this fact, we have employed a global optimization approach based on Simulated Annealing (Bonilla-Petriciolet et al., 2006) for performing both reactive bubble and dew point

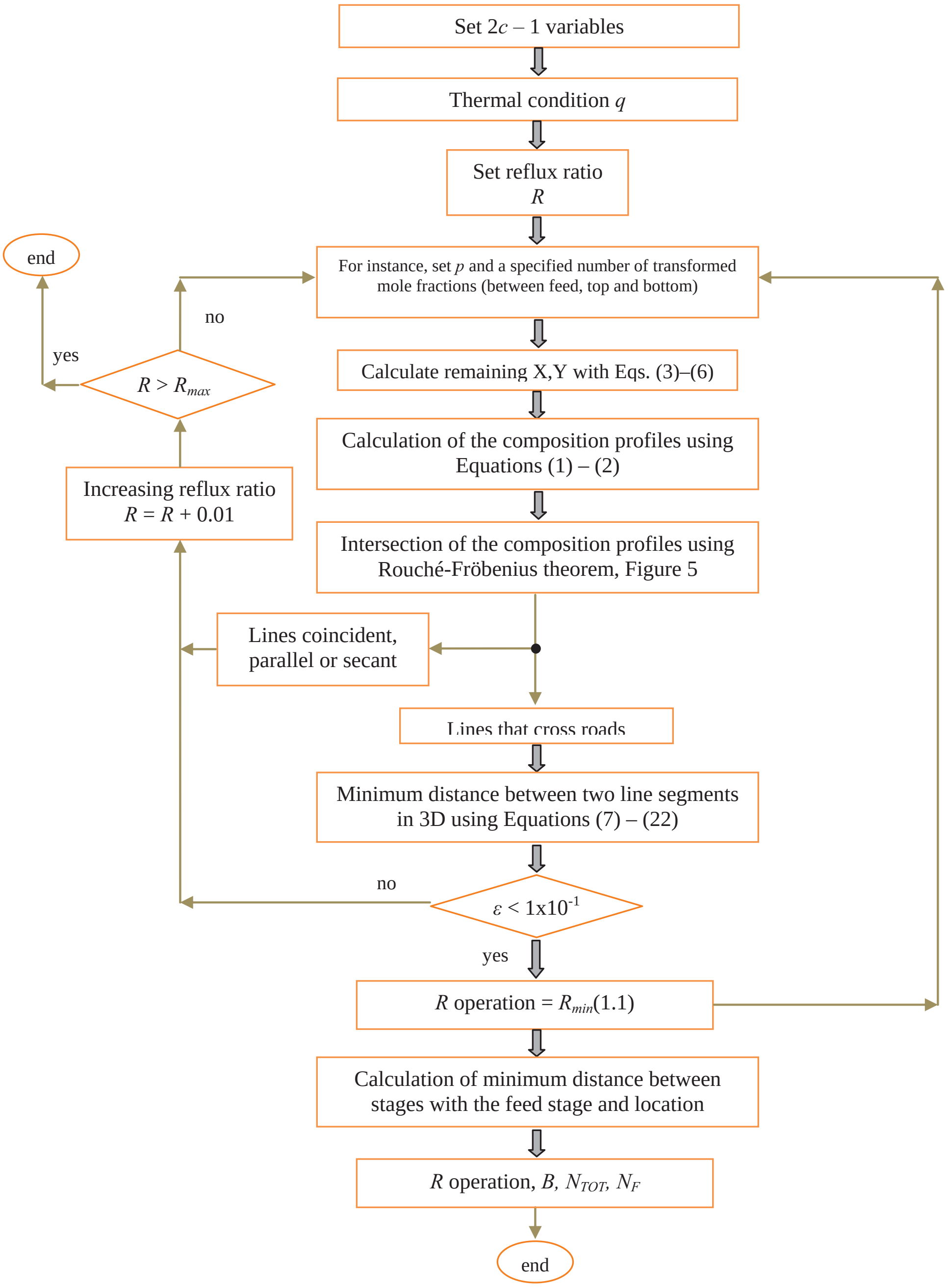


Fig. 7 – General procedure of short-cut method for the design of multicomponent reactive distillation columns.

calculations inside the proposed design method. In summary, the main contribution of this study is the implementation of an analytical strategy, based on a linear algebra theorem, to extend a short-cut method for the design of RD columns of multicomponent systems. Two points to be highlighted about this procedure: First, the feed composition is known for the analyzed mixture; the compositions of either the top or bottom products are fixed depending on the component to be recovered as main component. The third composition is obtained when the previous two compositions are located in a distillation curve in the composition map; as a result, the three compositions are thermodynamically consistent. It is important to mention that the composition of the third product (top or bottom products) depends on the positions of the previous two compositions (feed, bottom or top products). Second, as a short-cut design method, the design variables can be fixed almost arbitrary, but in order to ensure a good design, these design variables are set according to the components, compositions and expected products. It is true that these initial values can give an expensive design, but the main scope of this short-cut design method is to provide a good initial point for an optimization procedure.

