Designing reactive distillation processes: present and future

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Abstract

The potential benefits of applying reactive distillation (RD) processes are taxed by significant complexities in process development and design. The design problem is formulated in the wider context of process development and engineering. From that perspective design methods for RD units developed over the last decades are classified and described. A fingerprint of the most representative work in the three categories, graphical, optimisation- and heuristic-based, is presented and deficiencies are identified. In response to a need for a more integrated design methodology, a conceptual model is offered which uses a hierarchy of embedded design spaces of increasing refinement and conjugates the strengths of both the graphical- and optimisation-based methods.

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Keywords: Reactive distillation; Conceptual design; Residue curves; Distillation lines; Optimisation-based methods; Heuristics

1. Introduction

When chemical reactions and physical separations have some overlapping operating conditions the combination of these tasks in a single process unit can offer significant benefits. These benefits could involve: avoidance of reaction equilibrium restrictions, higher conversion, selectivity and yield, removal of side reactions and recycling streams, circumvention of non-reactive azeotropes and last but not least reduction of number of units (investment cost) and energy demands (heat integration) (Jimenez, Wanhschafft, & Julka, 2001; Malone & Doherty, 2000; Schenbecker & Tlatlik, 2003; Stichlmair & Frey, 1999; Subawalla & Fair, 1999). However, there is a price to pay in terms of increased complexity in design and operations. The non-linear coupling of reactions, transport phenomena and phase equilibria can give rise to highly system-dependent features, possibly leading to the presence of reactive azeotropes and/or the occurrence of steady-state multiplicities. Also the number of design decision variables for such an integrated unit will be high. This paper will focus on the available design issues and techniques for reactive distillation (RD) processes. Industrial relevance requires design issues not to be separated from the context of process development and plant operations. Hence, the review will start from a process life span perspective.

The aim of chemical process design has conventionally been considered as finding equipment sizes, configurations and operating conditions that will allow for the economical, safe and environmental responsible conversion of specific feed stream(s) into specific product(s). This task is in principle carried out only by specifying the state of the feeds and the targets on the output streams of a system (Buzad & Doherty, 1995; Doherty & Buzad, 1992). Frequently, however, the design activity turns to be severely complicated by the difficulty of identifying feasible equipment configurations and ranges of suitable operating conditions. This situation can be explained by the fact that the design of chemical process units is only a constitutive part of a larger scale—and therefore more complex—problem: the joint consideration of process unit development and design. At that higher level of aggregation, the objective of the design problem includes not only sizing the unit but also establishing the requirements of the design, screening the process feasibility and—at the top—identifying the process opportunities (Fig. 1).

From this point of view, two parallel and inter-related activities can be identified: the design program and the development program. For a given level of design detail all the
The design problem regarded as the combination of a design program and a development program.

- **Identification of opportunities**: This task permits one to qualitatively select the set of competing process technologies/equipment configurations, which might convert the given feeds to the desired products. Schoenmakers and Bessling (2003, Chapter 2), for instance, use the physical/chemical characteristics of the system (e.g., reaction velocity and relative volatility) to choose the equipment configuration. Proven technologies together with novel configurations might arise at this stage (e.g., dividing wall columns, pump-around reactors, side-reactors, etc.) (Baur & Krishna, 2003; Krishna, 2003, Chapter 7; Mutaib & Smith, 1998a, 1998b).

- **Screening of feasibility**: The feasibility of the selected opportunities is then screened with respect to the attainable products of a given set of feed streams. In this stage, the concepts of attainable region (Feinberg, 1999; Nisoli, Malone, & Doherty, 1997) and \( \infty/\infty \) approach (Fein & Liu, 1994; Güttinger, 1998; Güttinger & Morari, 1997, 1999a, 1999b; Westerberg & Wahnschafft, 1996, Chapter, 23) might be used.

- **Design requirements**: The set of functional requirements for the design can be deemed as the basis of design. This information involves the boundary conditions, the process structure, its physical behaviour (i.e., operability and availability) and minimum performance (e.g., safety and economics).

- **Design of units**: The final stage in the overall design problem defines the spatial and temporal variables of the unit(s), together with its (their) operation window(s) and mode(s) of operation. An extended description of this design task is given in Section 3.

The first three tasks in the design program are related to the scope of design, whereas the last task involves essentially the design of the units. If the general design paradigm (Biegler, Grossman, & Westerberg, 1997; Sirola, 1996a, Chapter 23, 1996b) is used as the backbone for the design task, the overall design problem can be represented as a multi-stage goal-directed process, with dynamic flow of information between the design tasks, the method development and the knowledge development (Fig. 2).

In the case of RD, design issues are by far more complex than those involved in conventional distillation and may differ significantly from case to case. For instance, the design variables for conventional distillation include the number of trays, the feed tray location and the reflux ratio for a constant molar overflow (CMO) system with single-feed tray. In contrast, in a RD column the liquid hold-up is the major design parameter that determines the extent of reaction, the feed might be distributed within the unit and a CMO cannot be assumed unless the reaction is thermally neutral and stoichiometrically balanced (Ciric & Gu, 1994). All these facts have led to a smaller number of RD applications in the chemical industry (Grotissen, 2003), than could be expected given the economic benefits that this combined process offers (Doherty & Buzad, 1992; Georgiadis, Schenk, Pistikopoulos, & Gani, 2002; Taylor & Krishna, 2000). Due to this intricate feature all the endeavours of the RD scientific community have resulted in the development of design algorithms mostly based upon equilibrium models applied to systems with simplified thermodynamics and reactions kinetics (Malone & Doherty, 2000; Ökästinski & Doherty, 1997, 1998; Smejkal & Soos, 2002; Ung & Doherty, 1995a, 1995b; Venkataraman, Chan, & Boston, 1990).
however, non-equilibrium (NEQ) models have been developed to assist in the accurate modelling of RD units, accounting for mass transfer limitations and considering its interaction with chemical reaction (Baur, Higler, Taylor, & Krishna, 2000; Baur & Krishna, 2002, 2003; Baur, Taylor, & Krishna, 2001a, 2001b, 2001c; Higler, 1999; Higler, Krishna, & Taylor, 1999, 2000; Higler, Taylor, & Krishna, 1998, 1999; Krishna, 2003, Chapter 7; Krishna-murthy & Taylor, 1985; Taylor & Krishna, 1993, 2000, 2003, Chapter 9; Wesselingh, 1997). Although the NEQ-based models are highly recommended for a more realistic description of the process—especially in advanced stages of the design cycle—their implementation is still relying upon the designer’s expertise. Furthermore, inappropriate parameters’ estimators might introduce an increased number of uncertainties.

In reviewing the currently available design methods for RD processes three core questions are considered:

- What output information is requested from the design program?
- To what extent are the current methods able to provide this output?
- What resources (time wise, tools, costs) are required for the design program?

The statement of the design problem (Table 1) shows that the desired outputs from the design program might be grouped in two main categories: those related to the process structure and performance (i.e. minimum economic performance) and those related to temporal features of the unit(s) (i.e. operability and availability). For the sake of clarity, the definitions adopted for each category have been included in Table 2.

