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# Feasibility Analysis, Synthesis, and Design of Reactive Distillation Processes: A Focus on Double-Feed Processes

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*A new approach for the feasibility analysis of reactive distillation processes based on the reactive extractive curve maps (rExCM) concept is introduced. A method dedicated to reactive distillation feasibility analysis, and design has been developed in our team since 1999. 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. Currently, the procedure permits the conceptual design of hybrid reactive column configuration with one or two feed plates, for any number of equilibrium reactions (provided that the degree of freedom of the system is equal to 2) occurring in liquid or vapor phase. This contribution focuses on the most recent developments: the generalization of the feasibility analysis step to double-feed processes thanks to the introduction of the rExCM concept. This methodology is illustrated through two examples: the emblematic methyl acetate example and the production of dimethyl methyl glutarate.*

**Keywords:** reactive distillation, feasibility analysis, conceptual design, double-feed columns, reactive extractive curve

## Introduction

Despite the many advantages of reactive distillation (RD) processes<sup>1</sup> the industrial community still hesitates on firmly adopting that multifunctional process, mainly by lack of systematical and universal design tools. During the past decades, many studies have been published to provide systematic procedures for the feasibility analysis, and the design of RD processes but only few of them propose a systematic and complete procedure which combines feasibility analysis, synthesis, and design of RD column. To fill this lack, a tool has recently been developed in the Laboratoire de Génie Chimique.<sup>3</sup> The main interest of this tool lies on a progressive introduction of the process complexity. From a minimal set of information concerning the physicochemical properties of the system—pure components physical properties, phase and reaction equilibria—three successive steps (feasibility analysis, synthesis, and design) lead to the design of the unit and the specification of its operating conditions. Since 1999, this methodology has also been extended through various PhD thesis and post doctoral studies. Figure 1 highlights the successive extensions of the methodology developed in the Laboratoire de Génie chimique and its applications to aca-

demic and industrial case studies proposed by Rhodia and other industrial partners.

Currently, the procedure permits the conceptual design of hybrid reactive column configuration with one or two feed plates, for any number of equilibrium reaction (provided that the degree of freedom of the reactive system is equal to 2) occurring in liquid or vapor phase. The feasibility analysis of reactive liquid liquid vapor reactive distillation (LLV RD) has also been studied.<sup>8</sup>

This contribution focuses on one of the most recent development of the procedure: the extension of the feasibility analysis step to double-feed processes. After a review of the general methodology, the second part of this article focuses on the feasibility analysis of double-feed reactive distillation process by introducing the reactive extractive curve map (rExCM). This concept was applied to industrial cases but for confidentiality reasons, the method will be illustrated through the emblematic methyl acetate example in the last part of this article.

## Presentation of the Methodology

The original methodology dedicated to the feasibility analysis and conceptual design of RD process is extensively described and illustrated through various academic examples in earlier work.<sup>3</sup> 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

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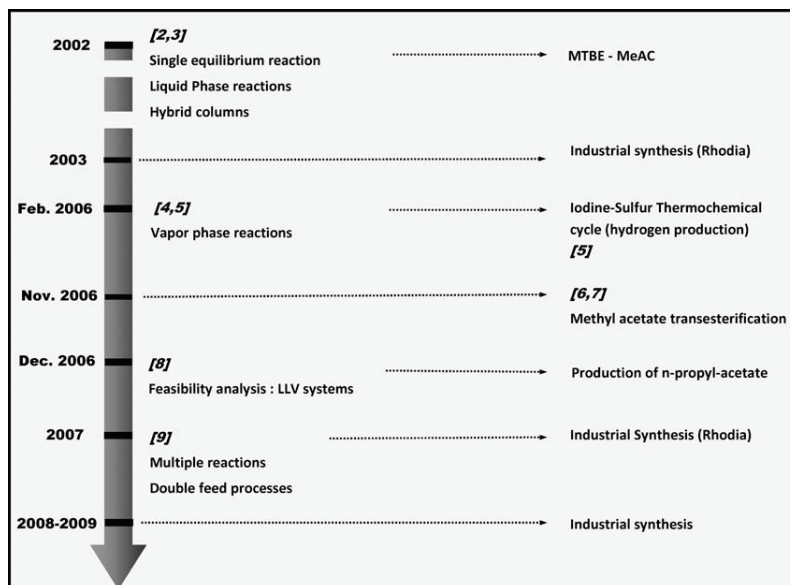


Figure 1. Sequential methodology developed in the LGC for the design of RD processes: historic of developments and industrial case studies.<sup>2-9</sup>

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.

Figure 2 presents a detailed flowchart of this approach and highlights its recent developments. The application of the methodology is currently limited to equilibrium reactive systems where degree of freedom is equal to 2 or less than 2.

Given 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 three steps of the methodology are:

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, and so forth.

Third, the design step enables to determine the operating parameters of the process (reflux ratio, heat duty, etc.). At the end of this third step, a configuration and a set of parameters relevant with the specifications are available.

### Feasibility analysis step

*First case: Single-Feed Unit: Reactive Residue Curve Maps Analysis.* The study of the reactive residue curve map gives a first idea of the feasibility and interest of investigating reactive distillation. The software we developed 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. 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 nonreactive 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 reactive residue curve maps (rRCM) is written using adimensional variables. It is given hereafter for systems consisting of  $N_c$  components and involving  $N_r$  reactions.<sup>10</sup>

$$\frac{dx_i}{d\tau} = (x_i - y_i) + \sum_{k=1}^{N_r} (v_{i,k} - v_{i,k} \cdot x_i) \cdot \psi_k \quad \text{for } i = 1, \dots, N_c - 1 \quad (1)$$

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

$$d\tau = \frac{V}{U} dt \quad (2)$$

$\psi_k$  is also a nondimensional variable defined by:

$$\psi_k = \frac{\xi_k}{V} \quad (3)$$

where  $\xi_k$  is the extent of reaction  $k$ .

The DAE system is solved with DISCO, an in house index one and two DAE solver based on the Gear method.<sup>11</sup> 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.<sup>11</sup> When the degree of freedom exceeds 2, the graphical analysis becomes difficult even impossible.

