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PRELIMINARY DESIGN OF REACTIVE DISTILLATION COLUMNS

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A procedure that combines feasibility analysis, synthesis and design of reactive distillation columns is introduced. The main interest of this methodology lies on a progressive introduction of the process complexity. From minimal information concerning the physicochemical properties of the system, three steps lead to the design of the unit and the specification of its operating conditions. Most of the methodology exploits and enriches approaches found in the literature. Each step is described and our contribution is underlined. Its application is currently limited to equilibrium reactive systems where degree of freedom is equal to 2 or less than 2. This methodology which provides a reliable initialization point for the optimization of the process has been applied with success to different synthesis. The production of methyl-tert-butyl-ether (MTBE) and methyl acetate are presented as examples.

Keywords: reactive distillation; process synthesis; feasibility analysis; process design.

INTRODUCTION

In the current context of cost reduction, environmental protection combined with a significant increase of computational power, chemical engineering equipments based on the integration of several functions in a single apparatus are more and more studied (Stankiewicz and Moulijn, 2000). In that field, multifunctional reactors can be defined as reactors that also perform other operations, like heat exchange or separation, in order to enhance the chemical conversion. Reactive distillation process (RD) is certainly one of the most significant examples. Combining reaction and separation in a single apparatus presents numerous advantages from a reaction point of view—improved conversion and selectivity, reduced catalyst requirement, heat integration benefits and avoidance of azeotropes—and can be applied in various areas of chemical engineering: esterification reactions (Bessling *et al.*, 1997), hydrolysis of esters (Giessler *et al.*, 2001), etherification (Sundmacher *et al.*, 1999) and alkylation reactions (Shoemaker and Jones, 1987). Reaction can also be used to improve distillation so that reactive columns become useful to consider separations difficult to operate through conventional distillations: azeotropic systems or close boiling points components (Stein *et al.*, 2000).

However, the lack of systematical and universal design tools makes the industrial community hesitate on firmly

adopting this new kind of process. The interaction between reaction and phase equilibrium in the same device makes the design and control of these processes much more difficult than it is for conventional reactors or traditional distillation processes. Nowadays, industrial processes of reactive distillation result more from a long experience acquired for years than from the existence of systematic methods to design these processes (Harmsen and Chewter, 1999).

The general principle of the approach usually adopted for the design of complex processes is schematized in Figure 1. Prerequisite data are a thermodynamic model to describe the phase equilibrium, the equilibrium constant of the chemical reaction and specifications concerning the purity of the products, the recovery ratio or the yield of the reaction. The approach is divided into four steps as enounced by Huss *et al.* (1999) and Tuchlenski *et al.* (2000):

- First, the feasibility analysis aims at discriminating the thermodynamically attainable specifications. A set of distillate and residue compositions complying with the purity, the recovery ratio or the yield specifications is determined. If the feasibility is not achieved, the process objectives are to be corrected.
- Second, the synthesis, based on a more rigorous analysis of the phenomena, confirms (or waives) the results obtained through the first step. A column configuration able to achieve the goals formerly specified is also determined: number of stages, localization and size of the reactive zone, number and location of the feed stages.
- Third, the design step enables to determine the operating parameters of the process (reflux ratio, heat duty, etc.).

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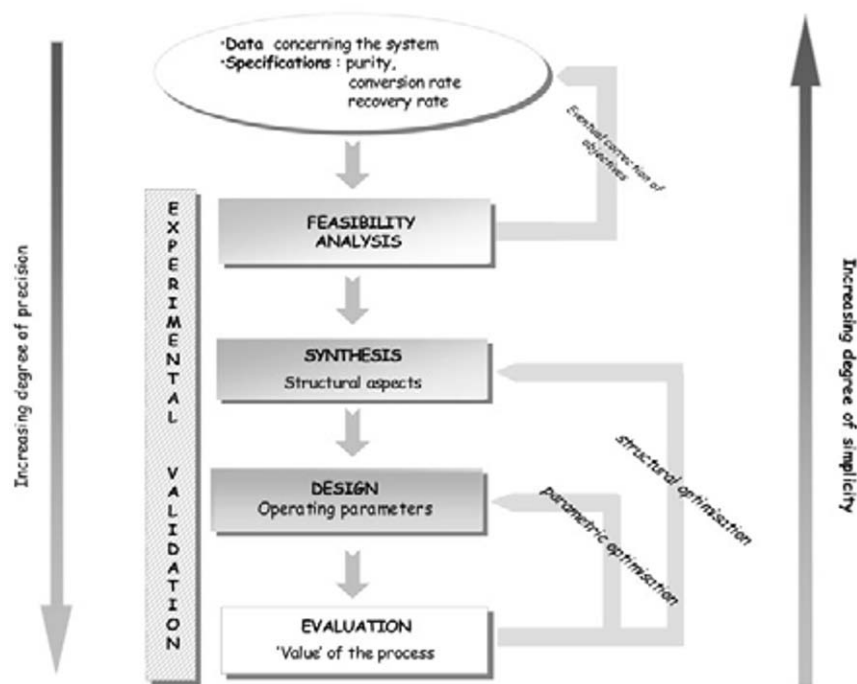


Figure 1. General principle of the design methodology.

At the end of this third step, a configuration and a set of parameters relevant with the specifications are available.

- The last step evaluates the process from an economical, energetical and environmental point of view. A sensitivity analysis to various parameters of the process and a process optimization are performed.

As shown in Figure 1, each of these steps should be coupled to an experimental validation.

During the past decades, many studies have been published to provide methods for the feasibility analysis and the design of RD processes. The first family of approaches relies on the extension of methods already existing for nonreactive distillation processes. The computation and the analysis of reactive residue curve maps exploit the reactive composition concept to analyse the coupling between reaction and vapour liquid equilibrium (Barbosa and Doherty, 1987b). The McCabe and Thiele and the Ponchon Savarit methods have also been adapted for reactive distillation processes but remain useful for binary systems only (Lee *et al.*, 2000a, b). Conceptual approaches rely on mass balances and sometimes also on heat balance to compute the composition and temperature profile inside the column and to evaluate the required configuration of the process—number of stages, location of feed (Melles *et al.*, 2000; Okasinski and Doherty, 1998). Barbosa and Doherty (1987c, d) developed such a procedure to design entirely reactive distillation columns for systems involving instantaneous chemical equilibria. Espinosa *et al.* (1996) extended this approach to hybrid processes with a pure stripping section. Okasinski and Doherty (1998) and Buzad and Doherty (1994) applied the same concept to study the influence of kinetics on the configuration of the process. Mahajani and Kolah (1996) introduced a model based upon the film theory to take into account the axial

dispersion that may occur in packed columns. Finally, methods based upon MINLP optimization were presented by Ciric and Gu (1994) and Gumus and Ciric (1997).

Some approaches consist in an extension of existing methods for the design of reactor like the attainable region method proposed by Glasser *et al.* (1987).

Specific approaches were developed for RD processes: the static analysis introduced by Giessler *et al.* (1999a, 1999b, 2001) and the phenomena based analysis developed by Hauan *et al.* (2000). As reported in Table 1, these different approaches only address one or two out of the four steps listed in Figure 1. Feasibility analysis relies on very large assumptions and need to be completed by a more rigorous approach. The synthesis and design steps require accurate data like attainable product composition to be exploited. Until 1999—*PREDICTOR* European project (Kenig *et al.*, 1999)—no systematic and consistent procedure which combines feasibility analysis, synthesis and design of reactive distillation column has been proposed. The methodology presented in this article contributes to fill this lack. Considering the complexity of the problem, it relies on a graphical analysis which limits its application to reactive systems with a degree of freedom less than 3. This sequential and hierarchical approach is based on some methods encountered in the literature. It enriches them in order to ensure a consistent linking between the consecutive steps. It relies on a progressive introduction of the process complexity: starting from a minimal set of information concerning the physico-chemical properties of the system and the reaction, a reactive column can be designed in three successive steps (feasibility analysis, synthesis and design): number of theoretical stages, location and length of the reactive zone, location and number of feed plates, reflux ratio, heat duties.

First, a detailed presentation of the implemented procedure is exposed. For each stage the key concepts are

Table 1. Inventory of existing approaches for the feasibility analysis, the synthesis or the design of reactive distillation processes.

Approach	Authors	Advantages	Drawbacks	Feasibility analysis	Synthesis	Design
Computation and analysis of reactive residue curve maps	Ung and Doherty, 1995 Espinosa <i>et al.</i> , 1995	Coupling between reaction and LV equilibrium is considered	Can not analyse the feasibility of hybrid processes	✓		
Phenomena based approach	Hauan <i>et al.</i> , 2000	Evaluates the extent of reaction	Complicated graphical analysis	✓		
Static analysis	Giessler <i>et al.</i> , 1999, 2000	*Qualitative analysis *Provides indications concerning the configuration of the process	Very strict assumptions	✓		
Attainable regions	Glasser <i>et al.</i> , 1987	Takes the mixing effect into account	Complicated graphical analysis	✓		
MacCabe Thiele Ponchon Savarit	Lee <i>et al.</i> , 2000	*Fast analysis *Analogy with nonreactive systems	Restricted application field		✓	✓
Conceptual approaches	Barbosa and Doherty, 1987 Espinosa <i>et al.</i> , 1996 Buzad and Doherty, 1998 Okasinski and Doherty, 1994 Mahajani and Kolah, 1996 Melles <i>et al.</i> , 2000	*Easy analysis *Can take a lot a phenomena into account (single feed plate or double feed plate, kinetically controlled or equilibrium reaction, heat effects or not)	Graphical analysis which restricts its application field to system whose degree of freedom is less than 3		✓	✓
Optimization approaches	Ciric and Gu, 1994 Gumus and Ciric, 1997	Very wide application field *handles multi-reaction systems	*Need for complicated numerical tools *Difficult initialization		✓	✓

briefly recalled and our contribution is developed. Finally, the potential of the methodology is illustrated through two applications.

A SEQUENTIAL AND HIERARCHICAL PROCEDURE FOR THE DESIGN OF RD PROCESSES

This paper focuses on the preliminary design of a reactive distillation process. A systematic procedure is developed which enables to determine the attainable compositions of products and the configuration and operating parameters of the column that can achieve these products. This approach is called 'Preliminary design' because it provides elements necessary to analyse the feasibility and the opportunity to adopt reactive distillation preferentially to a more classical process and does not intend to optimize the process. For that reason, this paper mainly deals with the three first steps of the design procedure but unlike Huss *et al.* (1999) and Tuchlenski *et al.* (2000) who mostly stayed at a conceptual level, our methodology provides a practical implementation of all three steps. The final results can then be considered as an initial value for the fourth step of the design procedure which is an optimization step, not developed in this paper. Figure 2 presents the procedure in a more detailed flow chart and highlights the complementarities of the various approaches.

Construction and Analysis of Reactive Residue Curve Maps (rRCM)

When considering complex processes and highly non ideal systems, it is necessary to identify the

thermodynamical limits of the process as soon as possible. The study of the reactive residue curve map gives a first idea of the feasibility and interest of investigating reactive distillation. This first step permits to localize the distillation boundaries of the system and to estimate the compositions of feasible pairs of products.

The software we developed for the preliminary step of feasibility analysis exploits the work initiated by Meyer *et al.* (1999). It generates entire reactive residue curves maps for reactive systems with a freedom degree less or equal to 2 and automatically displays the resulting distillation boundaries.

Concerning the construction and analysis of reactive residue curve maps, the new contributions presented in this paper mainly rely on the development of systematic methods to calculate the 'direct' and 'opposite' reactive residue curve maps and to generate the distillation boundaries as explained further.

Direct and opposite reactive residue curves

A reactive residue curve is defined by the locus of the liquid compositions remaining from a simple batch reactive distillation process. A reactive residue curve map is obtained through the simulation of the reactive distillation process for various initial liquid compositions. As for non-reactive residue curve maps, the reactive residue curve maps computed for instantaneous equilibrium reactions do not depend on the heat policy. The initial liquid holdup and the heat duty only influence the rate of the phenomenon but not the pathway followed by the liquid compositions.