The present contribution is outlined as follows: based upon a detailed review on the design methodologies developed during the last decades for RD (Section 2), a methods’ fingerprint is obtained, focussing particularly upon the method outputs, assumptions, advantages and limitations. Then, the identification of missing opportunities is carried out, leading to the development of an integrated design methodology, which intends to systematically merge the strengths and overcome the limitations of the given design methods (Section 3). It is worthwhile mentioning that the present contribution focuses upon the definition of the RD process structure, paying less explicit attention to a detailed
Table 1

Design problem statement

The design problem of reactive distillation processes can be seen as the creative task of structuring and sizing the RD process provided a set of constraints, windows of feed specifications and ranges of product targets. The design problem might be formulated as:

Given:
A set of components and chemical reactions
The characteristics of the feed streams ($P$, $T$, $x$)
A set of different modes of operation for the process
A set of product specifications and safety and operational constraints for each mode of operation
Data regarding the process economic targets based upon prices of the products and the reactants as well as correlations for the investment and utility costs
Ranges of possible values for the major model parameters and ranges of variation for key process variables
Disturbances' scenarios
Targets of availability of the unit(s)

Determine:
The number/type of units and their tasks (reaction, distillation, reactive distillation)
The connectivity of the units (flowsheet)
The type of internal contacting structure (continuous, discontinuous and/or diving wall) and hydrodynamic features (i.e. $\Delta P$, RTD, contacting area and volumetric hold-up)
The total number of stages in the column (reactive/non-reactive)
The location of the feed, withdraw and turn-around stages
The hold-up of the liquid phase for homogeneous reactions or the catalyst load for heterogeneous reactions
Flow regimes, column diameter
Control structure, controllers type and tuning parameters, placing of actuators and sensors
Operating conditions (e.g. operating pressure)
Reboil and reflux ratios
Reactant ratio
Economic, safety and environmental performance

Table 2

Categories of information resulting from the design process in reactive distillation

<table>
<thead>
<tr>
<th>Structure</th>
<th>Includes the complete spatial structure of the process, together with the control loops and operating conditions (ranges of temperature, pressure and reboil/reflux ratios)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Performance</td>
<td>Involves the estimation of the capital and operational cost of the process during the time horizon; normally the total annualised cost is calculated</td>
</tr>
<tr>
<td>Operability</td>
<td>Involves the ability to operate the unit(s) at preferred conditions in spite of disturbances and changes in operational policies</td>
</tr>
<tr>
<td>Availability</td>
<td>Is rarely considered and is a measure of the degree to which the unit(s) is in an operable state at any time</td>
</tr>
</tbody>
</table>

analysis of the actual dynamics of the unit, which might be described by NEQ-models. An extended review on this last topic can be found in the publications by Krishnamurthy and Taylor (1985) and Taylor and Krishna (1993, 2000, 2003, Chapter 9). Furthermore, the temporal features of the process unit(s) (e.g. operability and availability) are not fully considered in the proposed methodology, as availability is foreseen to be taken into account at the next level of engineering detail.

2. Methods for conceptual design of RD columns

The available approaches for the design of RD may be categorised into three main groups: those based upon graphical/topological considerations, those based upon optimisation techniques and those derived from heuristic/evolutionary considerations.

2.1. Graphical methods

The graphical methods are called so, because the decisions are made upon the basis of graphical information. This information is often generated by means of models. These approaches rely upon the behaviour of residue curves or distillation lines and may be classified into two well-defined trends: (a) methods based upon thermodynamic-topological analysis of distillation lines; and (b) methods based upon composition transformations.

2.1.1. Statics analysis

The design method based upon statics analysis in RD units involves finding the complete set of steady-state modes and the set of corresponding operating parameters (Serafinov, Pisarenko, & Kardona, 1999). Since separation is by far the most costly task, the prime purpose of statics analysis method is the synthesis of RD processes with
Parameters (Serafimov et al., 1999). For this purpose, several approaches are proposed, which are in general terms based upon thermodynamic-topological analysis of distillation diagrams (Giessler et al., 1998; Giessler, Danilov, Serafimov, Hasebe, & Hashimoto, 1999).

Assumptions: (a) The vapour and liquid flow rates in the column are infinitely large; (b) the capacity of the reaction part in the column is large enough to carry out a given conversion rate; (c) the plant is operated at steady-state and theoretical stages are chosen; and (d) one reversible equilibrium reaction is considered.

These assumptions allow one to estimate the liquid composition on a tray as the composition of vapour one tray below, i.e. $x_i = y_{i+1}$, and the profiles may be estimated by using usual distillation lines.

Description: This method considers that composition change due to reaction is negligible on each stage and that RD is a succession of reaction and distillation operations (Giessler et al., 1998), where the feed is firstly converted to a pseudo-initial mixture—with composition $X^*$ assuming a certain extent of reaction $\epsilon$—which is then separated in a distillation column (Fig. 3a). For that pseudo-initial mixture feasible steady states occur when: the composition $X^*$ and the product compositions satisfy the mass balance and a part of the distillation line lies inside the forward reaction rate region.

The number of theoretical and reactive stages is determined from the distillation line and from the intersection of the distillation line and CEM (i.e. chemical equilibrium manifold and represents the boundary of the forward and backward reactions) (Giessler et al., 1999). Since there are multiple pairs of $X^*$ and product composition that satisfy the mass balance, the method sets one of the product composition as reference point and solves for the other two (for a three-component system) by using material balance expressions. Thus, two of the components’ compositions and $X^*$ lie on the same line—referred to as line of mass balance (LMB)—in the diagram and allow the estimation of the ratio $D/B$ at a certain reboil ratio only by exploring the ratio of the line segments (Fig. 3b). After fixing the reference point, all the compositions of LMB are explored to estimate the degree of conversion required in the reaction step. The highest conversion value is found by iteration among the feasible degrees of conversion and defines the limiting steady state—LSS—i.e. condition of maximum conversion for a certain reactant (Giessler et al., 1999). At this condition, the location and the length of the reactive zone in the RD column are estimated by counting all reactive stages present in the forward reaction section. Attaining the LSS can proceed by several limiting paths, depending on the nature of the stability of the fixed point from which the distillation lines start or end. According to Giessler et al. (1998), if LSS is not convenient, the composition of the initial mixture, the structure of the phase equilibrium diagram and the reactions conditions ($P, T$) have to be changed and the iteration loop is performed again. The proposed method stresses the importance of identifying all feed composition regions, since they lead to the complete set of column configurations. Thus, the entire feed region is classified into several sub-regions, each of which has the same characteristics with respect to the product configurations (Giessler et al., 2001).

Advantages: (a) This method gives a straightforward solution to the question whether or not a reaction should be performed in a RD column; (b) allows one to synthesise flowsheets qualitatively (e.g. maximum degree of conversion, reactive zone location and length and column sequencing); (c) for its application this method requires little data (i.e. feed composition, phase equilibrium model parameters, chemical equilibrium model parameters and reaction stoichiometry); (d) provides an effective tool for the study of strongly non-ideal mixtures with multiple chemical reactions and number of components; (e) allows the selection of the appropriate steady states from their complete set; (f) simplifies troublesome calculations (including expensive full-scale experiments) reducing dramatically computational time (up to five times); (g) represents...
a general method that does not depend on the concrete column structure. (b) does not require that product compositions, extent of reaction and number of stages are fixed a priori; and (i) allows one to determine the stability of various product regimes and derive the possible product compositions and the column structure for not only one fixed fed composition but for the entire feed region.

Limitations: (a) This method assumes infinite separation efficiency; and (b) matching the operating lines with the assumed product composition can be sometimes troublesome.