3. Results and discussion

To show the effectiveness of the proposed method, we have used the synthesis of *tert*-amyl methyl ether (TAME) with inert at 4.052 bar as case of study. Note that this operating condition is commonly used in industry for this reactive mixture (Subawalla and Fair, 1999; Baur and Krishna, 2002). To the best of our knowledge, few design methods have been proposed and used to analyze the synthesis of TAME mainly due to the multicomponent character of this reactive system (Klöker et al., 2003; Kołodziej et al., 2004; Vanaki and Eslamloueyan, 2012). According to literature, the manufacturing process and the industrial implementation for this reactive system consist of a reactor and a hybrid reactive column. Simulation tools such as non-equilibrium (i.e., rate-based) and equilibrium-stage models can be used to model this reactive system. Traditional equilibrium-stage model assumes that vapor leaving a stage is at equilibrium with liquid on that stage, while the rate-based model assumes the equilibrium only at the vapor–liquid interface and uses mass and heat transfer correlations to determine molar flux across the interface. In particular, the rate-based model uses the actual number of trays or packed height in contrast to ideal equilibrium stages. Therefore, it is important to perform proper choices prior to the process design including the selection of an accurate vapor–liquid-equilibrium model and a reliable reaction kinetics model. This kinetic model should accurately predict the reaction rates under reactive distillation conditions, particularly, for systems where reactive column conditions differ considerably from the typical test or operating conditions (Subawalla and Fair, 1999; Baur and Krishna, 2002). Based on these facts, we have considered an equilibrium model for illustrating the capabilities of our design method.

For equilibrium-limited systems, a clear advantage of reactive distillation is the conversion enhancement via the product removal. For systems not limited by chemical equilibrium, the advantages are less obvious and include increased the selectivity to the desired product, the reduced equipment cost and an increased catalyst life. On the other hand, the use of an isothermal pre-reactor offers some advantages because high overall TAME production rates can be obtained (Subawalla and Fair, 1999; Baur and Krishna, 2002). Traditionally, a feed stream to the pre-reactor is considered in TAME production, which may consist of four o more inert components, e.g.: isopentane, *n*-pentane, 1-pentene and 2-pentene. In order to reduce the complexity of the system, we have decided to consider only a single inert component (i.e., *n*-pentane) for illustrating the application of our design method. Although, the boiling points of the inert components differ by about 8 K at 4.052 bar pressure, the choice of a single inert component does not significantly alter the thermodynamic behavior of the reactive mixture. Note that the activity coefficients for the inert C_5 components are close to unity and show almost an ideal behavior (Baur and Krishna, 2002).

In summary, we assume that the reaction for this case of study is reversible and in thermodynamic equilibrium. In this case, we used the heuristic of $1.1R_{min}$ to fix the operation 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. The most important feature of our methodology is that just considers mass balances and simple analytical equations for obtaining design parameters of multicomponent RD columns.

Our method provides an estimation of R, the top (D) or bottom (B) flow, the total number of stages (N_{TOT}) including reboiler and total condenser and, feed tray (N_F) when Eqs. (25) and (26) are minimized. The composition profiles 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 this reactive system using AspenONE Aspen Plus®, it is only necessary to use the four design parameters obtained (R, B, N_{TOT}, N_F) without any other restrictions. In addition, the operation pressure, feed thermal condition of the column and N_{TOT} are given. In performed simulations, we assume that all stages are reactive and the column involves a partial reboiler and considers the use of 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 via material and energy balances in each stage. To obtain thermodynamic consistency, we have used both the same model parameters for the calculation of thermodynamic properties and the chemical equilibrium constants in our method and Aspen Plus®. Results of all simulations are reported in Tables 1–2 and a detailed analysis of this example is given below.