Therefore, the dynamic model used to generate the rRCM is written using nondimensional variables. It is

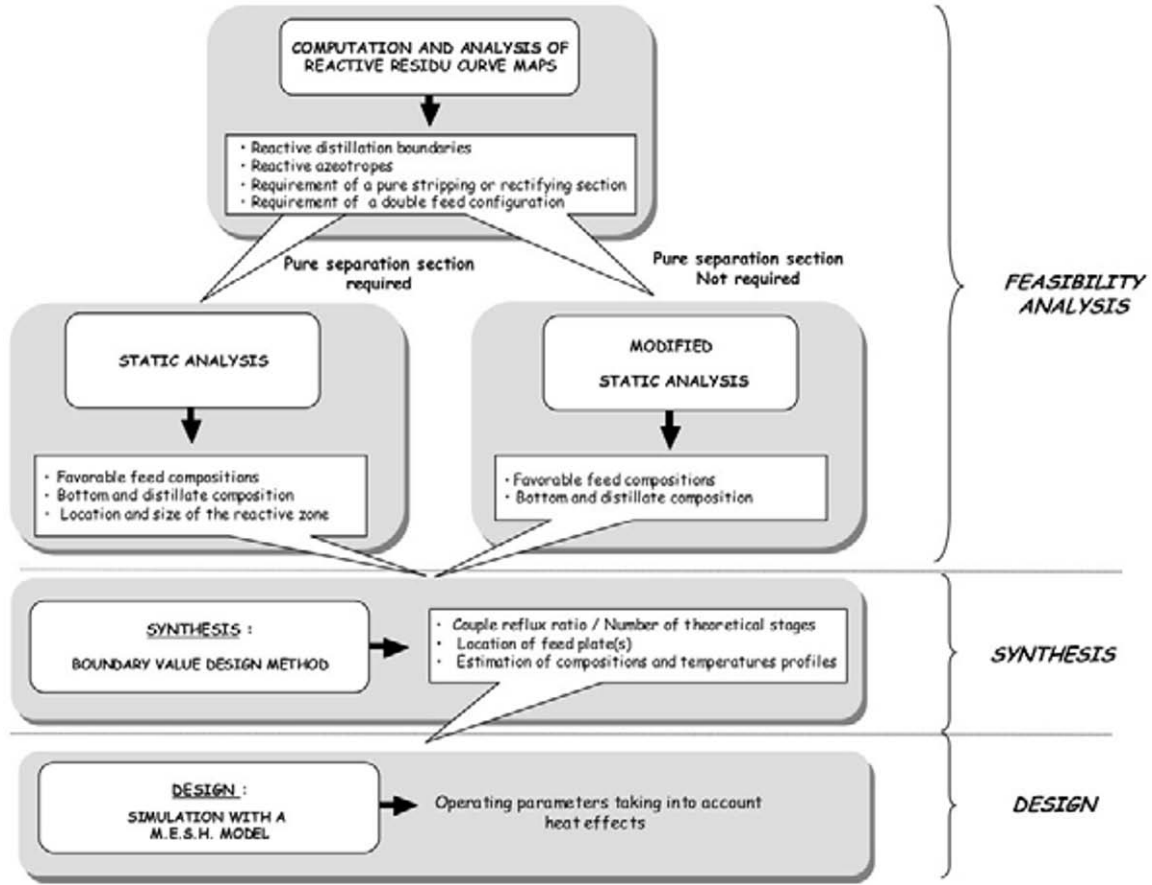


Figure 2. Constitutive approaches of the design methodology.

developed hereafter for systems consisting of N_c components and involving N_r reactions.

Component mass balance

$$\frac{dx_i}{d\tau} = (x_i - y_i) + \sum_{r=1}^{N_{re}} (v_{i,r} - v_{t,r} \cdot x_i) \cdot \psi_r \quad i = 1, \dots, N_c - 1 \quad (1)$$

x summation equation

$$\sum_{i=1}^{N_c} x_i - 1 = 0 \quad (2)$$

y summation equation

$$\sum_{i=1}^{N_c} y_i - 1 = 0 \quad (3)$$

Physical equilibrium equation

$$y_i - K_i \cdot x_i = 0 \quad i = 1, \dots, N_c \quad (4)$$

Chemical equilibrium equation

$$K_{eq,r} - \prod_{i=1}^{N_c} (a_i)^{v_{i,r}} = 0 \quad i = 1, \dots, N_c; \quad r = 1, \dots, N_{re} \quad (5)$$

VL equilibrium constant model

$$K_i - mK_i(T, P, x, y) = 0 \quad i = 1, \dots, N_c \quad (6)$$

Chemical equilibrium constant model

$$K_{eq,r} - mK_{eq,r}(T) = 0 \quad r = 1, \dots, N_{re} \quad (7)$$

Activity model

$$a_i - ma_i(T, P, x) = 0 \quad i = 1, \dots, N_c \quad (8)$$

Here, $d\tau$ is a nondimensional variable and is expressed as follows

$$d\tau = \frac{V}{U} \cdot dt \quad (9)$$

ψ_r is also a nondimensional variable defined by

$$\psi_r = \frac{\chi_r}{V} \quad (10)$$

where χ_r is the extent of the reaction r .

At fixed pressure, this set of equations consists in a $4N_c + 1 + N_{re}$ differential algebraic equations system (DAE) for which the $4N_c + 1 + N_{re}$ unknowns are: $(x_i)_{i=1,N_c}$, $(y_i)_{i=1,N_c}$, T , $(K_i)_{i=1,N_c}$, $(K_{eq,r})_{r=1,N_{re}}$, $(\psi_r)_{r=1,N_{re}}$, $(a_i)_{i=1,N_c}$.

The resolution of this DAE system for positive values of τ generates just a part of the reactive residue curve: the so-called ‘direct reactive residue curve’. In accordance with the physical phenomenon, this residue curve moves towards the stable node (i.e., the least volatile component) and the integration of the initial DAE system does not enable to identify the unstable nodes (i.e., the more volatile component). To generate a residue curve moving towards an unstable node (‘opposite reactive residue curve’), it is necessary to integrate the same system for negative values of t from $-\infty$ to 0 (Doherty and Perkins, 1978). To preserve a positive independent variable σ , the variable $\tau = -\sigma$ is introduced. Equations (1) become

$$\frac{dx_i}{d\sigma} = (y_i - x_i) - \sum_{r=1}^{N_{re}} (v_{i,r} - v_{i,r} \cdot x_i) \cdot \psi^r \quad (11)$$

all other equations remaining the same.

The DAE system is solved with DISCO, an in house index one and two DAE solver based on the Gear method (Sargousse, 1999).

The residue curve map can be plotted in the composition space. But for systems with a degree of freedom equal to 2, the analysis can be facilitated if the residue curve map is plotted in the reactive composition space according to the formalism developed by Barbosa and Doherty (1987a). When the degree of freedom exceeds 2 the graphical analysis becomes difficult, even impossible.

Analysis of the singular points

First of all, the singular points of the reactive system must be listed, located and characterized (stable nodes, unstable nodes, saddle points). They can be:

- a pure component;
- a nonreactive azeotrope: all the nonreactive azeotrope involving two components that do not react remain singular points. But, some nonreactive azeotrope involving two species that can react may disappear from the residue curve map, thanks to the coupling with the reaction;
- a reactive azeotrope: it is a consequence of the coupling between reaction and separation. A reactive azeotrope appears when the effect of the reaction is completely cleared by the separation.

Finally, for reactive systems, other noticeable points must also be investigated: the reactive pseudo azeotrope. This point nearly behaves like a reactive azeotrope but although the residue curves are heavily curved toward it, they do not stop and move toward a stable node. It was so called pseudo reactive azeotrope by Ung and Doherty (1995a, b).

These singular points give birth to distillation boundaries that must be determined to study the feasibility of the process.

Computation of distillation boundaries

Inventory of distillation regions: The generation of the reactive residue curves is carried out for several initial points, uniformly distributed. First, the stable SN_i and unstable UN_j nodes are listed: they are the endpoints of the residue curves. As a distillation region is characterized by a single couple (unstable node, stable node) an identification number is assigned to it as follows:

$$Id = 10 \cdot i + j \quad (12)$$

i and j , respectively representing the identification numbers of the stable and unstable nodes.

As an academic example, the system represented on Figure 3 is considered. It consists in four components (R_1 , R_2 , P and I) involved in one chemical equilibrium ($R_1 + R_2 \rightleftharpoons P$). Figure 3 represent the reactive residue curve maps in the reactive composition space. For that reason, no vertex corresponds to the component P because P can not exist alone in an equilibrium mixture. Figure 3 stresses two stable nodes (SN), two unstable nodes (UN) and three saddle points, defining four distillation regions listed in Table 2.

Computation of boundary distillation using dichotomy: Once the distillation regions have been indexed, the distillation boundaries are computed by dichotomy, assuming that it is a residue curve. A distillation boundary delimits two distinct distillation regions with a common stable node or unstable node. In our case, this corresponds to the equality of one of the constitutive figure of the identification number Id .

The dichotomy illustrated on Figure 4 runs as follows: two initial points Q_0 and P_0 are chosen on reactive residue curves with a common stable node (SN_2) but different unstable nodes (UN_1 for P_0 and UN_2 for Q_0). For P_1 , chosen as the middle of segment $[Q_0P_0]$, the residue curve is computed. If its unstable node is UN_1 (resp. UN_2), then P_1 belongs to the same distillation region as P_0 (resp. Q_0), that is region 21 (resp. region 22). Then P_0 is replaced by P_1 and the dichotomy is reiterated until the distance between two current points becomes as small as possible. The last plotted reactive residue curve—for which the distance between points Q_n and P_n is less than

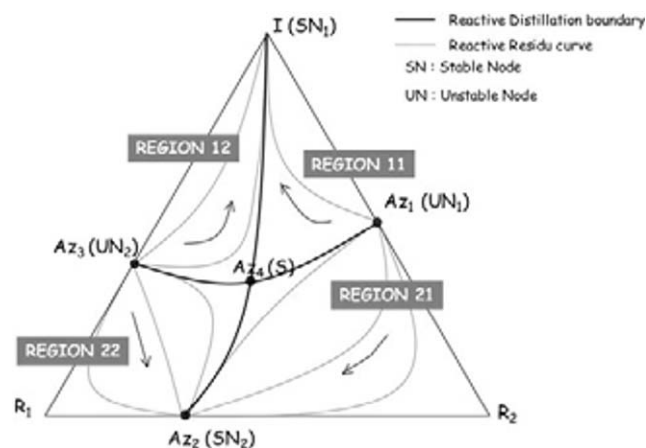


Figure 3. Example of distillation regions and boundary lines for a reactive system involving.

Table 2. Inventory of reactive distillation regions for the theoretical quaternary system (R_1, R_2, P, I) involving one equilibrium reaction $R_1 + R_2 \rightleftharpoons P$.

Region	Stable node	Unstable node
11	SN ₁ (I)	UN ₁ (Az ₁)
12	SN ₁ (I)	UN ₂ (Az ₃)
21	SN ₂ (Az ₂)	UN ₁ (Az ₁)
22	SN ₂ (Az ₂)	UN ₂ (Az ₃)

a fixed criterion—is then supposed to be the reactive distillation boundary.

Design rules from the reactive residue curve maps

Two rules which were enounced by Bessling *et al.* (1997) for equilibrium reactive systems can be exploited to analyse the residue curve maps. The first one concerns the requirement of a second feed stage.

Rule no. 1a:

Reactive distillation is a feasible and probably an economic operation if both products are connected by a reactive distillation curve, the products are nodes in a reactive distillation curve diagram and the boiling point difference between the products is large. If one or both products are saddles, the concentration profile can be shifted in the direction of the saddle by using a column with two feed stages.

The second rule is related to the requirement of nonreactive plates.

Rule no. 1b:

If it is necessary to separate a product that can not exist alone in an equilibrium mixture, a section with non reactive distillation trays must be added.

The reactive residue curve map is restricted to the feasibility analysis of an entirely reactive distillation column. But it may sometimes be necessary to introduce nonreactive stages into the column. The feasibility of hybrid columns consisting in nonreactive and reactive sections can be analysed with static analysis as seen in the following section.

Static Analysis

The static analysis is exploited to provide a complete set of attainable products complying with the yield of reaction, the purity or the recovery ratio specifications. The static analysis approach requires the thermodynamic model representing the system, the chemical equilibrium model, the stoichiometry of the reaction and the operating pressure.

The assumptions drawn are:

- only one reversible equilibrium reaction is considered;
- the column is operated under infinite separation efficiency (infinite number of stages and infinite liquid and vapor flow rates);
- the column is operated at steady state and the liquid holdup or the catalyst quantity is large enough to reach the equilibrium on each stage.

From these assumptions, one can say that the static analysis can also be considered as an infinite-infinite analysis. As demonstrated by Giessler *et al.* (1998), considering infinite flow rates enables to neglect the composition change due to the reaction on each tray and the reactive distillation column can then be considered as a combination of two successive steps:

- A reaction step during which the feed is converted into a 'pseudo-initial mixture' (composition x^*). Contrary to a conventional process, here, the coupling of reaction and separation enables to exceed the equilibrium limit.
- A separation step in which, the resulting mixture is separated by a nonreactive distillation column. Thanks to the assumption of infinite flow rate, the composition profiles in this column correspond to the traditional distillation lines introduced by Stichlmair (1991) and largely studied by Widagdo and Seider (1996).

The static analysis (Giessler *et al.*, 1998, 1999a, b, 2001) is particularly interesting to study the feasibility of the hybrid process. If pure separation sections are not required, a modified static analysis (*mSA*) has been developed. It consists in the resolution of a set of mass balance and specification equations.

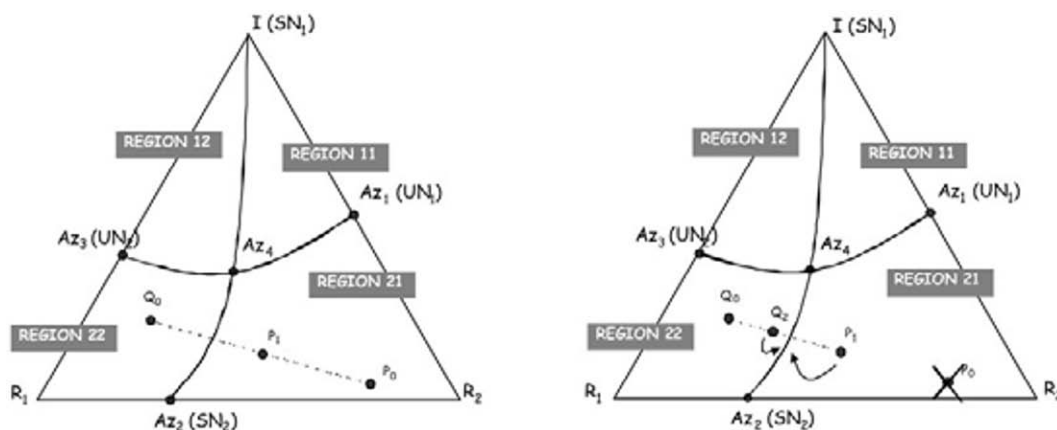


Figure 4. Algorithm for the computation of distillation boundaries—system involving one reaction $R_1 + R_2 \rightleftharpoons P$ with an inert I—reactive composition space.