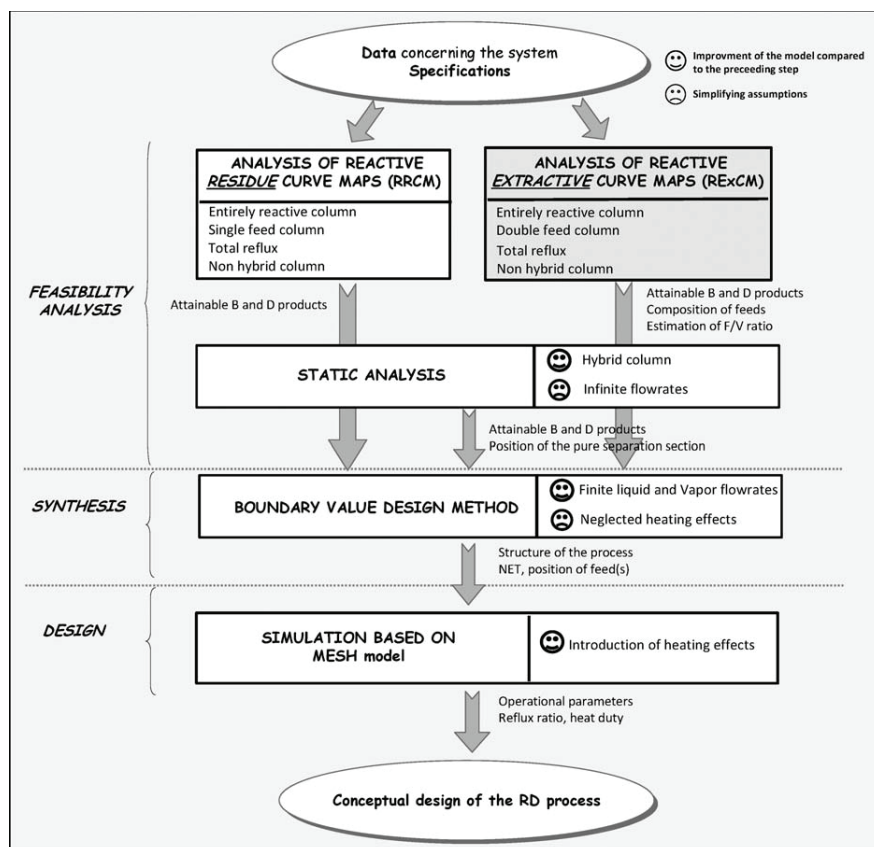


Figure 2. Methodology of the RD design (in gray, the recent development of the procedure).

Then, the analysis of the rRCM consists in the determination and the characterization of the singular points of the reactive system (stable nodes, unstable nodes, and 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.<sup>12–14</sup> These singular points give birth to distillation boundaries that must be determined to study the feasibility of the process.

Given the singular points and the distillation boundary, the following rules enable to determine the most favorable feed composition and the column structure necessary to obtain the desired product according to the following rules:<sup>15</sup>

**Rule No. 1** (see Figure 3): Single-feed reactive distillation is a feasible operation if:

- the distillate and bottom products and the feed satisfy the material balance.

- both products (bottom product B and distillate product D) are connected by a reactive distillation curve.

**Rule No. 2:** If it is necessary to separate a product that cannot exist alone in mixture whose compositions are constrained by equilibrium equations, a section with nonreactive distillation trays must be added. For example, in the case of the  $R_1 + R_2 \rightleftharpoons P$  system, a pure separation section is required to obtain pure P.

In that case, for the feasibility analysis of hybrid processes, the static analysis introduced by Giessler et al.<sup>16–18</sup> is applied.

**Rule No. 3:** If one or both products are saddles, the concentration profile can be shifted in the direction of the saddle using a column with two feed stages.<sup>15</sup>

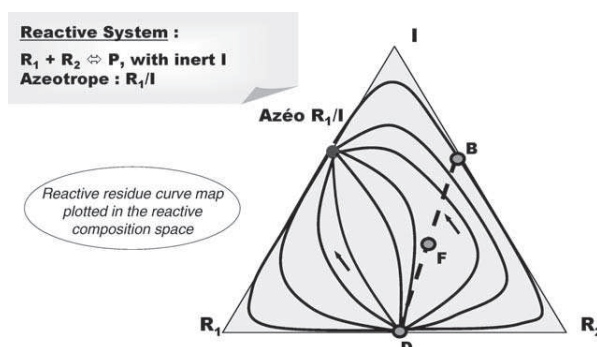
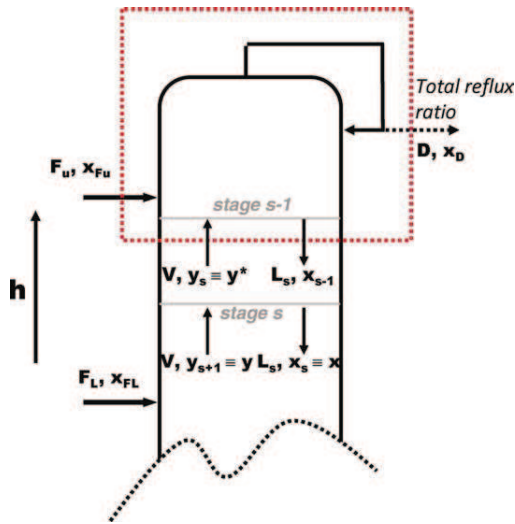


Figure 3. Feasibility analysis of a single-feed reactive distillation column.



**Figure 4. Material balance in the reactive middle section.**

[Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

However, this latter rule is only a heuristic rules which would need to be validated by a rigorous feasibility analysis. The following section provides hints for this analysis by introducing the rExCM concept.

*Second case: Double-Feed Unit: rExCM Analysis.* Some approaches have been developed in the literature to assess the feasibility or to design double-feed reactive distillation columns.

