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Synthesis and Design of Reactive Distillation Columns

A thesis submitted to the
University of Manchester Institute of Science and Technology

for the degree of
Doctor of Philosophy

by
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under the supervision of
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and
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March 2004
Declaration

No portion of the work referred to in this thesis has been submitted in support of an application for another degree or qualification of this or any other university, or any other institution of learning.

Ramona Manuela DRAGOMIR
Abstract

During the past decades, reactive distillation has received intensive attention due to the well known benefits of integrating distillation with reaction in a single unit. Significant capital savings, improved conversion and selectivity, avoidance of azeotropes, together with heat integration are some of the main advantages of using reactive distillation. Many applications have proven to be economically advantageous by using reactive distillation (e.g. MTBE and TAME synthesis, production of methyl-acetate, manufacture of di-isopropyl-ether, oligomerisation of linear butenes and others). Whereas there are many procedures available for the synthesis of non-reactive columns or reactive-separation systems, the synthesis of reactive distillation columns is still a challenge, due to the complexity and the high number of design parameters involved. Available conceptual design methods generally address three (or four) components and fully reactive columns, but there is still a lack of systematic conceptual design methods for more general column configurations and for multi-component systems.

The aim of this work is to develop a methodology to identify promising column configurations and to obtain column design parameters (number of reactive and non-reactive stages, reflux and reboil ratios, feed condition) for a given feed mixture and a set of desired products. A new systematic design method for reactive systems reaching equilibrium allows the analysis of the impact of different configurations (fully reactive or hybrid columns) and feed policies (single- or double-feed columns) on column performance. The methodology is extended to account for kinetically-controlled reactions in synthesis and design of reactive distillation columns. Systems with two degrees of freedom (according to the Gibbs phase rule) were considered for equilibrium reactions, and ternary and quaternary systems for kinetically-controlled reactions. Reactive distillation column designs generated by the methodology are
presented as illustrative examples. Their predicted performances are shown to be in good agreement with those predicted by rigorous simulation using HYSYS.

The approach can easily be automated and typically generates multiple designs, allowing a design engineer to efficiently compare various design options including hybrid and fully reactive columns, single- and double-feed configurations, and different sets of operating parameters for a given column configuration. The new methodology developed in this work facilitates a step change in conceptual design practice, offering a systematic and easy to use tool for the synthesis and design of reactive distillation columns.
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1. INTRODUCTION

1.1. Reactive distillation: from concept to industrial application

Several decades ago, the occurrence of reaction in a distillation column was considered a problem, chemical engineers usually looking for ways of eliminating the unwanted hydrolysis, dimerisation and polymerisation reactions which affected the efficiency of the separation process. The advantages of deliberately combining distillation with reaction in a single unit were first recognized in 1921, with the awarding of several patents for esterification processes to Backhaus (1921a-d; 1922a-d; 1923a,b). However, no industrial applications of these processes were realized until 1984, when Agreda and co-workers (Agreda, 1984) at Eastman Chemicals Co. took a step forward in inventiveness and patented their commercial process for methyl acetate production using a homogeneous catalysed reaction. The process was such a success, that in the following years the interest in reactive distillation has exploded, in both research area and industry.

Every year new applications for reactive distillation are developed, e.g. production of fuel ethers as MTBE, ETBE and TAME, production of ethylene glycol, metathesis of 1-butene and many others (Sharma and Mahajani, 2001) proving again that the hybrid process is a viable and economic alternative to conventional reaction-separation process. Some of the major advantages of reactive distillation include the simplification of the flowsheet leading to significant capital savings, improved conversion and selectivity, which gives a benefit of reduced recycle costs and significantly reduces the catalyst requirement, avoidance of azeotropes (e.g. in MTBE and methyl acetate production) and also sometimes significant heat integration benefits due to the continuous release of heat from reaction (Krishna, 2000). However, despite the industrial success of reactive distillation for many etherification and esterification
applications, there are situations when reactive distillation is not advantageous, or not even feasible (Towler and Frey, 2000). There are certain conditions a system should satisfy for reactive distillation to be a feasible and economic alternative. The most important condition for a system is that the relative volatilities must be suitable to maintain high concentrations of reactants and low concentrations of products in the reaction zone, i.e. the products should have extreme relative volatilities. If the volatility constraint is met, then it is important also to match the process conditions for distillation and reaction: in some processes the optimum conditions of temperature and pressure for distillation may be far from optimal for reaction. Other difficulties encountered in developing a reactive distillation process are linked with the control of residence time inside the column, a very important parameter for kinetically controlled reactions, and with the scale-up to large flows, still an area with many unknowns.

Because of the increased interest in finding new process alternatives, driven by the need for sustainable processes, cleaner and purer products and minimum environmental impact, the interest in developing new reactive distillation applications is growing, and so does the need for fast and effective methods for the feasibility and design of such processes. When a process engineer has to choose between various process alternatives, a robust and relatively fast method for process evaluation is needed.

In reactive distillation synthesis the best column structure is selected which, for given reactants and given specifications of the process, will lead to maximum yield and minimum cost. During reactive distillation synthesis, choices about the column configuration (fully reactive or hybrid column), the feed distribution pattern or the amount of the holdup in the column have to be made. Also, it is worth investigating whether complex configurations (e.g a reaction-separation system rather than a reactive distillation column) would be more beneficial for the proposed reaction-separation task. Some of the decisions are simple to make, at least qualitatively, such as using a hybrid column or a fully reactive
column, but some require further analysis and screening of many alternatives. Once a column structure has been selected, the optimum design (e.g. number of reactive and non-reactive stages, feed stage location) and operating parameters (e.g. reflux or reboil ratio and feed condition) have to be obtained, with respect to our objective (e.g. total annualised cost, energy requirement, total number of stages).

Because of the interactions between reaction and distillation in the combined unit, the modelling and design of reactive distillation is very complex. The reaction influences the composition on each tray, and thus mass transfer and vapour and liquid loads; for kinetically-controlled reactions liquid hold-up represents a very important design parameter, because the reaction extent is not only a function of tray compositions and temperature, but also of residence time.

For the synthesis and design of reactive distillation, there are two main approaches: optimisation methods (Ciric and Gu, 1994; Pekkanen, 1995; Groemping, 2002), and conceptual design methods. Generally, optimisation methods can cover both the synthesis and the design steps; they can accommodate various column configurations and provide the optimum structure and operating parameters. The conceptual design methods mainly focus on the initial stages of the design of a reactive distillation column for which a structure has been already chosen, such as obtaining the number of stages, the feed location and the operating parameters for a desired separation task. The conceptual design methods available can be divided into two main groups: graphical methods (Lee, 2000; Hauan, 2000) and conceptual design methods based on BVM (Bessling et al. 1997; Barbosa and Doherty, 1998; Groemping, 2002). All methods will be reviewed in more detail in Chapter 3.

Whereas the optimisation methods are quite well established, and are able to represent complex reactive distillation structures and kinetically controlled reactions, the conceptual design methods are not developed at the same level.
However, optimisation methods are very time consuming and they are more appropriate for analysing a wide variety of flowsheet configurations than for the synthesis and design of a single reactive distillation column. Also, they provide only one optimised design, and they are not very helpful for developing insights and understanding the phenomena underlying the reactive distillation process.

Overall, there is still a lack of a systematic and comprehensive approach for synthesis of reactive distillation processes, especially for multicomponent and complex column configurations. So far, conceptual design methods mostly consider equilibrium reaction, and usually non-hybrid columns (i.e. fully reactive columns) and simple systems (e.g. single reactions and a maximum of four components). There is a need in research in this area, for improving the existing methods or finding new approaches which would be able to deal with more complex reactions, and more complex configurations of reaction-separation systems.

1.2. Aims and scope

In the context of growing interest in developing new reactive distillation applications, a systematic and reliable tool is needed to aid design engineers in identifying, for a given reactive mixture and a set of desired products, promising column configurations and column design parameters (number of stages, reflux and reboil ratios, feed condition). In this work, a new systematic design method for reactive systems reaching equilibrium is developed, allowing the analysis of the impact of different configurations (fully reactive or hybrid columns) and feed policies (single- or double-feed columns) on column performance. The methodology is extended to account for kinetically-controlled reactions in synthesis and design of reactive distillation columns. The approach can easily be automated and typically generates multiple designs, allowing a design engineer to compare efficiently various design options including hybrid and fully reactive columns, single- and double-feed configurations, and different sets of operating parameters for a given column configuration. The new methodology
developed in this work facilitates a step change in conceptual design practice, offering a systematic and easy to use tool for the synthesis and design of reactive distillation columns.

1.3. Assumptions and restrictions

The methodology developed in this work, based on the BVM, uses a graphical approach, i.e. intersections of composition profiles and/or stage composition lines. Because of the limitation of the approach caused by the graphical representation, systems with two degrees of freedom according to the Gibbs phase rule were considered for equilibrium reactions and a maximum of four components for kinetically-controlled reactions. However, most of the systems of interest in reactive distillation are systems with two degrees of freedom and a maximum of four components including esterification, etherification and hydrolysis (Sharma, 2001). Therefore, even though the methodology does not solve the general problem of conceptual design of multicomponent and complex reactive systems, it still offers a very useful tool for the conceptual design of many systems of interest.

Most of the reactive systems are non-ideal systems; therefore appropriate models for the calculation of liquid and vapour fugacities are needed. Wilson, NRTL or UNIQUAC models were used to calculate the liquid phase activity coefficients and the virial equation was used to calculate the fugacity in the vapour phase. The interaction parameters for these models are obtained from a commercial simulator, HYSYS v2.4. The interaction parameters in HYSYS v2.4 are obtained from DEHEMA Vapour-Liquid Equilibrium Data Collection (Gmehling, 1977-1980). The interaction parameters which are not available in the simulator database are estimated using the UNIFAC method. For highly non-ideal systems in both the liquid and vapour phases (such as the methyl acetate system) a real-time interface with HYSYS v2.4 was used for all thermodynamic calculations. The pure component vapour pressure is calculated using the extended Antoine equation, using parameters from HYSYS v2.4.
This work does not assume constant molar overflow (in transformed variables for the reactive sections). This assumption is widely used in BVM, but it introduces errors affecting accuracy, especially for systems where the number of moles changes due to reaction. Heat balances were introduced in composition profile calculations for the cases where the constant molar overflow assumption proved to be unrealistic. An initial test was performed for each system to assess the validity of the assumption of constant molar overflow (in transformed variables for the reactive sections).

Mass transfer was considered to be ideal in this work, so that vapour-liquid equilibrium is assumed on each stage. However, this assumption is not fundamental to the approach and non-ideal rate based models can be relatively easily implemented, in an approach analogous to that of Castillo (1997).

1.4. Software implementation

The methodology developed in this work is easily automated, and has been implemented in FORTRAN 77, with good computational efficiency. The program has been included in DPI-UMIST software COLOM©. The simulations presented in the case studies were carried out on the commercial process simulator HYSYS v2.4. All calculations presented in this work were carried out on a Pentium IV 1.5 GHz personal computer.

1.5. Thesis outline

A few general considerations and definitions useful for understanding the concepts developed in this work are presented in Chapter 2. Chapter 3 presents a literature review of the available methods for synthesis and design of reactive distillation column is presented in. Chapters 4 and 5 focus on equilibrium reactions. Chapter 4 introduces a new methodology for the design of single-feed hybrid reactive distillation columns (columns featuring both reactive and
non reactive sections). The methodology developed in Chapter 4 is extended in Chapter 5 to accommodate two-feed columns. Both fully reactive and hybrid columns are considered. In Chapter 6, the assumption of reactive equilibrium is eliminated. This chapter presents a methodology for the conceptual design of fully-reactive and hybrid kinetically-controlled reactive columns separating ternary and quaternary mixtures. The thesis is concluded in Chapter 7.
2. REACTIVE DISTILLATION: GENERAL CONSIDERATIONS

This chapter briefly introduces some of the key concepts and definitions in modelling and design of reactive distillation columns. Some of the advantages and restrictions of established concepts (e.g. transformed variables) will be briefly discussed, together with their implication in reactive distillation column design.

2.1. Key definitions

The term equilibrium reactive distillation indicates that reactive process where the reactions, assumed to take place in the liquid phase, are infinitely fast. Thus, the system is able to reach chemical equilibrium on a distillation tray. For simplicity of analysis, usually a simultaneous chemical and vapour-liquid equilibrium (VLE) is assumed. The assumption of chemical equilibrium holds quite reasonably for fast reactions, but in some cases, where slow reactions take place in the column, kinetic considerations should be considered (Sundmacher and Kienle, 2003).

For systems with equilibrium reactions, all compositions have to satisfy the combined phase and reaction equilibrium; therefore not all compositions are feasible. The reaction space defines the locus of reachable compositions for a system undergoing an equilibrium reaction (Bessling et al., 1997). The reaction space is a subspace of lower dimension in the physical composition space. Figure 2.1 shows the reaction space for two reactive systems. For a ternary system A, B, C, undergoing the equilibrium reaction $A + B \leftrightarrow C$, the reaction space for a specific equilibrium constant ($K_{eq}$) is represented by a line between the two reactants A and B (Figure 2.1a). If an inert is present in the system (Figure 2.1b), the reaction space is stretched between the chemical equilibrium line for the reactive ternary system A, B, C and the inert component D (Bessling et al., 1997).
Two main implications are derived from the thermodynamic constraint related to the simultaneous phase and reaction equilibrium (Espinosa et al., 1995a). Firstly, because not all the concentrations from the concentration space can be considered as thermodynamically feasible, there are upper bounds for the concentrations of some components according to the chemical equilibrium. This leads to a second implication: some components cannot be obtained pure from a reactive section. In Figure 2.1 can be observed that pure C cannot be obtained from a reactive section, as the equilibrium line (or surface) does not contain C. In this case a non-reactive section must be added in the column to facilitate the separation of C from the reactant A and B.

A column featuring both reactive and non-reactive sections is usually known as a hybrid reactive distillation column. Hybrid reactive distillation columns contain a reactive section where catalyst is present and one or more pure distillation sections (rectifying and/or stripping sections). Consequently, non-hybrid columns denote columns where all trays (including condenser and reboiler in some cases) are reactive. An important question arising here is when to consider a hybrid column? Bessling et al. (1997) stated that if it is necessary to separate a product that is not in the reaction space, a section with non-reactive distillation region must be added. A product is located in the reaction space if it
needs a reactant for forward or backward reaction. Additionally, all inert components are located in the reaction space. For example, in reaction \(A \leftrightarrow B\) none of the components is located in the reaction space. For reaction \(A + B \leftrightarrow C\), A and B are located in the reaction space, C is not. If component C is the educt (i.e. is consumed in the reaction), a simple reactive distillation is feasible to obtain pure products B and C, whereas if C is the desired product (e.g. the two cases in Figure 2.1), a combination of reactive and non-reactive distillation is necessary. Hybrid columns commonly use a heterogeneous (solid) catalyst, which can be distributed on certain stages in the column; a homogeneous (liquid) catalyst would lead to a non-hybrid column design, unless the reaction can be prevented from being present at certain stages (e.g. by using an intermediate separation).