2.1.2. Residue curve mapping technique

The residue curve mapping (RCM) technique has traditionally been considered a powerful tool for flowsheet development and preliminary design of conventional multi-component separation processes. It does not only represent a good approximation of actual equilibrium behaviour, but it also allows one to perform feasibility analysis of separation processes where non-ideal and azeotropic mixtures are involved (Malone & Doherty, 2000; Sirola, 1996a, Chapter 23, 1996b). Furthermore, residue curves have been used to predict the liquid composition trajectories in continuous distillation units in the presence of azeotropes (Barbosa & Doherty, 1998a; Espinosa, Aguirre, & Perez, 1996). Although for finite columns those profiles differ slightly compared to the residue curves under same isobaric conditions (Fien & Liu, 1995a; Espinosa, Aguirre, & Perez, 1996a, Chapter 23, 1996b), the difference is normally considered negligible at finite columns those profiles differ slightly compared to the residue curves under same isobaric conditions (Fien & Liu, 1995a; Espinosa, Aguirre, & Perez, 1996a).

The RCM problem is solved by specifying the relation between the transformed compositions of the vapour and liquid phases and by using relevant properties of the transformed compositions.

Description: (a) Specify the compositions of the mixture at the minimum reflux ratio (Espinosa, Aguirre, Frey, & Julka, 2000; Westerberg, Lee, & Hauan, 2000). Although for finite columns those profiles differ slightly compared to the residue curves under same isobaric conditions (Fien & Liu, 1995a; Espinosa, Aguirre, & Perez, 1996a, Chapter 23, 1996b), the difference is normally considered negligible at

Advantages: (a) This method provides a reliable tool to perform feasibility analysis in RD; (b) for its application this method requires little data (e.g. feed compositions, phase equilibrium model parameters, chemical equilibrium model parameters and reaction stoichiometry).

Limitations: (a) Although relevant improvements have been made towards multiple component \( n_c > 3 \) mixtures (Malone & Doherty, 2000), the RCM technique is limited...
by its intrinsic graphical nature; and (b) accurate thermodynamic data are required in order to correctly describe the RD process (Barbosa & Doherty, 1988b).

RCM techniques have been used as feasibility tools to develop a generalised and systematic design approach for reactive feeds outside conventional composition ranges (Almeida-Rivera & Grieves, 2002, 2004). For the synthesis of MTBE, two separation sequences have been found, which depend upon the location of the reacting feed in the composition space.

2.1.3. Attainable region technique

The concept of attainable region (AR) has been extensively employed in the synthesis of reactor structures (Feinberg, 1999) and successfully extended to processes combining simultaneous reaction, mixing and separation (Nisoli et al., 1997). In combination with graphical methods, an activity-based reaction-separation vector has been defined, which satisfies the same geometric properties as the reaction vector does, and therefore, allows one to construct the attainable region by means of the existing procedure for reaction-mixing systems. In general terms and for a given system of reactions with given reaction rates, an activity-based reaction-separation vector has been defined, which satisfies the same geometric properties as simple reactor models, allowing the application of the theory derived for PFRs and CSTRs, and therefore, allows to follow the same procedure for the construction of the AR (Fig. 4).

Assumptions: (a) Economic considerations are not taken into account to rank the design alternatives.

2.1.4. Fixed-point algorithm

A sound understanding of fixed points (Table 3) and the prediction of their behaviour as a function of design parameters have been lately used as a design tool for RD columns. The researchers devote considerable effort in defining a design strategy for equilibrium chemical reactions in staged columns, although it is not always convenient to op-
Table 3

<table>
<thead>
<tr>
<th>Fixed points in RD</th>
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| At total reflux conditions, certain points in the concentration space are reached where the composition on successive stages is constant (Buzad & Doherty, 1994, 1995) and in the vicinity of which the columns profiles behave in a peculiar manner (Mahajani, 1999a, Mahajani & Kolah, 1996). These fixed points occur at the pure component and azeotropic compositions (Buzad & Doherty, 1994; Okasinski & Doherty, 1998) and move to new positions as the reflux ratio (or external reboil ratio or Damköhler number) is changed. Fixed points can be nodes (stable or unstable) or saddles and have a significant influence on the column composition profiles, minimum reflux, etc. (Okasinski & Doherty, 1998). However, unlike stable and unstable nodes, the location of fixed points is dependent upon process parameters and represents chemical and physical equilibrium conditions. According to Espinosa et al. (1996), fixed points can be obtained by finding tangents to residue curves that pass through the distillate or bottom streams. In order to solve for the fixed-point compositions in terms of the Damköhler number—particularly in terms of the critical value $Da_c$—the continuation method is commonly used. This method involves solving the design equations for a range of Damköhler numbers, where the lower bound corresponds to zero and the upper bound to the critical Damköhler number. The criterion for fixed-point location establishes that for low $Da$, the end of the profile will be located in the negative reaction space (i.e. where the backward reaction is predominant), whereas for $Da$ above the critical value the end of the profile will be located in the positive reaction space. If the balance expressions along the column are written as explicit finite difference equations (i.e. $x_{n+1} = f(x_n, p)$), the stability of the fixed points is determined by the eigenvalues $\lambda$ of the Jacobian of $f$ evaluated at the fixed points (Okasinski & Doherty, 1998).

Fig. 4. Procedure for the construction of the attainable region.

<p>|</p>
<table>
<thead>
<tr>
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</tr>
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| These fixed points occur at the pure component and azeotropic compositions (Buzad & Doherty, 1994; Okasinski & Doherty, 1998) and move to new positions as the reflux ratio (or external reboil ratio or Damköhler number) is changed. Fixed points can be nodes (stable or unstable) or saddles and have a significant influence on the composition profiles, minimum reflux, etc. (Okasinski & Doherty, 1998). However, unlike stable and unstable nodes, the location of fixed points is dependent upon process parameters and represents chemical and physical equilibrium conditions. According to Espinosa et al. (1996), fixed points can be obtained by finding tangents to residue curves that pass through the distillate or bottom streams. In order to solve for the fixed-point compositions in terms of the Damköhler number—particularly in terms of the critical value $Da_c$—the continuation method is commonly used. This method involves solving the design equations for a range of Damköhler numbers, where the lower bound corresponds to zero and the upper bound to the critical Damköhler number. The criterion for fixed-point location establishes that for low $Da$, the end of the profile will be located in the negative reaction space (i.e. where the backward reaction is predominant), whereas for $Da$ above the critical value the end of the profile will be located in the positive reaction space. If the balance expressions along the column are written as explicit finite difference equations (i.e. $x_{n+1} = f(x_n, p)$), the stability of the fixed points is determined by the eigenvalues $\lambda$ of the Jacobian of $f$ evaluated at the fixed points (Okasinski & Doherty, 1998).

Fig. 5. Representation of reactive distillation lines for the reactive system $A-B-C$ undergoing the reaction $A + B \rightarrow C$. $\pi$ denotes the pole at which stoichiometric lines coincide; $x_{i\pi} = n_i / \sum y_j$. Redrawn from Frey and Stichlmair (1999).
These definitions present convenient and simplifying properties: (a) the dimensions of the system are reduced, simplifying the depiction of equilibrium (Fig. 6) (Barbosa & Doherty, 1987a; Frey & Stichlmair, 1999); (b) they have the same numerical values before and after reaction; (c) they sum up to unity; (d) they clearly indicate the presence of reactive azeotropes when \( X_i = Y_i \); (e) the non-reactive limits are well defined; (f) the number of linear independent transformed composition variables coincides with the number of independent variables that describe the chemical equilibrium problem; and (g) the lever rule is valid as the chemical reaction no longer impacts the material balance.

However, the introduction of transformed variables reduces the understanding of the phase equilibrium as a whole, hiding eventually some non-reactive azeotropes (Frey & Stichlmair, 1999).