The specifications concerning the yield of the reaction, the purity or the recovery ratio of products are inherited from the *rRCM* analysis.

Case of an entirely reactive distillation column: modified static analysis (mSA)

If a pure stripping or rectifying section is not required, the modified static analysis aims at determining the attainable products compositions complying with purity and recovery ratio specifications.

It is assumed that the RD process can be decomposed into two successive steps: a reaction step and a separation step. The reaction step is characterized by the yield of the chemical reaction and the separation step is characterized by the recovery ratio and the purity of the components.

Mass balance in the reaction zone: The total molar flow rate F^* is defined as follows:

$$F^* = F + \nu_t \cdot \chi = F \cdot \left[1 - \frac{\nu_t}{\nu_{\text{ref}}} \tau_r \cdot x_{\text{ref},F} \right] \quad (13)$$

$x_{\text{ref},F}$ is the feed composition of the reactant in default chosen as a reference to define the yield.

The molar flow rate of each component i can be expressed in the following way:

$$F_i^* = F_i^* \cdot x_i^* = F \cdot \left[x_{i,F} + \frac{\nu_i}{\nu_{\text{ref}}} \cdot \tau_r \cdot x_{\text{ref},F} \right] \quad (14)$$

By fixing the value of the yield of the chemical reaction, the pseudo initial mixture is exactly determined.

Mass balances in the separation zone:

Global mass balance

$$F^* = D + B \quad (15)$$

Component mass balances

$$F^* \cdot x_{i,F^*} = D \cdot x_{i,D} + B x_{i,B} \quad i = 1, \dots, N_c - 1 \quad (16)$$

As the column is totally reactive, the bottom and distillate products must satisfy the chemical equilibrium constraints and are saturated liquids. For these products, the following equations are written:

Chemical equilibrium

$$\left\{ \begin{array}{l} K_{\text{eq},B}(T) = \prod_{i=1}^{N_c} (a_{i,B})^{\nu_i} \\ a_{i,B} - m a_{i,B}(T_B, P, x_B) = 0 \quad i = 1, \dots, N_c \end{array} \right. \quad (17a) \quad (18a)$$

$$\left\{ \begin{array}{l} K_{\text{eq},D}(T) = \prod_{i=1}^{N_c} (a_{i,D})^{\nu_i} \\ a_{i,D} - m a_{i,D}(T_D, P, x_D) = 0 \quad i = 1, \dots, N_c \end{array} \right. \quad (17b) \quad (18b)$$

Liquid–vapor equilibrium

$$\left\{ \begin{array}{l} y_{i,B} = K_{i,B} \cdot x_{i,B} \quad i = 1, \dots, N_c \end{array} \right. \quad (19a)$$

$$\left\{ \begin{array}{l} k_{i,B} - m K_{i,B}(T_B, P, x_B, y_B) = 0 \quad i = 1, \dots, N_c \end{array} \right. \quad (20a)$$

$$\left\{ \begin{array}{l} y_{i,D} = K_{i,D} \cdot x_{i,D} \quad i = 1, \dots, N_c \end{array} \right. \quad (19b)$$

$$\left\{ \begin{array}{l} K_{i,D} - m K_{i,D}(T_D, P, x_D, y_D) = 0 \quad i = 1, \dots, N_c \end{array} \right. \quad (20b)$$

Summation

$$\sum_{i=1}^{N_c} y_{i,B} = 1 \quad \text{and} \quad \sum_{i=1}^{N_c} x_{i,B} = 1 \quad (21a)$$

$$\sum_{i=1}^{N_c} y_{i,D} = 1 \quad \text{and} \quad \sum_{i=1}^{N_c} x_{i,D} = 1 \quad (21b)$$

Bottom and distillate recovery ratios

$$\tau_{i,B} = \frac{B \cdot x_{i,B}}{B \cdot x_{i,B} + D \cdot x_{i,D}} \quad \text{or} \quad (22)$$

$$\tau_{i,D} = \frac{D \cdot x_{i,D}}{B \cdot x_{i,B} + D \cdot x_{i,D}}$$

We obtain a system consisting of $7N_c + 7$ equations involving $8N_c + 6$ unknown variables ($x_D, x_B, y_D, y_B, T_D, T_B, B, D, P, \tau_{i,B}$ (or $\tau_{i,D}$) K_D, K_B, a_D and a_B). Assuming that the process is operated under a given pressure, $N_c - 2$ variables must be specified to perfectly define the outputs. The degree of freedom is saturated by fixing $N_c - 2$ variables among the recovery ratio and the purity of the components of the system.

Case of a hybrid column

This part mainly relies on the work of Giessler *et al.* (1998), but some precisions are introduced here to make the results consistent with a further design step.

This analysis enables to get the maximum conversion yield, the distillate and bottom composition and flowrates of the products for each studied feed composition.

The procedure, described below is illustrated on Figure 5 on a three components system involving one reaction,

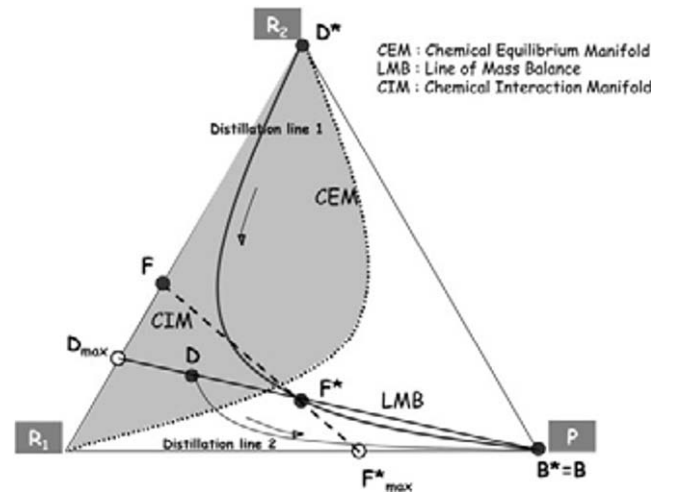


Figure 5. Characteristic points and lines in static analysis—ternary system involving one reaction $R_1 + R_2 \rightleftharpoons P$ —real composition space.

$R_1 + R_2 \Leftrightarrow P$ where the product P is assumed to be the less volatile compound.

For a given feed composition x_F (point F on Figure 5), the SA can be divided into nine steps:

- (1) Initialize the reaction extent ξ to its maximal value that is: $\xi = \xi_{\max} = 100\%$.
- (2) Compute the pseudo-initial composition x^* by mass balance on the reactor (point F^*). x^* lies on the *chemical interaction manifold* (CIM) which represents the change in mixture concentration resulting from the reaction. Sometimes, this line is also called *Stoichiometric Line* (Frey and Stichlmair, 1999). It starts at the point corresponding to no conversion and ends at an entire conversion (point F^*_{\max} on Figure 5).
- (3) Compute the distillation line going through point F^* and determines its stable and unstable nodes (points B^* and D^* and distillation line no. 1).
- (4) In the static analysis, one of the product composition must be fixed in advance. Two possibilities are taken into account: for the direct separation, the lightest product attainable from the pseudo-initial mixture is fixed as the distillate product (point D^*). Then, give the distillate composition x_D . On the other hand, in the indirect regime, the heaviest product is fixed as the bottom product (point B^*) and it is necessary to give the bottom composition x_B . In a first approach, aimed at selecting the most favourable feed proportions, these compositions can be set to the stable or unstable node composition (point B^*). Then, the calculation can be made again for a specified distillate or bottom composition different from the stable or unstable node composition.
- (5) For a direct separation, initialize the ratio $K_D = D/B$ value to its maximal value ($K_{D\max}$). For an indirect separation, initialize the ratio $K_I = B/D$ value to its maximal value ($K_{I\max}$). These maximal values depend on the feed and product specified composition. They can be calculated as:

$$\begin{cases} K_{D\max} = \text{Max}_{K_D, x_B} (K_D) \\ 0 \leq x_B = (K_D + 1) \cdot x_{i,F^*} - K_D x_{i,D^*} \leq 1 \quad i = 1, N_c \\ K_{I\max} = \text{Max}_{K_I, x_D} (K_I) \\ 0 \leq x_D = (K_I + 1) \cdot x_{i,F^*} - K_I \cdot x_{i,B^*} \leq 1 \quad i = 1, N_c \end{cases}$$

- (6) For a direct separation, compute the corresponding bottom, x_B , (respectively distillate, x_D for an indirect separation) composition by mass balance and plot the distillation line going through the calculated point (point D).
- (7) If the distillate and the bottom product do not belong to the same distillation line, than we can conclude that they do not belong to the same distillation region. That means that these products cannot be obtained in the same reactive distillation column. In that case, decrease the K_D (respectively K_I) ratio and go back to step 5. On Figure 5 this amounts to move point D closer to F^* (respectively moving point B closer to F^*) If no recovery ratio value is feasible, decrease the reaction extent and go back to step 2.

- (8) If the distillation line does not intersect the *chemical equilibrium manifold* (CEM)—grayed region on Figure 5—that is no point on the distillation verifies the condition $K(T) > \prod_{i=1}^{N_c} (a_i)^{v_i}$, decrease the reaction extent and go back to step 2. If no reaction extent respecting the former condition can be found, the specified feed composition x^F is not feasible, choose another one and go back to step 1.
- (9) If both K_D (K_I) and ξ are feasible, compute a new set of feed composition and go back to step 1.

Consistent feasible specifications: Because reaction and separation are studied separately, the SA may lead to results that are not consistent for the design. In fact, if the calculated distillate (or a bottom) lies in the reaction region a reactive rectifying (stripping) section is required. As long as an instantaneous chemical equilibrium is assumed, the distillate (or bottom) composition obtained in a reactive section must satisfy the chemical equilibrium and then must lie on the CEM. To obtain consistent results, the predicted distillate and bottom compositions can be corrected. The corrected distillate results from the change in mixture concentration due to the reaction. Then the point D^{corr} lies in the intersection between the CIM passing through the former point D and the CEM as illustrated on Figure 6. This correction remains small as long as the objective is to determine specifications which maximize the conversion of the reaction as well as the recovery ratio and the purity of the product P . In this case, the reactant should be nearly completely converted and the expected product D should be nearly deprived of reactant.

Specification selection—number of stages estimation: The SA iterative procedure generates a table in which the maximum conversion yield, the distillate and bottom composition and the ratio K_D (K_I) is given for each feed composition studied.

As it takes into account both the reaction and the separation performance, the mathematical product ‘recovery ratio ($\tau_{i,D}$ or $\tau_{i,B}$) \times reaction yield (τ_r)’—called ‘performance indicator’ (PI)—should be analysed to evaluate the feed composition that leads to the best performances of the reactive distillation.

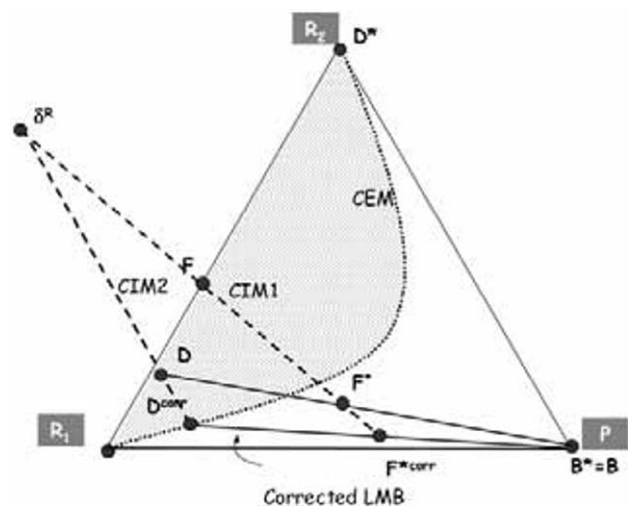


Figure 6. Correction of static analysis LMB predicted compositions – real composition space –

As the trajectory is computed stage by stage from the distillation line equation, the number of theoretical stages and the number of reactive stages can be estimated. Regarding the many assumptions that tend to overestimate the performances of the process, this result can be considered as a consistent evaluation of the minimum number of theoretical stages.

The SA is based upon a decoupling of reaction and separation phenomena. Therefore, contrary to the SA methods initially presented in the literature (Giessler *et al.*, 1998, 1999a, b, 2001), the use of SA is only suggested for hybrid columns. For entirely reactive distillation columns, the analysis of reactive residue curve map is preferred because it takes the coupling between reaction and separation phenomena. Furthermore, the correction of attainable composition and a performance indicator have also been introduced.

For the moment this method is restricted to one reversible reaction because it relies on a parametric analysis in relation to the extent of the reaction(s). Then, the complexity of this parametric analysis would exponentially rise with the number of reactions.

Synthesis Step: Boundary Value Design Method (BVD)

Given the compositions of the attainable products, the synthesis step consists in determining the configuration and the operating parameters of the process that enable to achieve these compositions.

To carry out this step, an approach based upon the boundary value design method proposed by Barbosa and Doherty (1987c, d) for entirely reactive distillation columns, extended to hybrid processes by Espinosa *et al.* (1996), has been developed. Meanwhile, this method can be used only if feasible specifications are specified which underlines the interest of coupling it to the data obtained from the previous feasibility analysis. The synthesis step provides more precise information concerning the

configuration of the process: minimum reflux ratio, and, for a given reflux ratio, location of the reactive zone, number of theoretical stages, position of the feed plates. Compared to the approaches existing in the literature (Table 3), our development permits to consider a broad range of configurations (Table 4): one or two pure separation sections, one or two feed plates, finite or infinite reflux ratio and offers a more precise definition of the minimum reflux ratio.

