

# A SHORT METHOD FOR THE DESIGN OF REACTIVE DISTILLATION COLUMN

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## ABSTRACT

In this study, a short method for the design of reactive distillation is presented. The method is based on distillation lines and tray-by-tray calculations, and a new strategy is suggested to locate the reflux ratio, the number of stages, and feed tray. The material balances are solved from the outside (top and bottom) to the inside of the distillation column (feed), to ensure that the product compositions are met. To reduce the numerical difficulties, the method is based on the application of reaction-invariant composition variables. The synthesis of MTBE with the presence of inert is used as case of study to show the effectiveness of the proposed method. Our strategy provides the number of theoretical stages, operating reflux ratio, and the feed tray location. The results obtained with our strategy show a significant agreement compared with those obtained with commercial simulator ASPEN PLUS®.

**Keywords:** reactive distillation; distillation lines maps; azeotropic points.

## 1. INTRODUCTION

Within the broad range of topics related to Reactive Distillation (RD), the complex design of these processes has received significant attention from many researchers due to the simultaneous occurrence of distillation and reaction, high thermodynamic non-ideality of the mixtures in question, and the formation of azeotropes. The implementation of RD is attractive for energy savings as well as equipment costs when the reactions show reasonable conversion and selectivity data at pressures and temperatures that are compatible with the distillation conditions (Taylor and Krishna, 2000).

Until now, some methods for the design of RD have been developed. For example, Barbosa and Doherty (1988) extended the boundary value method (BVM) for the design of 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 plates in each section of the column. The differential equations are solved from the outside to the inside of the column, finding the feed stage when the liquid compositions of both 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 (Van Dongen and Doherty, 1985). As consequence, in many cases, the composition of the feed tray is quite different from the feed composition. Another problem is finding the appropriate integration step to solve the differential equations

and a small integration step is usually recommended, but it rather depends on the system under study. This design method assumes constant molar flows, theoretical stages, and feed as saturated liquid. On the other hand, there are studies that apply graphical methods as the McCabe-Thiele or Ponchon-Savarit assuming equilibrium conditions, and design methods for reactive systems under kinetic control, which enable the analysis and design of RD process (Sanchez-Daza *et al.*, 2003). These methods are generally based on the concept of *element*, which has the main disadvantage that limit the number of systems that can be studied using this concept.

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 problems considered, the nonlinearity of the models caused by the presence of simultaneous chemical and physical equilibrium, and also by the type of variables involved in defining the problem, which are generally composition variables in molar units and extents of reaction (Malone and Doherty, 2000).

In this study, a short method for the design of RD is presented. The method is based on distillation lines, which constitute a more appropriate tool than residue curve lines for staged columns (Stichlmair and Fair, 1998). The proposed strategy avoids finding a suitable integration step with the use of residual curves. Our method is based on tray-by-tray calculations and a strategy is suggested to locate the reflux ratio and the feed tray location that minimizes the total number of stages. The material balances are solved from the outside (top and bottom) to the inside of the distillation column (feed), to ensure that the product compositions are met. 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. Using these transformed variables, the solution space is restricted to compositions that are already at chemical equilibrium and, as a consequence, the problem dimension is also reduced favoring the implementation of numerical strategies (Ung and Doherty, 1995). These advantages allow to study a variety of real and complex reactive systems because there are several combinations between the number of reactions ( $r$ ) and the number of components ( $c$ ) that can be analyzed in ternary diagrams in terms of transformed variables.

## **2. DESIGN OF REACTIVE DISTILLATION COLUMN**

For designing a distillation column, the operating minimum reflux ratio, the number of theoretical stages and feed stage should be calculated. These operating parameters can be determined using reactive distillation lines, which constitute a more appropriate tool than residue curve lines for staged columns (Stichlmair and Fair, 1998). The use of distillation lines allows the material balances to be written in algebraic form. The material balances are solved from the outside to the inside of the distillation column, to ensure that the product compositions are met. In this study, ideal stages and constant molar overflows are assumed.