### 2.2. Reactive composition transformation

Considering a system of \(R\) independent reactions among \(C\) reacting components and \(I\) inert components, the total number of species will be \(NC = C + I\) (Ung and Doherty, 1995b). The inert components do not participate in any of the reactions but they may exhibit non-ideal solution behaviour with each other and with the reacting species. The chemical reactions are represented in the following way:

\[
\nu_{ir} A_i + \nu_{2r} A_2 + \ldots + \nu_{Cr} A_C \leftrightarrow 0, \quad r = 1, 2, \ldots, R
\]  

(2.1)

where \(A_i\) are the reacting species and \(\nu_{ir}\) is the stoichiometric coefficient of component \(i\) in reaction \(r\). It is considered that \(\nu_{ir} < 0\) if component \(i\) is a reactant and \(\nu_{ir} > 0\) if component \(i\) is a product in the reaction \(r\); \(\nu_{ir} = 0\) if component \(i\) is an inert.

The number of degrees of freedom for a reactive system in both reactive and thermodynamic equilibrium is given by the extended Gibbs Phase Rule (Wales, 1985) (Eq. 2.2):

\[ \text{Eq. 2.2} \]
\[ DOF = (C + I) - R + 2 - \Pi \] (2.2)

where \( DOF \) is the degrees of freedom, \((C + I)\) the total number of components, \( R \) the total number of independent reactions, and \( \Pi \) the number of phases.

For a two-phase system, at either constant pressure or temperature, the number of degrees of freedom becomes \( DOF = (C + I) - R - 1 \). This is the number of mole fractions that must be specified in isobaric or isothermal phase equilibrium calculations for reacting mixtures. The number of degrees of freedom from the extended phase rule gives also the dimension of the subspace of reachable compositions, the reaction space (Section 2.1). Each linearly independent reaction reduces the dimensions of the reaction space by one. For example, a four component mixture with one reaction will have two degrees of freedom according to (Eq. 2.2); the reaction space will be a surface in the three-dimensional physical composition space (Figure 2.2a). This surface can be projected onto a two-dimensional plane (Figure 2.2b). Generally, a feasible reaction space in \( C-1 \) dimensions can be projected onto a lower \( (C-1-R) \) dimension space. The projection is a mapping procedure, based on the use of transformed variables.

![Real and transformed composition space for an etherification reaction A+B↔C with inert component D.](image)

(a) Reaction space in the 3-D mole fraction space; (b) The reference component C is eliminated; reaction space is converted to a 2-D transformed composition space.
First introduced by Barbosa and Doherty (1988c) and modified later by Ung and Doherty (1995b), transformed variables are defined using Eq. 2.3.

\[
X_i = \frac{x_i - \nu_i^T \gamma_{\text{ref}} x_{\text{ref}}}{1 - \nu_{\text{tot}}^T \gamma_{\text{ref}} x_{\text{ref}}} \quad \forall \ i = 1, \ldots, C - R - 1,
\]

where:

- \(X_i\) – transformed composition of component \(i\)
- \(x_i\) – mole fraction of component \(i\)
- \(x_{\text{ref}}\) – column vector of \(R\) reference component mole fractions
- \(\nu_i\) – column vector of \(R\) stoichiometric coefficients for component \(i\)
- \(\nu_{\text{tot}}\) – column vector of \(R\) sums of stoichiometric coefficients
- \(\gamma_{\text{ref}}\) – square matrix of dimension \((R,R)\) of stoichiometric coefficients for the \(R\) reference components in the \(R\) reactions
- \(C\) – number of components
- \(R\) – number of reactions

The transformed compositions \((X)\) exhibit the following properties (Ung and Doherty, 1995a; Ung and Doherty, 1995b):

1. \(X\) expresses the conservation of mass for any value of the extent of reaction; they are reaction-invariant compositions;
2. The \(X\)-vector sums to unity;
3. The transformed representation does not depend on the combination of the reaction equations chosen (i.e. one reaction can be replaced by a linear combination of other reactions), as long as this combination is linearly independent;
4. Reactive azeotropes occur if and only if \(X = Y\) (the transformed liquid composition is equal to the transformed vapour composition) (Ung and Doherty, 1995b). Reactive azeotropes pose the same difficulties and limitations in reactive distillation as non-reactive azeotropes pose in traditional distillation, creating reactive distillation boundaries and limiting the separation.
The main advantage of using transformed variables in column design is that the operating lines written in terms of transformed compositions and flowrates have the same form as for non-reactive systems; therefore the extension of the methodologies developed for the design of non-reactive systems to reactive systems is relatively easy (Ung and Doherty, 1995c). Another advantage of using transformed variables is that graphical methods can be applied to mixtures with more than three components, as long as the reaction space is at most two-dimensional. Therefore, in this work, transformed variables were used for the design of equilibrium reactive columns.

It is worth mentioning here that transformed compositions can be calculated for kinetically controlled as well, as long as $x_{\text{ref}}$ is known. Mass balances written in transformed variables hold for both equilibrium and kinetically controlled reactions (Appendix B). But whereas for equilibrium reactions there is a unique correspondence between real and transformed compositions (Ung and Doherty, 1995a), for kinetically controlled reactions there is an infinite number of compositions leading to the same transformed value. This is caused by the fact that for kinetically-controlled reactive systems the compositions are not restricted to lie on the reactive surface. Therefore the use of transformed variables for kinetically-controlled reactive column design is not appropriate. However, they can be used for visualisation purposes.

Taking into account the above considerations, the use of transformed variables for column design is restricted in this work only to equilibrium reactions; for kinetically-controlled reactive systems, real composition space is used.
3. LITERATURE REVIEW

3.1. Introduction

When investigating the possibility of using reactive distillation for a specific system, a fast and effective tool is needed, to guide the design engineer through the decisional steps from idea to commercial application. The first problem to be solved is to assess the feasibility of the process, e.g. to establish if the combined reaction and separation task can be achieved in a reactive distillation column and, if yes, what product compositions and yield we would expect to obtain? This area is widely covered in the open literature; many procedures for assessing the feasibility of reactive distillation processes have been developed in the past few decades, mainly based on the similarities between the reactive distillation process and conventional distillation or reaction separation processes. A review of the most commonly used methods for identifying the feasibility of a proposed reactive distillation task is presented in the first section of this chapter.

Identifying the feasible product compositions for a reactive distillation column is a vital step for the next level, the process development, which include synthesis, design and optimisation of the reactive distillation column. These three steps are in some studies addressed separately, but many studies address them in the same framework. For example, optimisation methods, either using MINLP (Ciric and Gu, 1994), local optimisation (Pekkannen, 1995) or stochastic optimisation (Cardoso et al., 2000; Groemping, 2002) provide the best structure and the optimum design and operating parameters simultaneously. Other methods, such as conceptual design methods (Hauan and Lien, 1996, 1998; Hauan et al.; Lee, 2000; Barbosa and Doherty, 1988a-d; Espinosa et al. 1995a,b, 1996), focus mainly on the feasibility and design of a reactive distillation column for which a configuration type (e.g. fully reactive or hybrid column, single- or double-feed configuration) has already been chosen. The
available conceptual design methods and their strengths and limitations will be discussed in more detail later in this chapter.

The process development step is very important in the implementation of a reactive distillation process, as it gives, quantitatively, the starting points for deriving a basic design using the equilibrium stage model (Sundmacher and Kienle, 2003). This can be later refined using the mass-transfer model. Suitable equipment for the reactive distillation column can then be chosen. Some aspects influencing the choice of the equipment (e.g. the type of reaction: fast or slow, homogeneous or heterogeneous catalysed; or the relative volatilities of the components present in the reactive mixture) are discussed in detail in Sundmacher and Kienle (2003).

The methodologies presented in this work combine the synthesis and conceptual design steps. Therefore, the literature reviewed in this chapter is focused on the available methodologies for synthesis and design of reactive distillation columns. However, because the choice of a feasible pair of product compositions is a very important step for almost all available conceptual design methods, an extensive review of available procedures for assessing feasibility of a proposed reactive separation task is presented.

### 3.2. Feasibility of proposed splits

The determination of feasible product compositions and feasible operating conditions is crucial for synthesis, design, optimisation or control of a reactive distillation column. For a reactive distillation column, not only should the composition of the products lead to a feasible profile in the column, but the overall mass balance has to be satisfied as well. Therefore, there exists a limited set of product compositions satisfying the two constraints. In addition to this, it has to be checked whether reactive distillation, compared to the conventional process, improves the process, e.g. in terms of conversion, or yield (Giessler, 1998).
Extensive studies, based on the analysis of residue curve maps (RCM) and distillation regions for reactive mixtures were published during the past decade. A reactive residue curve is defined by Barbosa and Doherty (1988b) as the locus of the liquid compositions remaining from a reactive simple distillation. A distillation region is a region of a RCM where all residue curves have the same pair of initial and end points. Barbosa and Doherty (1988b) and later Ung and Doherty (1995a-c) analysed the RCMs for ternary and quaternary systems for equilibrium-limited reactions, and introduced the concept of transformed variables to map the composition space to a lower-dimensional feasible composition space (Chapter 2). The similarities between the RCMs in transformed variables and the RCMs for non-reactive mixtures lead to the development of the boundary value methods (BVM) for reactive systems, discussed in more detail later in this chapter. Similar studies were carried out by Espinosa et al. (1995a and b, 1996). Focused more on the effect of inerts on the feasibility of proposed splits, they identified that in some reactive systems (e.g. MTBE), non-reactive components play a key role in both the design and synthesis of reactive distillation columns, acting as conventional entrainers. Also, the importance of using hybrid columns to obtain pure products for certain reactive systems (e.g. MTBE) is discussed. Buzad and Doherty (1994), Song et al. (1998) and Jimenez et al. (2002) analysed the effect of reaction kinetics on RCMs, and the influence of the holdup on the feasibility of reactive distillation columns. An important parameter emerged from their studies, the Damköhler number ($Da$) defined as the ratio between the characteristic residence time and the characteristic reaction time (Eq. 3.1). Buzad and Doherty (1994) identified minimum and maximum $Da$ numbers and minimum and maximum reflux (or reboil) ratios for the proposed product compositions to be feasible.

$$Da = \frac{k_f \cdot H}{F}$$  \hspace{1cm} (3.1)

where:

$k_f$ - forward reaction constant
The geometric methods using reactive RCMs are very useful for providing insights into the behaviour of reactive systems, identifying the feasible distillation regions and analysing the influence of inert components and kinetics on the feasibility of a proposed split.

A more systematic approach to identify the feasible compositions that can be achieved in processes combining simultaneous reaction, mixing and separation was developed by Nisoli et al. (1997). They combined the attainable region approach for reaction-mixing systems, using a series of CSTRs with vapour removal, with geometric methods for assessing the feasibility of separation in order to find the feasible compositions that can be achieved in processes combining simultaneous reaction, mixing and separation. The method was later extended by Gadewar et al. (2002) to accommodate a reactive distillation column, using a countercurrent cascade of two-phase CSTRs to emulate the stripping and rectifying sections. The attainable region method, used in both approaches, is useful for identifying promising flowsheets in a design procedure, but being a graphical method, it cannot readily be applied in multicomponent reactive mixtures. Nevertheless, the method can be used for multiple components and multiple reactions and can be a useful tool for identifying the regions of feasible product composition, but because in multidimensional space the graphical visualisation is not possible, the utility of the method in finding promising flowsheets cannot be extended in this case.

Giessler et al. (1998) developed a feasibility analysis method based on the Static Analysis (SA). The method was applied to analyse feasible separation modes for a series of industrial examples (Giessler, 1999) and then extended to a systematic structure generation method (Giessler, 2001). A dominant assumption in the SA is that the vapour and liquid flow rates in the column are very large; therefore the composition change caused by the reaction on each tray can be neglected. Based on this assumption, the combined process can be divided into two separate unit operations: a reaction unit in which the feed is converted into a pseudo-feed by assuming a certain extent of reaction, and a
simple distillation unit which separates the pseudo-feed into desired products. The concept of limiting path (a trajectory for a limiting steady state) is very useful in delimiting the feasible composition regions, but the drastic assumptions of the method and the graphical interpretation of the results limit its applicability only to simple systems. Moreover, by decomposing the process into two processes, the often significant interaction between reaction and distillation is ignored.

Another approach for feasibility analysis, which also considers the limiting conditions in a reactive distillation column, is $\infty/\infty$ analysis (Guettinger, 1998). The $\infty/\infty$ analysis considers that the reactive distillation column has infinite separation capabilities: infinite reflux and infinite number of stages. The main advantage of this analysis is that it was developed both for non-hybrid and for hybrid columns. A reactive distillation column with given feed composition, flowrate and quality, has only one operational degree of freedom in the $\infty/\infty$ case. Guettinger (1998) used this single degree of freedom to parametrise all possible profiles and to perform a bifurcation study (continuation of solutions) by tracking the distillate and bottom compositions to obtain all feasible transformed composition profiles. A series of bifurcation diagrams are obtained, which can be used for detecting the feasible product compositions for given operational parameters. Apart from the possibility of identifying feasible product compositions, the method can successfully identify the presence of multiple steady states (MSS), for both fully reactive and hybrid columns.

A similar method for finding feasible compositions, also based on bifurcation analysis and very useful for kinetically-controlled reactions, was used by Venimadhavan et al. (1999). They studied the implications of reaction rate, catalyst level and liquid holdup (lumped in Damköhler number, $Da$) on the feasibility and product purities, and used the bifurcation analysis to obtain feasible product compositions for reactive distillation. Critical $Da$ numbers were found for which a distillation boundary can disappear, or a reactive azeotrope can appear. The analysis is very useful for setting the intervals for the $Da$
number in order to obtain a certain residue curve map (RCM) structure. As the method uses the $Da$ number for estimating the kinetic effects, it can capture the essential features of kinetically-controlled reactive distillation even if very little kinetic information is available, as a specific Da number can be obtained by manipulating design and operation parameters (e.g. holdup and feed flowrate). However, the method is applicable only to fully reactive columns, and kinetically-controlled reactions.

Gadewar et al. (2001) used an infinite series of CSTR with vapour removal (a series of flash cascades) to predict the feasible direct and indirect splits from a single feed, fully reactive column, using a bifurcation analysis. Based on the results from bifurcation analysis, some rules can be derived for sharp splits in a non-hybrid reactive distillation column:

- *unstable nodes* in the rectifying bifurcation diagram are feasible distillates for a single feed reactive column;
- *stable nodes* in the stripping bifurcation diagram are feasible bottoms from a single feed reactive column.

The main advantage of the method is that it can be used for any number of components and reactions in the system. The authors (Gadewar et al., 2001), stated that the method can be extended to study the feasibility of hybrid, double-feed and complex columns, but so far only methods for non-hybrid columns have been published.