For kinetically controlled reactions, the approach involves specifying all the degrees of freedom of the system and performing expanding envelope balances (material balances around the rectifying, stripping sections and the entire column) from the ends of the column towards the middle (Buzzad & Doherty, 1994; Huss, Chen, Malone, & Doherty, 1999). The methodology is supported by the residue curve map techniques and allows both a fast screening for reactive azeotropes and feasible designs, and the computation of the number of trays and the minimum reflux ratio (Ciric & Gu, 1994).

Mahajani and Kolah (1996) successfully extend the approach of Doherty and co-workers to packed columns, where liquid phase backmixing is totally absent. This approach relies on the performance of mass balances over differential elements of length \( dz \) in both rectifying and stripping sections, which can be re-written as functions of dimensionless numbers (e.g. \( Da, HTU, \) dimensionless flux \( \psi \) and ratio of characteristic times in the vapour and liquid sides \( \beta = \pi C_j^V \times k_v / C_i^L \times k_l \)).

Rectifying section (\( \forall i \in \{1, 3\} \)):

\[
\frac{dY_i}{dx} = -\frac{\psi}{HTU}V,
\]

\[
\frac{dX_i}{dx} = \left( \frac{s + 1}{s} \right) \left[ \frac{-\psi}{HTU} + \frac{Da}{F} g(s, T) \right].
\]

Stripping section (\( \forall i \in \{1, 3\} \)):

\[
\frac{dY_i}{dx} = \frac{-\psi}{HTU}V,
\]

\[
\frac{dX_i}{dx} = \left( \frac{s + 1}{s} \right) \left[ \frac{-\psi}{HTU} + \frac{Da}{L + F} g(s, T) \right].
\]

Although the fixed-point algorithm was not recommended by (Ciric & Gu, 1994; Espinosa et al., 1996) for systems where the reaction kinetics, heat of reaction, liquid hold-up and residence times the determining design variables, this method was used by Okasinski and Doherty (1998) to successfully reproduce the ethylene glycol synthesis example of Ciric and Gu (1994).
Vapour-liquid equilibrium in the interface ($\forall i \in [1, 3]$):

$$y_i - y_i = f(\nu_i \beta + x_i),$$  \hspace{1cm} (12)

where $\xi$ is the dimensionless height of the column, and $r$ and $s$ are the reflux and reboil ratios, respectively.

The extent of reaction is given as:

$$x_j = \frac{1}{\rho_j} \int_{0}^{z_j} r dz + \frac{1}{\rho_j} \int_{0}^{z_s} r dz, \quad \forall i \in [1, 3],$$  \hspace{1cm} (13)

where $z_j$ and $z_s$ are the lengths of the rectifying and stripping sections, respectively.

The solution procedure reported by Mahajani and Kolah (1996) for packed columns is quite similar to that described by Buzad and Doherty (1994) for staged columns: (a) expressions (10)–(12) are solved simultaneously for various values of $Da$, determining the range where the stripping and rectifying profiles intersect; (b) the satisfaction of the second necessary condition is then evaluated; and (c) the sizing of the RD column is performed.

New from Mahajani’s contributions is the parametric analysis of the design, in terms of identifying the dependence of HTUV with $Da$. It was concluded that for kinetically controlled reactions accompanied by slow mass transfer, the dimensionless number (HTUV $\times Da$) plays a major role in the feasibility of the design. Thus, profiles intersect if and only if (HTUV $\times Da$) falls in a specific range, whose width depends on the relative position of the fixed points (Mahajani, 1999b).

For RD columns where equilibrium controlled reactions are involved, the design methodology follows the same guidelines developed by Barbosa and Doherty (1988a, 1998b) for staged columns. Thus, transformed variables can be introduced, reducing the dimensionality of the reactive system and simplifying the set of design equations.

It is revealed from this approach that the liquid hold-up has no direct influence on the performance of the column, highly resembling the non-reactive distillation case. Furthermore, the reflux ratio is found to determine exclusively the feasibility of the design. Thus, for low reflux ratio values stable nodes are reached before the concentration profiles intersect (i.e., non-feasible design), whereas at high reflux ratios the profiles intersect and the design turns to be feasible. The value at which the profiles just touch corresponds to the minimum reflux ratio. Although the parameters HTUV and $\beta$ do not play a role in the intersection of the profiles, they determine the column height and the extent of reaction.

Advantages: (a) This method is highly flexible in generating alternative designs at various design parameters (e.g., Damköhler number, reboil ratio or liquid hold-up in reactive zones), allowing one to put realistic bounds on those parameters (Okasinski & Doherty, 1998); and (b) the mass and energy balances can be decoupled, allowing the determination of the column profile only by means of the mass balance and equilibrium equations (Espinosa et al., 1996).

Limitations: This algorithm is limited by its inherent graphical nature, that imposes practical limitations and complicates its extension to systems where the number of components minus the number of independent stoichiometric reactions exceeds 3.

Fortunately, several modifications and extensions of the fixed-point method for staged and packed columns are available in the open literature, aiming to relax part of the assumptions on which the original algorithm was based. These relaxations include: (a) double-feed columns (Okasinski, 1998); (b) kinetically controlled reactions, which account for the liquid hold-up in the column design and economics (Barbosa & Doherty, 1987a, 1987b, 1988a, 1988b; Buzad & Doherty, 1994, 1995; Doherty & Buzad, 1992; Mahajani, 1992a); (c) multiple reactions (Ung & Doherty, 1995b); (d) different hold-ups per section (Melles, Grievink, & Schrans, 2000; Okasinski & Doherty, 1998); (e) heat effects (Melles et al., 2000; Okasinski & Doherty, 1998); and (f) reactions where $\sum \nu_i \neq 0$ (Melles et al., 2000; Okasinski, 1998).

2.1.5. Reactive cascades

Chadda, Malone, and Doherty (2003) and Gadewar et al. (2003, Chapter 6) use the concept of reactive cascades to screen the feasibility of hybrid RD systems. This approach has been successfully applied to the preliminary design of single-feed and double-feed RD columns. The governing expressions for the stripping ($N$ stages) and rectifying ($M$ stages) cascades are:

rectifying : $y_{i,j-1} = \phi_j \times y_{i,j} + (1 - \phi_j) \times x_{i,j}$

$$- \nu_i \left( \frac{k_i}{k_i^{ref}} \right) \left( \frac{D}{1 - D} \right) r(x_j), \quad \forall i \in [1, n_r - 1], j \in [2, M],$$  \hspace{1cm} (14)

stripping : $x_{i,j-1} = \phi_j \times y_{i,j} + (1 - \phi_j) \times x_{i,j}$

$$- \nu_j \left( \frac{k_i}{k_i^{ref}} \right) \left( \frac{D}{1 - D} \right) r(x_j), \quad \forall i \in [1, n_r - 1], j \in [2, N],$$  \hspace{1cm} (15)

where $\phi_j = (V_j/L_{j-1})$ is the fraction of feed vapourised in the $j$th unit, and $D$ a normalised Damköhler number ($D = (Da/1 + Da)$).