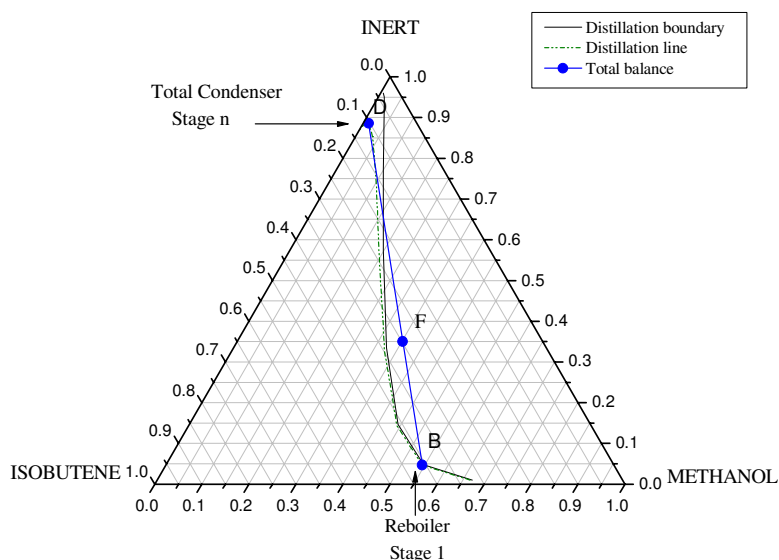
### *2.1 Calculation of Feasibility Zone*

The first step of the design procedure is check the feasibility of the split. The feasible zone for the bottom and top products for a given feed is delimited by the composition space, the distillation boundary, and the distillation line that contain the desired products. Fig. 1 illustrates how the feasible region can be identified in a ternary composition diagram. 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. In this figure, D-F-B line represents the overall mass balance of the column of RD in terms of transformed variables. The points D

and B refer to the desired products to obtain in the top and bottom of the column, respectively. The point F also represents the feed composition in terms of transformed variables. If the desired split is not feasible, a new feasible split can be easily specify using this type of diagram. Note that the transformed variables (Ung and Doherty, 1995) are defined as:

$$X_i = \frac{x_i - v_i N^{-1} x_{ref}}{1 - v_{TOT} N^{-1} x_{ref}} \quad i = 1, \dots, c - r \quad (1)$$

where  $X_i$  is the transformed composition of component  $i$ ,  $x_{ref}$  is the column vector of  $r$  reference component mole fractions,  $v_i$  is the row vector of stoichiometric number of component  $i$  for each reaction,  $v_i$  is a row vector where each element corresponds to reaction  $r$  and it is the sum of the stoichiometric number for all components that participate in reaction  $r$ , and  $N$  is a square matrix formed from the stoichiometric number of the reference components in the  $r$  reactions, respectively.



**Figure 1: Zone of feasibility products for a given feed F in the synthesis of MTBE; D denotes the distillate product, and B is the bottom product**

## 2.2 Design Method

The following equations represent the mass balance for a reactive column using transformed variables for the rectifying section (Eq. 2) and for the stripping section (Eq. 3):

$$X_{i,m} = \frac{R+1}{R} Y_{i,m-1} - \frac{1}{R} X_{i,D} \quad i = 1, \dots, c - r \quad (2)$$

$$X_{i,n+1} = \frac{S}{S+1} Y_{i,n} + \frac{1}{S+1} X_{i,B} \quad i = 1, \dots, c - r \quad (3)$$

where  $X_{i,j}$  is the transformed composition in the liquid phase of component  $i$  in step  $j$ ,  $Y_{i,j}$  is the transformed composition in the vapor phase of component  $i$  in step  $j$ ,  $R$  is the reflux ratio of liquid  $L$  that returns to the column with respect to distilled  $D$ ,  $S$  is the reflux ratio of vapor  $V$  that returns to the column with respect to 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 top, respectively.

The mass balance equations must be used with a thermodynamic model that relates the vapor–liquid equilibrium conditions. An analysis of the number of degrees of freedom for a reactive mixture of  $c$  component indicates that  $2c - 1$  variables must be specified (Barbosa and Doherty, 1998). For quaternary systems in molar fractions, this means that we must specify seven parameters. The way to specify these variables depends on the interest of the designer, so we can specify the operating pressure or temperature, the condenser or reboiler reflux ratio, and five transformed composition (between feed, top and bottom). For complementing the number of degrees of freedom, the summation constraints and mass balances can be used.