Identifying feasible product compositions is a very important step prior to any conceptual design attempt. Most of the conceptual designs methods available in the open literature are based on BVM (as will be presented later in this chapter), and the specification of the product composition is an essential step; therefore using a reliable method to identify the feasibility of a proposed pair of products will be most helpful, avoiding tedious iterations and unfeasible design results. Methods of Guettinger (1998), Venimadhavan et al. (1999) and Gadewar (2001) are particularly useful for this step. Other methods (e.g. Ung and Doherty, 1995a-c; Espinosa et al., 1995a,b, 1996; Buzad and Doherty, 1994, Nisoli et al., 1995a-c; Espinosa et al., 1995a,b, 1996; Buzad and Doherty, 1994, Nisoli et al., 1995a-c; Espinosa et al., 1995a,b, 1996; Buzad and Doherty, 1994, Nisoli et al.,
1997; Giessler, 1998, 1999, 2001; Gadewar et al., 2002 are also helpful in offering insights on the behaviour of a reactive system and identifying the feasible regions of product compositions. By identifying first what product compositions are feasible in a reactive column will significantly speed up the conceptual design process.

3.3. Synthesis and design of reactive distillation columns

Whereas there are many procedures available for the synthesis of non-reactive columns or reactive-separation systems, the synthesis of reactive distillation columns cannot be performed in the same way. The reactions influence the composition on each tray and thus the mass transfer, the vapour and liquid loads and the minimum reflux ratio. Furthermore, the hold-up on each tray needs to be considered because for kinetically-controlled reactions the generation of components is not only a function of temperature and composition but also of residence time and thus of hold-up.

The methods available for synthesis and design of reactive distillation column can be divided into two main categories: optimisation methods and conceptual design methods, with the latter including various graphical methods and Boundary Value methods.

3.3.1. Optimisation methods

Reactive distillation design via optimisation methods is based on the main idea that the system can be represented as a special case of a multiphase reactor network. In a single reactive distillation column, reaction and distillation occur simultaneously on every stage and the flows are counter-currently contacted. Therefore, synthesis of reactive distillation columns is strongly related to the synthesis of multiphase reactor networks including reaction and separation.
Ciric and Gu (1994) formulated a mixed integer non-linear programming model (MINLP), incorporating reaction kinetics, heats of reaction and liquid holdup volumes, solution of which yields the optimal number of stages, the optimal feed stage location(s) and feed rates and the optimal reflux ratio at a minimal total annualised cost.

Pekkanen (1995) described a local optimisation method for the design of reactive distillation (a “stage by stage specification method”). This approach does not optimise the column as a whole, i.e. all the parameters optimised simultaneously, but the design procedure starts from both column ends and makes the design specifications at each stage as calculation progresses. The basic idea behind the local optimisation method is to minimise, in composition space, the difference between the direction of the liquid phase operating line, moving from stage $n$ to stage $n+1$, and the direction from stage $n$ to a target point (which is the distillate for stripping operating line and bottom for the rectifying operating line). The main advantage of the method is that it can be applied for multi-component and multiple reaction systems, and it considers kinetically controlled reactions. Also, minimising the directions of composition changes could be useful in some other decisional steps, for example whether a reactive or a non-reactive stage is more beneficial.

Groemping (2002) presented a new approach for optimisation of reaction separation systems by using the concepts first developed for reactor systems synthesis (Mehta, 1997). In his approach, the reactive distillation column is considered as a special case of a general multiphase reactor network. A superstructure accommodating reaction/distillation units, reboilers, condensers, mixers and splitters, is optimised using a simulated annealing algorithm for obtaining the most promising flowsheet structure. For each reaction/distillation unit, the options for mass transfer, reaction, number of stages, flow direction and depth of modelling effort can be controlled, so that each unit can represent either a well mixed reactor (CSTR), a cascade of CSTR’s, a plug flow reactor (PFR), a reactive distillation section in co- or counter-current mode, an inert
distillation section or a short cut distillation column. During the simulated annealing optimisation, novel and complex network structures with many recycle streams and interactions between the flowsheet sections are generated.

The simulated annealing algorithm was also used by Cardoso et al. (2000) to optimise a single reactive distillation column. They adopted the MINLP model of Ciric and Gu (1994) and performed an optimisation by simulated annealing, to obtain the optimum configuration and operational parameters of the reactive distillation column. The proposed method can be applied to single or multiple reactions, ideal or non-ideal vapour-liquid equilibrium and distributed or single-staged reaction zones.

The optimisation methods proved to be viable methods for the design of reactive distillation systems. They are able to provide solutions which are very close to the global optimum, even for highly non-ideal systems with multiple reactions. However, for the synthesis and design of a single reactive distillation column, the optimisation methods are very time consuming, and they are more appropriate to analyse a wide variety of flowsheet configurations. This, combined with the lack of insights into the reactive systems behaviour makes optimisation methods not very appropriate for the synthesis and design steps of a reactive distillation column. Also, they usually offer only one optimised solution, not several alternatives for the design engineer to choose from, which would be very useful in the decision making steps, especially if retrofit is considered.

### 3.3.2. Graphical methods

A very useful approach for obtaining insights into the behaviour of reactive systems behaviour is based on the graphical representation of the combined reaction and separation phenomena.
Hauan and co-workers (Hauan and Lien, 1996, 1998; Hauan, Westerberg and Lien, 2000b) have developed a phenomena-based method for the analysis and design of reactive separation processes. Within this framework the change in the composition of any particular phase is given by the vector equation:

\[
\frac{dx}{dt} = mix + sep + rx
\]

(3.2)

where \( x \) is the composition vector of component mole fractions of the phase in question and \( mix, sep \) and \( rx \) are vectors that represent the composition changes due to mixing, separation and reaction, respectively. The direction of these combined vectors indicates the feasibility of a particular process; their length is a measure of the process efficiency. More importantly, this formulation admits the possibility of using a properly formulated model of mass transfer in multicomponent systems. A fixed point exists when the \( mix, sep \) and \( rx \) vectors cancel each other:

\[
mix + sep + rx = 0
\]

(3.3)

Hauan et al. (2000a) have provided a comprehensive analysis of the kinds of fixed points that can arise from cancellation of different combinations of these vectors. They also introduce the concept of reaction difference point \( (\delta_r) \), defined as the difference between an arbitrary composition and a singular point (Eq. 3.4). The reaction difference point acts like a focus for chemical reactions and in composition space the reaction moves along straight lines, all of which pass through the difference point. Thus, this reaction difference point behaves similarly to a difference point for an extractive distillation column and is essential to realising the geometric implications of material balances in a reactive distillation column. However, in a reacting system where the total number of moles does not change by the reaction, the reaction difference point vector points at infinity. This is inconvenient both for geometric and numerical reasons and unfortunately rather common in systems where reactive distillation might be applied.
\[ \delta_r = \frac{1}{\sum_i v_i} \begin{bmatrix} v_1 \\ v_2 \\ \vdots \\ v_C \end{bmatrix} = \frac{\nu}{\sum_i v_i} \quad \forall \sum_i \neq 0, i = 1, \ldots, C \quad (3.4) \]

In a later study, Hauan et al. (2000b) apply the concept of difference points to analyse the interactions between reaction and separation in extractive and reactive cascades. The compositions of the difference points for a reactive cascade (\( \delta^r_R \), for a rectifying section and \( \delta^s_R \), for a stripping section) are defined as linear combinations of their product composition and the difference point of the chemical reaction (\( \delta_t \)). The difference point composition for a reactive cascade will in general not be the same from stage to stage, but it will move along the line corresponding to all linear combinations of the cascade end product and the reaction difference point (e.g. Eq. 3.5 for a rectifying section).

\[ \delta^r_R = \alpha_r \cdot \chi_D + (1 - \alpha_r) \cdot \delta_t \quad (3.5) \]

The step size along this line reflects the internal reaction distribution in the cascade (i.e. dependant on the molar reaction turn-over on each stage). The overall molar turn-over \( \xi_n \) is, as the stage number \( n \) goes to infinity, theoretically limited to values keeping the vapour and liquid compositions inside the composition simplex and in practice further restricted by chemical equilibrium. Hauan (2000b) showed that the maximum valid range for \( \xi_n \) is a function of the chosen end product compositions. The range of possible compositions resulting from selection of a particular molar turn-over on stage \( n \) will, however, subsequently affect the calculation on corresponding \( x-y \) pairs on stage \((n+1)\) and higher.

Based on this concept, an algorithm for computing cascade section profiles was described (Hauan, 2000b). The major problem of this algorithm is how to compute the reaction distribution. Except for this step, the rest of the algorithm is analogous with the algorithm of computing non-reactive section cascade profiles (e.g. Julka and Doherty, 1993).
To avoid this drawback, a general approach was developed (Lee et al., 2000), which looks directly at the overall conversion in the cascade and avoids the parametric family of solutions resulting from alternative ways to distribute a given molar turn-over between the rectifying and stripping sections. This method, although very useful in the synthesis of various design alternatives, does not offer any information about the column design and associated operating parameters. Also, the method is limited by the graphical representation to a maximum of 4 components.

In subsequent papers, Lee et al. (2000b; 2001) focused on solving some of the drawbacks of the earlier work, by including the difference point concept in a method using the lever rule for tray-by-tray calculations. Thus, details about the design and operation parameters for a particular column can be obtained. Single-feed and double-feed columns can be accommodated, as can hybrid columns. However, at each stage, important decisions have to be made, accounting for the amount of reaction taking place on a particular stage, the second feed location or whether to start a non-reactive section. Of all these decisions, specifying the reaction extent on each stage is the most restrictive. Even though for kinetically-controlled reactions the reaction extent can be theoretically adjusted by adjusting the liquid holdup on each tray, for equilibrium reaction the assumption of a specific reaction extent on a tray is not realistic, as the actual value of reaction extent is a function of the tray composition and temperature, in chemical and phase equilibrium. Therefore, the methodology has a very limited applicability, but still offers great insights about the behaviour of reactive systems. For example, by manipulating the amount of reaction on a particular stage, it is possible to break azeotropes (Lee et al. 2000c). Also, the understanding of the lever rule in reactive distillation columns lead to the development of two very important graphical methods for binary mixtures: the McCabe Thiele and Ponchon-Savarit methods (Westerberg et al. 2000; Lee et al., 2000d);
The geometric approach has proved to be very useful for specific systems (e.g. systems with a maximum of 4 components and 1 reaction) because it offers an easy-to-understand methodology for evaluating the feasibility of reactive distillation and for identifying promising flowsheets. Even if it is restricted by the graphical representation only to simple systems, the insights offered are very valuable in understanding the behaviour of more complex systems.

3.3.3. Boundary value methods

The most common methods used for the conceptual design of reactive distillation columns are the boundary value methods (BVM). Developed for both equilibrium and kinetically-controlled reactions, BVM for reactive systems are an extension of those developed for non-reactive systems by Levy et al. (1985).

For an equilibrium reaction, the methodology uses the concept of transformed variables (Chapter 2), first introduced by Ung and Doherty (1995a), which simplifies the mass balances and leads to equations for the operating line analogous to those for non-reactive systems. Generally, BVMs assume equilibrium stages (Taylor & Krishna, 2000); some recent developments have opened up the possibility of using non-equilibrium models for reactive distillation design (e.g. Mahajani, 1996).

Barbosa and Doherty (1988a) first extended the BVM of Levy et al. (1985) for the design of single-feed RD columns. The method is based on the following assumptions:

- the column is adiabatic;
- the molar heat of vaporisation of the mixture is constant;
- the heat of mixing is negligible in both liquid and vapour phases;
- the heat of reaction is negligible compared to the enthalpy of vaporisation;
- the feed is a saturated liquid;
- phase equilibrium is achieved on each stage.
These assumptions, common to most of the conceptual methods developed so far, ensure that the vapour and liquid flows inside the column are constant, thereby the energy balances are decoupled from the component and general mass balances.

The BVM uses intersection of rectifying and stripping profiles as a feasibility criterion. Column design details are obtained from the intersection point, for a specified pair of product compositions. Composition profiles are calculated from material balance in transformed variables around each stage in a column section (either above or below the feed stage) and the corresponding product (distillate or bottom product) (Eqs. 3.6 and 3.7).

\[
X_{i,j} = \frac{r_j^* + 1}{r_j} Y_{i,j-1} - \frac{1}{r_j} Y_{i,D}
\]

(3.6)

\[
X_{i,j+1} = \frac{s_j^*}{s_j + 1} Y_{i,j} - \frac{1}{s_j + 1} X_{i,B}
\]

(3.7)

In the work of Barbosa and Doherty (1988a), the transformed reflux and reboil ratios are defined as follows:

\[
r_j^* = \frac{L(v_k - v_T x_{k,j})}{D(v_k - v_T y_{k,D})}
\]

(3.8)

\[
s_j^* = \frac{V(v_k - v_T y_{k,j})}{B(v_k - v_T x_{k,B})}
\]

(3.9)

To derive a general method for assessing the feasibility and calculating the minimum reflux ratios for single-feed reactive distillation columns, Barbosa and Doherty (1988a) converted these equations into differential equations. To obtain a feasible design, the equations are integrated numerically starting with desired product compositions. If the trajectories intersect, then the resulting column is feasible. The minimum reflux can be found from the special case of two trajectories that just touch each other.
A later paper (Barbosa and Doherty, 1988b) extended the method to accommodate double-feed columns. The same approach was used; in this case feasible designs were obtained by intersecting the composition profile for a rectifying or stripping section with the composition profile for the middle section. In order to calculate the middle section composition profile, the location of one of the feeds needs to be specified.

Espinosa et al. (1995a) used the same approach for the conceptual design of reactive distillation columns separating mixtures containing inerts. The entrainer effect of the inert components was discussed, leading to the conclusion that for reactive mixtures inerts play a key role in design and synthesis. In a following paper, Espinosa et al., (1996) pointed out the necessity of using hybrid columns for separating certain mixtures (e.g. MTBE system), and the need for the non-reactive composition profile to intersect the reactive surface for a feasible hybrid column to exist. However, the algorithm provided for the calculation of the intersection of an adiabatic profile with the reactive surface is only approximate, as there is rarely an exact solution for the intersection of a composition profile calculated for a fixed reflux or reboil ratio with the reactive surface. In this work, this approach was extended by using stage composition lines (SCLs), which allows the calculation of the reflux or reboil ratio at the intersection point. An exact solution for the intersection of a composition profile with the reactive surface can be calculated, as described in Appendix C.

A more systematic approach to column design was introduced by Groemping (2000, Groemping et al. 2003). He developed a tool based on reactive stage composition lines, which is applicable to systems with two degrees of freedom (reactive systems with three transformed compositions). The method takes into account the discrete nature of stages and stacked packing. He extended the concept of stage composition lines first introduced by Castillo (1997) for conventional distillation columns, to reactive distillation. Similar to non-reactive systems, the reactive stage composition lines represent the locus of compositions leaving a certain reactive stage at any reboil and reflux ratio. In
transformed compositions space, each intersection between rectifying and stripping reactive stage composition lines indicates a feasible reactive column design.