Input and analysis of data

The data required for the synthesis step and inherited from the feasibility analysis step are:

- the feed composition;
- the distillate and bottom compositions;
- the configuration of the column: requirement or not of a pure separation section, requirement or not of two separate feed stages, finite or infinite reflux or reboil ratios.

Depending on the chosen configuration of the column (one or two feed plate, finite or infinite reflux ratio, finite or infinite reboil ratio), one or several additional parameters must be specified to saturate the degree of freedom of the system. These parameters are listed in Table 5.

Table 3. Applicability of the existing approaches based upon the boundary value design method.

Authors	Application range
Barbosa and Doherty, 1987d	Entirely reactive distillation column, one feed plate
Barbosa and Doherty, 1987e	Entirely reactive distillation column, two feed plates
Espinosa <i>et al.</i> , 1996	Reactive distillation column with a pure stripping section, one feed plate

Table 4. Considered configurations for the synthesis and the design of reactive distillation processes.

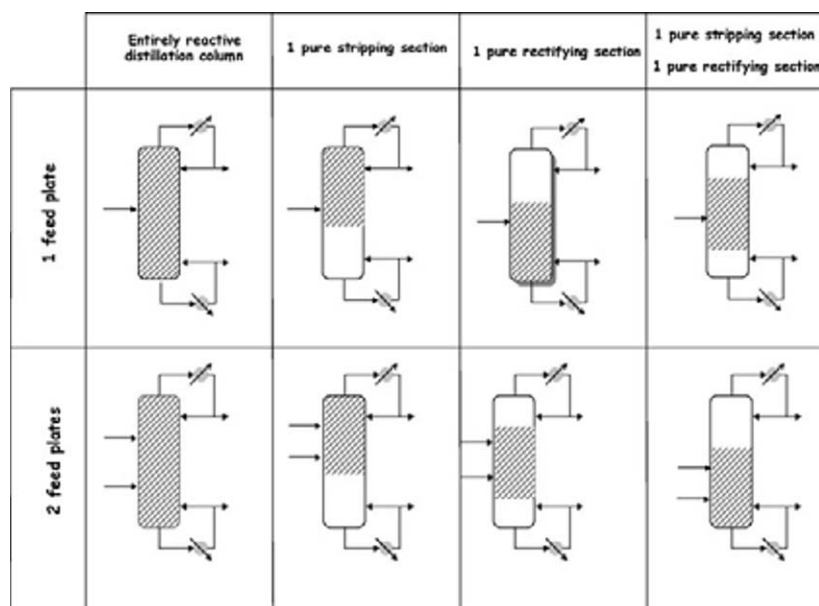


Table 5. Input data for the synthesis step.

Reflux ratio and reboil ratio	Single feed plate column	Double feed plate column
Finite reflux ratio or infinite reboil ratio	Reflux ratio	Reflux ratio Location of the lower feed plate
Infinite reflux ratio	Reboil ratio	Reboil ratio Location of the lower feed plate

From these data, preliminary calculations are made to determine the distillate and bottom flow rates and the reboil ratio.

Using the reactive composition system (Barbosa and Doherty, 1987b), the mass balance can be written as follows:

$$\frac{X_{i,B} - X_{i,F}}{X_{i,F} - X_{i,D}} = \frac{X_{j,B} - X_{j,F}}{X_{j,F} - X_{j,D}} \quad (23)$$

$$i, j = 1, \dots, N_c, i, j \neq k$$

where k is the index of a component chosen as a reference (Barbosa and Doherty, 1987a).

For a double feed column, the composition of the feed is given by (Barbosa and Doherty, 1987c):

$$X_{i,F} = \frac{F_U \cdot X_{i,FU} + F_L \cdot X_{i,FL}}{F_U + F_L} \quad (24)$$

$$i, j = 1, \dots, N_c, i, j \neq k$$

Then, the distillate and bottom flow rates and the reboil ratio can be calculated:

$$D = F \cdot \left(\frac{v_k - v_t \cdot x_{k,F}}{v_k - v_t \cdot x_{k,D}} \cdot \frac{X_{i,B} - X_{i,F}}{X_{i,B} - X_{i,D}} \right) \quad (25)$$

$$i, j = 1, \dots, N_c, i, j \neq k$$

$$B = D \cdot \left(\frac{v_k - v_t \cdot x_{k,D}}{v_k - v_t \cdot x_{k,B}} \cdot \frac{X_{i,F} - X_{i,D}}{X_{i,B} - X_{i,D}} \right) \quad (26)$$

$$i, j = 1, \dots, N_c, i, j \neq k$$

$$\text{and } s = (r + 1) \cdot \frac{v_k - v_t \cdot x_{k,B}}{v_k - v_t \cdot y_{k,\text{cond}}} \cdot \frac{X_{i,B} - X_{i,F}}{X_{i,F} - X_{i,D}} \quad (27)$$

$$i, j = 1, \dots, N_c, i, j \neq k$$

$y_{k,\text{cond}}$ refers to the molar fraction of the reference component in the vapor going (or coming from) to the condenser.

Computation of profiles

During this second step, the composition and temperature profiles in the different sections of the column are computed stage by stage: pure separation section, reactive sections, intermediate section (section located between two feed plates). Figure 7 presents the notations adopted in each section of the column. The approach used to

compute the composition and temperature profiles in each section of the column is described below:

Pure stripping profile (balance region 1 on Figure 7a):

Starting from the liquid composition on the stage s , the vapour composition and the temperature on the same stage are determined using a liquid–vapour equilibrium calculation procedure. Then, the liquid composition on stage $s+1$ is calculated through a mass balance on the stripping section. In this section, no reaction occurs, the mass balance is expressed with the real compositions. The equation of mass balance is defined as follows:

With a finite reboil ratio

$$x_{i,s+1} = \frac{s}{s+1} y_{i,s} + \frac{1}{s+1} x_{i,B} \quad i = 1, \dots, N_c \quad (28a)$$

With an infinite reboil ratio, the profile is equivalent to a distillation line (Widagdo and Seider, 1996)

$$x_{i,s+1} = y_{i,s} \quad i = 1, \dots, N_c \quad (28b)$$

Stages are added to the pure stripping section until the liquid compositions satisfy the chemical equilibrium. This corresponds to the intersection of the stripping profile with the chemical and phase equilibrium surface. For each plate, a test detailed in Appendix A is carried out to detect this intersection. When the test is satisfied, the computation of the pure stripping profile is stopped and the computation of the reactive stripping profile is initiated.

Reactive stripping profile (balance region 2 on Figure 7a):

To compute the reactive stripping profile, equations modeling the chemical equilibrium must be added. Thus, starting from the liquid composition on the stage s , the vapor composition and the temperature on the same stage are determined using a chemical and liquid–vapour equilibrium calculation procedure. Then, the liquid composition on stage $s+1$ is calculated through a mass balance written using the reactive compositions:

With a finite reboil ratio:

$$X_{i,s+1} = \frac{s_s^*}{s_s^* + 1} Y_{i,s} + \frac{1}{s_s^* + 1} X_{i,B} \quad (29a)$$

$$i = 1, \dots, N_c \text{ and } i \neq k$$

s_s^* is the modified reboil ratio

$$s_s^* = s \cdot \frac{v_k - v_t \cdot y_{k,s}}{v_k - v_t \cdot x_{k,B}} \quad (30)$$

With an infinite reboil ratio

$$X_{i,s+1} = Y_{i,s} \quad i = 1, \dots, N_c \text{ and } i \neq k \quad (29b)$$

If the column has two feed plates, the reactive stripping profile is computed until the lower feed plate is reached. If the column has a single feed plate, the reactive stripping profile ends when it reaches a pinch point.

Middle section profile (balance region 3 on Figure 7b):

For double feed columns, the middle section is supposed to be a reactive section. The composition profile in the middle section is computed as follows: starting from the liquid composition on stage m , a chemical and physical equilibrium calculation enables to get the temperature of the stage and the vapour composition leaving this same stage. Then a mass balance on the region 3 illustrated on

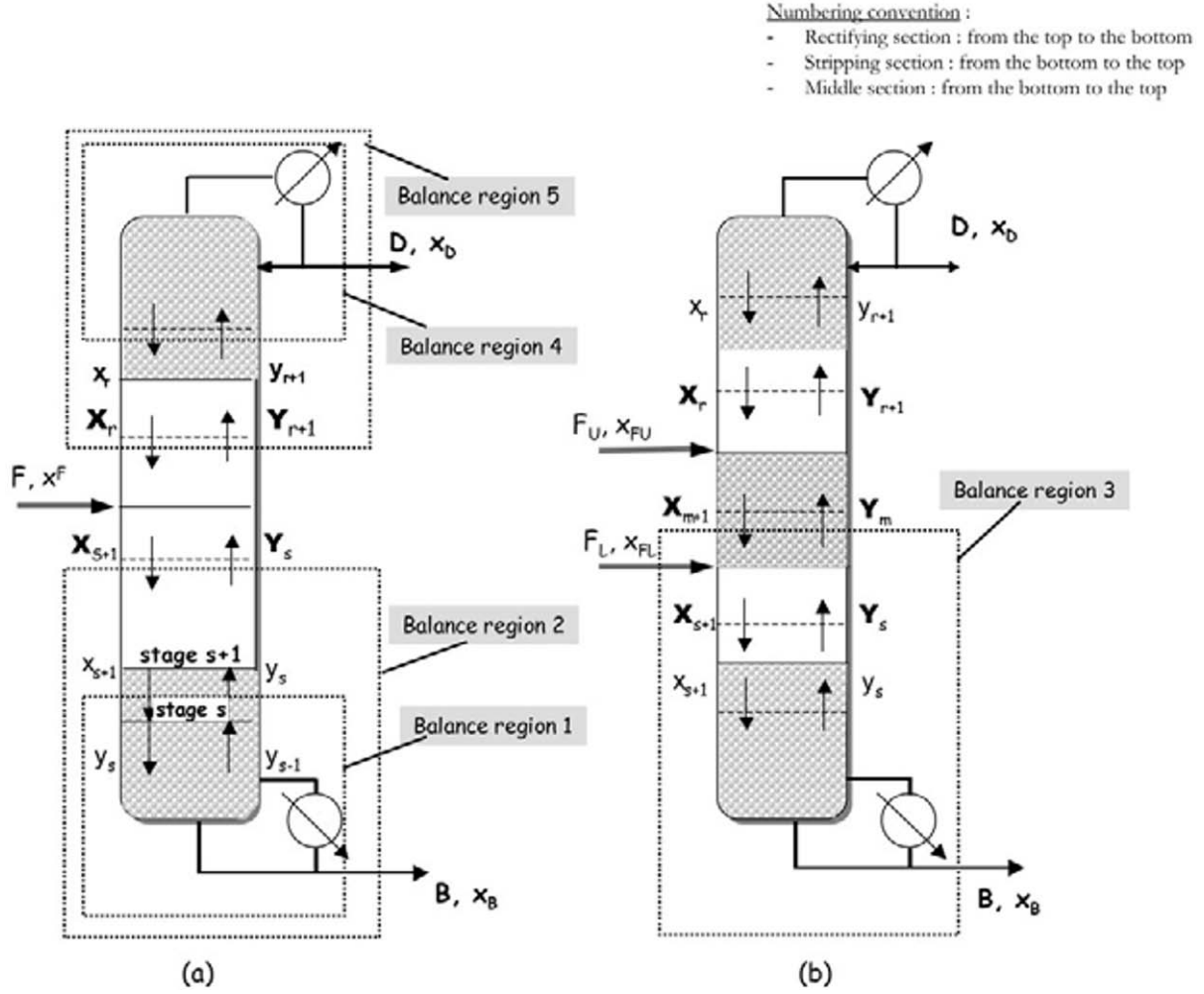


Figure 7. Schematic representation of a reactive distillation column.

Figure 7b permits to calculate the liquid compositions on plate $m + 1$.

With a finite reflux ratio

$$X_{i,m+1} = \frac{(r_m^* + 1) \cdot E_m}{r_m^* \cdot E_m + F_R^*} Y_{i,m} + \frac{F_R^* \cdot X_{i,FU} - E_m \cdot X_{i,D}}{F_R^* + r_m^* \cdot E_P} \quad (31a)$$

$i = 1, \dots, N_c$ and $i \neq k$

With a infinite reflux ratio

$$X_{i,m+1} = \frac{(F_R^* + 1) \cdot s_p^*}{F_R^* + s_p^* \cdot (1 + F_R^*)} \cdot Y_{i,m} + \frac{F_R^*}{F_R^* + s_p^* \cdot (1 + F_R^*)} \cdot X_{i,FU} \quad (31b)$$

$i = 1, \dots, N_c$ and $i \neq k$

with

$$F_R^* = \frac{F_U(v_k - v_t \cdot x_{k,FU})}{F_L(v_k - v_t \cdot x_{k,FL})} = F_R \left(\frac{v_k - v_t \cdot x_{k,FU}}{v_k - v_t \cdot x_{k,FL}} \right) \quad (32)$$

$$F_R = \frac{F_U}{F_L} \quad (33)$$

$$E_m = \frac{s_m^*(F_R^* + 1)}{s_m^* + r_m^* + 1} \quad (34)$$

r_m^* is the modified reflux ratio

$$r_m^* + 1 = \frac{v_k - v_t \cdot y_{k,m}}{v_k - v_t \cdot y_{k,cond}} \cdot (r + 1) \quad (35)$$

Contrary to a stripping profile, the liquid compositions profile in the middle section does not systematically reach a fixed point. Indeed, on the basis on the mass balance in this section, it can be shown that the reactive liquid composition on stage m can reach a nonphysical value (Théry, 2002). In that case, the calculation stops before reaching a fixed point. On the contrary, if X_m remains in a physical field the profile stops when reaching a fixed point.