3.1. *TAME synthesis*

As stated, TAME is an important chemical for gasoline and is commonly produced by liquid-phase etherification between methanol and iso-amylenes, in the presence of an acidic catalyst. Among the three iso-amylenes, only 2-methyl-l-butene (2M1B) and 2-methyl-2-butene (2M2B) are reactive, whereas 3-methyl-1-butene (3M1B) is non-reactive (Chen et al., 2002). In this study, we have considered the lumped single reaction with inert (*n*-pentane) for this system, which can be written as: 2M1B (x_1) + 2M2B (x_2) + 2 methanol (x_3) ⇔ 2 TAME (x_4) and *n*-pentane (x_5) as inert. Wilson and ideal gas models have been used to calculate thermodynamic properties of this mixture. Model parameters are taken from Chen et al. (2002). The reaction equilibrium constant is determined from $K_{eq} = 1.057 \times 10^{-4} e^{(4273.5/T)}$, where T is in K. Note that K_{eq} is given in terms of activities of all reactive species. Reaction-invariant mole fractions, considering TAME as reference component (x_4), are defined as

$$X_1 = \frac{x_1 + 0.5x_4}{1 + x_4} \tag{25}$$

$$X_2 = \frac{x_2 + 0.5x_4}{1 + x_4} \tag{26}$$

$$X_3 = \frac{x_3 + x_4}{1 + x_4} \tag{27}$$

$$X_5 = \frac{x_5}{1 + x_4} = 1 - X_1 - X_2 - X_3 \tag{28}$$

The target of this reactive separation is to obtain the maximum flow of TAME by the column bottom. Feed composition, top and bottom product compositions established for the column design are reported in Table 1. Our results show that the thermodynamic behavior of this reactive mixture is complex. According to AspenONE Aspen Plus®, this system forms four binary non-reactive azeotropes (2M1B-methanol, 2M2B-methanol, *n*-pentane-methanol and *n*-pentane-2M2B) and one ternary non-reactive azeotrope (*n*-pentane-2M1B-methanol); and then, there are various distillation boundaries that divide the composition diagram. Therefore, it is very important to verify that both the distillate point and the bottom point fall into feasible separation region, and also the co-linearity with respect to feed composition. Design results for this system are shown in Table 2. In this case, the total number of stages varies only in one stage for all the feed thermal conditions (i.e., N_{TOT} ranged from 39 to 40), and the feed stage is closer to the reboiler as the vapor fraction in the feed stream decreases (i.e., $N_F = 22$ for saturated vapor and $N_F = 26$ for saturated liquid, respectively). R increases with the feed vapor fraction (i.e., $R = 4.29$ for saturated liquid and

Table 1 – Design specifications using transformed molar fractions and molar fractions of feed (F), distillate product (D), and bottom product (B).

Systems	Component	X_F	X_D	X_B	x_F	x_D	x_B
TAME	2M1B	0.54350	0.89774	0.24946	0.54350	0.89795	0.14095
	2M2B	0.17351	0.01671	0.30366	0.17351	0.01645	0.21861
	Methanol	0.24264	0.00058	0.44355	0.24264	0.00004	0.20256
	TAME	–	–	–	0	0.00054	0.43312
	n-Pentane	0.04035	0.08497	0.00333	0.04035	0.08502	0.00476

Table 2 – Design specifications for the synthesis of TAME using a RD column.

Feed thermal condition	Design specifications		Component	Molar fractions of products			
				Proposed method		AspenONE Aspen Plus®	
				Top	Bottom	Top	Bottom
Saturated liquid			2M1B	0.89795	0.14095	0.88227	0.15158
	N_{TOT}	40	2M2B	0.01645	0.21861	0.00196	0.24409
	N_F	26	Methanol	0.00004	0.20256	0.02620	0.18660
	R	4.29	TAME	0.00054	0.43312	0.00256	0.41692
	B (lbmol/h)	37.811	*n*-Pentane	0.08502	0.00476	0.08701	0.00081
Liquid–vapor mixture	$q = 0.25$		2M1B	0.89795	0.14095	0.87825	0.15196
	N_{TOT}	40	2M2B	0.01645	0.21861	0.00220	0.24596
	N_F	25	Methanol	0.00004	0.20256	0.02989	0.18467
	R	4.41	TAME	0.00054	0.43312	0.00310	0.41655
	B (lbmol/h)	37.811	*n*-Pentane	0.08502	0.00476	0.08656	0.00076
	$q = 0.5$		2M1B	0.89795	0.14095	0.88362	0.14989
	N_{TOT}	39	2M2B	0.01645	0.21861	0.00188	0.24425
	N_F	23	Methanol	0.00004	0.20256	0.02489	0.18832
	R	4.95	TAME	0.00054	0.43312	0.00238	0.41698
	B (lbmol/h)	37.811	*n*-Pentane	0.08502	0.00476	0.08723	0.00056
	$q = 0.75$		2M1B	0.89795	0.14095	0.87859	0.15152
	N_{TOT}	39	2M2B	0.01645	0.21861	0.00222	0.24596
	N_F	23	Methanol	0.00004	0.20256	0.02947	0.18521
	R	5.115	TAME	0.00054	0.43312	0.00306	0.41666
	B (lbmol/h)	37.811	*n*-Pentane	0.08502	0.00476	0.08665	0.00065
Saturated vapor			2M1B	0.89795	0.14095	0.87962	0.15170
	N_{TOT}	39	2M2B	0.01645	0.21861	0.00075	0.24754
	N_F	22	Methanol	0.00004	0.20256	0.03095	0.18377
	R	5.50	TAME	0.00054	0.43312	0.00189	0.41637
	B (lbmol/h)	37.811	*n*-Pentane	0.08502	0.00476	0.08679	0.00062