The method was developed for non-hybrid columns, because of the difficulties associated with feasibility test at the interface between the reactive and non-reactive sections (Groemping, 2002). However, considering that transformed compositions can represent both reactive and non-reactive systems, an extension of the methodology to hybrid columns is possible (Chapter 4).

The method of Groemping (2002) showed that using stage composition lines can provide accurate initialisation of reactive distillation problems for systems with two degrees of freedom. However, reactive stage composition lines cannot address reactive distillation column featuring multicomponent systems. The intersection of stage composition lines, which would satisfy the feasibility criterion, is unlikely in multidimensional space. To accommodate multicomponent mixtures, Groemping (2002) extended the design method for non-reactive columns developed by Thong (2000). This method specifies the product purity or the recovery, which leads to an incomplete specification of product composition ahead the design. Composition manifolds for reactive and non-reactive sections can then be constructed, which represent all possible compositions leading to a product region for a certain value of the reflux ratio and a certain stage number. The manifolds are constructed at discrete values of the reflux or reboil ratio; there are gaps between one manifold and its succeeding manifold at the next. A combined manifold comprises all compositions that for a certain stage number and reflux or reboil ratio leads to the specified product region. A combined manifold is therefore analogous to segments on the stage composition line. For a saturated liquid or a saturated vapour feed, each intersection between a pair of reactive composition manifolds indicates a potentially feasible design. A preliminary cost model allows all feasible designs to be ranked.
The method of Groemping (2002) based on the intersection of composition manifolds is the first conceptual design method to address both multicomponent and hybrid columns. However, the method considers only the limiting cases of saturated liquid or saturated vapour feed. This restriction has to be relaxed in the future and complex column configurations should also be considered. In particular, a reaction distillation column with a reactive core has proved to be the best configuration for several industrial applications (MTBE synthesis, ethylene glycol production); so far only fully reactive columns were considered. The possibility of including kinetically controlled reactions also needs to be studied.

Extending the above BVM methodologies to account for kinetic effects pose inherent limitations and specific constraints. In kinetically-controlled reactions the composition profiles are not confined to the reactive surface, therefore the use of graphical methods for column design can be applied to a maximum of 3 components. However, kinetically-controlled composition profiles can be calculated and the concepts used for the design of equilibrium reactive distillation columns can be applied, to a certain extent, to kinetically-controlled reactions. Buzad and Doherty (1994, 1995) adapted their BVM for equilibrium reactions to accommodate kinetically-controlled reactions. The importance of a new design parameter – the amount of holdup – emerged in their studies, usually expressed in terms of the \( Da \) number. Critical values for the \( Da \) number were identified for specified reflux and reboil ratios, below which the proposed separation is not feasible. Also, the studies of Buzad and Doherty (1994, 1995) identified that the intersection of the rectifying and stripping profiles is a necessary but not sufficient condition for a feasible column. In order for a feasible solution to occur, the reaction extent at the intersection point (e.g. the reaction extent in the rectifying section plus the reaction extent in the stripping section) must equal the total reaction extent given by the overall mass balance. Therefore, column design for kinetically-controlled reactive systems using the method of Buzad and Doherty (1994, 1995) is highly constrained, and leads to a highly iterative process of selecting the product compositions and the
combination between the reflux (or reboil) ratio and the amount of holdup in order to obtain a feasible design. However, the BVM developed by Buzad and Doherty (1994, 1995) provides a framework for creating a more general design procedure that is capable of handling multi-component systems, non-ideal mixtures, non-ideal mass transfer and reactions with significant heat effects as well as various holdup distributions (e.g. allowing holdup to have different values for the rectifying and stripping sections).

Okasinski and Doherty (1998), included heat effects, non-ideal vapour-liquid equilibrium, non-isomolar reactions and variable holdups in reactive zones in a more systematic method for the design of kinetically controlled staged RD columns. The methodology, developed for fixed composition and feed quality is based on calculating the stripping profile bottom-up in the column and identifying a feed stage region. The feed stage region is defined as that segment of the stripping profile which will ensure that the rectifying profiles calculated upwards in the column will be attracted towards the distillate composition. Rectifying profiles are calculated then from the feed stage upwards in the column using mass balances around the bottom of the column including the feed. Using this approach ensures that the profiles intersect. However, this approach will not guarantee a feasible design, as the distillate specification needs to be met, and the overall mass and energy balances need to be satisfied. Therefore, even though the methodology overcomes some of the drawbacks of previous approaches by considering non-ideal phase equilibrium, heat effects and non-isomolar reactions, it still does not make the design of kinetically-controlled reactive distillation columns less iterative, as the choice of reflux (or reboil) ratio is arbitrary, as is the Da number. Theoretically, the method can be applied to multicomponent systems, as from the bottom product composition a continuous profile is traced in the column towards the distillate, and no intersection between composition profiles is performed. However, certain difficulties are encountered when dealing with multicomponent mixtures; the probability of the end point satisfying the distillate constraint to
satisfy the total reaction extent constraint decreases as the number of components increases.

Another extension of the methodology of Buzad and Doherty (1994) by including non-ideal mass transfer was developed by Mahajani and Kolah (1996) and Mahajani (1999). They extended the BVM to packed reactive distillation columns, in which backmixing is absent. The rate-limited mass transfer was modelled using the film theory of diffusion for mass transfer in both liquid and vapour phases. Critical $Da$ numbers were found to limit the feasibility of packed reactive distillation columns in the same manner as for staged columns. Additionally, another design parameter revealed its importance: that is the height of the transfer unit ($HTU^V$). Also, it has been established that the path followed by the composition profiles does not change as long as the product $Da \cdot HTU^V$ is constant. This product, a dimensionless number, consolidates the two parameters: $Da$, related to the extent of reaction and $HTU^V$, which influences the distillation efficiency. For a given design problem, profiles intersect if and only if the value of these numbers fall within a specific range. If the product $Da \cdot HTU^V$ is beyond the desired range, in other words if either reaction (i.e. $Da$) or distillation (i.e. $HTU^V$) dominates over the other, profiles will not intersect and the design will be infeasible.

Methodologies based on intersection of composition profiles are limited by the graphical representation to a maximum of 3 components, as in multi-component systems the intersection of the two profiles is improbable. However, an extension of this approach to quaternary mixtures was published by Mahajani (1999). The method is highly iterative, as the already constrained problem of feasibility in kinetically-controlled reactive systems is increased by the condition that the mass balance for the fourth component must be satisfied. The approach of Mahajani (1999) actually tries to find an intersection of profiles in 3-D, using 2-D transformed composition space for easy visualisation. Many trials are needed to obtain a feasible design, leading to the conclusion that if multi-component mixtures are to be considered, then some of the constraints need to
be relaxed. Chapter 6 of this work provides a new approach, more systematic and much more efficient in providing feasible designs for kinetically-controlled reactive systems.

3.4. Conclusions

Overall, many graphically based approaches are available for conceptual design of reactive distillation columns, for both equilibrium and kinetically-controlled reactive systems. Most of the methods are developed for fully reactive columns; very few attempts were made to accommodate more complex configurations. Also, most of the methods are based on the assumption of constant molar overflow, which is not realistic for many reactive systems. Exact models for the heat balances need to be included, to account for the heat of reaction and for the change in the enthalpy of the streams due to the change in composition. As reactive products are sometimes very different chemicals than the reactants, considering constant liquid and vapour enthalpies along the column is not realistic. Also, a fixed feed condition is considered in almost all approaches, which restricts the feasible space. Fixed holdup for kinetically-controlled reaction restricts the problem even further. To extend the feasible space, these assumptions need to be relaxed. Furthermore, the available conceptual design methods are more focused on the feasibility of a proposed pair of product compositions and finding one design which satisfies the specifications. There is a need for a more systematic methodology able not only to assess feasibility of a proposed reactive separation task, but also to accommodate multiple configurations and provide design alternatives. However, the BVMs developed so far offer a very good basis for a more comprehensive and systematic methodology, able to accommodate various column configurations: hybrid column, columns with a reactive core, as well as multiple feed columns. This work introduces new methodologies that able to obtain fast and efficient multiple column configurations and multiple designs, for both equilibrium and kinetically-controlled reactions.
4. CONCEPTUAL DESIGN OF SINGLE-FEED REACTIVE
DISTILLATION COLUMNS: COLUMNS FEATURING BOTH
REACTIVE AND NON-REACTIVE SECTIONS (HYBRID
COLUMNS)

4.1. Introduction

As reactive distillation becomes an increasingly promising alternative to
conventional processes, due to its well-known advantages, there has been an
increase in the interest in conceptual design of such process, able to provide an
accessible tool for design engineers. Many methods for optimisation and design
of a reactive distillation column have been developed during the past decade,
but there is still a lack of systematic conceptual design methods for complex
column configurations.

Many of the design methods available currently consider fully reactive columns.
However, in some cases a fully reactive column cannot be used to obtain the
desired product. Hybrid configurations, such as columns with a rectifying or
stripping reactive section or columns with a reactive core, will extend the
applicability of reactive distillation.

Figure 4.1 Reactive surface for an etherification reaction (A+B ⇌ C, with inert D)

Assuming reactive equilibrium, a pure component can be obtained from a
reactive section only if it is located on the reactive surface. If the component is not on the reactive surface, then a non-reactive section is necessary to be added in the column in order to obtain the desired product (Hauan et al. 2000a).

For example, in the system presented in Figure 4.1, C cannot be obtained pure from a reactive section because it will always decompose into reactants A and B. C can be obtained pure only if a non-reactive section is used in the column. Components A, B and the inert D are located on the reactive surface; therefore they can be obtained in a pure form from a reactive section.

A column featuring both reactive and non-reactive sections is usually known as a *hybrid* reactive distillation column.

The benefit of using hybrid columns, in the form of top/bottom-section reactive columns or columns with a reactive core, is dictated not only by the reactive system topology (as the case in Figure 4.1) but by economics, as well. It is known that reactive stages (or reactive packing) are much more expensive than non-reactive stages (or packing), sometimes by as much as a factor of 5. The catalyst makes an important contribution to the cost of the reactive stages. In addition, some special arrangements are needed to ensure appropriate residence time distribution in the reactive sections of the column. Overall, the number of the reactive stages used in a hybrid column will have a significant impact on the capital cost.

Several simulations performed for various systems (using Hysys v2.4) showed that in single-feed columns, especially for fast reactions reaching equilibrium in the column, the reaction extent is actually concentrated around feed stage, where the concentration of the reactants is higher. In the top and in the bottom of a reactive section, where pure products are collected, the reaction extent is insignificant, which makes the use of the reactive stages in these sections unnecessary. Significant cost reduction can be obtained by analysing the column behaviour, identifying the sections where reaction extent is low, and
replacing the reactive stages (or packing) with non-reactive internals, without affecting the overall performance of the reactive column. However, a hybrid configuration is suitable only for heterogeneous catalytic reactions, when we can distribute the catalyst to specific sections only. For homogeneous and autocatalytic reactions the hybrid configurations are not valid, as the reaction takes place everywhere in the column.

Investigating the possibility of using different column configurations for a given task is a very important part of reactive distillation column design. Even if the system allows the use of a fully reactive column, a hybrid configuration (top/bottom-section reactive or a column with a reactive core) might be much more economic. Published methods (Espinosa et al., 1996) have considered hybrid configurations in their studies, but there is still a lack of a systematic design method, which allows rapid screening of different configurations to achieve a specified performance.

In this chapter, a design methodology based on the BVM will be presented, which allows rapid screening for the best configuration and operating parameters for a reactive distillation column with a specified performance (reaction conversion and product purities). Hybrid configurations – top/bottom-section reactive and columns with a reactive core – will be considered. The methodology is applicable to columns with a single feed and two products. Multiple designs will be obtained; these will be ranked using appropriate cost models.

4.2. Previous work

Available methods for conceptual design of reactive distillation columns with equilibrium reactions are generally based on the use of intersection of composition profiles in transformed variables (Section 3.3). Composition profiles are calculated starting from fully defined top and bottom compositions, for specified reflux and reboil ratios. If an intersection in 2D transformed space
occurs between the two profiles, then a feasible design exists, characterised by the specified reflux and reboil ratios and the number of stages resulting from the intersection point (Figure 4.2). The method generally considers a fixed feed condition, so there will be only one degree of freedom remaining to search for feasible designs: either the reflux or the reboil ratio. The other parameter will be calculated based on Eq. 4.1, valid for the assumption of constant molar overflow in transformed variables (Barbosa and Doherty, 1988c)

$$\frac{s_{ext}(v_k - v_T y_{k,N-1})}{\left(1 + r_{ext}^* (v_k - v_T x_{k,B})\right)} = \frac{X_{i,B} - X_{i,F}}{X_{i,F} - Y_{i,D}} \quad i = 1, \ldots, C-1; \ i \neq k$$  \hfill (4.1)

where:
- $s_{ext}$ is the external reboil ratio
- $r_{ext}^*$ is the external transformed reflux ratio
- $v_k$ is the stoichiometric coefficient for component K
- $X_i$, $Y_i$ are the liquid and vapour transformed mole fractions of component $i$

**Reaction:** $A + B \rightleftharpoons C + D$

<table>
<thead>
<tr>
<th>Transf. mole fr.</th>
<th>$X_F$</th>
<th>$X_D$</th>
<th>$X_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-0.5</td>
<td>-1.0</td>
<td>-1E-13</td>
</tr>
<tr>
<td>B</td>
<td>-0.5</td>
<td>-0.99</td>
<td>-0.01</td>
</tr>
<tr>
<td>C</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>D</td>
<td>0</td>
<td>-0.99</td>
<td>0.99</td>
</tr>
</tbody>
</table>

**Figure 4.2 Feasible design from intersection of composition profiles in transformed variables (Barbosa and Doherty, 1988c)**
This method, widely used for the conceptual design of reactive systems (Barbosa and Doherty, 1988c,d; Espinosa et al., 1995a,b, 1996) is restricted by the fixed feed condition and result in a highly iterative procedure. It is generally focused on assessing the feasibility of the specified products and finding one design which satisfies the specifications.

From the synthesis point of view, it would be more useful to analyse and compare multiple designs to find either the best design based on total cost, or the best few design satisfying specific constraints, such as a specified number of stages (useful in retrofit studies). A simple way to achieve this is by relaxing the constraint of specified feed condition, which will allow the reflux and reboil ratios to be specified independently, and thus increasing the probability of finding a feasible design. The number of feasible designs can be further increased by specifying a range of reflux and reboil ratios for which the composition profiles to be calculated. By rearranging the information contained in the composition profiles calculated for a range of reflux or reboil ratios, Stage Composition Lines (SCLs) can be obtained. They represent all possible compositions on a specific stage for a range of reflux or reboil ratios. Looking for intersections between stripping and rectifying SCLs will result in multiple designs, each characterised by a specific reflux and reboil ratio. Feed quality can then be calculated using Eq. B.104.