Description: (a) For a given operating pressure, the feasibility diagram is drawn, which is obtained by solving the component balances for the liquid/vapour molar compositions in the stripping/rectifying sections. The independent variable $\phi$ is assigned a convenient value, whereas $D$ is used as parameter to move from equilibrium to kinetically controlled regimes; (b) for a given $D$-value the column configuration (reactive or hybrid) is selected based upon the satisfaction of the product specifications; (c) the rectifying and stripping cascades expressions are solved for $D = 0$; (e) the transformed compositions in the liquid/vapour phases are estimated according to expressions (3) for the stripping/rectifying sec-
RD is a feasible and cost-effective alternative if one of the desired products behaves as a saddle point. In the event that one of the desired products behaves as a saddle point, the conversion of a two-feed column reaches a maximum of 100%. However, this method does not have any restriction in the number of components or reactions; it is deemed to be feasible if the lever rule intersects both the rectifying and stripping cascade lines.

Advantages: (a) A global feasibility analysis can be performed as a function of the production rate, catalyst concentration and liquid hold-up; (b) this method does not have any restriction in the number of components or reactions; and (c) this method is deemed to be easily implemented.

Limitations: (a) The Damköhler numbers are assumed to be invariant on all the reactive stages; (b) the effect of structural and separation borders are identified.

A thorough analysis of the behaviour of reactive distillation lines with respect to the volatility values of the involved components and the feed staging suggests the following (Bessling et al., 1997; Bessling, Loning, Ohlfschlagger, Schenbecker & Sundmacher, 1998; Bessling, Schenbecker, & Simmrock, 1997):

- RD is a feasible alternative for systems where the desired products are the nodes in a reactive distillation line diagram and their boiling points differ considerably.
- The event that one of the desired products behaves as a saddle point, the conversion may be increased by adding a second feed stream in the column. This is called the synthesis of methyl acetate.
- The conversion of a two-feed column reaches a maximum at finite reflux in the case of products that behave as saddle points.
- RD is a feasible and cost-effective alternative if one of the desired products behaves as a saddle point and:
  - high conversion is required at stoichiometric reactants ratio;
  - separation between desired and undesired products is difficult;
  - boiling point difference between desired products is large;
  - there is no distillation boundary line;
  - chemical equilibrium is on the side of the desired products (e.g. synthesis of methyl acetate).

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Table 4 presents a general overview for the combination of reactive and non-reactive sections for several stoichiometries.

Advantages: (a) This approach can be applied to both fast and slow chemical equilibrium reactions; and (b) feasible products can be determined within a RD column.

Limitations: (a) Finding the reactive azeotropes might be sometimes troublesome; and (b) detailed knowledge of phase equilibrium, reaction kinetics and residence time within the column is required.

2.1.7 Conventional graphical techniques

These techniques allow the distribution of reaction zones within a column using the McCabe–Thiele and Ponchon–Savarit methods for a given reaction conversion by adjusting the catalyst, hold-up on each stage. Although the methods are currently limited to binary reactive mixtures, they provide fundamental insights towards multiple component systems. In general terms, it is suggested that if the reaction has a heavy reactant and a light product, the reaction zone should be placed in the rectifying section, whereas if the reaction has a light reactant and a heavy product, the reaction zone should be located in the stripping section (Lee, Han, Lien, & Westerberg, 2000b, 2000c; Lee, Han, & Westerberg, 2000).

Assumptions: (a) Binary system with a single chemical reaction; (b) CMG; and (c) vapour–liquid equilibrium.

Ponchon–Savarit method: This method is traditionally considered a powerful visualisation tool for the synthesis of distillation columns for binary mixtures. Thus, it allows the designer to account graphically for the enthalpy effects that cause a varying molar overflow when stepping off stages (Lee et al., 2000b). The main issue of this approach is the definition of the reactive cascade difference point, which
for an exothermic isomerisation reaction occurring in the rectifying zone moves towards the reactant and downward as the calculation goes down the column. The following nomenclature is adopted for the diagram co-ordinates (Lee & Westerberg, 2000):

\[
\begin{align*}
\delta_{R,n} &= \frac{DQ - cP \epsilon_n + cR \epsilon_n}{D}, \\
hr_{R,n} &= \frac{bD + qc + SDelta \phi h_R \epsilon_n}{D},
\end{align*}
\]

where \(\delta_{R,n}\) and \(hr_{R,n}\) are the composition and enthalpy co-ordinates in the Ponchon–Savarit diagram, \(D\) the distillate flow, \(cP\) the product coefficient vector, \(cR\) the reactant coefficient vector, \(\epsilon_n\) the sum of the extent of reactions occurring in stages \(n\) and above, \(h\) is the liquid enthalpy, \(Qc\) is the condenser duty and \(SDelta \phi h\) the heat of reaction. It is concluded from this study that the number of reactive stages and the location of the feed stage are highly dependent upon the extent of reaction \(\epsilon\) in the RD column. Thus, the determination of the optimal feed stage is possible by connecting the bottom difference point and the final difference point of the rectifying section, which in turn depend upon the assumed extent of reaction on each stage (Lee et al., 2000b).

McCabe–Thiele method: This method is used to assess qualitatively the impact of changing a design variable (Lee et al., 2000c). For the RD case, two main features are tracked to sketch the diagram for a binary mixture of reactants undergoing an isomerisation reaction and under CMO assumption:

- The intersection point of the operating line with the \(y = x\) line defines the reactive cascade difference point, which moves proportionally as the ratio molar extent of reaction to product flow rate (i.e. \(x_n = x_D - \epsilon_n/D\), where \(n\) denotes the stage number).
- The heat supplied by the reaction decreases the slope of the operating line provided that the location of the reactive cascade difference point is not changed.

A simplified procedure for sketching the McCabe–Thiele diagram is depicted in Fig. 7 for an isomerisation reaction.**Advantages:** (a) These methods allow a transparent visualisation of tray-by-tray calculations; (b) they might be fundamental tools for the conceptual design of RD column; and (c) they allow one to visualise the impact of the location of the reactive sections and the feed location within the column.**Limitations:** (a) These methods are exclusively applied to isomerisation reactions; and (b) they are limited by their inherent graphical nature.

2.1.8. Phenomena-based approach

According to this method—proposed by Hauan (1998)—three independent phenomena take place simultaneously in a RD column: mixing, separation and reaction (Hauan &
Lien, 1996; Westerberg et al., 2000). These phenomena may be represented by vectors (Fig. 8) and allow the description of the total process profile of the system as a trajectory in position space.

Thus, each step along the profile may be represented by the vectorial addition of the phenomena vector mixture ($\mathbf{M}$), separation ($\mathbf{S}$) and reaction ($\mathbf{R}$):

$$
\frac{ds}{dt} = \mathbf{M} + \mathbf{S} + \mathbf{R}
$$

where $s$ is the phase composition and the phenomena vectors are given by:

$$
\mathbf{M} = M \times \begin{bmatrix} x^f_i - x^i_i \\ x^g_i - x^0_i \\ \vdots \\ x^i_n - x^0_n \end{bmatrix},
$$

$$
\mathbf{S} = S \times \begin{bmatrix} x_i - y_i \\ \vdots \\ x_n - y_n \end{bmatrix},
$$

$$
\mathbf{R} = R \times \begin{bmatrix} v_1 - x^0_1 \times \sum v_i \\ \vdots \\ v_n - x^0_n \times \sum v_i \end{bmatrix},
$$

where $x^f$ and $x^0$ denote feed and initial values, respectively, $M$ the length of the mixing vector and is determined by the relative amount of material in the streams being mixed, $S$ a matrix reflecting average mass transfer rates, $v$ the stoichiometric coefficient and $R$ a scalar calculated from catalyst activity, hold-up, temperature and pressure. Each vector has a unique local direction (i.e. process feasibility) and vector length (i.e. process efficiency). Vector directions are calculated by physical and chemical data only, whereas vector lengths depend upon the operating parameters and design variables.