Pure rectifying profile (balance region 5 on Figure 7a):

For the pure rectifying profile, the liquid composition of plate r is determined by calculating a dew point based on the known vapour composition leaving this plate. The vapour composition on stage $r + 1$ is calculated the mass balance on the pure rectifying section.

With a finite reflux ratio

$$y_{i,r+1} = \frac{r}{r+1} x_{i,r} + \frac{1}{r+1} x_{i,D} \quad i = 1, \dots, N_c \quad (36a)$$

With a infinite reflux ratio, the profile can be considered as classical distillation lines

$$y_{i,r+1} = x_{i,r} \quad i = 1, \dots, N_c \quad (36b)$$

Reactive rectifying profile (balance region 4 on Figure 7a):
Equations representing the reactive rectifying section are the followings:

With a finite reflux ratio,

$$Y_{i,r+1} = \frac{r_{r+1}^*}{r_{r+1}^* + 1} X_{i,s} + \frac{1}{r_{r+1}^* + 1} X_{j,D} \quad i = 1, \dots, N_c \text{ and } i \neq k \quad (37a)$$

With an infinite reflux ratio

$$Y_{i,r+1} = X_{i,r} \quad i = 1, \dots, N_c \text{ and } i \neq k \quad (37b)$$

Equation (37a) shows that the composition of the vapour phase Y_{s+1} depends on the modified reflux ratio r_{r+1}^* , itself depending on the real vapour composition y_{r+1} [see equation (35)] Then, to compute the reactive rectifying profile, it is necessary to calculate all variables at the same time solving a nonlinear algebraic set of equations consisting in the mass balance equations (37), the modified reflux ratio equation (35) and the chemical and physical equilibrium equations. This reactive rectifying profile stops when it reaches a pinch point.

Influence of the reflux ratio

The synthesis step permits to compute the composition and temperature profiles for different values of the design parameters (reflux ratio, reboil ratio for column operating at infinite reflux ratio, position of the lower feed plate for double feed columns). Among these parameters, the reflux ratio strongly influences the profiles. The first purpose of the boundary value design method consists in determining the minimum reflux ratio. The approach adopted for this step depends on the column configuration.

Minimum reflux ratio for an entirely reactive column:

Barbosa and Doherty (1987b) studied the influence of the reflux ratio on entirely reactive distillation columns. For such a column, a minimum reflux ratio is found when

one of the reactive profile (the reactive stripping profile or the reactive rectifying profile) just ends on the other. In that case, an infinite number of stages is required to perform the separation.

Minimum reflux ratio for a hybrid reactive column: To define the minimum reflux ratio for hybrid columns, Espinosa *et al.* (1996) kept the same definition without taking into account the non reactive section. However, as illustrated on Figure 8a for the reaction $R_1 + R_2 \rightleftharpoons P$, if the chosen reflux ratio is too small, the pure stripping profile reaches a fixed point before one can observe an intersection with the reactive surface.

In that case, it seems that two different minimum reflux ratios must be defined:

- The pure stripping or the pure rectifying section minimum reflux ratio r_{\min}^{pure} corresponds to the value of the reflux ratio for which the pure stripping or the pure rectifying profile reaches an end point.
- The reactive section minimum reflux ratio r_{\min}^{react} corresponds to the Barbosa and Doherty's definition (1987b).

Two cases can occur:

- The minimum reflux ratio is defined by the reactive profiles: $r_{\min} = r_{\min}^{\text{react}}$

This case occurs when $r_{\min}^{\text{pure}} < r_{\min}^{\text{react}}$. Here three situations can be highlighted: first, the pure stripping profile reaches a fixed point before it reaches the chemical and phase equilibrium surface ($r < r_{\min}^{\text{pure}}$: Figure 8a); second, the pure stripping profile reaches the chemical and phase equilibrium surface but the reactive profiles do not intersect each other ($r_{\min}^{\text{pure}} < r < r_{\min}^{\text{react}}$: Figure 8b); lastly, the reactive profiles intersect each other (Figure 8c).

- The minimum reflux ratio is defined by the pure separation profile: $r_{\min} = r_{\min}^{\text{pure}}$

In that case, when $r > r_{\min}^{\text{pure}}$, we observe an intersection between the reactive profiles (Figure 9).

Finally, if the separation appears to be infeasible for any value of the reflux ratio, a two feed plates column is investigated.

Minimum reflux ratio for a double feed column: For a double feed column, two parameters must be given: the

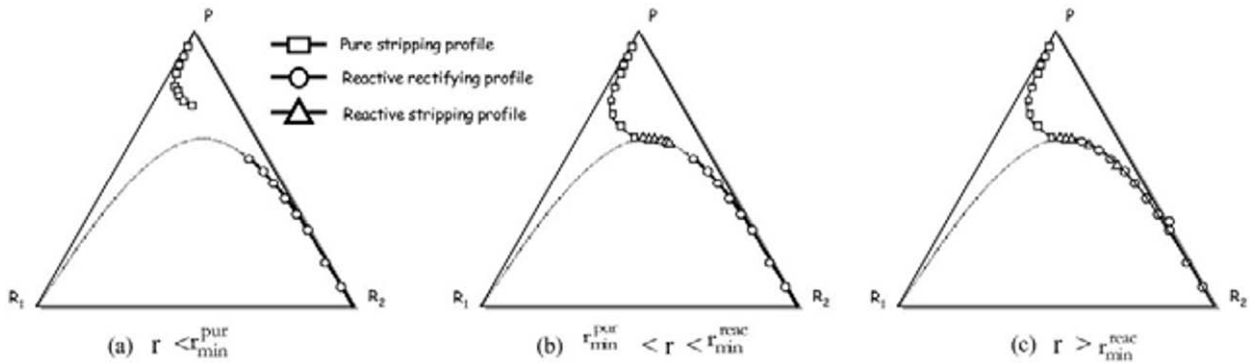


Figure 8. Synthesis step: determination of the minimum reflux ratio for a reactive distillation column with a pure stripping section: case where $r_{\min} = r_{\min}^{\text{react}}$.

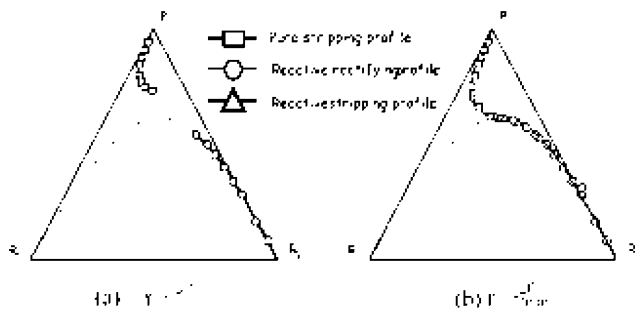


Figure 9. Synthesis step: determination of the minimum reflux ratio for a reactive distillation column with a pure stripping section: case where $r_{\min} = r_{\min}^{\text{pure}}$.

value of the reflux ratio and the location of the lower feed plate. To guide the choice, two rules are usually used:

Rule no 2a:

The lower feed plate must not disturb the liquid composition profiles.

Rule no 2b:

The location of the lower feed plate should be chosen so as to minimize the total number of plates in the column (Barbosa and Doherty, 1987d).

Once the location of the lower feed plate is given, the minimum reflux ratio must be determined. For a double feed column this concept must also be adapted. A feasible column design is found when a continuous path from the distillate composition to the bottom product composition can be plotted. The minimum reflux ratio can be found in one of the two following cases:

- The reactive rectifying profile just ends on the middle-section profile; or
- The middle-section profile just ends on the reactive rectifying profile.

However, another situation can be encountered: we have formerly shown that the middle-section profile could stop before having reached a fixed point. For values of r slightly lower than r_{\min} , the middle section profile ends before the intersection with the rectifying profile and for values slightly higher than r_{\min} , the profile ends after the intersection. Consequently, for double feed column, we recommend to use the following definition for the minimum reflux ratio: for a double feed column whose location of lower feed plate has been fixed, the minimum reflux is the smallest value of r for which we observe an intersection between middle-section profile and the reactive rectifying profile.

Choice of a feasible reflux ratio: The minimum reflux ratio corresponds to an infinite number of stages. To determine a feasible reflux ratio corresponding to a feasible column configuration, the Gilliland's law usually used for non reactive processes has been extended to reactive columns (King, 1980).

$$0,1 \leq \frac{r - r_{\min}}{r + 1} \leq 0,33 \quad (38)$$

Note that a maximum reflux ratio can also exist: beyond this ratio, the reactive profiles do not present an intersection anymore. This phenomenon will be examined in detail in the last part of this study.

Design Step: Simulation

The previous steps lead to a column configuration and a reflux ratio that permits to reach the initial product specifications. But, these results have been obtained neglecting all thermal phenomena (heat of reaction, thermal loss, heat of mixture, etc.). The objective of the simulation step is to recalculate the operating parameters without modifying the column configuration by taking into account the heat balances.

Case of a finite reflux ratio

When the reactive mixture contains impurities or leads to the formation of secondary products, the reactive distillation column usually requires a finite reflux ratio to remove these components.

Until now, the specifications were described as a function of the purity, the recovery ratio or the yield. To take both recovery ratio and yield of the reaction at the same time, the problem is defined by fixing the molar flow rate of one component as the first constraint: either the distillate molar flow rate of the key component for a direct separation (see *Case of a hybrid section* for a definition of a direct separation)

$$D_i = D \cdot x_{i,D} = \tau_{i,D} \cdot \tau_r \cdot F \cdot x_{\text{key}} \quad (39)$$

or the bottom molar flow rate of the key component for an indirect separation (see *Case of a hybrid section* for a definition of an indirect separation)

$$B_i = B \cdot x_{i,B} = \tau_{i,B} \cdot \tau_r \cdot F \cdot x_{\text{key}} \quad (40)$$

This qualifies the *quantity* of product.

To qualify the *quality*, the second constraint chosen to saturate the problem is the distillate or the bottom purity of the key component.

Case of an infinite reflux ratio

Contrary to non reactive distillation processes for which the single purpose is to separate product and which require a finite reflux ratio, the static analysis revealed the interest of a infinite reflux ratio, especially when the reaction leads to a single and low boiling product.

Here the distillate flow rate is set to 0 and the bottom molar flow rate of the key component is fixed.

Case of an infinite reboil ratio

In the same way, an infinite reboil ratio can be useful when the reaction leads to a single high boiling product.

Table 6. Input data for the design step.

Finite reflux ratio	Distillate or bottom purity Distillate or bottom partial molar flowrate
Infinite reflux ratio	Bottom partial molar flowrate
Infinite reboil ratio	Distillate partial molar flowrate

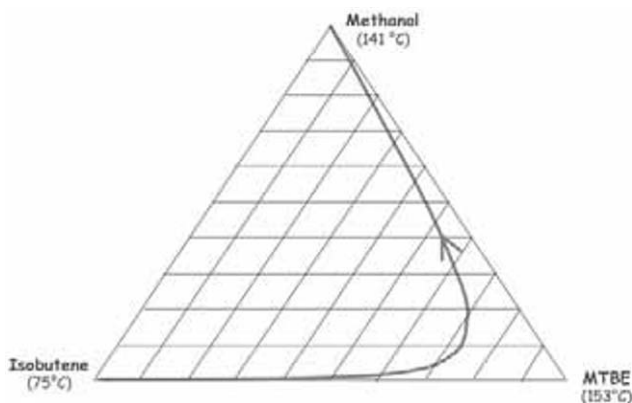


Figure 10. Reactive residue curve map for the ternary system methanol–MTBE–isobutene ($P = 11$ atm).

In that case, the bottom flow rate is equal to 0 and the distillate molar flow rate of the key component is fixed.

Table 6 summarizes the constraints which must be given to define the design problem. The mathematical model of the reactive distillation process is composed of highly nonlinear equations (MESH equations) solved with a NLAE solver (nonlinear algebraic equations) based upon the Newton–Raphson method. To ensure the convergence, the liquid and temperature composition profiles are initialized using the profiles estimated during the synthesis step.

APPLICATIONS

Two examples are developed to illustrate the different points of the methodology formerly presented.

Production of Methyl Tert Butyl Ether

The production of MTBE is a very significant example of industrial application of reactive distillation columns (Backaus, 1921, 1923; Smith, 1990):



For the optimal temperature window of the catalyst to be consistent with the operating temperature of the process,

the reaction is performed at 11 atm (Espinosa *et al.*, 1996). The thermodynamic data of this system and the equilibrium data are listed in Appendix B.

Feasibility analysis

The reactive residue curve map of the methanol–isobutene (MTBE) comes down to a single curve is plotted in the real composition space (Figure 10). Two pure components appear as singular points of the reactive residue curve: the isobutene which behaves as an unstable node and the methanol which behaves as a stable node.

The two physical azeotropes existing under 11 atm concern components reacting together do not appear as singular point for reactive distillation. MTBE does not appear as a singular point of the residue curve because it can not exist alone in the reactive mixture. Consequently, the recovery of pure MTBE in an entirely reactive column is impossible and a pure stripping section is required.