First introduced by Castillo (1997) and Thong (2000) for non-reactive systems, the method based on intersection of Stage Composition Lines (SCLs) proved to be a more efficient and accurate method to assess feasibility and obtain multiple designs for simple and complex distillation columns separating azeotropic mixtures. The methodology was successfully extended by Groemping (2002) to equilibrium reactive systems with two degrees of freedom. The methodology was developed for single-feed fully reactive columns, where both rectifying and stripping SCLs are on the reactive surface, so their intersection in transformed variables will indicate a feasible design (Figure 4.3).
The method developed by Groemping (2002) cannot accommodate hybrid configurations. Some amendments are needed to apply these concepts for conceptual design of columns featuring both reactive and non-reactive section.

In this chapter, based on the methodology presented by Groemping (2002) for fully reactive columns and systems with two degrees of freedom, a systematic conceptual design method will be developed, able to address hybrid reactive distillation columns, either top or bottom-section reactive or columns with a reactive core.
4.3. Calculation of composition profiles/stage composition lines and internal reflux/reboil ratios.

Stage composition lines (SCLs) contain the same information as composition profiles. While a composition profile represent a tray-by-tray profile in a column section at a specified reflux or reboil ratio, a SCL represent the locus of compositions of a specific tray for all reflux/reboil ratios (Castillo, 1997). To obtain SCLs, composition profiles for a series of reflux/reboil ratios are calculated first.

The equations for reactive composition profiles (operating lines) in transformed variables are similar to the equations used for non-reactive systems (Barbosa and Doherty, 1988c) (Appendix B):

- the operating line for the rectifying section

\[
Y_{r,n-1} = \frac{R_n}{R_n + 1} X_{r,n} + \frac{1}{R_n + 1} X_{B,i}, \quad i = 1, \ldots, C - R - 1 \tag{4.2}
\]

- the operating line for the stripping section

\[
X_{s,m+1} = \frac{S_m}{S_m + 1} Y_{s,m} + \frac{1}{S_m + 1} X_{B,i}, \quad i = 1, \ldots, C - R - 1 \tag{4.3}
\]

- the operating line for a rectifying middle section

\[
Y_{p+1} = \frac{A_p}{A_p + 1} X_{p,j} + \frac{A_0 + 1}{A_p + 1} Y_{1,j} - \frac{A_0}{A_p + 1} X_{0,j} \quad \forall \ j = 1, \ldots, C - R - 1 \tag{4.4}
\]

- the operating line for a stripping middle section

\[
X_{p+1} = \frac{B_p}{B_p + 1} Y_{p,j} + \frac{B_0 + 1}{B_p + 1} X_{1,j} - \frac{B_0}{B_p + 1} Y_{0,j} \quad \forall \ j = 1, \ldots, C - R - 1 \tag{4.5}
\]

where \( X \) and \( Y \) denote the transformed liquid and vapour compositions, \( \bar{R} \) and \( \bar{S} \) are the transformed reflux and reboil ratios as defined by Barbosa and
Doherty (1988c), and $\overline{A}$ and $\overline{B}$ are transformed ratios as defined by Eqs 4.8 and 4.9.

$$\overline{R}_n = \frac{L_n}{D}$$  \hspace{1cm} (4.6)

$$\overline{S}_m = \frac{V_m}{B}$$  \hspace{1cm} (4.7)

$$\overline{A}_\rho = \frac{L_p}{V_1 - L_0}$$  \hspace{1cm} (4.8)

$$\overline{B}_\rho = \frac{V_\rho}{L_1 - V_0}$$  \hspace{1cm} (4.9)

Under the assumption of constant molar overflow in transformed variables, the local transformed reflux and reboil ratios are linked with the external reflux and reboil ratios through the composition of the reference component (Eqs. 4.10 and 4.11).

$$\overline{R}_n = \frac{L_n}{D} = \frac{L_0}{D} \cdot \frac{\left(1 - v_{\text{tot}} Y^{-1} x_{\text{ref},0}\right)}{\left(1 - v_{\text{tot}} Y^{-1} x_{\text{ref},D}\right)} = R_{\text{ext}} \cdot \frac{\left(1 - v_{\text{tot}} Y^{-1} x_{\text{ref},0}\right)}{\left(1 - v_{\text{tot}} Y^{-1} x_{\text{ref},D}\right)}$$  \hspace{1cm} (4.10)

$$\overline{S}_m = \frac{V_m}{B} = \frac{V_0}{B} \cdot \frac{\left(1 - v_{\text{tot}} Y^{-1} y_{\text{ref},0}\right)}{\left(1 - v_{\text{tot}} Y^{-1} y_{\text{ref},D}\right)} = S_{\text{ext}} \cdot \frac{\left(1 - v_{\text{tot}} Y^{-1} y_{\text{ref},0}\right)}{\left(1 - v_{\text{tot}} Y^{-1} y_{\text{ref},D}\right)}$$  \hspace{1cm} (4.11)

For a total condenser, $x_{\text{ref},0} = x_{\text{ref},D}$ and the transformed reflux ratio $\overline{R}_n$ is the same as the external reflux $R_{\text{ext}}$, even for reactive systems with a change in the number of moles. However, the internal reflux ratio $R_n$ and reboil ratio $S_n$ depend on the change in the number of moles; they represent the change in the internal flows due to reaction (Eqs. 4.12 and 4.13).

$$R_n = R_{\text{ext}} \cdot \frac{\left(1 - v_{\text{tot}} Y^{-1} x_{\text{ref},0}\right)}{\left(1 - v_{\text{tot}} Y^{-1} x_{\text{ref},n}\right)}$$  \hspace{1cm} (4.12)

$$S_n = S_{\text{ext}} \cdot \frac{\left(1 - v_{\text{tot}} Y^{-1} y_{\text{ref},0}\right)}{\left(1 - v_{\text{tot}} Y^{-1} y_{\text{ref},m}\right)}$$  \hspace{1cm} (4.13)

The internal transformed ratios $\overline{A}$ and $\overline{B}$ are calculated from local transformed liquid and vapour flows. Because the middle section composition profiles are
usually calculated starting from the interface between a reactive and a non-reactive section and at the interface the liquid and vapour flows are affected by the reaction, an energy balance is always used at the first reactive stage. After the first stage, a constant molar overflow in transformed variables may be used if appropriate.

Alternate application of the rectifying operating line and a dew point calculation (or reactive dew point if the rectifying section is a reactive section) will give the rectifying composition profile. Similarly, the stripping profile is obtained by alternate application of the stripping operating line and a bubble point calculation (reactive bubble point if the stripping section is a reactive section). Calculating the composition profiles for a set of reflux and reboil ratios and rearranging the information obtained will provide the SCLs.

4.4. Hybrid reactive distillation column design using intersection of SCLs in transformed variables.

Hybrid reactive distillation columns, featuring a rectifying or a stripping reactive section are usually used for systems such as that shown in Figure 4.1. A top reactive section is used when the product is a heavy component (obtained as bottom product), and a bottom reactive section is used when the product is a light component (obtained as top product). Also, hybrid columns can be applied for systems of type \( A + B \leftrightarrow C + D \) (when a fully reactive column is feasible as well) if one of the products is much lighter or heavier than the other components.

A conceptual design methodology was developed for single-feed fully reactive columns (Groemping, 2002), based on the intersection of SCLs in transformed composition space. The mass balance in transformed variables holds for both hybrid and non-hybrid columns: non-reactive stages can be considered a special case of reactive stages, with zero reaction extent. Therefore the method of Groemping (2002) can easily be extended for the design of hybrid columns.
For equilibrium reactions, the reactive SCLs are confined on the reactive surface (Groemping, 2002). The non-reactive SCLs lie in the entire composition space – they have $R$ extra dimensions compared to reactive SCLs. We can plot both reactive and non-reactive SCLs in transformed variables, and test for intersection, similarly to fully reactive columns. However, not all their intersection points will represent feasible designs. Because composition space in a non-reactive section has $R$ additional dimensions compared with the composition space of the reactive section (where $R$ represents the no. of reactions), simple intersection of SCLs will not indicate feasible designs, but only potentially feasible designs. For each intersection in transformed composition space, $R$ additional feasibility criteria have to be satisfied. Because in transformed variables the reference components are eliminated from the composition space, the additional feasibility criterion will be the mass balances for the $R$ reference components at the intersection point. This will ensure that all component balances hold for both reactive and non-reactive sections.

![Figure 4.4 Hybrid reactive distillation column. (a) Top-section reactive distillation column; (b) Bottom-section reactive distillation column](image-url)
For the design procedure, constant molar overflow can be assumed (in transformed variables for reactive sections); alternatively, if this assumption does not hold, composition profiles may be calculated incorporating energy balances (Appendix B). Also, no pressure drop is assumed in the column.

The design procedure starts with choosing a set of fully specified product compositions for the top and bottom products. For the overall mass balance, if feed flowrate and reference component composition are specified, only one degree of freedom remains to be specified, which can be chosen between D/F, B/F ratios and feed composition for any other component than the reference component. Ranges of reflux and reboil ratios have to be set in order to generate SCLs.

A search for all intersections between rectifying and stripping SCLs is then performed; the intersection points indicate potentially feasible designs. For each intersection found, the additional feasibility criterion is applied. The feed stage is taken to be the first reactive stage, i.e. the feed stage will be the first rectifying stage for top reactive columns and the first stripping stage for bottom reactive columns. The modified feasibility criteria for hybrid reactive distillation columns are:

a) Top reactive distillation column (Figure 4.4a)
   - General feasibility test: intersection of liquid profiles in transformed variables (Groemping, 2002)
     \[ X_n = X_{m-1} \]  \hspace{1cm} (4.14)
   - Additional feasibility test: mass balance for reference component for the non-reactive stripping section (envelope in Figure 4.4a)
     \[ L_{m+1} \cdot X_{m+1,ref} = V_m \cdot y_{m,ref} + B \cdot x_{B,ref} \]  \hspace{1cm} (4.15)

A graphical representation of the general feasibility test is presented in Figure 4.5. [AB] represents a segment on a liquid stage composition line \(NR\), between
two reflux ratios $R_A$ and $R_B$. Similarly, $[CD]$ represents a segment on a liquid stage composition line $NS$, between two reboil ratios $S_C$ and $S_D$.

![Diagram of top-section reactive distillation column](image)

Figure 4.5 General feasibility criterion for a top-section reactive distillation column. Intersection point indicates a potentially feasible design

A 2D line-line intersection is performed, between a reactive rectifying segment $[AB]$ and non-reactive stripping segment $[CD]$. The intersection point $I$ is characterised by $X_{int}$, $NR$, $R_{int}$, $NS$, $S_{int}$. Also, two linear parameters can be calculated using the details at the intersection: $\alpha$ for the rectifying section and $\beta$ for the stripping section (Appendix G). For the intersection to indicate a feasible design, the parameters $\alpha$ and $\beta$ should be within the interval $[0,1]$. The reflux and reboil ratios at the intersection (in transformed variables) are calculated by linear interpolation, Eqs. 4.16 and 4.17:

$$R_{int} = R_A + \alpha (R_B - R_A)$$  \hspace{1cm} (4.16)

$$S_{int} = S_C + \beta (S_D - S_C)$$  \hspace{1cm} (4.17)

The design details for the column are:

- Number of reactive rectifying stages: $NR$ (feed stage is the first rectifying stage)
- Number of non-reactive stripping stages: $NS-1$
- Reflux ratio: $R = R_{int}$ if total condenser; otherwise use Eq. 4.10
- Reboil ratio: $S$ calculated from $S_{int}$ using Eq. 4.11
b) Bottom-section reactive distillation column (Figure 4.4 b)

- General feasibility test: intersection of vapour profiles in transformed variables (Groemping, 2002)

\[ Y_{n+1} = Y_m \]  \hspace{1cm} (4.18)

- Additional feasibility test: mass balance for reference component for the non-reactive stripping section (envelope in Figure 4.4 b)

\[ V_{n+1} \cdot y_{n+1,ref} = L_{n+1} \cdot x_{n+1,ref} + B \cdot x_{D,ref} \]  \hspace{1cm} (4.19)

Similar to the top-section reactive distillation column, a 2D line-line intersection is performed between a non-reactive rectifying segment \([AB]\) on a vapour stage composition line \(NR\), and reactive stripping segment \([CD]\) on a vapour stage composition line \(NS\). The resulting line parameters \(\alpha\) (for the rectifying section) and \(\beta\) (for the stripping section), satisfying the condition \(\alpha \in [0,1]\) and \(\beta \in [0,1]\), are used to calculate reflux and reboil ratios at the intersection (Eqs. 4.16 and 4.17).

If the additional feasibility criterion is satisfied (Eq. 4.19) for the intersection point then \(X_{int}(NR, R_{int}, NS, S_{int})\) will indicate a feasible design. The design details for the column are:

- Number of non-reactive rectifying stages: \(NR - 1\)
- Number of reactive stripping stages: \(NS\) (feed stage is the first stripping stage)
- Reflux ratio: \(R = R_{int}\) if total condenser; otherwise use Eq. 4.10
- Reboil ratio: \(S\) calculated from \(S_{int}\) using Eq. 4.11

Once the column details are calculated, only one parameter remains to be calculated, that is the feed condition. An overall heat balance is used to calculate the feed condition (Eq. B.104).

All feasible design found are then ranked based on total cost. Total cost is
calculated as a sum of annualised capital cost of the column (catalyst cost is considered for reactive sections) and utility cost (Appendix F). The conceptual design methodology allows one to obtain multiple designs, and design details: number of stages, reflux/reboil ratios, column diameter, condenser/reboiler duties and column cost, with very few specifications and practically no intermediate decision steps.

4.5. Hybrid reactive distillation column design using intersection of SCLs with the reactive surface.

In Section 4.4 a design methodology for hybrid reactive distillation column was presented, based on the intersection of SCLs in transformed variables. A search for intersection for all segments of SCLs will offer information about potentially feasible designs. For each intersection found, additional feasibility criterion is applied to find feasible designs. In many cases, the restriction that the intersection to be a point on both a reactive SCL, hence on the reactive surface, and on a non-reactive SCL (represented by the additional feasibility criterion), is satisfied only by very few designs. Because all segments have to be checked for intersection, the methodology is very time consuming and inefficient. A new methodology will be presented in this chapter, based on the intersection of non-reactive SCLs with the reactive surface, which will avoid the difficulties encountered in the previous approach and will reduce the time by limiting the search only to points which are likely to lead to feasible designs.