Description: Any composition change in the system due to chemical reaction may be represented by a straight line from the singular point—termed difference point (i.e. $x^p = v/\sum v$)—through the local composition $x^0$ (Hauan, Lee, Westerberg, & Lien, 2000):

$$
x = x^0 + (x^f - x^0) \frac{\sum v}{N^f + \epsilon \sum v}
$$

where $N$ is the number of moles and $\epsilon$ the extent of reaction.

As the local compositions may be those of feeds and chemical reaction products, the composition in the desired point may be expressed as a normalised linear combination of the reaction difference points and distillate, bottom or feed composition vectors. From expression (17), a kinetic fixed point occurs when the vectorial contributions of the non-zero phenomena balance each other:

$$
\frac{ds}{dt} = \mathbf{M} + \mathbf{S} + \mathbf{R} = 0.
$$

Fixed points—which become evident by the presence of flat concentration profiles for large portions of the column—are by no means desired in RD and indicate a weak design or operation. Therefore, several ways to move away from a fixed point in the composition space are suggested:

- altering the mixing vector: by changing process variables (e.g. reflux and reboil policies, external feeds and hold-ups);
- altering the reaction vector length: by manipulating process variables (e.g. catalyst density, hold-up) or by introducing non-reactive stages in the reactive zone;
- incorporating ‘pump-around’ reactors: to avoid a counter-productive separation vector.

Advantages: (a) Only physical and chemical data are required to estimate the phenomena vectors, which are independent of the structural design of the unit; and (b) this approach allows the designer to assess independently the effect of equipment structure and operating policies upon the composition change in RD.

Limitations: (a) Although this method is driven by fundamental considerations, its applicability requires further studies.

2.1.9. Scalar/vectorial difference points technique

The concepts of reactive cascade and scalar/vectorial difference points in reactive cascades (Table 5) have been successfully applied by Hauan, Citic, Westerberg, and Lien (2000), Lee, Hauan, Lien, and Westerberg (2000a) and Lee and Westerberg (2001) in the design of RD processes.

Assumptions: (a) Known top and bottom compositions; (b) known reflux ratio; (c) CMO; and (d) chemical reaction of the type $2R = P_1 + P_2$.

Based upon rigorous graphical considerations, the number and location of the reactive and non-reactive stages is obtained. For the system studied by Lee and Westerberg (2000), the reaction conversion of the feed stage is found to be always larger than that of any single stage in the rectifying and stripping sections. This situation allows one to guarantee the conversion on the feed stage at any reflux ra-
tio. The location of the bubble point (BP) curve with respect to the chemical equilibrium curve plays a key role in the feasibility of the process within the stripping and rectifying sections. Thus, if the BP curve lies to the right of the reaction equilibrium curve, the rectifying section shows a better performance towards reactants’ conversion than that of the stripping section. In this case, the forward reaction always takes place and enhances the separation task.

This approach is tested in the gas-phase disproportionation of toluene and in the dehydration of methanol into water and dimethyl ether. In the first case study the most competitive configuration is reported to be the reaction zone in the stripping and rectifying sections. The effect of the reaction equilibrium constant is analysed in the second example, resulting in feasible configurations with a single reactive stage.


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novel approaches demand huge computational time and lack robustness when solving highly constrained problems. Ciric and Gu (1994) present a MINLP-based approach for the design of RD columns for systems where multiple reactions take place and/or where reactive equilibrium or thermal neutrality cannot be assured. This method is based on the combination of a rigorous tray-by-tray model and kinetic-rate-based expressions to give basic constraints of an optimisation model that minimises the total annual cost. The major variables are the number of trays in the column, the feed tray location, the temperature and composition profiles within the column, the reflux ratio, the internal flows within the column, and the column diameter.

Lately, Poth et al. (2001) apply MINLP technique to the synthesis of MTBE and compare the optimal processes for the assumption of chemical equilibrium and kinetically limited reactions. Their results show that the total cost of the kinetic column is higher than that of the equilibrium case. Cardoso et al. (2000) apply a simulated annealing-based algorithm to solve a non-equilibrium RD column in the synthesis of ethylene glycol. The results obtained from this approach coincide satisfactorily with those reported by Ciric and Gu (1994) using commercial optimisation packages. Pekkanen (1995) applies a local optimisation algorithm to take advantage of the large number of degrees of freedom (\( n + n_c \)) in the design of RD columns. In that study, the stage hold-ups and tray efficiencies are taken as optimisation variables and the local optimum is found by tracking the directions of the concentration vectors in successive stages. Frey and Stichlmair (2001) optimise the RD column for the synthesis of methyl acetate in the kinetically controlled regime with respect to total annualised cost. Multiple feeding of reactants is allowed in the optimisation routine leading to a decrease in the energy demand. Stichlmair and Frey (2001) design RD columns for the synthesis of MTBE and methyl acetate. Their starting point is the definition of the process superstructure, which in turn is derived from thermodynamic fundamentals (e.g. stoichiometric lines and lines of possible reactive azeotropes). A generalised modular representation for process synthesis is presented and extended by Papalcanu and Pistikopoulos (1996) and Ismail, Proios, and Pistikopoulos (2001), respectively. That approach is supported by fundamental mass and heat transfer principles, which allow the definition of a “multiscale mass/heat transfer module”. The optimised combination of building blocks defines the process superstructure. The effectiveness of this steady-state approach is tested in homogeneous and two-phase-reactions, absorption/extraction and RD processes. Ismail et al. (2001) include Gibbs free energy-based driving forces as constraints to guarantee the feasibility of the reaction/separation/RD processes. The design of RD units with VLL equilibrium is studied by Gunus and Ciric (1997). That optimisation problem is formulated as a MINL-bilevel exercise; the underlying feature of that approach is the development of a single level optimisation problem whose solution is a lower bound for the solution of the bilevel problem. The objective function is the Gibbs free energy on each tray subjected to the mass, energy balances, constitutive expressions and integer variables defining the number of trays at the minimum total annualised cost.

2.2.2. Orthogonal collocation on finite elements (OCFE)

MINLP has been found to be troublesome for units with large number of trays and for the simultaneous design of more than one distillation unit due to the considerable computational time required for attaining the solution. OCFE techniques is suggested by Seferelis and Grievink (2001). Furthermore, special attention must be paid in the MINLP model formulation and initial guesses outside the feasibility domain may lead into convergence difficulties. OCFE techniques is suggested by Seferelis and Grievink (2001) for the design and optimisation of staged RD columns. This approach transforms the discrete number of stages in the column into a continuous variable and treats the composition and temperature as functions of the position. Assumptions: (a) Complete mixing of each phase at each stage; (b) constant liquid hold-up and no vapour hold-up at each stage; (c) no liquid entrainment from stage to stage; (d) adiabatic stages; and (e) thermal equilibrium between the liquid and vapour streams leaving each stage. Description: (a) The column is separated into sections; (b) each column section is divided into smaller sub-domains (i.e. fine elements); (c) for each fine element a number of collocation points is specified, where the mass and energy balances are exclusively satisfied; (d) the collocation points are chosen as the roots of the discrete Hahn family of orthogonal polynomials; and (e) Lagrange interpolation polynomials are used within each finite element to approximate the liquid- and vapour-component flow rates, the total stream flow rates and the liquid and vapour stream enthalpies.