To complete the feasibility analysis, the static analysis (SA) is performed (Table 7). The following conclusions can be drawn:

- An equimolar feed leads to the highest recovery ratio and yield with a global conversion of 99.5%. Note that the ratio K_1 predicted in that case is higher than 50. Consequently, a process operating with an infinite reflux ratio is required and the region of attainable compositions at the distillate is defined on Figure 11(a) and (b). The two physical azeotropes methanol/MTBE and isobutene/MTBE generate a distillation boundary which affects the behavior of the system in the pure stripping section: the single part of chemical equilibrium manifold attainable is located below this distillation boundary.
- For an excess of isobutene, a bottom product composed of pure MTBE and a distillate composed of isobutene and traces of methanol is predicted.
- If the quantity of residual methanol exceed 60% molar, it is not possible to get pure MTBE. In fact, beyond that value, methanol will be recovered in the bottom product instead of MTBE, because of the boundary line of the nonreactive residue curve generated by the binary azeotrope MTBE–methanol.

Table 7. Results of the static analysis for the production of MTBE— $P = 11$ atm. The lines in italics refer to the compositions selected for the further step.

Feed molar liquid composition		Distillate molar liquid composition			Bottom molar liquid composition			τ (%)	$K_1 = B/D$	$\tau_{\text{MTBE,B}}$ (%) Recovery ratio of MTBE	PI (%) Performance indicator
IB	MEOH	IB	MEOH	MTBE	IB	MEOH	MTBE				
0.1	0.9	0.09	0.49	0.42	0.00	1.00	0.00	83	3.68	0.00	0.00
0.2	0.8	0.05	0.51	0.44	0.00	1.00	0.00	90	1.02	0.00	0.00
0.3	0.7	0.05	0.51	0.44	0.00	1.00	0.00	90	0.20	0.00	0.00
0.4	0.6	0.05	0.50	0.45	0.00	0.00	1.00	95	0.41	47.4	0.45
0.45	0.55	0.05	0.50	0.44	0.00	0.00	1.00	97	1.52	77.4	0.75
0.5	0.5	0.12	0.20	0.68	0.00	0.00	1.00	100	68.31	99.5	0.99
0.55	0.45	0.94	0.01	0.05	0.00	0.00	1.00	99	4.26	100	0.99
0.6	0.4	0.98	0.01	0.01	0.00	0.00	1.00	99	1.94	100	0.99
0.7	0.3	0.98	0.01	0.01	0.00	0.00	1.00	99	0.72	100	0.99
0.8	0.2	1.00	0.00	0.00	0.00	0.00	1.00	97	0.32	100	0.97
0.9	0.1	1.00	0.00	0.00	0.00	0.00	1.00	95	0.12	100	0.99

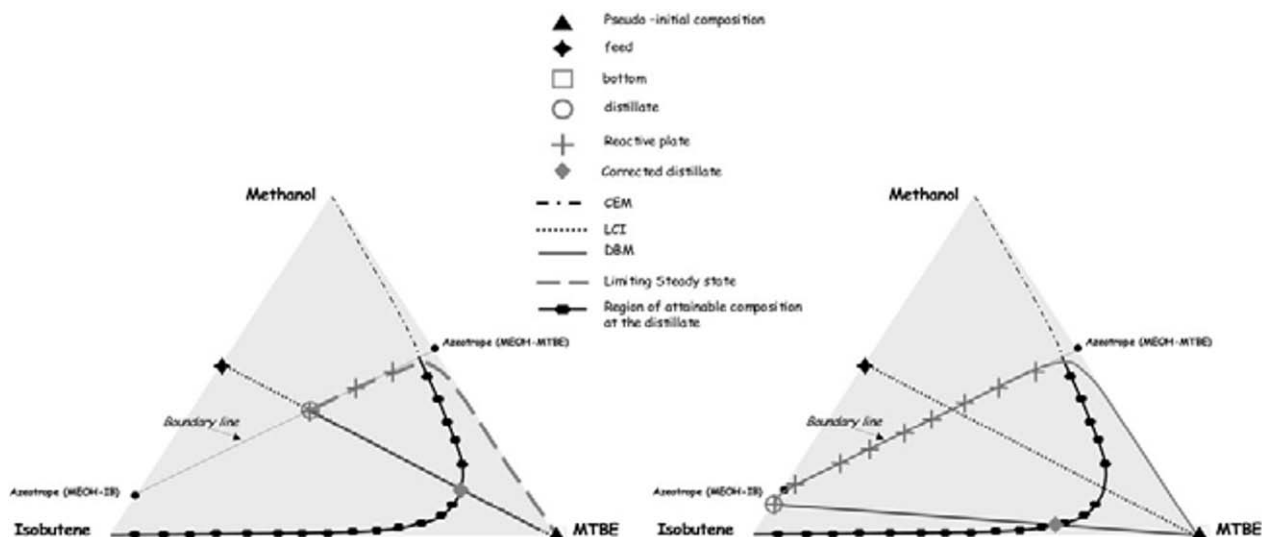


Figure 11. Production of MTBE—static analysis—equimolar feed.

Synthesis

To illustrate various aspects of the methodology, two feed compositions will be studied: the equimolar feed and slight excess of isobutene feed.

Equimolar feed: Table 8 presents the first data set inherited from the static analysis and exploited as starting data for the synthesis step (see Figure 11a). On Figure 12, the reactive stripping profile, the reactive rectifying profile and the pure stripping profile are represented for an equimolar feed and distillate and bottom specifications listed in Table 7. The variable parameter for a process operating with an infinite reflux ratio and a single feed plate is the reboil ratio. But in that case, whatever the reboil ratio, the reactive profiles do not intersect. Indeed both reactive profiles go toward opposite directions. With this example, we show that an operation considered as feasible by the feasibility analysis can appear to be infeasible through the synthesis step which underlines the necessity of coupling different approaches.

Another distillate specification must be investigated: according to Figure 12, a distillate richer in isobutene would better lead to an intersection between the reactive profiles. Figure 13 represents the profiles observed with the composition set presented in Table 9. For a reboil ratio equal to 0.8 (Figure 13a), the pure stripping profile reaches a fixed point before it reaches the chemical and phase equilibrium surface. For a reboil ratio equal to 0.95 (Figure 13b), the pure stripping profile reaches a fixed point as it intersects with the chemical and phase equilibrium surface. Finally for a higher value of the reboil ratio, $s = 0.98$ (Figure 13c), the reactive stripping profile intersect with the reactive rectifying profile. In that case,

Table 8. Production of MTBE— $P = 11$ atm—input data for the synthesis step: first distillate composition for an equimolar feed.

	Molar compositions		
	Feed	Distillate	Bottom
Isobutene	0.5	0.1173	1.1926×10^{-3}
Methanol	0.5	0.2002	1.1253×10^{-3}
MTBE	0.0	0.6825	0.9968

the minimum reboil ratio is defined by the pure stripping profile and its value set to $s_{\min} = 0.95$.

Given the minimum reboil ratio, an effective reboil ratio can be chosen between 1.2 and 1.9. For $s = 1.5$, the column configuration can be deduced from the analysis of Figure 14:

- two reactive rectifying stages (including the condenser);
- two reactive stripping stages;
- eight pure stripping stages (including the reboiler).

The resulting liquid composition and reaction rate profiles are represented on Figure 15. The cumulative production rate on stage k is defined as follows:

$$r_k^{\text{cum}} = r_{k-1}^{\text{cum}} + r_k \quad \text{for } 1 \leq k \leq N_s \quad (41)$$

$$r_1^{\text{cum}} = r_1 \quad (42)$$

where r_k is the production rate of MTBE on stage k . In that particular configuration, the reactants are introduced at the top of the column, and the reaction takes place mostly in the two first plates. Reactants which did not react are recycled and the MTBE is recovered at the bottom.

Excess of isobutene: Table 10 present the starting data used for the synthesis step. In that situation, the variable parameter is the reflux ratio. Given the minimum reflux ratio ($r_{\min} = 3.3$) the column configuration is determined

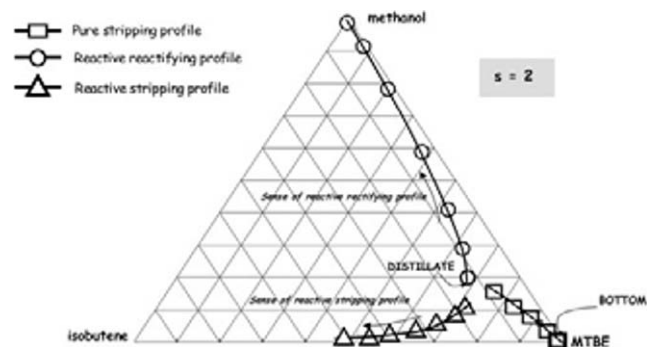


Figure 12. Production of MTBE—synthesis step for an equimolar feed.

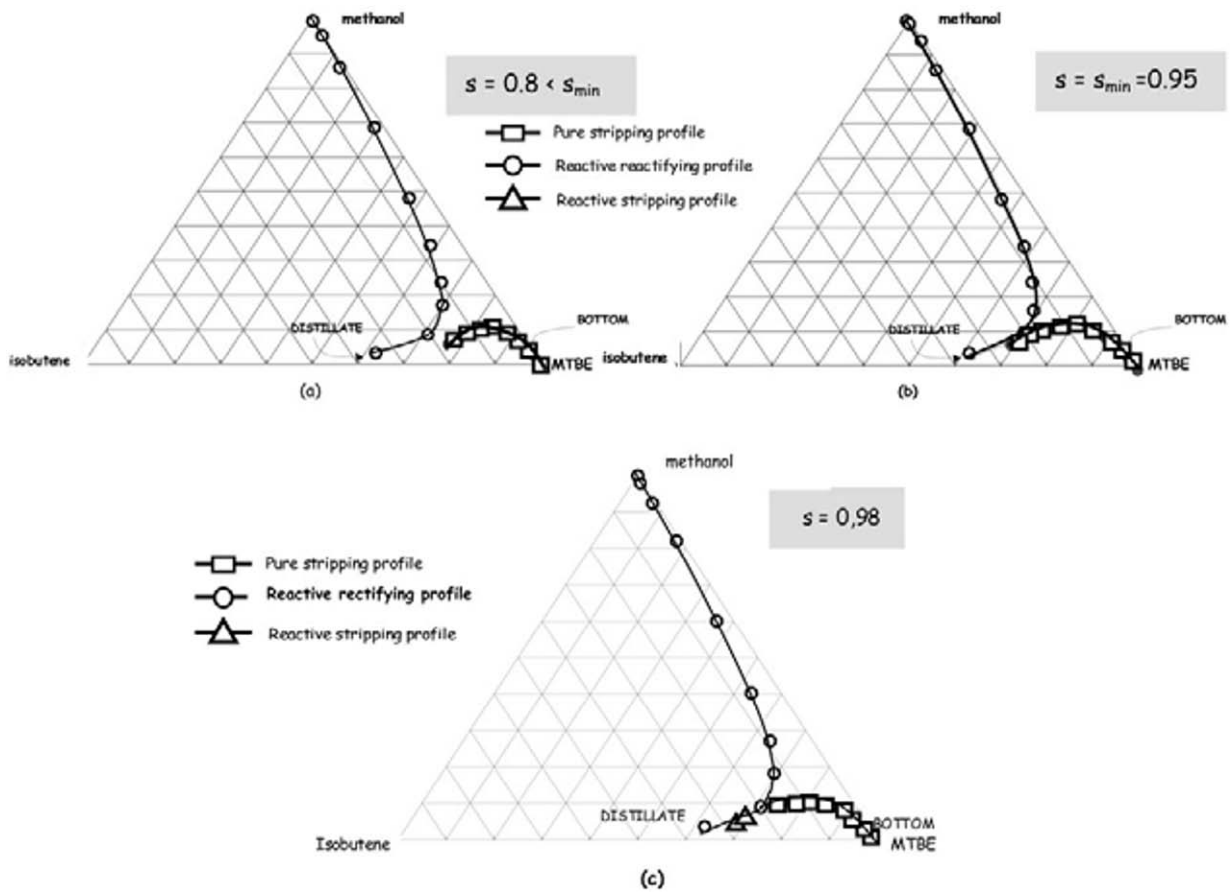


Figure 13. Production of MTBE—synthesis step for an equimolar feed.

Table 9. Production of MTBE— $P = 11$ atm—input data for the synthesis step: second composition for an equimolar feed.

	Molar composition		
	Feed	Distillate	Bottom
Isobutene	0.5	0.3498	0.1926×10^{-2}
Methanol	0.5	0.02467	0.1253×10^{-2}
MTBE	0.0	0.62553	0.9968

for a reflux ratio equal to 5 (see Figure 16). The resulting column configuration is as follows:

- ten pure stripping stages (including the reboiler);
- three reactive stripping stages;
- five reactive rectifying stages (including the condenser).