4.5.1. Calculation of the intersection of non-reactive SCLs with the reactive surface

The principle underlying the BVM is that a continuous profile should exist between the top and the bottom product compositions for a column to be feasible (Levy, 1985; Barbosa and Doherty, 1988c). For a hybrid reactive distillation column that means that the intersection is situated on both non-reactive SCL (either stripping or rectifying SCL, depending whether the column
has a top or a bottom-section reactive) and on the reactive SCL, hence on the reactive surface. Therefore, for a hybrid column to be feasible, the non-reactive SCL have to intersect the reactive surface at least once. For ideal systems, the non-reactive SCLs are pseudo-linear curves in 3D space, so a non-reactive SCL will intersect the reactive surface at one point (as illustrated in Figure 4.6). However, not all SCLs will have an intersection point with the reactive surface, for example a minimum number of stages may be needed for the specified task. For non-ideal systems, the SCLs are curved, so more than one point of intersection is possible between a SCL and the reactive surface. Therefore, by intersecting all SCLs with the reactive surface, one or more sets of intersection points can be generated. These points are more likely to lead to feasible designs, so we can restrict the search by looking only at the intersection points of non-reactive SCLs with the reactive surface in relation to reactive SCL.

Figure 4.6 Intersection points of non-reactive SCLs with the reactive surface for a system \(A + B \rightleftharpoons C\) with inert \(D\) \((K_{eq} = 10)\)

Because all intersection points lie on the reactive surface, no additional feasibility criteria are needed. Also, we can use for visualisation the concept of transformed variables. We can plot in transformed variables the reactive SCLs
and the intersection points of the non-reactive SCLs with the reactive surface, as shown in Figure 4.7.

![Figure 4.7 The reactive rectifying operating leaf and the non-reactive stripping operating leaf in transformed variables for two product compositions. Intersection points of non-reactive stripping SCLs with the reactive surface are represented (points 1-6). System A + B ⇔ C with inert D (K_{eq} = 10)](image)

Each intersection point is characterised by a specific reflux/reboil ratio (Figure 4.8). The intersection point was calculated using a non-linear root search routine (Brent, 1971), looking for that value of reflux/reboil ratios which will give at a certain stage a composition satisfying the reactive equilibrium (Appendix D). One (or more) sets of intersection points will result, characterised by a specific number of stages \( NR_{intersect} \) with an associated reflux ratio \( R_{intersect} \), for a non-reactive rectifying section, or \( NS_{intersect} \) with an associated reboil ratio \( S_{intersect} \), for a non-reactive stripping section.

For a non-reactive stripping section (Figure 4.9a) the intersection of a non-reactive stripping SCL with the reactive surface will represent the composition of the liquid leaving the last rectifying stage \( n \), whereas for a non-reactive
rectifying section (Figure 4.9b) the intersection of non-reactive rectifying SCLs with the reactive surface will represent the composition of the liquid in reactive equilibrium with the vapour leaving the last stripping stage \( m \). The stages are numbered starting from the column ends towards the feed stage. The actual number of non-reactive stages will always be equal to the number of stages at the intersection point less one, as the composition at intersection point represents the composition leaving the reactive stage at the interface.

![Figure 4.8 Specific values for reflux ratios at intersection points. Detail from Figure 4.7.](image)

The composition and the number of stages at the intersection of non-reactive SCLs with the reactive surface are:

a) Stripping non-reactive section (Figure 4.9a)

\[
X_{\text{intersect}} = X_{m-1} \tag{4.20}
\]

\[
NS = NS_{\text{intersect}} - 1 \tag{4.21}
\]
b) Rectifying non-reactive section (Figure 4.9b)

\[ X_{intersect} = X_{n+1} \quad (4.22) \]
\[ NR = NR_{intersect} - 1 \quad (4.23) \]

![Diagram of hybrid reactive distillation columns and the intersection of non-reactive SCL with the reactive surface](image)

Figure 4.9 Hybrid reactive distillation columns and the intersection of non-reactive SCL with the reactive surface

The reactive stage at the interface may or may not be a feed stage, and depending on where the feed stage is placed in the column, various hybrid configurations can be obtained: top or bottom-section reactive with the feed within the reactive section or with the feed at the interface between the reactive and the non-reactive sections. Also, the intersection of the non-reactive SCLs with the reactive surface can be calculated for both rectifying and stripping section, resulting in reactive core configurations. The feed stage is always taken to be a reactive stage (the last reactive stage if the feed is located at the
interface), therefore the feasibility criterion will be different for different types of hybrid configurations. The next section discusses in detail the feasibility criteria for various hybrid reactive column configurations.

4.5.2. Feasibility criteria for hybrid reactive distillation columns

The previous section showed why a non-reactive SCL must intersect the reactive surface for a hybrid configuration to be possible, for a specified pair of product compositions. The intersection point will represent the composition leaving the first reactive stage (the interface stage), which may or may not be a feed stage. Depending on the feed location (at the interface between the reactive and non-reactive sections or within the reactive section) and on the general type of the reactive system, four types of hybrid configurations can be analysed (Figure 4.10):

- Type I – top/bottom-section reactive column with the feed at the interface between the reactive and non-reactive sections
- Type II – top/bottom-section reactive column within the reactive section
- Type III – reactive core configuration with the feed at the interface of the reactive core (top/bottom)
- Type IV – reactive core configuration with the feed within the reactive core

Hybrid configurations of Type I typically apply to systems where a non-reactive section is necessary to obtain the desired product (e.g. etherification reactions), while hybrid configurations of Type II apply to systems where the desired products can be obtained from a fully reactive column as well, but a non-reactive section might be more economical (e.g. esterification or decomposition reactions).
Figure 4.10 Possible hybrid column configurations. T – Top-section reactive; B – Bottom-section reactive

The reactive core configurations, Types III and IV, can be applied to all systems with two degrees of freedom described previously: etherification, esterification or decomposition reactions. They are generally used to minimise the total cost of the column, by replacing the stages where the reaction extent is very small with non-reactive stages.

Table 4.1 summarises the function of the sections for hybrid reactive column configurations. A hybrid column Type I has two sections, a reactive section and a non-reactive section, which can be either reactive or stripping, depending on the column type. A hybrid column Type II features three sections: a reactive section (rectifying for top-section reactive and stripping for bottom-section reactive), a middle reactive section and a non-reactive section (stripping or
rectifying). A column with a reactive core features three sections as well, a rectifying non-reactive section, a stripping non-reactive section and a middle reactive section.

For a feasible design to be possible the rectifying (or middle rectifying) composition profile should intersect the stripping (or middle stripping) composition profile in transformed variables. For the hybrid columns in Figure 4.10, the feed stage is always located on a reactive stage. Therefore, depending on the column configuration, the feed stage could be either in the rectifying or in the stripping section, the general feasibility criterion changing accordingly.

Table 4.1 Section functions for various hybrid reactive column configurations.

<table>
<thead>
<tr>
<th>Section</th>
<th>Type I (T)</th>
<th>Type I (B)</th>
<th>Type II (T)</th>
<th>Type II (B)</th>
<th>Type III (T)</th>
<th>Type III (B)</th>
<th>Type IV (T)</th>
<th>Type IV (B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rectifying</td>
<td>R</td>
<td>Non-R</td>
<td>R</td>
<td>Non-R</td>
<td>Non-R</td>
<td>Non-R</td>
<td>Non-R</td>
<td>Non-R</td>
</tr>
<tr>
<td>Middle Rectifying</td>
<td>-</td>
<td>-</td>
<td>R</td>
<td>-</td>
<td>R</td>
<td>-</td>
<td>R</td>
<td></td>
</tr>
<tr>
<td>Middle Stripping</td>
<td>-</td>
<td>-</td>
<td>R</td>
<td>-</td>
<td>-</td>
<td>R</td>
<td>R</td>
<td></td>
</tr>
<tr>
<td>Stripping</td>
<td>Non-R</td>
<td>R</td>
<td>Non-R</td>
<td>R</td>
<td>Non-R</td>
<td>Non-R</td>
<td>Non-R</td>
<td>Non-R</td>
</tr>
</tbody>
</table>

R: Reactive; Non-R: non-reactive

Taking into account the type of the hybrid reactive distillation column (top-section reactive, bottom-section reactive or reactive core) and depending on the position of the feed (at the bottom, at the top, or within the reactive section) - three feasibility criteria can be formulated.

A. **Feed at the bottom of the reactive section**

In this case the feed stage is considered to be the last rectifying stage (stages numbered from the top) as in Figure 4.11. This arrangement is characteristic of configurations Types I(T) and III(T).
The feasibility criterion in this case is that the composition of the liquid leaving the reactive feed stage $n$ must be the same as the composition of the liquid entering the non-reactive stripping stage $m$, or equivalently, the composition of the intersection point of non-reactive SCL $m+1$ with the reactive surface. In Figure 4.11 this point is denoted by a star, and is referred to as $x_{intersect}$. Using the intersection of non-reactive SCLs with the reactive surface in the feasibility criterion formulation allows the use of transformed variables for visualisation and column design, as all liquid composition points of interest will be located on the reactive surface. Thus, the feasibility criterion for a hybrid column with a rectifying (or middle rectifying) reactive section in transformed variables will be:

$$x_n = x_{intersect} \quad (4.24)$$

**B. Feed at the top of the reactive section**

In this case the feed stage is considered to be the last stripping stage (stages numbered from the bottom) as in Figure 4.12. This arrangement is characteristic of configurations Types I(B) and III(B).
Figure 4.12 Feed stage arrangement for a column with a stripping (or middle stripping) reactive section

By analogy with the case where feed is situated at the bottom of the reactive section (Case A), the feasibility criterion in this case should be an intersection of the vapour profiles. That is, the composition of the vapour leaving the reactive feed stage \( m \) should be the same as the composition of the vapour entering the non-reactive rectifying stage \( n \). However, we can reformulate this in terms of liquid composition, knowing the intersection point of non-reactive SCL \( n+1 \) with the reactive surface – the point denoted by the star in Figure 4.12 and referred to as \( x_{\text{intersect}} \). As described in previous section, in this case \( x_{\text{intersect}} \) represents the liquid composition in reactive and phase equilibrium with the vapour leaving feed stage. If this composition coincides with the composition of the liquid leaving stage \( m \), then the feasibility criterion for this type of feed arrangement is satisfied (Eq. 4.25). Also, because all composition points of interest are located on the reactive surface, the feasibility criterion can be expressed in transformed variables (Eq. 4.25):

\[
X_m = X_{\text{intersect}} \tag{4.25}
\]

C. Feed stage within the reactive section

This arrangement is characteristic of configuration Types II and IV. Both rectifying (or middle rectifying) and stripping (or middle stripping) sections are reactive sections, and considering the feed stage the last stripping stage
(stages numbered starting from the ends of the column towards the feed stage), the general feasibility criterion is similar to the general feasibility criterion for non-reactive sections: the liquid composition leaving feed stage \( m \) should coincide with the composition leaving stage \( n+1 \).

For reactive sections, the same feasibility criterion applies, and we can use transformed variables, as all liquid compositions are located on the reactive surface. Thus, the feasibility criterion for a column with the feed in the middle of the reactive section can be written as:

\[
X_m = X_{n+1} \quad (4.26)
\]

For all the configurations above, no additional feasibility criteria are necessary, as all compositions are located on the reactive surface: intersection points of non-reactive SCLs with the reactive surface and reactive rectifying, stripping or middle section profiles.

The feasibility criteria presented in this section will be used for hybrid column design in following sections and for easy reference are summarised in Table 4.2.
Table 4.2. Feasibility criteria for hybrid column configurations

<table>
<thead>
<tr>
<th>Hybrid configuration</th>
<th>Feasibility criterion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type I</td>
<td>( X_n = X_{\text{intersect}} )</td>
</tr>
<tr>
<td></td>
<td>( X_m = X_{\text{intersect}} )</td>
</tr>
<tr>
<td>Type II</td>
<td>( X_m = X_{n-1} )</td>
</tr>
<tr>
<td></td>
<td>( X_m = X_{n-1} )</td>
</tr>
<tr>
<td>Type III</td>
<td>( X_n = X_{\text{intersect}} )</td>
</tr>
<tr>
<td></td>
<td>( X_m = X_{\text{intersect}} )</td>
</tr>
<tr>
<td>Type IV</td>
<td>( X_m = X_{n-1} )</td>
</tr>
</tbody>
</table>

4.5.3. Design methodology for hybrid reactive distillation columns

In the previous section feasibility criteria were described for each type of hybrid reactive column configuration. As it can be observed in Table 4.2, they are all based on liquid compositions represented in transformed variables. Depending on the type of column configuration, the liquid composition can be a point on a reactive SCL, an intersection point of a non-reactive SCL with the reactive surface or a point on a middle composition profile.

Reactive SCLs for the rectifying and stripping sections are calculated using Eqs. 4.2 and 4.3, for a range of reflux and reboil ratios. Section 4.5.1 describes how to calculate intersection of non-reactive SCLs with the reactive surface. Middle section profiles will be calculated starting from each intersection point using the specific reflux or reboil ratios (Eqs. 4.4. or 4.5).

Figure 4.14 shows middle section profiles calculated from the intersection points for a system A + B ⇔ C (inert D). Each intersection of a non-reactive SCL with the reactive surface is characterised by a specific reflux/reboil ratio, e.g. for stripping stage no. 9, the corresponding reboil ratio is 16.4 (Figure 4.14). The reflux/reboil ratio and the composition at the intersection with the reactive
surface are used to initiate the calculation of middle section composition profiles (Eqs. 4.4 and 4.5). At the interface between a non-reactive and a reactive section internal vapour and liquid flows change significantly due to reaction; therefore a heat balance is used on the first reactive stage to obtain internal flows. After the first stage (the interface stage) constant molar overflow, in transformed variables, may be a reasonable assumption for the middle reactive section.

![Figure 4.14 Middle composition profiles starting from intersection points of non-reactive SCLs with the reactive surface. A + B ⇔ C (with inert D); Keq = 50](image)

To obtain feasible designs, a search for intersections between different combinations of segments on reactive SCLs, middle composition profiles, or segments between two adjacent points of intersection of non-reactive SCLs with the reactive surface is performed, depending on the hybrid configuration type. Table 4.3 lists the types of intersections checked to obtain feasible designs for various hybrid configurations.
Table 4.3 Types of intersections checked in the search for feasible hybrid columns designs.

<table>
<thead>
<tr>
<th>Section</th>
<th>Type I</th>
<th>Type II</th>
<th>Type III</th>
<th>Type IV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(T)</td>
<td>(B)</td>
<td>(T)</td>
<td>(B)</td>
</tr>
<tr>
<td>Rectifying SCLs</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stripping SCLs</td>
<td></td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Rectifying SCL-RS points*</td>
<td>X</td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Stripping SCL-RS points*</td>
<td>X</td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Middle rectifying CPs**</td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Middle stripping CPs**</td>
<td>X</td>
<td></td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>

* Intersection points of non-reactive SCLs with the reactive surface
**CP – composition profiles

The main drawback of this approach is that the intersection of non-reactive SCLs with the reactive surface, as well as the composition profiles for the middle sections, are sets of discrete points. That means that the segment between two adjacent points of intersection of non-reactive SCLs with the reactive surface, or between two stages on a composition profile, has no physical meaning, as fractional stages cannot exist. However, because reactive systems are usually highly constrained, an approximation given by the interpolation between the two points, even if fractional stages will result, will still provide a good initialisation for simulation or detailed design.