In the study by Seferelis and Grievink (2001), the oscillatory behaviour in the composition space of highly-diluted components is circumvented by transforming the molar fractions of those components. Additionally, a second alternative is proposed, where inert components with low concentrations are removed from the energy and mass balances. Both approaches are found to increase the stability and robustness of the solution at the same level of accuracy. This technique is successfully applied to the design of a RD column for the synthesis of ethyl acetate (Seferelis & Grievink, 2001), using a single element with four collocation points in the recrystallising section, three elements with three collocation points per element in the reactive section, and two elements with two collocation points per element in the stripping section. The study concludes that the production of ethyl acetate is strongly favoured by large liquid-stage hold-ups in the reactive and stripping sections because of the relatively low rate of reactions. Furthermore, a double-column production flowsheet is selected, which allows the production of high purity ethyl acetate.
variables corresponding to the best primal solution; (c) solve the primal problem at the solution found in step (b) with the full set of search variables and constraints included. Convergence will be achieved in one iteration. Obtain the Lagrange multipliers needed to construct the 4th master problem; (d) solve the 4th master problem to obtain a solution \( y^* \). Update the lower bound, \( LB = y^* \), and (e) if \( UB - LB \leq \epsilon \), or the master problem is infeasible, then stop. The optimal solution corresponds to the values stored in step (b). Otherwise set \( k = k + 1 \), go back to step (b).

Advantages: (a) optimisation-based approaches are applicable for multiple reactions and where reactive equilibrium or thermal neutrality cannot be assured; and (b) it allows the generation of optimum designs with respect to economics and controllability.

Limitations: (a) Special care should be paid to the model formulation and the physical significance of the solution; scaling of optimisation variables might be required to reduce computational effort; (b) the optimisation problem might be difficult to solve; (c) huge computational time can be required for multiple alternative optimisations; (d) it is difficult to perform sensitivity analysis of the optimum solution; and (e) local limitations can be found when the initial guess lies outside the feasibility region.

2.3. Evolutionary/heuristic methods

A third trend of conceptual design approaches may be identified from the evolution of RD as a derivative from conventional distillation processes. As stated by Subawalla and Fair (1999), residue curve map techniques and fixed-point algorithms have been traditionally very useful tools for preliminary screening and design of RD systems. However, they cannot be used for detailed design, since they rely on several limiting assumptions and do not account for the special nature of reactive column internals. This post-design algorithm has been successfully applied to catalytic distillation of equilibrium-limited reactions and allows the estimation of several parameters (i.e. column pressure, reactive zone location, catalytic mass, reactant feed location, reflux ratio, column diameter, number of equilibrium stages and packed height) and the feasibility of up-stream pre-reactor. The proposed guidelines (Subawalla & Fair, 1999) involve the following issues:

- Use of a pre-reactor: Incorporating a pre-reactor could profitably enhance the conversion of equilibrium-limited reactions, especially when it handles a substantial part of the reaction duty (rule of thumb: use a pre-reactor when reaction rate at 80% conversion is more than half the initial rate).
- Operating pressure: The column pressure ranges from the condenser pressure (determined by the condenser coolant temperature) to the reboiler pressure (fixed by the heating medium temperature and the column pressure drop).
In general terms, and within this range, the operating pressure depends upon the reaction temperatures, relative volatility and the effect of pressure upon azeotropes. An upper pressure limit exists beyond which rates decrease because of reaction depletion due to relative volatility and/or azeotropic effects, and due to departure from chemical equilibrium.

- **Reactive zone location**: This parameter represents the best trade-off between conversion and product purity. Thus, the reactive zone section should be located where the concentration of at least one reactant (preferably the limiting reactant) is the maximum. For instance, when the limiting reactant is the most volatile component and the product is the heaviest component, the reactive zone is located towards the top of the column. For high purity requirements, stripping or rectifying sections must be incorporated below or above the reaction zone.

- **Feed location**: A right choice of feed location guarantees high concentrations of reactants in the reactive zone (Fig. 9). The following considerations should be taken into account:
  - if the reactants are the most volatile components, then the feed should be introduced at the bottom of the reactive zone;
  - if the volatilities of the reactants are very different, an additional feed location may be required to ensure stoichiometric reactant quantities;
  - a pre-reacted product-containing feed enters the column at some distance from the reactive zone, ensuring thereby that separation between reactants and products takes place on stages between the feed point and the reactive zone.

- **Reactant ratio**: Reactants’ requirements can be calculated from product specifications, desired conversion and azeotropic compositions at different operating pressures.

- **Catalyst mass**: The minimum catalyst requirements are determined by simulating a series of isothermal PFR’s and ideal separators in series. As depicted in Fig. 10, the feed to the first PFR contains the necessary quantity of unconverted reactants; the partially reacted effluent is fed to an ideal separator that completely separates reactants from products. This procedure is repeated for different temperatures until the desired conversion is reached, where the operating temperature defines the minimum amount of catalyst. Since there is a relevant influence of operating temperature upon catalyst life, chemical equilibrium and column pressure, the adopted operation temperature value differs from the highest possible value. In order to account for the non-isothermal operation and for the imperfect separation on each stage, the mass of catalyst should be 20–30% greater than the estimated value. Additionally, inadequate catalyst volume reduces residence time and gives poor conversion.

- **Number of theoretical stages**: the number of stages may be estimated to a certain extend by shortcut methods (e.g. Fenske Underwood), especially for the non-reactive zones (stripping and rectifying). The procedure—shown in Fig. 11—may be adopted to estimate the number of stages in the stripping and rectifying sections. According to Solokhin and Blagov (1996), there is an optimum number of reactive stages which allows one to obtain the highest reaction extent for given vapour flow and column height.

- **Reactive zone height and column diameter**: The diameter of the column is determined by the flooding velocity, vapour–liquid traffic, pressure drop and packing catalyst density; the reactive zone height, on the other hand, depends upon the catalyst mass, packing catalyst density and column diameter.

- **Reflux ratio**: In RD columns, the rate and ratio of reflux play an important role in reaction and separation phenomena. For equilibrium-controlled systems, a high reflux
rate increases the separation of products from reactants, thereby increasing the reaction driving force. Excessive reflux leads to operating problems and insufficient reaction hold-up, leading to incomplete conversion (Fig. 12) (rule of thumb: use a factor of 1.2–1.4 × the minimum ratio). Shortcut methods derived from conventional distillation have been found to be inappropriate for the estimation of reflux ratio for reactive case and new approaches have been adopted. Methods derived from the boundary-value approach allow the determination of the minimum and real reflux ratio, which are key factors in the determination of vapour and liquid velocities. The reflux ratio can be calculated by means of an iterative procedure, described in Subawalla and Fair (1999) and summarised in Fig. 13.

- Reboil ratio: The feasibility of RD processes has been closely related to the minimum reboil ratio ($R_{\text{min}}$), at which the composition of the rectifying fixed point equals the composition of the stripping fixed point (Okasinski & Doherty, 1998). The reboil ratio normally ranges from 3 to 8 and reaches a minimum when plotted versus the total number of stages.

- Actual tray/packed height: For the stripping and rectifying sections experimental tray efficiency or packing HETP should be used, whereas for the reactive section mass-transfer coefficients should be calculated from experimental data at the operating conditions of the system. In the event that thermophysical data, transport phenomena data and hydraulic models are available, non-equilibrium design approaches are found to provide a better agreement between experimentation and simulation.

The proposed approach may be extended by incorporating hydraulic models which account for the column capacity in terms of pressure drop and percent flood, and for mass-transfer efficiency estimations in terms of liquid hold-up, mass-transfer coefficients and interfacial area.

**Advantages:** This method estimates easily several equipment and/or operational variables.

**Limitations:** This method is basically a post-design algorithm and as such it requires an already defined process structure.