Wahnschafft and Westerberg<sup>19</sup> suggested a method based on the analysis of pinch point curves. However, this analysis relies on quite complex graphical analysis performed in the real composition space. It is so restricted to ternary systems. Malone and Doherty<sup>20,21</sup> described a hierarchy of methods, models, and calculation techniques to support the design of reactive distillation columns. On the basis of the very classical example of methyl acetate production, they apply the synthesis procedure developed by Barbosa and Doherty<sup>22</sup> to propose a double-feed distillation configuration which enables to get pure methyl acetate on the distillate. However, prior to this synthesis step, a rigorous feasibility analysis similar to the analysis of reactive residue curve maps would be required to determine the best feed conditions and the attainable product in bottom and the distillate. To fill this gap, Gadewar et al.<sup>23</sup> recently developed a feasibility analysis methodology based on a counter current cascade of vapor–liquid continuous stirred-tank reactor (CSTRs) that enables to predict the feasible splits for continuous double-feed reactive distillation processes. Furthermore, the use of reactive composition enables the application of this methodology to systems with several reactions (provided that the degree of freedom remain equal to 2).

The approach we propose is very similar to the former one but rather consists in an adaptation of the extractive profile concept defined by Lelkes et al.<sup>24</sup> for batch nonreactive extractive distillation. Using the reactive composition, the rExCM concept enables to formulate a necessary condition for the feasibility of a reactive double-feed unit which is very similar to the necessary condition formulated for single-feed RD columns and based on the analysis of reactive residue curve maps.

- Definition and formulation of a reactive extractive curve

Figure 4 shows a balance region drawn between the distillate withdrawal and a stage  $s-1$  located in the middle section.

Assuming a total reflux ratio, a mass balance on this section leads to the following equation:

$$\begin{cases} L_{j-1} \cdot x_{j-1,i} = F_u \cdot x_{F_u,i} + V \cdot y_{j,i} + \sum_{k=1}^{Nr} v_{i,k} \cdot \xi_{k,j-1} \\ \text{for } i = 1, \dots, N_c - 1 \end{cases} \quad (4)$$

where  $\xi_{k,j-1}$  is the cumulative extent of the reaction  $k$  on the stage  $j-1$  starting from the top of the column.

Using a Taylor series,  $x_{j-1}$  can be approximated by  $x_{j,i} = x_{j-1,i} + \frac{dx_{j,i}}{dh}(\Delta h) + \vartheta\{(\Delta h)^2\}$

Here,  $\Delta h = (j-1) - j = -1$ , then we obtain  $\frac{dx_{j,i}}{dh} = x_{j-1,i} - x_{j,i}$

Moreover, combining Eqs. 4 and 5, we obtain

$$L_{j-1}(x_{j-1,i} - x_{j,i}) = F_u(x_{F_u,i} - x_{j,i}) + V(y_{j,i} - x_{j,i}) + \sum_{k=1}^{Nr} (v_{i,k} - v_{t,k} \cdot x_{j,i}) \xi_{k,j-1} \quad (6)$$

Taking into consideration that  $y_s$  is in equilibrium with  $x_j$  ( $x_{j,i} = x_i$  and  $y_{j,i} = y_i^*$ ), Eq. 6 becomes

$$\frac{dx_i}{dh} \cdot L_{s-1} = F_u(x_{F_u,i} - x_i) + V(y_i^* - x_i) + \sum_{k=1}^{Nr} (v_{i,k} - v_{t,k} \cdot x_i) \xi_{k,s-1} \quad (7)$$

Then,  $\frac{dx_i}{dh} \cdot L_{j-1} = x_i(-V - F_u - v_t \cdot \xi_{j-1}) + F_u \cdot x_{F_u,i} + V \cdot y_i^* + \sum_{k=1}^{Nr} v_{i,k} \cdot \xi_{k,j-1}$

Dividing each side of the equation by  $L_{j-1}$ , we get:

$$\begin{aligned} \frac{dx_i}{dh} = -x_i + \frac{F_u \cdot x_{F_u,i}}{V + F_u + \sum_{k=1}^{Nr} v_{t,k} \cdot \xi_{k,j-1}} \\ + \frac{V \cdot y_i^*}{V + F_u + \sum_{k=1}^{Nr} v_{t,k} \cdot \xi_{k,j-1}} + \frac{\sum_{k=1}^{Nr} v_{i,k} \cdot \xi_{k,j-1}}{V + F_u + \sum_{k=1}^{Nr} v_{t,k} \cdot \xi_{k,j-1}} \end{aligned}$$

Expressing this equation as a function of the parameter  $\frac{F_u}{V}$  and the nondimensional extent of the reaction  $k$ :  $\psi_k = \frac{\xi_{k,j-1}}{V}$ , we finally obtain:

$$\begin{aligned} \frac{dx_i}{dh} = -x_i + \frac{F_u/V}{1 + F_u/V + \sum_{k=1}^{Nr} v_{t,k} \cdot \psi_k} \cdot x_{F_u,i} \\ + \frac{y_i^*}{1 + F_u/V + \sum_{k=1}^{Nr} v_{t,k} \cdot \psi_k} + \frac{\sum_{k=1}^{Nr} v_{i,k} \cdot \psi_k}{1 + F_u/V + \sum_{k=1}^{Nr} v_{t,k} \cdot \psi_k} \end{aligned} \quad (8)$$

A reactive extractive curve (rExC) is so defined by the locus of liquid composition obtained through the resolution of Eq. 7 for given:

- initial composition,
- value of  $\frac{F_u}{V}$  parameter,
- and composition of the upper feed  $x_{F_u, i}$

As for the reactive residue curves, this differential algebraic equation (DAE) system is solved with the DAE solver Do Integrate by Software Component (DISCO) based on the Gear method.<sup>11</sup>

These curves are represented in the reactive composition space then allowing the feasibility analysis of system whose degree of freedom is equal to 2.

Whereas the reactive residue curve can be seen as an approximation of the composition profiles in the rectifying and stripping sections of a reactive column operating at total reflux, the rExC approximates the liquid compositions on the reactive middle section of the same column.

- Maximum value of parameter  $F_u/V$

The mass balance equation shows that the parameter  $F_u/V$  is necessarily correlated to the reflux ratio. We can demonstrate (see Appendix) that, to keep a positive reflux ratio, the  $F_u/V$  parameter values are restricted to the interval defined by:

$$\left[ 0, \frac{1 + \sum_{k=1}^{N_r} v_{t,k} \psi_k}{(1 - \alpha_B)(1 + \beta)} \right] \quad (9)$$

with  $\alpha_B = \frac{B}{F}$  and  $\beta = \frac{F_L}{F_u}$ .