A general representation of the feasibility criterion for a single-feed hybrid configuration is presented in Figure 4.15. To obtain feasible designs, a 2-D line-line intersection is performed between rectifying segments $[AB]$ and stripping segments $[CD]$. The rectifying segment $[AB]$ can be:

- a segment between two adjacent reflux ratios from a rectifying SCL;
- a segment between two consecutive stages from a middle rectifying composition profile;
- a segment between two adjacent points of intersection of non-reactive rectifying SCLs with the reactive surface.

Similarly, the stripping segment $[CD]$ can be:
- a segment between two adjacent reboil ratios on a stripping SCL;
- a segment between two consecutive stages on a middle stripping composition profile;
- a segment between two adjacent points of intersection of non-reactive stripping SCLs with the reactive surface.

Figure 4.15 Graphical visualisation of the feasibility test for single-feed hybrid reactive distillation columns.

For example, for a hybrid column Type I (T), $[AB]$ will represent a segment of a reactive SCL containing all possible compositions of stage $NR$ for reflux ratios between $RA$ and $RB$. Segment $[CD]$ will represent two adjacent points resulted from the intersection of non-reactive SCLs with the reactive surface, corresponding to stage $NSC$ (with intersection reboil ratio $Sc$) and stage $NSD$ (with intersection reboil ratio $SD$). A 2D line-line intersection is performed between the two segments $[AB]$ and $[CD]$, the resulting intersection point $I$ being characterized by $X_{int}, NR, NS_{int}, R_{int}, S_{int}$. $X_{int}$ represents the transformed liquid composition at the intersection and $NR$ represents the number of rectifying stages. $R_{int}$ (the reflux ratio at the intersection), $NS_{int}$ (the number of stripping stages) and $S_{int}$ (the reboil ratio at the intersection) are calculated by linear interpolation, using the two linear parameters $\alpha$ and $\beta$ resulting from the line-line intersection (Appendix G). For a feasible design, the two parameters $\alpha$ and $\beta$ should have values within the interval $[0,1]$, meaning that the two segments intersect.
Similarly, for other configurations, 2-D line-line intersections between segments on SCLs, middle CPs or between two adjacent non-reactive interface points are checked (as presented in Table 4.3). The design details at intersection point are estimated using linear interpolation (Eqs. 4.27 to 4.34):

1) Segments from SCLs

\[ R_{int} = R_A + \alpha (R_B - R_A) \]  \hspace{1cm} (4.27) \\
\[ S_{int} = S_C + \beta (S_D - S_C) \]  \hspace{1cm} (4.28) 

2) Segments from middle CPs

\[ NMR_{int} = NMR_A + \alpha (NMR_B - NMR_A) \]  \hspace{1cm} (4.29) \\
\[ NMS_{int} = NMS_C + \beta (NMS_D - NMS_C) \]  \hspace{1cm} (4.30) 

3) Segments between two adjacent points of intersection of non-reactive SCLs with the reactive surface

\[ R_{int} = R_A + \alpha (R_B - R_A) \]  \hspace{1cm} (4.31) \\
\[ NR_{int} = NR_A + \alpha (NR_B - NR_A) \]  \hspace{1cm} (4.32) \\
\[ S_{int} = S_C + \beta (S_D - S_C) \]  \hspace{1cm} (4.33) \\
\[ NS_{int} = NS_C + \beta (NS_D - NS_C) \]  \hspace{1cm} (4.34) 

where:

- \( R \) – Reflux ratio;
- \( S \) – Reboil ratio;
- \( NR \) – Number of stages in the rectifying section;
- \( NMR \) – Number of stages in the middle rectifying section;
- \( NMS \) – Number of stages in the middle stripping section;
- \( NS \) – Number of stages in the stripping section.

Using the information available from the intersection, the design details for various single-feed column configurations can then be estimated (Table 4.4).
Table 4.4 Design details for single-feed configurations shown in Figure 4.10.

### Rectifying section

<table>
<thead>
<tr>
<th>Configuration type</th>
<th>( R )</th>
<th>( NR )</th>
<th>( NMR )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type I (T)</td>
<td>( R_{int} )</td>
<td>( NR )</td>
<td>-</td>
</tr>
<tr>
<td>(B)</td>
<td>( R_{int} )</td>
<td>( NR_{int,non-R} - 1 )</td>
<td>-</td>
</tr>
<tr>
<td>Type II (T)</td>
<td>( R_{int} )</td>
<td>( NR - 1 )</td>
<td>-</td>
</tr>
<tr>
<td>(B)</td>
<td>( R_{intersect}(NR_{non-R}) )</td>
<td>( NR_{non-R} )</td>
<td>( NMR_{int} - 1^{(*)} )</td>
</tr>
<tr>
<td>Type III (T)</td>
<td>( R_{intersect}(NR_{non-R}) )</td>
<td>( NR_{non-R} )</td>
<td>( NMR_{int}^{(*)} )</td>
</tr>
<tr>
<td>(B)</td>
<td>( R_{int} )</td>
<td>( NR_{int,non-R} - 1 )</td>
<td>-</td>
</tr>
<tr>
<td>Type IV</td>
<td>( R_{intersect}(NR_{non-R}) )</td>
<td>( NR_{non-R} )</td>
<td>( NMR_{int} - 1^{(*)} )</td>
</tr>
</tbody>
</table>

### Stripping section

<table>
<thead>
<tr>
<th>Configuration type</th>
<th>( S )</th>
<th>( NS )</th>
<th>( NMS )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type I (T)</td>
<td>( S_{intersect}(NS_{non-R}) )</td>
<td>( NS_{non-R} - 1 )</td>
<td>-</td>
</tr>
<tr>
<td>(B)</td>
<td>( S_{int} )</td>
<td>( NS )</td>
<td>-</td>
</tr>
<tr>
<td>Type II (T)</td>
<td>( S_{intersect}(NS_{non-R}) )</td>
<td>( NS_{non-R} )</td>
<td>( NMS_{int}^{(*)} )</td>
</tr>
<tr>
<td>(B)</td>
<td>( S_{int} )</td>
<td>( NS )</td>
<td>-</td>
</tr>
<tr>
<td>Type III (T)</td>
<td>( S_{int} )</td>
<td>( NS_{int,non-R} - 1 )</td>
<td>-</td>
</tr>
<tr>
<td>(B)</td>
<td>( S_{intersect}(NS_{non-R}) )</td>
<td>( NS_{non-R} )</td>
<td>( NMS_{int}^{(*)} )</td>
</tr>
<tr>
<td>Type IV</td>
<td>( S_{intersect}(NS_{non-R}) )</td>
<td>( NS_{non-R} )</td>
<td>( NMS_{int}^{(*)} )</td>
</tr>
</tbody>
</table>

\(^{(*)}\) Middle composition profiles calculated from intersections of non-reactive SCLs with the reactive surface

\( NR_{non-R} \) or \( NS_{non-R} \) = No. of stages in the non-reactive rectifying or stripping section

\( R_{intersect}(NR_{non-R}) \) = Specific reflux ratio at intersection of non-reactive stage \( NR_{non-R} \) with the reactive surface

\( S_{intersect}(NS_{non-R}) \) = Specific reboil ratio at intersection of non-reactive stage \( NS_{non-R} \) with the reactive surface

\( NR_{int,non-R} \) = No. of stages in the non-reactive rectifying section, calculated by interpolation using Eq. 4.32

\( NS_{int,non-R} \) = No. of stages in the non-reactive stripping section, calculated by interpolation using Eq. 4.34

For each feasible design found, the remaining parameters can then be calculated: feed condition, column condenser and reboiler duties, column diameter and column capital and operating costs. Feed condition is calculated using an overall energy balance (Appendix B). The condenser and reboiler duties are direct functions of reflux and reboil ratios (Appendix D), and they can
be easily calculated from an energy balance around the condenser/reboiler. Based on the information obtained, the utility cost can be calculated, as can be the capital cost for the heat exchangers. The capital cost of the column will take into account different prices for the reactive and non-reactive stages. Thus, we can rank the feasible designs to obtain the best few designs with respect to any of the parameters above: number of stages, energy requirement or total cost.

The general procedure for the design methodology is as follows:

1. Set two fully specified product compositions for the top and bottom products. Also, set reflux and reboil ratios ranges (to calculate SCLs), feed flowrate and the feed reference component mole fraction $x_{i, \text{ref}}$. For the overall mass balance, in order to satisfy the number of degrees of freedom, only one more parameter is needed, chosen from $D/F$, $B/F$ and $x_{f,i} \neq \text{ref}$.

2. Calculate the remaining variables (remaining feed compositions, D and B flowrates and the reaction extent in the column) from the overall mass balance.

3. Calculate reactive and non-reactive SCLs for both rectifying and stripping sections using the specified ranges for the reflux and reboil ratios.

4. Calculate intersections of non-reactive SCLs with the reactive surface for both rectifying and stripping section.

5. If any intersection points are found at step 4, calculate for each of them middle-section composition profiles, using a heat balance to obtain internal liquid and vapour flows.

6. Search for feasible designs for all types of configurations: fully reactive columns (Groemping, 2002) and all types of hybrid configurations.

7. Rank the feasible designs obtained, based on total cost (or any other parameter e.g. number of stages, energy requirement).

8. Narrow the results to meet the constraints if necessary, e.g. feed condition, maximum number of stages, maximum total cost.
The design procedure can be easily automated, and offers a tool to rapidly generate various configurations (useful in the synthesis step) and to obtain feasible designs for reactive distillation columns. To generate multiple feasible designs it will take less than 1 min for an ideal system and less than 5 min for a highly non-ideal system, using a PIII 1.5 GHz personal computer.

The method using intersections of SCLs with the reactive surface offers certain advantages over the method using intersection of SCLs in transformed variables (Section 4.4). First, it is much faster, as the search is restricted only to the points which are more likely to lead to feasible designs. Secondly, it offers a basis for extending the design and synthesis methodology to more complex configurations, such as reactive core and various feed arrangements: at the interface between the reactive and non-reactive sections or within the reactive section. The extension of the methodology for double-feed columns is presented in the next chapter.

### 4.6. Case studies

#### 4.6.1. Ideal system

The design procedure will be illustrated for an etherification type reaction between species A and B, to obtain product C, in the presence of an inert D (Eq. 4.35).

\[
A + B \rightleftharpoons C \quad \text{(inert D)}
\]  

(Eq. 4.35)

The system is assumed to have an ideal thermodynamic behaviour, which is shown in the residue curve map presented in Figure 4.16. The reaction equilibrium constant is \( K_{eq} = 20 \). The parameters used to model this system are presented in Appendix E.1.
To obtain pure C, a non-reactive section is needed to be added to the column, because component C is not on the reactive surface. C is a heavy component which will be obtained as a bottom product of the column, so the final configuration will feature a stripping non-reactive section and a rectifying reactive section (or a middle reactive section) (configurations of Type I(a), II(a), III and IV).

For the design procedure, fully specified product compositions are necessary, along with feed specifications: feed flowrate and feed composition for the reference component (in this case component C). To satisfy the degrees of freedom for the overall mass balances, one other parameter needs to be specified, between D/F, B/F or feed composition for a component other than the reference component. In this case the composition of component D in the feed is specified to be 0.35. The remaining variables are calculated from the overall mass balances (Eqs. B.1 and B.2). For the specified product compositions, the reaction conversion will be 99.7%. To generate the stage composition lines, the ranges for reflux and reboil ratios were specified, as well as the maximum number of stages in each section (Table 4.6).
Table 4.5 Feed and product compositions for system $A + B \rightleftharpoons C$ (inert $D$)

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Stoichiometry</th>
<th>Boiling temp. (5 bar)</th>
<th>Distillate</th>
<th>Bottom</th>
<th>Feed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>[-] [°C] transfr. mole fr.</td>
<td>$x_D$</td>
<td>$x_D$</td>
<td>$x_B$</td>
</tr>
<tr>
<td>A</td>
<td>-1</td>
<td>1.7</td>
<td>0.003</td>
<td>0.003#</td>
<td>0.4992</td>
</tr>
<tr>
<td>B</td>
<td>-1</td>
<td>50.3</td>
<td>0.047</td>
<td>0.047#</td>
<td>0.5003</td>
</tr>
<tr>
<td>C</td>
<td>1</td>
<td>156.9</td>
<td>0</td>
<td>1.E-6#</td>
<td>0</td>
</tr>
<tr>
<td>D</td>
<td>0</td>
<td>37.9</td>
<td>0.95</td>
<td>0.95#</td>
<td>0.0005</td>
</tr>
</tbody>
</table>

# Specified values

Table 4.6 Specifications for generating stage composition lines

<table>
<thead>
<tr>
<th>Distillate flowrate</th>
<th>Bottoms flowrate</th>
<th>Feed flowrate</th>
<th>Feed quality</th>
<th>Reflux ratio range</th>
<th>Reboil ratio range</th>
<th>Rectifying stages range</th>
<th>Stripping stages range</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>B</td>
<td>F</td>
<td>$q$</td>
<td>$r$</td>
<td>$s$</td>
<td>$n$</td>
<td>$M$</td>
</tr>
<tr>
<td>[kmol/h]</td>
<td>[kmol/h]</td>
<td>[kmol/h]</td>
<td>[-]</td>
<td>[-]</td>
<td>[-]</td>
<td>[-]</td>
<td>[-]</td>
</tr>
<tr>
<td>36.79</td>
<td>31.64</td>
<td>100</td>
<td>App. B.23</td>
<td>0.2 – 20</td>
<td>0.2 – 20</td>
<td>1 – 30</td>
<td>1 – 30</td>
</tr>
</tbody>
</table>

Figure 4.17 Influence of constant molar overflow on composition profiles. (a) Reactive rectifying section; (b) Non-reactive stripping section
The constant molar overflow assumption is valid for this system for both reactive and non-reactive sections, as can be seen in Figure 4.17. However, because at the interface between the reactive and non-reactive sections there are always changes in the internals flows, energy balances were used at the interface stage, to calculate the initial points for middle section profiles. The rectifying SCLs and the middle composition profiles calculated from the intersection points of non-reactive stripping SCLs with the reactive surface are shown in Figure 4.18.