Design step

Equimolar feed: Given the column configuration, the purpose of the design step is to determine the operating

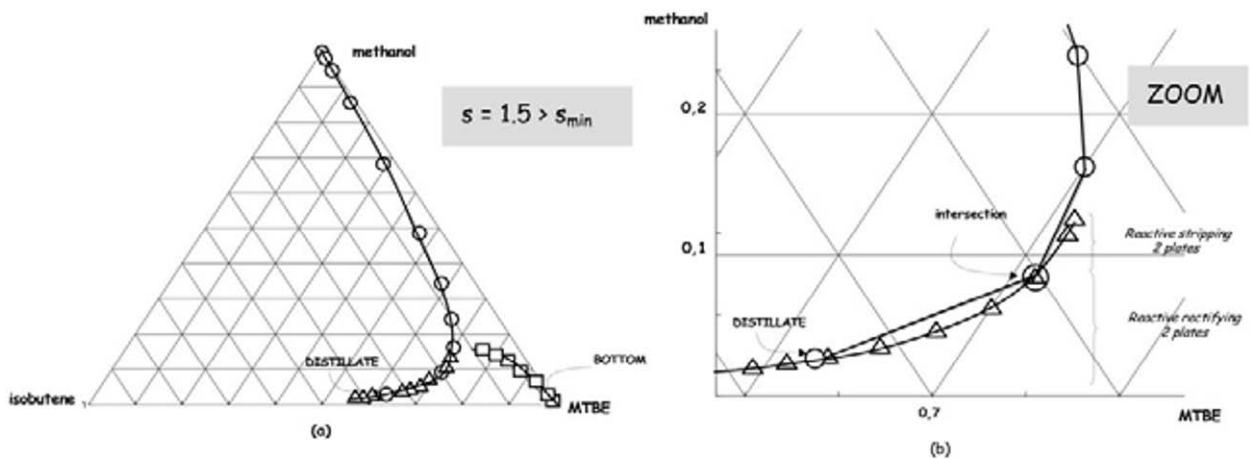


Figure 14. Production of MTBE—synthesis step for an equimolar feed—influence of the reflux ratio.

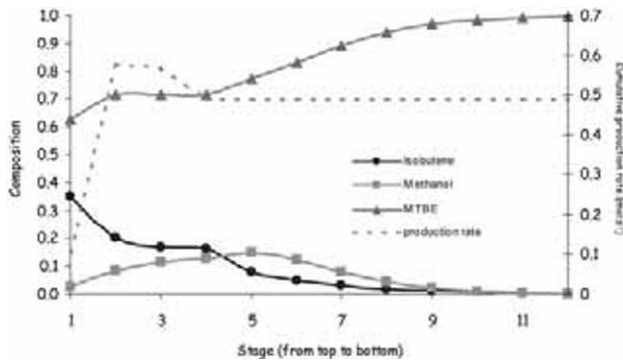


Figure 15. Production of MTBE—synthesis step: molar liquid composition profile and cumulative production rate of MTBE (equimolar feed; $s = 1.5$; feed flowrate: 1 mol s^{-1}).

Table 10. Production of MTBE: excess of isobutene— $P = 11 \text{ atm}$ —input data for the synthesis step—feed containing an excess of isobutane.

	Molar composition		
	Feed	Distillate	Bottom
Isobutene	0.55	0.9673	0.4317×10^{-2}
Methanol	0.45	0.396×10^{-4}	0.1253×10^{-2}
MTBE	0.0	0.0327	0.9957

parameters taking into account the heat effects. For an infinite reflux ratio, the single operating parameter is the heat duty. For a feed flow rate equal to 1 mol s^{-1} , the heat duty at the reboiler is equal to 15.9 kW .

Excess of isobutene: For a column operating with a finite reflux ratio, the design step adjusts the reflux ratio to take the heat effects into account. For an excess of isobutene, the required heat duty at the reboiler is equal to 13.1 kW and the reflux ratio is equal to 12.6 . This value is much higher than this obtained through the synthesis step. In fact, the reaction exothermicity: $Q_r = -62.7 \text{ kJ mol}^{-1}$ (Colombo *et al.*, 1983) increases the vapour flow rate on the reactive plates. Consequently, to obtain the same performances, a higher reflux ratio is necessary. The liquid composition profile obtained through the design step presented on Figure 17 shows that thanks to this parametric adjustment, it is possible to achieve the performances predicted by the feasibility analysis.

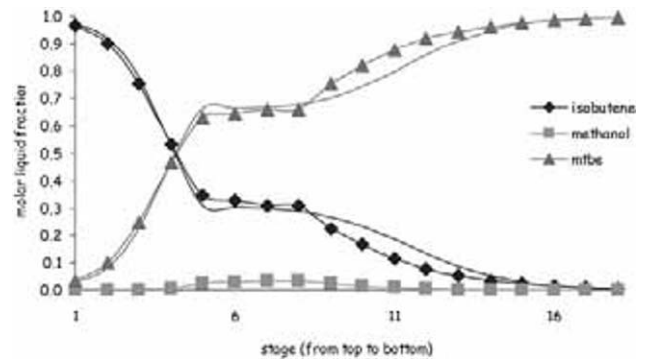
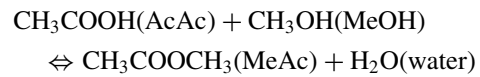


Figure 17. Production of MTBE—design step for an excess of isobutene: comparison of composition profiles obtained through the synthesis and the design step (line: synthesis; symbol: design).

Production of Methyl Acetate

The second example presented concerns the production of methyl acetate from acetic acid and methanol.



This reaction is performed under 1 atm . Thermodynamic data relating to this system taken from Song *et al.* (1998) are listed on Appendix C. The process was described in detail by Agreda *et al.* (1990), and patented by Eastman Chemical Company patent (Agreda and Partin, 1984). Although esterification reactions are usually modeled as kinetically controlled reactions, the residence time will be assumed to be high enough to consider that the chemical equilibrium is reached on each plate.

Feasibility analysis

The performances of classical processes for the production of high purity methyl acetate are usually limited by the chemical equilibrium and especially by the existence of two minimum azeotropes: methyl acetate/methanol and methyl acetate/water which make the purification of methyl acetate very difficult. As pointed out in the first part of this study, the conventional process not only requires a very important excess of one of the reactants in the reactive part of the process but also nine distillation or extraction columns in the purification part (Agreda and

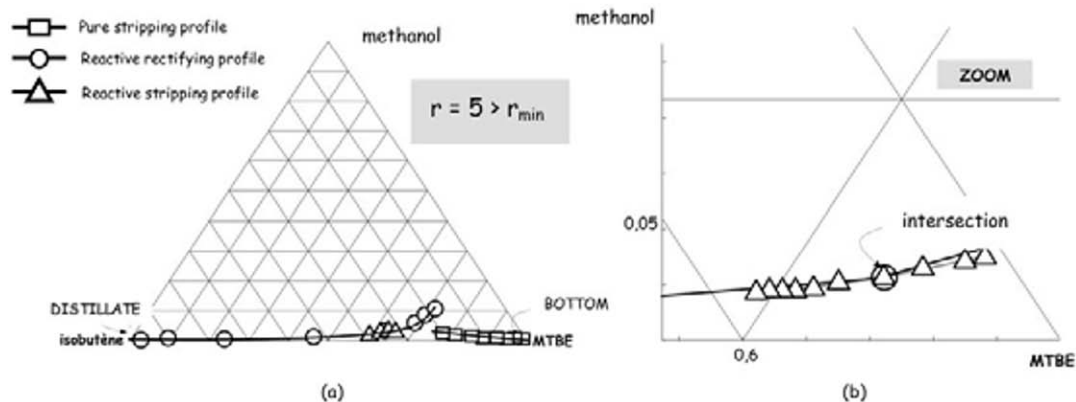


Figure 16. Production of MTBE—synthesis step for an excess of isobutene.

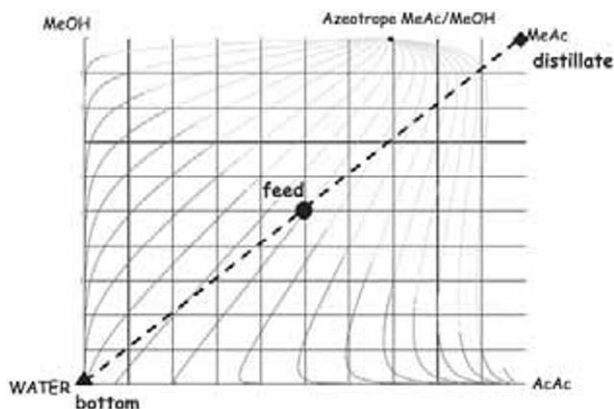


Figure 18. Reactive residue curve map of the quaternary system water-methyl acetate (MeAc)-acetic acid (AcAc)-methanol (MeOH) involving a reaction.

Partin, 1984). The design of a RD column for this process appears as important challenge for this system. The reactive residue curve maps of water-methanol-acetic acid-methyl acetate is represented on Figure 18. In that case, all the components appear in the reactive composition space as vertices of the diagram because these four pure components can exist alone in an equilibrium mixture. For that system, a pure separation section is not required. The single azeotrope surviving to the reaction involves two components which do not react together: methanol/methyl acetate. The stable and unstable nodes are respectively the acetic acid and the azeotrope methanol/methyl acetate. The system exhibits no reactive azeotrope and no distillation boundary line. According to the rule 1 b, although, the reactive residue curve map does not display any distillation boundary, methyl acetate appears as a saddle point of the system; consequently, the recovery of pure methyl acetate requires a two feed plates configuration. An upper feed plate made up of acetic acid (heavy reactant), and a lower feed plate made up of methanol (light reactant). Thanks to this double feed configuration, it would be possible to shift the concentration profile in the direction of the saddle MeAc, moreover, the equimolar feed appears to be the most favourable one because in that case, all acetic acid and methanol can be converted and pure methyl acetate can be recovered at the distillate and pure water can be recovered at the bottom (see Figure 18). As no pure separation section is required for that system, the modified static analysis is carried out. The yield of the reaction and N_c -2 specifications chosen among the purity or the recovery ratio of the desired product must be specified. According to the rRCM, the following specifications can be formulated:

- yield of the reaction: 98%;
- methyl acetate distillation composition: 98% molar;
- distillate methyl acetate recovery ratio: 99.9% molar.

The resulting bottom and distillate attainable composition are summarized in Table 11.

Synthesis of the process

Knowing the attainable composition in the distillate and in the bottom product, the synthesis step is performed to confirm the feasibility of the process and to determine the configuration of the column.

Table 11. Production of methyl acetate: equimolar feed— $P = 1$ atm—input data for the synthesis step.

	Molar composition		
	Feed	Distillate	Bottom
Acetic acid	0.5	4.39×10^{-3}	0.0191
Methanol	0.5	1.45×10^{-2}	9.18×10^{-4}
Methyl acetate	0.0	0.980	9.72×10^{-4}
Water	0.0	5.52×10^{-4}	0.971

Location of the lower feed plate: Figure 19 presents the liquid composition profiles obtained for various locations of the lower feed plate. For a methanol feed located on the second reactive stripping plate, the middle section profiles stops before it reaches a pinch point. If the lower feed plate is located on the plates 3 or 4, an important gap is noticed between the composition of the last reactive stripping plate and the composition of the first plate of the middle section: this gap characterizes a bad location of the feed plate. For a methanol feed located on the fifth plate, a path between the profiles in the three sections is continuous. Finally, for a lower feed plate located beyond the fifth plate, the reactive stripping profile reaches a fixed point. Consequently, the lower feed is introduced on the fifth plate.

Minimum reflux ratio: According to Figure 20, the minimum reflux ratio is equal to 1.3 and the operating reflux ratio can be chosen between 1.6 and 2.4. For $r = 2$, the column configuration is the following (see Figure 21):

- four reactive rectifying plates (including the condenser);
- twenty-five plates in the middle section (the feed stage is supposed to belong to the middle section);
- four reactive stripping plates (including the reboiler).

Design of the process

The heat of reaction for the production of methyl acetate can be considered as negligible ($Q_r = -20 \text{ kJ mol}^{-1}$). The heat of vaporization of the different components are very close. The assumptions formulated in the synthesis step are nearly satisfied, and the reflux ratio determined through the design step (1.6) is close to the reflux ratio determined through the synthesis step (equal to 2). Figure 22 presents the profiles and the configuration obtained for the production of methyl acetate. This configuration is very similar to the one proposed by Huss *et al.* (1999) who recommended a column made up of 39 plates to obtain a distillate composed of 98% molar of methyl acetate. The acetic acid feed is located on the third plate (starting from the top) and the methanol feed is introduced on the plate 36. The reflux ratio is equal to 1.7.