- Necessary condition for the feasibility of reactive double-feed operations

The necessary condition for the feasibility of reactive double-feed processes is illustrated on Figure 5. A double-feed reactive distillation operation is feasible, if:

- the distillate and bottom products and the feed satisfy the material balance.
- it is possible to draw a continuous path from the distillate to the bottom products thanks to a reactive residue curve (approximation of the composition profile in the reactive rectifying section), a reactive extractive curve (approximation of the composition profile in the reactive middle section), and another reactive residue curve (approximation of the composition profile in the reactive stripping section).

Consequently, the simultaneous analysis of the rRCM and rExCM enables to assess the feasibility of double-feed reactive distillation processes.

### Synthesis step

The synthesis step is based on the boundary value design method introduced by Barbosa and Doherty.<sup>21,25</sup> The specifications required for the synthesis (distillate, bottom and feed compositions, and structure of the column) are inherited from the feasibility analysis presented formerly. The synthesis provides more precise information concerning the process configuration: minimum reflux ratio, and for a given reflux ratio, location of the reactive zone, number of theoretical stages, and position of the feed plates. In the developed tool, a broad range of configurations can be considered: one or two pure separation sections, one or two feed plates, and finite or infinite reflux ratio. Within this framework, the constant molar overflow (CMO) assumptions are formulated: all the thermal effects are neglected and composition profiles

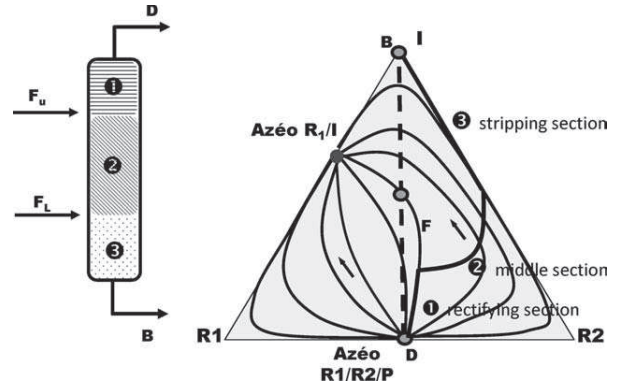


Figure 5. Feasibility analysis of a reactive double-feed distillation operation.

are deduced from the mass balance equations. The composition profiles in the rectifying, middle and stripping sections are calculated considering a RD column, and calculating the mass balance between the top of the column and a rectifying stage and between the bottom of the column and a stripping stage, respectively. The obtained profiles necessarily depend on the reflux ratio.

A feasible steady state is found when the rectifying, middle and stripping profiles intersect. As the synthesis step computes the profile stage by stage, the number of stages required in each section of the column can be estimated.

### Conceptual design step

The previous steps lead to a column configuration and a reflux ratio that permits to reach the initial product specifications. However, so far, the column configuration has been drawn up from the mass balances only. Thermal phenomena (heat of reaction, thermic loss, heat of mixture, etc.) have been ignored. Knowing the configuration of the required column which is not modified here, the design step consists in adjusting the operating parameters taking into account the overall complexity of the process. This is done with PROSIM<sup>®</sup> process simulation software. Given the pressure and the column configuration, the degree of freedom of the MESH model is equal to 2: to saturate this degree of freedom and 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 if the key component (component  $k$ ) is obtained in the distillate product:

$$D_l = D \cdot x_{l,D} \quad (10)$$

- or the bottom molar flow rate of the key component, if the key component (component  $k$ ) is obtained in the bottom product:

$$B_l = B \cdot x_{l,B} \quad (11)$$

This first specification 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 ( $x_{l,D}$  or  $x_{l,B}$ ).

Then, the required reflux ratio and heat duties are deduced from the model resolution. At the end of this step, a column structure and the associated operating parameters necessary to achieve the initial specifications are available.

**Table 1. Properties of the Components for the MGDM System**

| Name                                  | Chemical Formula                              | Molar Mass (g mol <sup>-1</sup> ) | Normal Boiling Point (K) |
|---------------------------------------|---|-----------------------------------|--------------------------|
| MGA<br>(2-methyl glutaric Acid)       | C <sub>6</sub> H <sub>10</sub> O <sub>4</sub> | 146.14                            | 627.25                   |
| MGMM<br>(Methyl 2-methyl Glutarate)   | C <sub>7</sub> H <sub>12</sub> O <sub>4</sub> | 160.17                            | 562.85                   |
| MGDM<br>(Dimethyl 2-methyl glutarate) | C <sub>8</sub> H <sub>14</sub> O <sub>4</sub> | 174.20                            | 498.45                   |
| H <sub>2</sub> O<br>(Water)           | H <sub>2</sub> O                              | 18.01                             | 373.15                   |
| MeOH<br>(Methanol)                    | CH <sub>3</sub> O                             | 32.04                             | 337.85                   |

At the end of the procedure, we finally obtain a configuration of a RD process and its operating condition. This configuration is a reliable initialization point for a further optimization of the process based on a more rigorous model (nonequilibrium equation, kinetically control reactions, etc.). In the following section, this procedure will be applied to the emblematic example of production of methyl acetate.

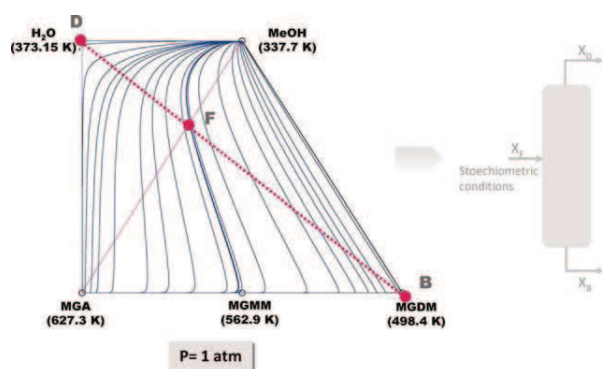
### Application: Production of Dimethyl Methyl Glutarate

The second example concerns an industrial case study proposed by Rhodia company and will permit to illustrate the methodology on a complex system consisting on five components and two reactions. This example concerns the production of dimethyl methyl glutarate (MGDM) from methyl glutarate acid (MGA) and methanol (MeOH) through two consecutive reactions: formation of the monoester 2-methyl-2-methyl glutarate (MGMM) and formation of the diester dimethyl-2-methyl glutarate (MGDM).