For example, one can specify the operation pressure, the reflux ratio ( $R$ ), two feed compositions ( $Z_1, Z_2$ ) and three product compositions ( $X_{1,D}, X_{2,D}, X_{1,B}$ ), then  $X_{2,B}$  can be calculated by material balances around the column using the following equation

$$X_{2,B} = Z_2 + (Z_2 - X_{2,D}) \left( \frac{S}{R+1} \right) \quad (4)$$

The reflux ratio of reboiler ( $S$ ) is a key variable and can be calculated using material balances around column and it is given by

$$S = (R + q) \left[ \frac{X_{1,B} - Z_1}{Z_1 - X_{1,D}} \right] + (q - 1) \quad (5)$$

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  $X_{3,D}$  and  $X_{3,B}$  are calculated by summation constraints

$$\sum_{i=1}^{c-r} X_{i,D} = 1 \quad (6)$$

$$\sum_{i=1}^{c-r} X_{i,B} = 1 \quad (7)$$

Eqs. 2 and 3 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 anywhere in the composition space is a necessary and sufficient condition to establish the feasibility of the split; therefore, this intersection should be checked (Castillo *et al.*, 1998). However, the intersection of the composition profiles does not necessarily provide a good

criterion for the feed tray, because it does not always locate the plate with the composition closest to that of the feed.

To determine the location of the feed stage, Gutierrez-Antonio *et al.* (2007) proposed a minimum difference criterion, in which a search is conducted for the tray with the minimum difference between the composition of each stage in the column and the feed composition. The search procedure for the minimum difference is performed for each section of the column, so that the number of stages in the stripping and the rectifying sections are obtained along with the location of the feed stage. The difference (i.e., distance) between the compositions is calculated using Eqs. 8 and 9, which are also defined using transformed variables and have been obtained by introducing small modifications of the models proposed by Gutierrez-Antonio *et al.* (2007), due to the reactive character of the model used in this study. So, we have

$$d_R = \sqrt{\sum_{i=1}^{c-r} (Z_i - X_{i,NR})^2} \quad (8)$$

$$d_S = \sqrt{\sum_{i=1}^{c-r} (Z_i - X_{i,NS})^2} \quad (9)$$

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 column, respectively.

The mass balance given by Eqs. 2 and 3 is calculated by minimizing Eqs. 8 and 9. It is convenient to indicate that the first equations are solved from the top to the rectifying zone and from the bottom to the stripping zone toward the center of the column, respectively. The operating minimum reflux ratio is calculated by trial and error until a pinch point for the operating profiles is detected. After determining the operating minimum reflux ratio, an operating reflux ratio can be fixed using a heuristic rule, or it can be optimized for some objective function, which can be defined in terms of energy saving or operation cost. The number of theoretical stages obtained involves a partial reboiler and considers the use of a total condenser.

### 2.2.1 Case of study: MTBE synthesis.

To show the effectiveness of the proposed method, the synthesis of MTBE in the presence of n-Butane (inert) from Isobutene and Methanol is analyzed (Sánchez-Daza *et al.*, 2003). The system pressure was 11 atm, and the Wilson and ideal gas models were used for determining the thermodynamic properties. The parameters of thermodynamic models were taken from Ung and Doherty (1995). In our analysis, the feed was assumed to be saturated liquid.

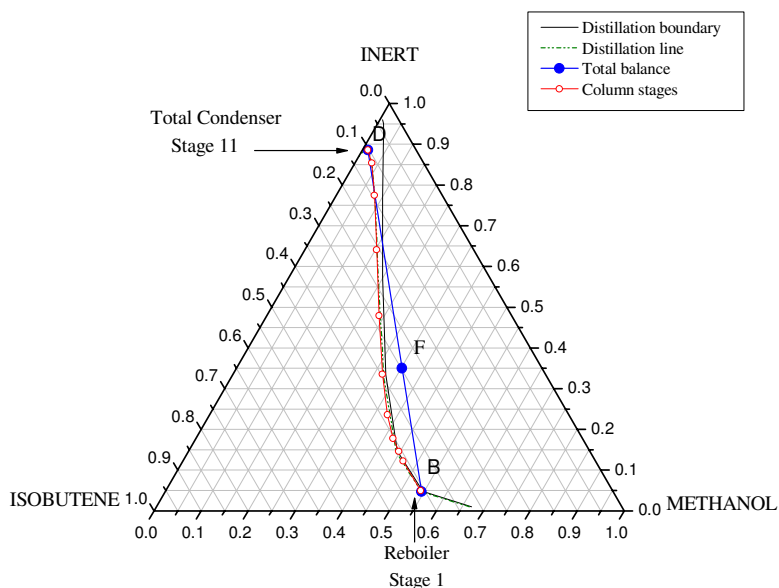
The feed composition and the top and bottom products that are required for the design are reported in Table 1. In this study, the reactive mixture shows only one distillation boundary. The purpose of separation is to obtain the maximum conversion of MTBE by the bottom of the column. Both the distillate point and the bottom point fall into feasible zone, and are