3. Future directions

Based upon their assumptions, limitations, and outputs a “fingerprint” chart has been produced for the methods described in Section 2. From this qualitative plot (Table 7) the following conclusions can be drawn: (a) most of the graphical methods provided fundamental insights on the feasibility of the RD process and define the initial process structure; (b) economic considerations are taken into account exclusively by optimisation-based methods; (c) the availability of the process has not been included as design output by any method, since this temporal feature is normally dealt at the next level of engineering design; (d) the heuristic-based methodology is based upon an already designed process and is therefore a post-design tool; (e) most of the design methods have been developed for steady-state operation; (f) the initial effort required for optimisation-based methods is by far more significant than that for graphical approaches, but the output generated by the programming-based design is more comprehensive.

The results in Table 7 clearly show the complementary aspects of the graphical and the programming methods. The graphical methods are capable of generating feasible process structure options under somewhat idealised chemical and physical conditions. Optimisation-based methods, once given a superstructure, can generate more detailed and complete designs from an engineering perspective, even striving to account for controllability aspects. It is obvious that the complexity and full range of design variables in process integrated RD units have not been considered yet in the scope of the current RD design methods. Process integrated de-
signs will not only account for the economic interactions with the process surroundings of the RD units but also comply with the desired dynamics and control of the overall process supply chain. In view of the size and of the conceptual and computational complexity of such a design problem a single comprehensive design technique will not be available for years to come. A multi-stage design strategy will be required. It allows the designer to combine in a systematic way the capabilities and complementary strengths of the available graphical and optimisation-based methods. As a step towards such an integrated design approach, Almeida-Rivera and Grievink (2001) propose a methodology, supported by

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**Notes:** G1, statics analysis; G2, RCM; G3, flammable region; G4, fixed points; G5, reactive cascade; G6, thermodynamic-based; G7, conventional graphic techniques; G8, photometra-based; G9, difference points; M1, MINLP; M2, OCPE; M3, MDOO; H1, heuristics. Key: □, applicable; □, non-applicable/missing. \*, original assumption relaxed by later contributions.
a decomposition in a hierarchy of imbedded design spaces of increasing refinement. As a design progresses the level of design resolution can be increased, while constraints on the physical feasibility of structures and operating conditions derived from first principles analysis can be propagated to limit the searches in the expanded design space. The general design paradigm of Sirola (1996a, Chapter 23, 1996b) is taken as the backbone of this multi-stage approach. As depicted in Figs. 14 and 15, different decisions are made at the different levels, supported by specific design tools. Furthermore, all the levels are inter-related by the flow of information originated at lower levels. As one steps up the design pyramid, the scope of design is decreased whereas the information flow is incremented.

The following guidelines have been derived for this integrated methodology in RD:

level 1. Formulation: Sustainability issues are considered, the basis of design (product and feedstock purities ranges, production modes, operating window and economics) are defined and the building model blocks are developed (e.g. thermodynamic, kinetic, hydrodynamic) (corresponds to levels "Formulation" and "Building blocks" in Fig. 2).

level 2. Feasibility analysis: By graphical methods the feasible product compositions are determined for a given set of input variables (e.g. feed composition and Damköhler number), incorporating all occurring phenomena (e.g. distillation boundaries, (non)-reactive azeotropy). If the process occurs to be feasible, economically attractive and satisfies SHE issues, proceed to level 2. Otherwise, stop.
the design and explore other processes alternatives (corresponds to level “Synthesis” in Fig. 2).

level 3. Temporal structure: The model of operation (batch, continuous or semibatch) is selected based on operational skills, production requirements and supply chain dynamics (corresponds to level “Synthesis” in Fig. 2).

level 4. Generation of separation sequences: Rigorous graphical methods allow the identification and organisation of feasible column sequences. Their type of task is estimated (fully reactive, hybrid and non-reactive columns), together with the number of units and their connectivity. A decision has to be made related to the type of packing (continuous or discontinuous) (corresponds to level “Synthesis” in Fig. 2).

level 5. Internal spatial structure: The process structure obtained from the previous level is used as starting point for this stage. By means of optimisation-based methods both continuous variables (e.g. column diameter, heat exchange areas, contacting area, catalyst concentration, pressure drop, reboil and reflux ratios) and discrete variables (e.g. feed staging, reactive and non-reactive stages, withdrawal staging) are obtained. If the process structure options are economically attractive, proceed to the next level. Otherwise, relax—if applicable—some of the constraining assumptions of level 1 and resume level 2 (corresponds to level “Synthesis” in Fig. 2).

level 6. Behaviour analysis: Steady-state simulations are carried out to explore the kinetics, gas/liquid mass transfer, hydrodynamics and multiplicities inside the units. Dynamic simulations are performed to check the robustness of the design, in terms of the ability to maintain product purities and conversion in a desired range when disturbances are occurring. If the process is controllable and economically attractive at the estimated operating conditions, go to the next level. Otherwise, relax—if applicable—some of the constraining assumptions of level 1 and resume level 2 (corresponds to level “Analysis” in Fig. 2).

level 7. Evaluation: The design options are checked with respect to Safety, Health and Environment-related issues. If one process satisfies all the SHE constraints the design task is finished. Otherwise, a trade-off between economic considerations and SHE issues is required (corresponds to level “Evaluation” in Fig. 2).

The successful application of the integrated design methodology relies upon considering the output of the graphical methods as initial structure for the optimisation-driven design approaches. In this way, the optimised design is likely to be embedded within the feasible space and the computational effort becomes less demanding due to the reduced number of design variables. This approach intends to reduce the complexity of the design problem, and it should not be considered as a mechanistic recipe.

4. Concluding remarks

Both the graphical and optimisation-based design methods have already proven their potential in RD process design but have also shown some significant limitations. Graphical methods are fairly flexible in generating alternative designs at various design parameters, allowing the designer to define realistic bounds on them. Furthermore, the graphical nature of the methods clarifies the understanding of those fundamental issues in RD, which might be disguised by other approaches (e.g. reactive azeotropes). On the other hand, graphical methods are strongly limited by their graphical nature (i.e. \( n_c - n_{c1} \leq 3 \)). Optimisation-based methods overcome the last limitation and have successfully solved design problems, where multi-component mixtures, multiple chemical reactions and multiple units are involved. However, additional caution is required in the problem formulation and inappropriate initial guesses of the optimisation variables may lead into convergence difficulties. The evolutionary method proposed by Subawalla and Fair (1999) covers in more detail some physical aspects of the design of RD columns. However, this approach requires a pre-defined structure and accordingly the optimum design is not guaranteed.

The multi-stage approach conjugates the strengths of both graphical and optimisation-based methods, aiming at an integrated and generalised methodology. Economic, controllability-related and environmental issues have been included as evaluation criteria and special attention has been paid to the definition of rigorous building blocks (dynamic models for the involved units and physical/chemical properties estimation). This approach proposes a decomposition of the design problem in a hierarchy of design spaces of increasing refinement.

The challenges in the design of RD are numerous and foreshadow to be exciting. The drive for process intensification and more sustainable plant operations can lead to more intricate geometric structures (e.g. packings, dividing walls, distributed heat exchange) and more refined models which couple mass and energy transfer in a more realistic way. Finally, incorporating supply chain motivated temporal features within the design task (e.g. switching modes) might increase tremendously the degrees of freedom and the problem complexity.

References


Higler, A., Krishna, R., & Taylor, R. (1999). Nonequilibrium cell model for packed distillation columns—The influence of maldistribu-