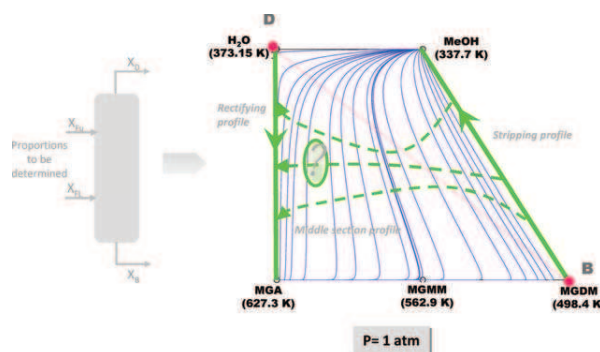
For this system a UNIFAC thermodynamic model has been chosen, and the chemical equilibria were defined as follows:

$$\ln(K_1) = -3788 + \frac{15,034.881}{T} \quad (12)$$



**Figure 6. Reactive residue curve map of MGDM system ( $P = 1$  atm).**

[Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

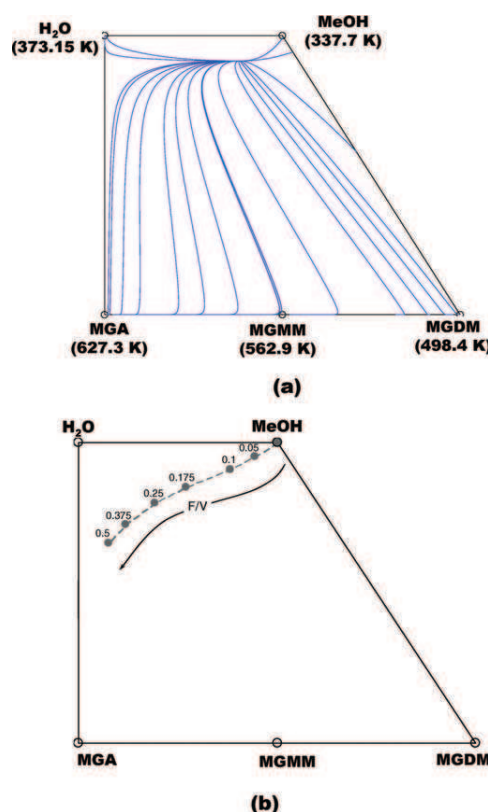


**Figure 7. Feasibility condition of a double-feed reactive distillation process for the MGDM system.**

[Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

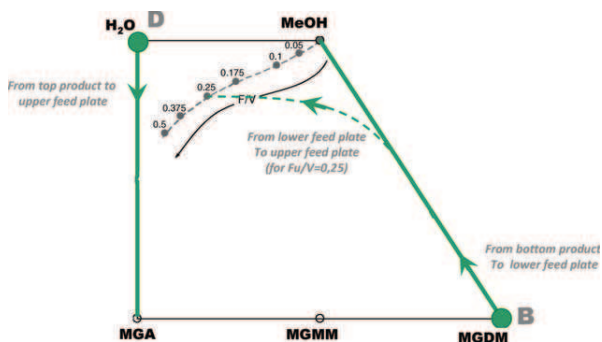
$$\ln(K_2) = -3062 + \frac{15,034.881}{T} \quad (13)$$

The five components are summarized in Table 1. The complexity of the operation relies on the very high relative volatilities of the components MGA/MeOH and MGMM/MeOH which prevent these reactants to coexist on the same stage. Then, it seems difficult even impossible to imagine a single stoichiometric feed reactive distillation column. The minimal excess of methanol will be discussed later.



**Figure 8. (a) rExCM ( $F_u/V = 0.1$ ;  $P = 1$  atm; upper feed = MGA) and (b) locus of the rExCM stable nodes.**

[Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 9. Unfeasibility of double-feed RD column to obtain pure MGDM and pure H<sub>2</sub>O.**

[Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

### Feasibility Analysis

Figure 6 represents the reactive residue curve map of the MGDM system under 1 atm and displays the mass balance line for a stoichiometric feed, that is, for proportion of reactant satisfying the following relation:

$$\frac{F_{\text{MeOH}}}{F_{\text{MGA}}} = 2 \quad (14)$$

**Pure Product Production.** The analysis of Figure 6 leads to the following conclusions:

- there is no distillation boundary;
- the stable node is the heavy reactant (MGA);
- the unstable node is the light reactant (MeOH);
- both desired products (MGDM and H<sub>2</sub>O) behave as saddle points.

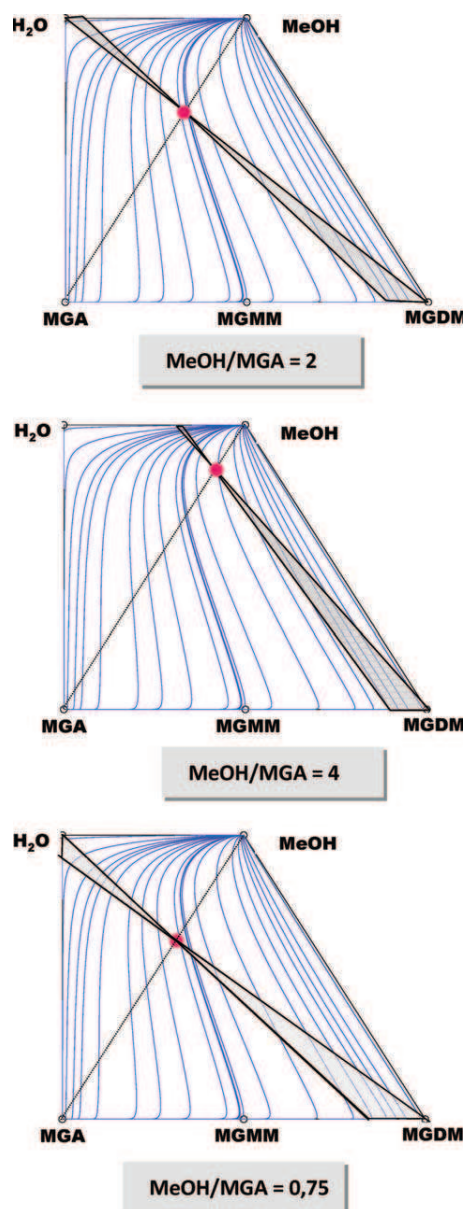
Distillate and residue do not belong to the same reactive residue curve; as a consequence, the recovery of pure MGDM is not feasible in a single-feed reactive distillation column with a stoichiometric feed. To get pure H<sub>2</sub>O and pure MGDM, the rectifying and stripping profiles need to follow paths, respectively, along to the nonreactive binary edges MGA–H<sub>2</sub>O and MeOH–MGDM. Introducing a new feed stage permit to consider a profile in the middle section which would connect rectifying and stripping profiles (see Figure 7).