collinear with feed, as explained in the section above (see Fig. 2). After verifying the feasibility zone, the calculation of operation minimum reflux ratio is started.

**Table 1: Design specifications in transformed molar fractions and molar fractions of feed (F), the distillate product (D), and the bottom product (B).**

Component	$X_F$	$X_D$	$X_B$
Isobutene	0.29806	0.10192	0.40807
Methanol	0.35194	0.01212	0.54538
n-Butane	0.35000	0.88596	0.04655
MTBE			
Component	$X_F$	$X_D$	$X_B$
Isobutene	0.29806	0.09447	0.07650
Methanol	0.35194	0.00392	0.28630
n-Butane	0.35000	0.89331	0.07706
MTBE	0	0.00830	0.56014

To find  $R$ , a trial and error procedure was performed to find the value where the operating profiles intersect for the first time. The profiles of the rectifying zone (Eq. 2) and the stripping zone (Eq. 3) are solved together with the thermodynamic model that describes the physical and chemical equilibrium. After the search, a value of  $R = 3.5$  is found as shown in Fig. 2.



**Figure 2: Operating profiles for the synthesis of MTBE**

Our method provides an estimation of  $R$ ,  $S$ , the number of stages in each section of the column and feed tray when Eqs. 8 and 9 are minimized. The compositions obtained through the short method were compared with results obtained by a rigorous method (using ASPEN ONE simulator) to show the effectiveness of our strategy. To perform the simulation of this system using ASPEN ONE, it is only necessary to enter the four parameters obtained without any other restrictions. The results are reported in Table 2, where  $N_F$  is the feed tray and  $N_{TOT}$  is the total number of stages including reboiler and total condenser. In this case, our results indicate that the purity of MTBE obtained by both methods is very

similar. This purity is very low but it can be improved using additional physical stages, so, a hybrid model that combines reactive stages and nonreactive stages will be used for this purpose. Finally, the difference in compositions is primarily due to our short method only uses mass balances and assumes constant molar flows along the column.

**Table 2: Design specifications for the synthesis of MTBE**

	Proposed method		Aspen One	
$N_{TOT}$	11		11	
$N_F$	6		6	
$R$	3.5		3.5	
$S$	2.52396		2.52396	
Molar fractions of products				
	Top	Bottom	Top	Bottom
Isobutene	0.09447	0.07650	0.15501	0.06429
Methanol	0.00392	0.28630	0.00903	0.39010
n-Butane	0.89331	0.07706	0.80393	0.00568
MTBE	0.00830	<b>0.56014</b>	0.03203	<b>0.53993</b>

### 3. CONCLUSIONS

A short method for the design of reactive distillation columns has been presented. The method is easy to implement and provides a quick pre-design (providing operating parameters as a starting point) for a design rigorous method. This avoids that the designer begins its rigorous design without information and employing more time in trial and error calculations to find the main operating parameters to provide the expected results. The method uses distillation lines with algebraic 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. As opposed to the concept of the intersection of the two operations profiles, our design method optimizes the feed location by searching for the minimum difference in composition between any given tray and the feed point. Due to a highly non-ideal thermodynamic behavior, the MTBE can not 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. Our design method is useful for analyzing reactive systems where  $c - r = 3$ , and for a feed as a saturated vapor or a liquid – vapor mixture.

### ACKNOWLEDGEMENTS

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

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#### **Brief Biography of the Presenter**

Adrián Bonilla-Petriciolet is Professor in the Department of Chemical Engineering of Instituto Tecnológico de Aguascalientes, México. His research interests are applied thermodynamics, process design and optimization. He has published several papers in international journals and presented a number of papers in conferences.