$R = 5.50$ for saturated vapor). Note that similar trends have been reported in the literature for non-reactive distillation (Douglas, 1988) and it implies an increment of the amount of heat needed in the reboiler. Another result to illustrate the reliability of our design method is the comparison between the TAME composition by the bottom stream obtained from AspenONE Aspen Plus® and those obtained from the proposed design methodology (see Table 2). In general, it is observed a satisfactory agreement between the TAME compositions calculated by both modeling approaches. Therefore,

Table 3 – Compositions and operation parameters obtained using the short-cut method proposed for the design of RD column of TAME synthesis.

Component	Methodology reported in literature and industrial data (Subawalla and Fair, 1999; Baur and Krishna, 2002)					Short-cut method		
	Pre-reactor		Hybrid reactive column			Reactive column		
	x_F	x_P	x_F	x_D	x_B	x_F	x_D	x_B
2M1B	0.06350	0.00798	0.00798	0.00267	0.00013	0.54350	0.89795	0.14095
2M2B	0.12180	0.07020	0.07020	0.01495	0.00333	0.17351	0.01645	0.21861
Methanol	0.23130	0.13043	0.13043	0.26985	–	0.24264	0.00004	0.20256
TAME	0.00010	0.13127	0.13127	0.00004	0.98292	0	0.00054	0.43312
n-Pentane	0.58330	0.66012	0.66012	0.71249	0.01362	0.04035	0.08502	0.00476
Pure methanol	–	–	1.0000	–	–			
Total flow (Kmol/h)	1353.00	1196.00	1411.00	1103.60	234.24	100.00	62.189	37.811
(M_{TAME}/M_{FEED}) (100%)			14.69%				16.37%	
N_{TOT}				45			40	
$N_{REACTIVE}$				22			40	
R				2.0			4.29	