An analysis of rExCM is then required to study the feasibility of a double-feed reactive distillation column. In that example, MeOH would be fed in the lower plate and according to Eq. 9, the maximum value of the  $F_u/V$  parameter is equal to 0.5. Figure 8a represents the rExCM for  $F_u/V = 0.1$ . As shown in this figure, all reactive extractive curves display a stable node located inside the reactive composition space. As shown in Figure 8b, which represents the locus of this stable node for values of all the possible values of  $F_u/V$ , the location of this stable node strongly depends on the value of  $F_u/V$ .

Figure 9 represents the profiles that would be observed on the stripping and on the rectifying sections starting from pure products (MGDM in the bottom product and H<sub>2</sub>O in the distillate product). A profile in the middle section for  $F_u/V = 0.25$  is also represented. This figure demonstrates that it is impossible to draw a continuous path from the bottom product to the distillate product. As a conclusion, even if with a double-feed plate column, a reactive distillation leading to pure MGDM and H<sub>2</sub>O is unfeasible.

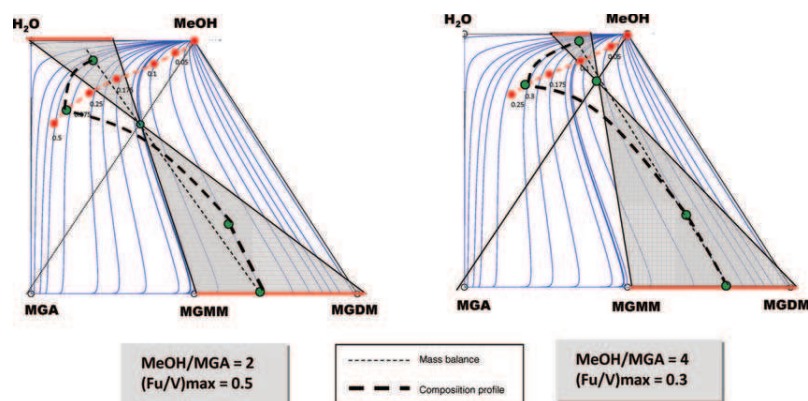
**Binary Mixture Production.** As production of pure MGDM is unfeasible, it is necessary to study the feasibility of a reactive distillation operation where the bottom and distillate product would be, respectively, MGMM/MGDM and H<sub>2</sub>O/MeOH binary mixtures. For this analysis, the minimal composition of MGMM in the bottom product is fixed to 80%. Figure 10 displays the mass balances regions for various reactants proportions (in light gray). As no reactive residue curve belong to both lower and upper mass balance regions, a single-feed RD operation is not feasible.

Figure 11 enables the feasibility analysis of a double-feed reactive distillation operation for an equimolar feed (MeOH/MGA = 2) or for an excess of MeOH (MeOH/MGA = 3). In both cases, it is possible to draw a continuous path from the bottom product to the distillate product. Consequently, a



**Figure 10. Feasibility analysis of single-feed RD operation for the production of binary mixtures.**

[Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 11. Feasibility analysis of double-feed RD operation for the production of binary mixtures.**

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double-feed reactive distillation column would enable to product a binary mixture composed of MGDM and MGMM with a MGDM molar fraction higher than 80%.

### Synthesis

According to the feasibility analysis, a double-feed reactive distillation column operating with infinite reflux ratio would permit to obtain a bottom product mainly composed of MGDM. To confirm this conclusion and to determine the required column configurations for finite reflux, it is necessary to perform the synthesis step. Bottom and distillate compositions are essential data for this study. To obtain a consistent set of data, the mass balances are solved with constraints on the conversion ratio of MGA, the selectivity of reaction R2 and conversion ratio of MGDM.

$$\tau_{MGA} = 1 - \frac{D \cdot x_{D,MGA} + B \cdot x_{B,MGA}}{\sum_{i=1}^2 (F_i \cdot x_{F_i,MGA})} = 0.99 \quad (15)$$

$$S_{MGDM} = \frac{D \cdot x_{D,MGDM} + B \cdot x_{B,MGDM}}{D(x_{D,MGDM} + x_{D,MGMM}) + B(x_{B,MGDM} + x_{B,MGMM})} = 0.95 \quad (18)$$

$$\tau_{MGDM} = \frac{B \cdot x_{B,MGDM}}{D \cdot x_{D,MGDM} + B \cdot x_{B,MGDM}} = 0.99 \quad (17)$$

**Table 2. Influence of the MeOH/MGA Ratio on the Performances of the RD Column**

|                    |                          | Steady state No.1 | Steady state No.2 |
|--------------------|--------------------------|-------------------|-------------------|
|                    | MeOH/MGA                 | 2                 | 3                 |
|                    | $F_{MGA}(\text{mol/s})$  | 100               | 100               |
|                    | $F_{MeOH}(\text{mol/s})$ | 200               | 300               |
| Distillate Product | $x_{MGA}$                | 0.00(traces)      | 0.00(traces)      |
|                    | $x_{MGMM}$               | 0.05              | 0.00(traces)      |
|                    | $x_{MGDM}$               | 0.95              | 0.00(traces)      |
|                    | $x_{H_2O}$               | 0.00(traces)      | 0.96              |
|                    | $x_{MeOH}$               | 0.00(traces)      | 0.03              |
| $D(\text{mol/s})$  |                          | 202               | 302               |
| Bottom Product     | $x_{MGA}$                | 0.00(traces)      | 0.00(traces)      |
|                    | $x_{MGMM}$               | 0.05              | 0.00(traces)      |
|                    | $x_{MGDM}$               | 0.95              | 0.00(traces)      |
|                    | $x_{H_2O}$               | 0.00(traces)      | 0.64              |
|                    | $x_{MeOH}$               | 0.00(traces)      | 0.35              |
| $B(\text{mol/s})$  |                          | 98                | 98                |

Notice that combining these three criteria, we obtain an aggregate criteria which refers to the global performance of the operation taking into account the efficiency of both reaction and separation effect at the same time.