To evaluate the consistency of the results of the design procedure, the industrial configuration (Agreda *et al.*, 1990) has also been compared to the estimated configuration. For a distillate composed of 98% molar of methyl acetate, Agreda *et al.* (1990) suggest an entirely reactive distillation column made up of 65 theoretical plates. The methanol feed plate is on the plate 20, the acetic acid plate is on plate 60 and the reflux ratio is equal to 1.7. Although the global structure and the operating conditions seem consistent, the number of plates required by the industrial column appears to be much more important. First, this can be explained by the assumption concerning

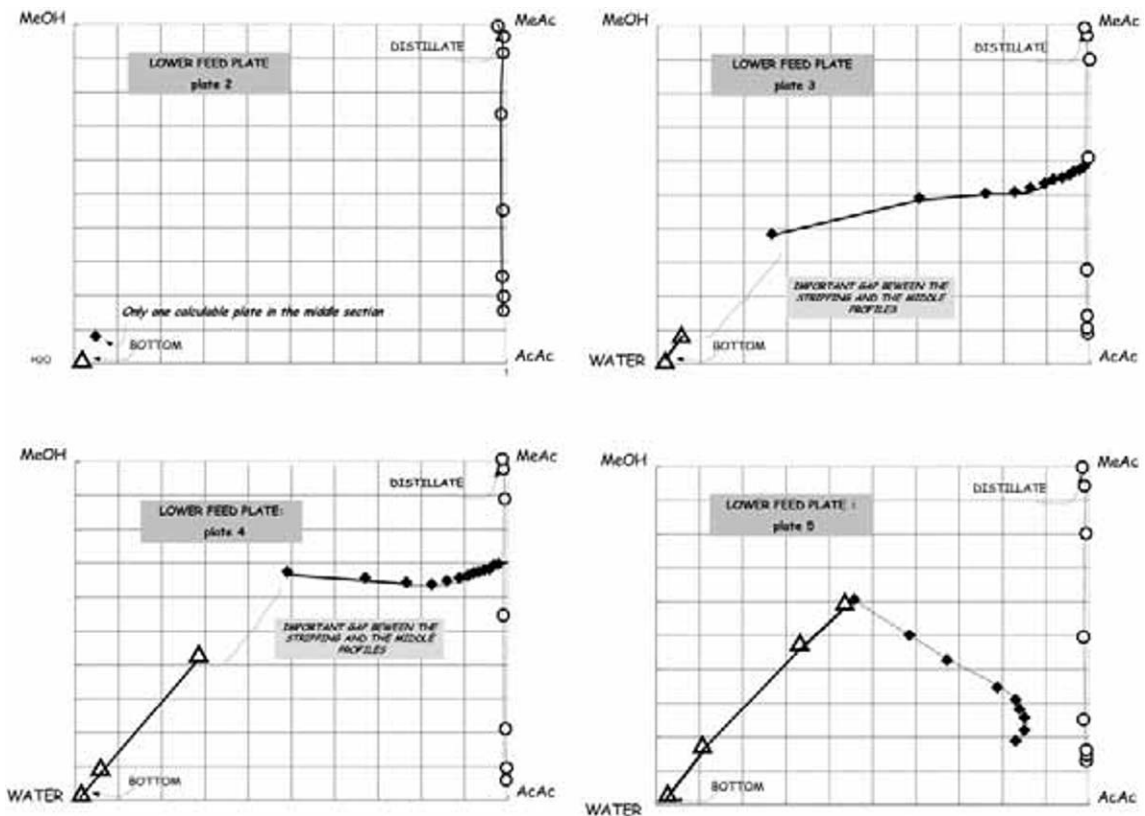


Figure 19. Production of methyl acetate—synthesis step for an equimolar feed: determination of the location of the lower feed plate.

the theoretical plates: this assumption is never satisfied and the theoretical number of plate is usually corrected to take the kinetics of the mass transfers into account. Second, the procedure considers instantaneous chemical equilibrium whereas the esterification of acetic acid with methanol is not known to be a very fast reaction. For that example, further developments of the procedure consisting in the introduction of kinetics would surely lead to better results. Huss *et al.* (1999) (Buzad and Doherty, 1994).

CONCLUSION AND OUTLOOKS

A new sequential and hierarchical approach for the feasibility analysis, the synthesis and the design of reactive

distillation processes undergoing one equilibrium reaction has been introduced. The main interest of this methodology lies on a progressive introduction of the process complexity and the coupling of different complementary approaches. From a minimal set of information concerning the physical and chemical properties of the system, three successive steps lead to the design of a column and the specification of its operating conditions. The results obtained through this method leads to a reliable initialization point for a further optimization of the operating conditions and the process design. It has been applied with success to different reactive systems. The production of methyl-ter-butyl-ether and methyl acetate reported in the paper shows its performance but also points out its limits.

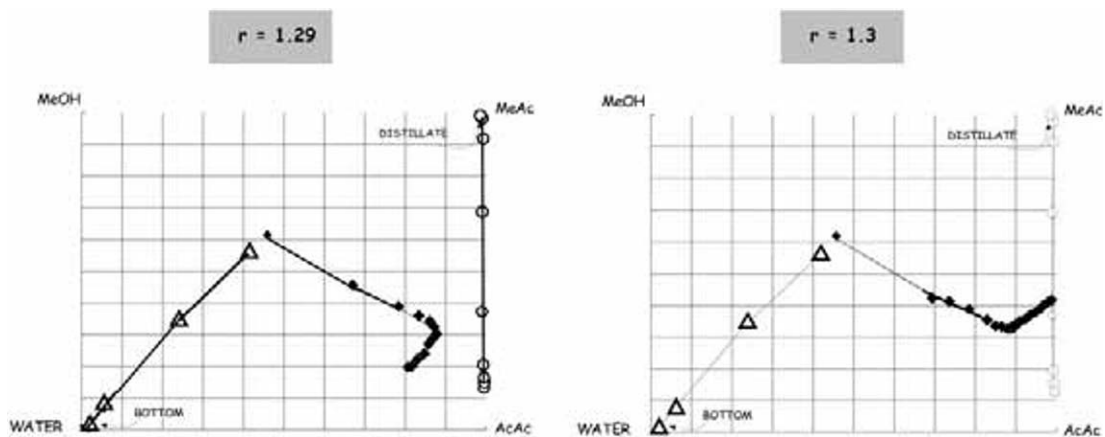


Figure 20. Production of methyl acetate—synthesis step for an equimolar feed: calculation of minimum reflux ratio (lower feed located on plate 5).

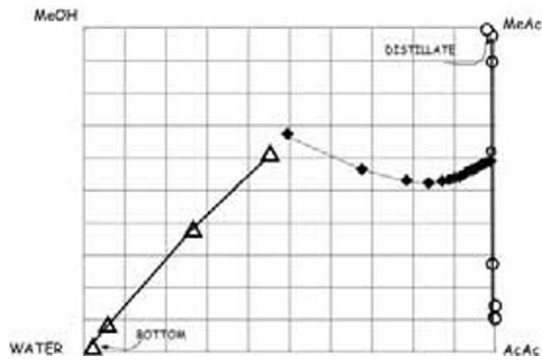


Figure 21. Production of methyl acetate: synthesis step (lower feed on plate 5; $r = 2$).

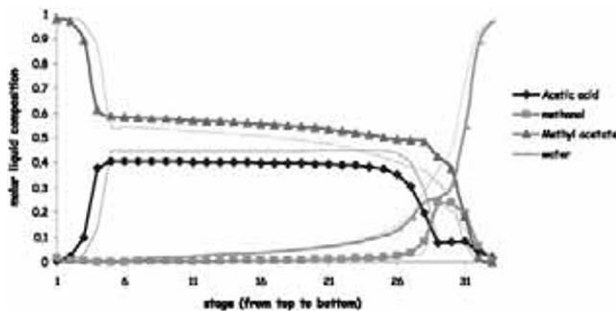


Figure 22. Production of methyl acetate—design step for an equimolar feed.

The procedure should be extended to kinetically controlled reaction. A pure numerical analysis should also be substituted to the graphical analysis to be able to investigate reactive systems whatever the number of components and reactions.

NOMENCLATURE

a_i	activity of component i
B	molar flowrate of bottom product, mol s^{-1}
D	molar flowrate of distillate product, mol s^{-1}
F	molar flowrate of feed, mol s^{-1}
F^*	molar flowrate of pseudo initial feed, mol s^{-1}
F_L	for a double feed column, molar flowrate of the lower feed, mol s^{-1}
F_U	for a double feed column, molar flowrate of the upper feed, mol s^{-1}
F_R	for a double feed column, ratio F_R/F_U
K_I	ratio B/D
K_D	ratio D/B
K_i	liquid-vapour equilibrium constant of component i
Keq	Chemical equilibrium constant, depends on the reaction
$mK_i(T, P, x, y)$	calculated liquid-vapour equilibrium constant for given T, P, x and y
$mKeq(T)$	calculated chemical equilibrium reaction depends on the reaction
N_{feed}	number of feed plates
N_c	number of components
N_{re}	number of equilibrium reactions
N_p	number of phases
N_s	number of stages of the column
P	pressure, bar
Q_r	heat of reaction, J mol^{-1}
r	reflux ratio
r_r^*	modified reflux ratio
$r_{\text{min}}^{\text{react}}$	reactive profile minimum reflux ratio
$r_{\text{min}}^{\text{pure}}$	pure stripping or pure rectifying profile minimum reflux ratio
r_k	reaction rate on stage k , mol s^{-1}

r_k^{cum}	cumulative production rate on stage k , mol s^{-1}
s	reboil ratio
s_s^*	modified reboil ratio
t	time, s
T	temperature, K
U	liquid molar holdup, mol
V	vapour flowrate, mol s^{-1}
x_i	liquid molar composition of component i
y_i	vapour molar composition of component i
X_i	reactive liquid molar composition of component i
Y_i	reactive vapour molar composition of component i
x^*	pseudo initial composition vector
x	liquid molar composition vector
y	vapour molar composition vector
X	liquid molar reactive composition vector
Y	vapour molar reactive composition vector

Greek symbols

δ_R	pole of the reaction R
$\nu_{i,k}$	stoichiometric coefficients of component i in reaction k
ν_t	sum of stoichiometric coefficients
ξ_j	extent of reaction j , mol
τ_r	yield of reaction
$\tau_{i,D}$	recovery ratio of component i in the distillate
$\tau_{i,B}$	recovery ratio of component i in the bottom product
χ_r	evolution of chemical reaction r , mol s^{-1}
ψ_r	nondimensional evolution of the reaction r
γ_i	activity coefficient of component i
σ	nondimensional time
τ	nondimensional time

Subscripts

B	bottom
D	distillate
F	feed
U	upper feed
L	lower feed
n	stage n
k	reference component
key	key component

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APPENDIX A: ALGORITHM DETECTING THE END OF THE NONREACTIVE PROFILES DURING THE SYNTHESIS STEP

To detect the end of pure stripping or rectifying profile in the synthesis step of the procedure, a test must be performed on each calculated plate to detect the intersection between the profile and the chemical and phase equilibrium surface. Let us consider a reaction $R_1 + R_2 \rightleftharpoons P$ where P is the highest boiling component. In that case, P is recovered at the bottom of the column and a pure separation section is required (see rule no. 1b). Figure A1 represents the pure stripping profile and the chemical and phase equilibrium surface of the considered system. Point A corresponds to the last calculated plate on the pure stripping profile before its intersection with the chemical and phase equilibrium surface. Each point on the pure stripping profile characterizes a liquid mixture with a composition x_n . For each stage, the composition x_n^{eq} (point A^{eq}) which corresponds to the composition change due to the reaction is calculated and the extent of the reaction is defined as follows:

$$\xi_n = \frac{N \cdot (x_{i,n} - x_{i,n}^{eq})}{x_{i,n}^{eq} \cdot \nu_i - \nu_i}$$

where N is the plate molar holdup.

Points A and A^{eq} belong to the stoichiometric line with represents the composition change resulting from the reaction. Due to varying initial components concentrations, a

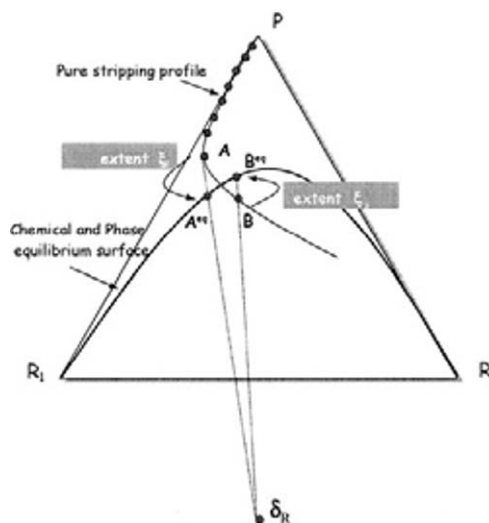


Figure A1. Intersection between the pure stripping profile and the chemical and phase equilibrium surface.

family of straight lines can be created, all including a common point δ_R and called the pole.

- If $\xi_n < 0$ (point A on Table B1), the plate n is a pure stripping plate.
- If $\xi_n > 0$ (point B on Table B2), the plate n must be a reactive plate. The number of pure stripping plate is equal to $n - 1$.

APPENDIX B: THERMODYNAMIC DATA FOR THE MTBE PRODUCTION SYSTEM

Wilson coefficients (cal/mol)

Table B1

	A_{ij} (cal/mol)	A_{ji} (cal/mol)
Isobutene/methanol	169.9953	2576.8532
Isobutene/MTBE	-30.2477	271.5669
Methanol/MTBE	1483.2478	-406.3902

Chemical equilibrium constant (Colombo *et al.*, 1983)

$$\ln(K) = -10.0982 + 4254.05/T + 0.2667 \ln(T)$$

The equilibrium is expressed as a function of activity coefficients.

Pure components and azeotropes ($P = 11$ atm)

Table B2

Pure component or azeotrope	Boiling point (°C)
Azeotrope isobutene (90.4% molaire)/methanol	71.9
Isobutene	75
Azeotrope MTBE (47% mol)/methanol	132
Methanol	141
MTBE	153

Vapour phase model

Equation of State: Soave-Redlich-Kwong.

APPENDIX C: THERMODYNAMIC DATA FOR THE MEAC PRODUCTION SYSTEM

Wilson coefficients (Song *et al.*, 1998)

	A_{ij} (cal/mol)	A_{ji} (cal/mol)
Acetic acid/methanol	2535.2019	-547.5248
Acetic acid/methyl acetate	1123.1444	-696.5031
Acetic acid/water	237.5248	658.0266
Methanol/methyl acetate	813.1843	-31.1932
Methanol/water	107.3832	469.5509
Methyl acetate/water	645.7225	1918.232

Equilibrium constant for the esterification reaction (Song *et al.*, 1998)

$$\ln(K) = -0.8226 + 1309.8/T$$

The equilibrium is expressed as a function of activity coefficients.

Equilibrium constant for the vapour phase dimerization

$$\log(K_d) = -10.241 + 3166/T$$

Pure components and azeotropes ($P = 1$ atm)

Pure component or azeotrope	Boiling point (°C)
Azeotrope methyl acetate (66% mol)/methanol	53.6
Azeotrope methyl acetate (92% mol)/water	57
Methyl acetate	56.9
Methanol	64.5
Water	100
Acetic acid	118.2