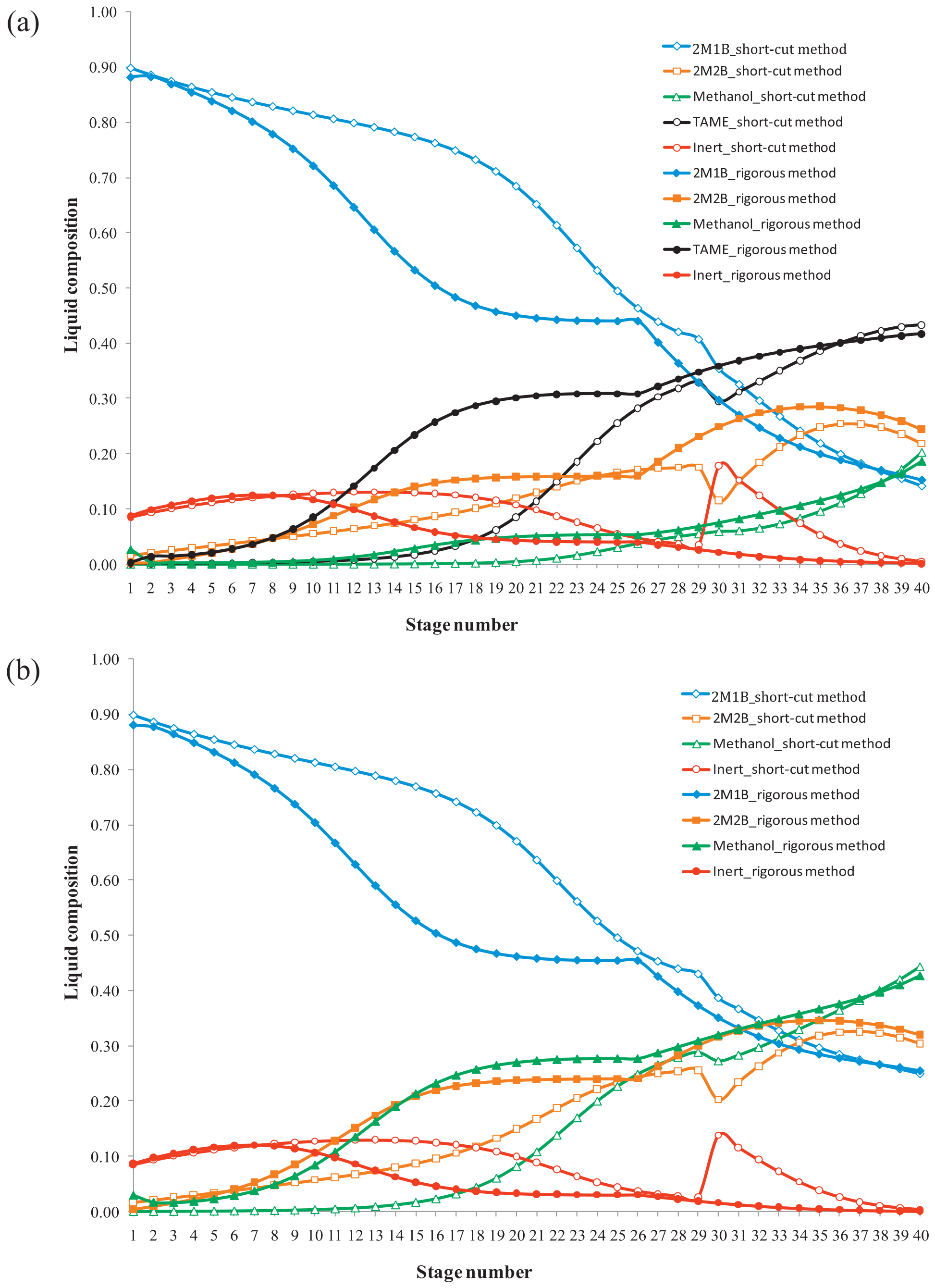


Fig. 8 – Composition profiles in the RD column for the TAME synthesis using saturated liquid as column feed: (a) mole fraction and (b) transformed mole fraction.

the most suitable design corresponds to that one with the least number of stages and lower R (in this case, the feed as saturated liquid). These conditions imply lower operating costs.

For illustration, Fig. 8 shows the composition profiles along of the column for TAME synthesis. In general, our results indicate that the key purities in the top and bottom of column obtained from AspenONE Aspen Plus® and those obtained from the proposed design methodology have good agreement. However, this agreement between both approaches may be less along of the column because of our method assumes constant molar flows along the RD column and only uses total and component mass balances. On the other hand, the rigorous model used in AspenONE Aspen Plus® considers that the moles of the reaction are not conserved due to the reaction heat. As a consequence, the vapor and liquid flowrates change along of the column and, to take account of these changes in RD model, mass and energy balances must be used for modeling each stage.

Finally, Table 3 shows the compositions and the principal operation parameters obtained from our short-cut method and their comparison with respect to the results obtained with the typical methodology from the literature and the data obtained from the industrial TAME production process (Subawalla and Fair, 1999; Baur and Krishna, 2002). The reliability of our design method can be illustrated via the comparison of the mass of TAME presents in the bottom stream obtained from the typical process and the result obtained from our design methodology (see Table 3). In general, there is a satisfactory agreement between the mass of TAME calculated by both modeling approaches (i.e., 14.69% for the typical process and 16.37% for the short-cut method). On the other hand, the purities obtained 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, results obtained using our approach are useful to obtain a quick pre-design that can be further optimized to reach the designer targets.

4. Conclusions

An extended short-cut method, related to an analytical approach based on a linear algebra theorem, for the design of multicomponent reactive distillation columns has been introduced. This method is easy to implement and provides a quick pre-design (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 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 operations profiles, our method optimizes the feed location by searching for the minimum difference in composition between any given tray and the feed point. From our results, it is clear that the design methodology proposed here provides a good agreement compared with the results obtained with commercial simulator AspenONE Aspen Plus®, principally for the target purities of our case of study (in this case, TAME) in the top o bottom of column. On the other hand, we have illustrated the effect of the feed thermal condition on the designs obtained. Analyzing these operating conditions, we can improve RD designs reducing the total number of stages and *R* because of 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 of study, the main product (TAME) cannot be obtained with high purity using distillation columns with only reactive stages. However, the purification target can be achieved with the addition of non-reactive 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 condition (i.e., saturated liquid, saturated vapor or a liquid–vapor mixture). It should be noted that although only a single chemical reaction example is presented, this design methodology is also applicable for systems containing a set of multiple chemical reactions.

Acknowledgements

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

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