Indeed, we can demonstrate that the global efficiency of the process (GlobalEff):

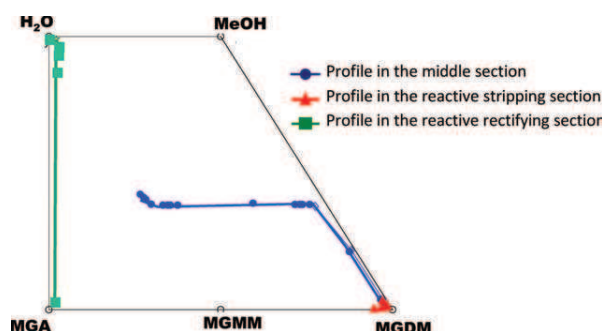
$$\text{GlobalEff} = \tau_{MGA} * S_{MGDM} * \tau_{MGDM} = \frac{B \cdot x_{B,MGDM}}{\sum_{i=1}^2 (F_i \cdot x_{F_i,MGA})}$$

Assuming that  $F_{MGA} = 100 \text{ mol/h}$ , Table 2 gives the compositions and flow rates of distillate and bottom products for two selected steady states. In these conditions, the global efficiency of the RD column is equal to 93.1 % which means that for 100 mol/hr of MGA, we can obtain 93.1 mol/hr of MGDM in the bottom product.

For the steady state No. 1 given in Table 2 and whatever the location of the lower feed plate and the value of the reflux ratio, the observed profile looks like the one represented in Figure 12. It means that the reactive distillation operation is unfeasible in stoichiometric conditions.

Figure 13 displays one of the reactive profiles obtained for the steady state No. 2 (small excess of MeOH). In that situation; the column configuration is as follows:

- 5 stages in the reactive stripping section,
- 11 stages in the reactive middle section,
- 2 stages in the reactive rectifying section.



**Figure 12. Typical profile obtained in the synthesis step for the steady state No. 1.**

[Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

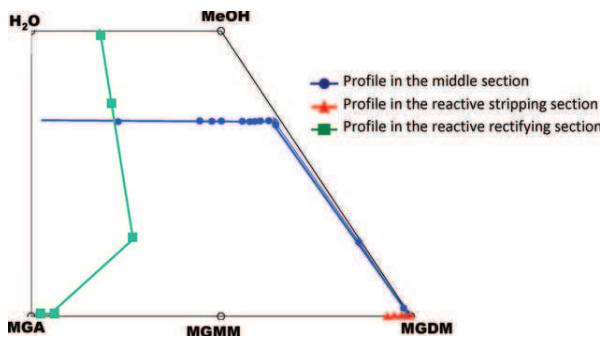


Figure 13. Feasible profile obtained in the synthesis step for the steady state No. 2.

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### Conceptual design

In the design step, the configuration given in the former part is simulated using a process simulation software. Given the degree of freedom of the reactive distillation process, Two specifications must be provided to the process simulator. To determine these two specifications, two strategies can be used:

- The first strategy consists in deducing these specifications from the performances predicted during the synthesis step; In our case study, the bottom flow rate and the composition of MGDM in the bottom product are given (see Figure 14a). Unfortunately, for this system, the relaxation of the CMO does not permit to reach the global efficiency determined during the synthesis step.
- The second strategy consists in fixing the distillate flow rate and analyzing the influence of the reflux ratio the global efficiency of the process (see Figure 14b). As illustrated in Figure 15, a reflux ratio equal to 5 can lead to an efficient operation with a global efficiency equal to 81%. Figure 16 represents the composition profiles obtained for this configuration.

### Conclusions

A general methodology for the conceptual design of reactive distillation processes has been presented. The main in-

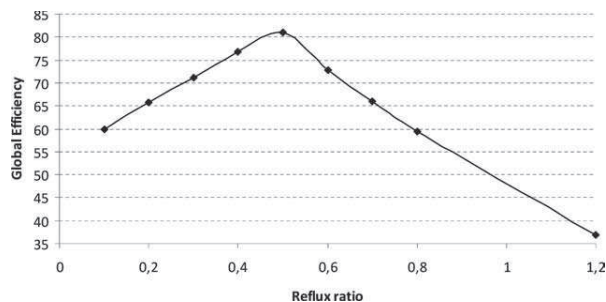


Figure 15. Influence of the reflux ratio on the global efficiency.

terest 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 a preliminary design of a column and the specification of its operating conditions. The results obtained leads to a reliable initialization point for a further optimization of the operating conditions and the process design. Of course, this optimization step should be based on a more rigorous model including not only nonequilibrium equations for the liquid vapor (LV) equilibrium but also kinetically controlled reactions.

The methodology is constantly extended. In this contribution, the most recent development concerning the introduction of a rigorous feasibility analysis for double-feed processes has been developed. The concept of the reactive extractive curve map appears here as a very efficient tool to quickly assess the feasibility of a double-feed reactive distillation process. These new functionalities have been validated not only through an academic example but also through various industrial case studies recently proposed by Rhodia or by other industrial partners.

However, although RD processes are really promising, the interactions existing between reaction and separation functions lead to nonlinearities which strongly complicate the control of such processes. For that reason, studies concerning

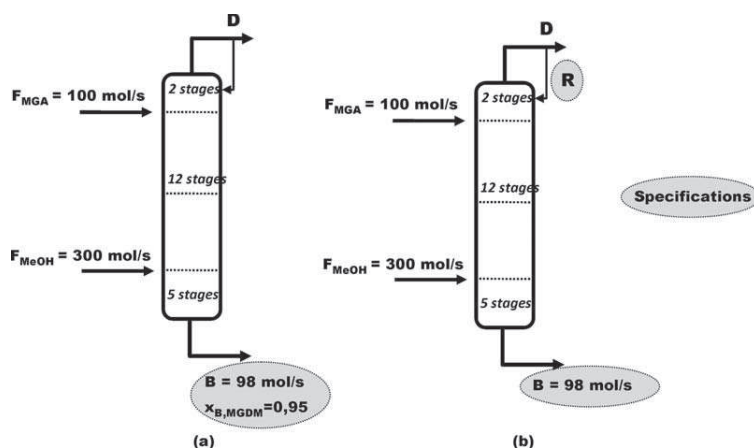


Figure 14. Definition of the problem for the design (a) or the sensibility analysis (b) of the RD distillation column.

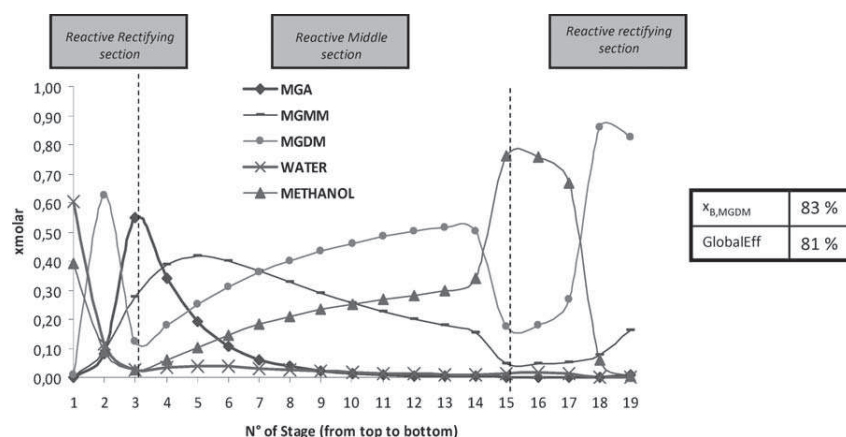


Figure 16. Composition profiles obtained in the design step.

the design of RD processes including controllability is currently in progress.

## Notation

### Indexes

- $j$  = stage
- $k$  = reaction
- $l$  = key component

### Variables

- $x$  = liquid composition
- $y$  = vapor composition
- $R$  = reflux ratio
- $B$  = bottom product flow rate (mol/s)
- $F$  = total feed flow rate (mol/s)
- $F_u$  = upper feed flow rate (mol/s)
- $F_l$  = lower feed flow rate (mol/s)
- $L$  = liquid flow rate (mol/s)
- $Nr$  = number of reactions
- $V$  = vapor flow rate (mol/s)
- $U$  = molar holdup (mol)
- $D$  = distillate flow rate (mol/s)

### Greek letters

- $\tau$  = adimensional time
- $v_{i,k}$  = sum of the stoichiometric coefficient of reaction  $k$
- $v_{i,k}$  = stoichiometric coefficient of reaction  $k$  for component  $i$
- $\xi_{k,j}$  = extent of reaction  $k$  on stage  $j$  (mol/s)
- $\psi_k$  = nondimensional extent of reaction

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## Appendix

The purpose of this appendix is to demonstrate the relation given by Eq. 8. This relation gives the maximal value of the parameter  $F_u/V$  for a double-feed reactive distillation column.

A material balance on the balance region drawn on the Figure A1 leads to the following relation:  $V + B + \sum_{k=1}^{Nr} v_{t,k} \zeta_k = F_u + F_l + L$ , where  $\zeta_k$  is the global yield of reaction  $k$  in the column.

Dividing this relation by  $V$ , we obtain:

$$\frac{F_u}{V} + \frac{F_l}{V} + \frac{r \cdot D}{V} = 1 + \frac{B}{V} + \frac{\sum_{k=1}^{Nr} v_{t,k} \zeta_k}{V} \quad (A1)$$

where the reflux ratio  $r$  is given by:  $r = \frac{L}{D}$

Defining three parameters:  $\alpha_B = \frac{B}{F}$ ,  $\alpha_D = \frac{D}{F}$ , and  $\beta = \frac{F_l}{F_u}$ , Eq. A1 becomes:

$$\frac{F_u}{V} (1 + \beta) + r \cdot \alpha_D \cdot \frac{F_u}{V} (1 + \beta) = 1 + \alpha_B \cdot \frac{F_u}{V} (1 + \beta) + \frac{\sum_{k=1}^{Nr} v_{t,k} \zeta_k}{V}$$

This equation can also be written as follows:

$$\frac{F_u}{V} (1 + \beta) (1 + r \cdot \alpha_D + \alpha_B) = 1 + \frac{\sum_{k=1}^{Nr} v_{t,k} \zeta_k}{V}$$

According to this equation, we can express the reflux ratio by:

$$r = \frac{1}{\alpha_D} \left[ \frac{1 + \frac{\sum_{k=1}^{Nr} v_{t,k} \zeta_k}{V}}{\frac{F_u}{V} (1 + \beta)} + \alpha_B - 1 \right] \quad (A2)$$

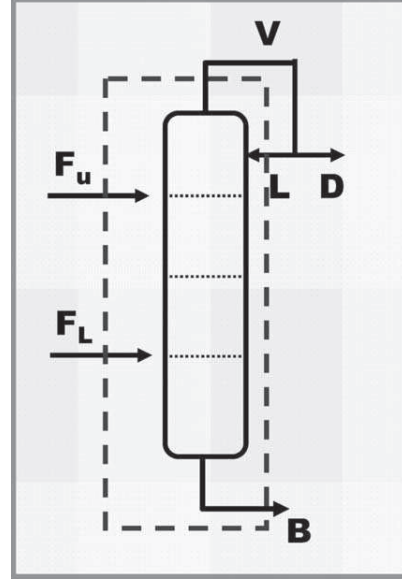


Figure A1. Mass balance on a double-feed RD column.

The reflux ratio must be a positive parameter, we can write the following condition:

$$1 + \frac{\sum_{k=1}^{Nr} v_{t,k} \zeta_k / V}{\frac{F_u}{V} (1 + \beta)} + \alpha_B - 1 \geq 0$$

This condition finally permits to obtain the upper bound for the  $F_u/V$  parameter:

$$\frac{F_u}{V} \leq \frac{1 + \frac{\sum_{k=1}^{Nr} v_{t,k} \zeta_k}{V}}{(1 - \alpha_B)(1 + \beta)}$$

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