![Figure 4.18 Rectifying reactive SCLs and middle composition profiles for the ideal system](image)

Multiple designs of various configurations are obtained from the design procedure; Table 4.7 shows the best 10 designs ranked based on total annualised cost (TAC). As expected, reactive core configurations are preferred, due to their low capital cost.
Table 4.7 First 10 feasible designs with respect to total annualised cost, obtained for the ideal system

<table>
<thead>
<tr>
<th>No</th>
<th>Type</th>
<th>NR</th>
<th>NMR</th>
<th>NMS</th>
<th>NS</th>
<th>N_{TOT}</th>
<th>R</th>
<th>S</th>
<th>q</th>
<th>Cond. Duty [kW]</th>
<th>Reb. Duty [kW]</th>
<th>Total Cost [MS/yr]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>III(T)</td>
<td>2</td>
<td>11.7</td>
<td>-</td>
<td>6.2</td>
<td>19.9</td>
<td>3.71</td>
<td>13.33</td>
<td>3.76</td>
<td>883</td>
<td>3283</td>
<td>0.981</td>
</tr>
<tr>
<td>2</td>
<td>IV</td>
<td>2</td>
<td>10.4</td>
<td>1.3</td>
<td>6</td>
<td>19.7</td>
<td>3.71</td>
<td>15.10</td>
<td>4.58</td>
<td>883</td>
<td>3718</td>
<td>1.026</td>
</tr>
<tr>
<td>3</td>
<td>I(T)</td>
<td>11</td>
<td>-</td>
<td>-</td>
<td>6.0</td>
<td>17.0</td>
<td>5.89</td>
<td>14.97</td>
<td>3.75</td>
<td>1291</td>
<td>3686</td>
<td>1.070</td>
</tr>
<tr>
<td>4</td>
<td>II(T)</td>
<td>10</td>
<td>-</td>
<td>1.0</td>
<td>6</td>
<td>17.0</td>
<td>5.85</td>
<td>15.10</td>
<td>3.83</td>
<td>1284</td>
<td>3718</td>
<td>1.072</td>
</tr>
<tr>
<td>5</td>
<td>I(T)</td>
<td>16</td>
<td>-</td>
<td>-</td>
<td>6.6</td>
<td>22.6</td>
<td>3.09</td>
<td>10.63</td>
<td>2.73</td>
<td>767</td>
<td>2618</td>
<td>1.207</td>
</tr>
<tr>
<td>6</td>
<td>I(T)</td>
<td>15</td>
<td>-</td>
<td>-</td>
<td>6.6</td>
<td>21.6</td>
<td>3.31</td>
<td>10.48</td>
<td>2.59</td>
<td>808</td>
<td>2581</td>
<td>1.208</td>
</tr>
<tr>
<td>7</td>
<td>I(T)</td>
<td>17</td>
<td>-</td>
<td>-</td>
<td>6.5</td>
<td>23.5</td>
<td>2.84</td>
<td>11.06</td>
<td>3.02</td>
<td>720</td>
<td>2724</td>
<td>1.216</td>
</tr>
<tr>
<td>8</td>
<td>I(T)</td>
<td>14</td>
<td>-</td>
<td>-</td>
<td>6.6</td>
<td>20.6</td>
<td>3.57</td>
<td>10.83</td>
<td>2.66</td>
<td>856</td>
<td>2666</td>
<td>1.235</td>
</tr>
<tr>
<td>9</td>
<td>I(T)</td>
<td>13</td>
<td>-</td>
<td>-</td>
<td>6.4</td>
<td>19.4</td>
<td>3.95</td>
<td>11.87</td>
<td>3.00</td>
<td>928</td>
<td>2922</td>
<td>1.300</td>
</tr>
<tr>
<td>10</td>
<td>I(T)</td>
<td>27</td>
<td>-</td>
<td>-</td>
<td>7.2</td>
<td>34.2</td>
<td>2.06</td>
<td>6.74</td>
<td>1.30</td>
<td>573</td>
<td>1659</td>
<td>1.354</td>
</tr>
</tbody>
</table>

For this case-study, the parameter specified to satisfy the number of degrees of freedom for the overall mass balances (Eqs. B.1 and B.2) was the composition of inert component D in the feed. For single-feed columns and for fully specified product composition, the composition of the inert in the feed stream affects the distillate and bottom product flowrates, the ratio of reactants A:B in the feed and, consequently, the reaction conversion (as shown in Table 4.8). However, even for a significant change in the inert feed composition, from 0.35 to 0.5, the reaction extent is still in reasonable limits, above 99%.

Table 4.8 Influence of inert on product flowrates, feed composition and conversion.

<table>
<thead>
<tr>
<th>x_{F,D}</th>
<th>F</th>
<th>D</th>
<th>B</th>
<th>x_{F,A}</th>
<th>x_{F,B}</th>
<th>Feed molar ratio A:B</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>[-]</td>
<td>[kmol/h]</td>
<td>[kmol/h]</td>
<td>[kmol/h]</td>
<td>[-]</td>
<td>[-]</td>
<td>[-]</td>
<td>[-]</td>
</tr>
<tr>
<td>0.35</td>
<td>100</td>
<td>36.79</td>
<td>31.64</td>
<td>0.3166</td>
<td>0.3334</td>
<td>0.9495</td>
<td>0.996</td>
</tr>
<tr>
<td>0.375</td>
<td>100</td>
<td>39.46</td>
<td>30.31</td>
<td>0.3035</td>
<td>0.3215</td>
<td>0.9441</td>
<td>0.996</td>
</tr>
<tr>
<td>0.4</td>
<td>100</td>
<td>42.08</td>
<td>29.02</td>
<td>0.2905</td>
<td>0.3095</td>
<td>0.9383</td>
<td>0.996</td>
</tr>
<tr>
<td>0.425</td>
<td>100</td>
<td>44.71</td>
<td>27.68</td>
<td>0.2774</td>
<td>0.2976</td>
<td>0.9320</td>
<td>0.995</td>
</tr>
<tr>
<td>0.45</td>
<td>100</td>
<td>47.34</td>
<td>26.35</td>
<td>0.2643</td>
<td>0.2857</td>
<td>0.9252</td>
<td>0.994</td>
</tr>
<tr>
<td>0.475</td>
<td>100</td>
<td>49.97</td>
<td>25.06</td>
<td>0.2513</td>
<td>0.2737</td>
<td>0.9178</td>
<td>0.994</td>
</tr>
<tr>
<td>0.5</td>
<td>100</td>
<td>52.60</td>
<td>23.72</td>
<td>0.2382</td>
<td>0.2618</td>
<td>0.9098</td>
<td>0.993</td>
</tr>
</tbody>
</table>

The constant molar overflow proved to be a valid assumption for this system, therefore the composition profiles were calculated using the operating lines
defined by Eqs. 4.3. and 4.4, functions of product compositions and reflux or reboil ratios only. As during this analysis the distillate and bottom product compositions and the reflux and reboil ratio ranges were fixed, the composition profiles for the rectifying and the stripping section do not change.

The middle section profiles were calculated using Eqs. 4.5 and 4.6 (under the assumption of constant molar overflow). A heat balance at the interface stage was used to obtain initial points for the calculation of the middle section profiles. The internal flowrates used in the energy balance are calculated based on the distillate and bottom flowrates and on the reflux and reboil ratios (Appendix B). However, for ideal systems, the energy balance has very little influence on the middle composition profiles. Overall, the design details obtained from the design procedure do not change much. Table 4.9 lists the design details and the operating parameters obtained for Design 10 in Table 4.7 (a top section reactive column Type I(T)). The concentration of the inert in the feed has practically no influence on the design details (number of rectifying and stripping stages) and operating parameters (reflux and reboil ratio). The only significant change is observed in the feed condition, caused mainly by the change in the condenser and reboiler duties (as the feed condition is calculated using an overall heat balance, Appendix B).

<table>
<thead>
<tr>
<th>Case</th>
<th>(X_{F,D})</th>
<th>(NR)</th>
<th>(NS)</th>
<th>(N_{TOT})</th>
<th>Reflux ratio</th>
<th>Reboil ratio</th>
<th>(q_{FU})</th>
<th>Cond. Duty</th>
<th>Reb. Duty</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>0.35</td>
<td>27</td>
<td>7.2</td>
<td>34.2</td>
<td>2.06</td>
<td>6.74</td>
<td>1.30</td>
<td>573</td>
<td>1659</td>
</tr>
<tr>
<td>1</td>
<td>0.375</td>
<td>27</td>
<td>7.2</td>
<td>34.2</td>
<td>2.06</td>
<td>6.74</td>
<td>1.16</td>
<td>614</td>
<td>1590</td>
</tr>
<tr>
<td>2</td>
<td>0.4</td>
<td>27</td>
<td>7.2</td>
<td>34.2</td>
<td>2.06</td>
<td>6.74</td>
<td>0.93</td>
<td>654</td>
<td>1521</td>
</tr>
<tr>
<td>3</td>
<td>0.425</td>
<td>27</td>
<td>7.2</td>
<td>34.2</td>
<td>2.06</td>
<td>6.74</td>
<td>0.89</td>
<td>695</td>
<td>1452</td>
</tr>
<tr>
<td>4</td>
<td>0.45</td>
<td>27</td>
<td>7.2</td>
<td>34.2</td>
<td>2.06</td>
<td>6.74</td>
<td>0.76</td>
<td>736</td>
<td>1382</td>
</tr>
<tr>
<td>5</td>
<td>0.475</td>
<td>27</td>
<td>7.2</td>
<td>34.2</td>
<td>2.06</td>
<td>6.74</td>
<td>0.62</td>
<td>777</td>
<td>1313</td>
</tr>
<tr>
<td>6</td>
<td>0.5</td>
<td>26</td>
<td>7.2</td>
<td>33.2</td>
<td>2.06</td>
<td>6.76</td>
<td>0.49</td>
<td>819</td>
<td>1248</td>
</tr>
</tbody>
</table>

Therefore, we can obtain the proposed set of product compositions using a feed containing 40% (molar) inert D, in a column with 27 reactive rectifying stages.
(including the condenser) and 8 non-reactive stripping stages (including the reboiler). The operating parameters for this column are: a reflux ratio of 2.06, a reboil ratio of 6.74 and a feed temperature of 25 °C (saturated liquid). These design details and operating parameters were used as specifications in a rigorous simulation using HYSYS 2.4. The product compositions predicted by simulation are compared to those specified in the conceptual design method in Table 4.10. The simulation results show very good agreement with the conceptual design method.

Table 4.10 Product compositions obtained by simulation, based on the results from the conceptual design procedure, for the design in Case 2 (Table 4.9)

<table>
<thead>
<tr>
<th>Component</th>
<th>Simulation results</th>
<th>Conceptual design specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$x_F$</td>
<td>$x_D$</td>
</tr>
<tr>
<td>i-Butene</td>
<td>0.2905</td>
<td>0.0011</td>
</tr>
<tr>
<td>MeOH</td>
<td>0.3095#</td>
<td>0.0457</td>
</tr>
<tr>
<td>MTBE</td>
<td>0#</td>
<td>1.5E-05</td>
</tr>
<tr>
<td>n-Butane</td>
<td>0.4#</td>
<td>0.9532</td>
</tr>
</tbody>
</table>

*Specified values

4.6.2. MTBE production

The second example to illustrate the automated feasibility assessment and design procedure for hybrid columns is methyl tertiary butyl ether (MTBE) production. The reaction between iso-butene (IB) and methanol (MeOH) (Eq. 4.36) takes place in the rectifying section, and pure MTBE is obtained as a bottom product. The reactive mixture contains the inert component n-butane. The thermodynamic and kinetic data are listed in Appendix E.2.

\[
\text{IB} + \text{MeOH} \xrightleftharpoons{\text{Cat.}} \rightarrow \text{MTBE}
\] (4.36)

Figure 4.19 shows the residue curve map of the reactive MTBE system in the transformed composition space. The reference component is MTBE. Two reactive azeotropes are formed: one binary light-boiling azeotrope and one quaternary saddle-azeotrope, located very close to the n-butane vertex.
In Figure 4.20 the non-reactive azeotropes and reaction equilibrium surface are shown in mole fraction space. A distillation boundary divides the composition space into two distillation regions. Pure MTBE can only be produced from a conventional distillation column if the methanol concentration in the feed is low. The reactive residue curve map indicates that the methanol/n-butane azeotrope is a potential product composition of a reactive rectifying section. If this reactive section is combined with an inert stripping section, pure MTBE can be withdrawn as the bottom product.

A composition close to the quaternary reactive azeotrope is chosen as the top product, and almost pure MTBE for the bottom product. The methanol conversion for the specified products is 99.8%. Product and feed specifications are given in Table 4.11. Table 4.12 presents the range of operating conditions used to generate reactive stage composition lines.
Figure 4.20 Non-reactive distillation behaviour and reaction space (in mole fraction space) for the MTBE system at 8 bar. The non-reactive mixture forms three binary azeotropes, two distillation regions and one distillation boundary. The singular points are numbered in order of increasing boiling temperature at 8 bar (Groemping, 2002)

Table 4.11 Products and feed compositions for MTBE example

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Stoichiometry</th>
<th>Boiling temp. (8 bar)</th>
<th>Distillate</th>
<th>Bottom</th>
<th>Feed</th>
</tr>
</thead>
<tbody>
<tr>
<td>i-Butene</td>
<td>-1</td>
<td>61.4</td>
<td>0.0977</td>
<td>0.0009</td>
<td>0.0978</td>
</tr>
<tr>
<td>MeOH</td>
<td>-1</td>
<td>128.0</td>
<td>0.0099</td>
<td>0.0015</td>
<td>0.0009</td>
</tr>
<tr>
<td>MTBE</td>
<td>1</td>
<td>136.4</td>
<td>0.0</td>
<td>0.0085</td>
<td>0.0</td>
</tr>
<tr>
<td>n-Butane</td>
<td>0</td>
<td>69.4</td>
<td>0.8924</td>
<td>0.9</td>
<td>0.0</td>
</tr>
</tbody>
</table>

# Specified values

Table 4.12 Specifications for generating stage composition lines

<table>
<thead>
<tr>
<th>Distillate flowrate</th>
<th>Bottoms flowrate</th>
<th>Feed flowrate</th>
<th>Feed quality</th>
<th>Reflux ratio range</th>
<th>Reboil ratio range</th>
<th>Rectifying stages range</th>
<th>Stripping stages range</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>B</td>
<td>F</td>
<td>q</td>
<td>r</td>
<td>s</td>
<td>n</td>
<td>m</td>
</tr>
<tr>
<td>[kmol/h]</td>
<td>[kmol/h]</td>
<td>[kmol/h]</td>
<td>[-]</td>
<td>[-]</td>
<td>[-]</td>
<td>[-]</td>
<td>[-]</td>
</tr>
<tr>
<td>44.35</td>
<td>27.94</td>
<td>100</td>
<td>Eq. B.23</td>
<td>0.2 – 20</td>
<td>0.2 – 20</td>
<td>1 – 30</td>
<td>1 - 30</td>
</tr>
</tbody>
</table>
For this highly non-ideal system, constant molar overflow in transformed variables is not a valid assumption for the reactive section, as can be observed in Figure 4.21, therefore energy balances were used in calculation of the rectifying reactive SCLs. For the non-reactive section, there is little influence of heat balances on composition profiles, constant molar overflow may be assumed to speed up the calculations.

![Figure 4.21. Influence of constant molar overflow on composition profiles. (a) Rectifying reactive section; (b) Stripping non-reactive section](image)

Because the distillate composition is very close to the quaternary reactive azeotrope, the feasible designs are grouped close to a distillation boundary, as can be seen in Figure 4.22. For the feasibility study, small steps for reflux and reboil ratios are needed to generate the stage composition lines near to the distillation boundary accurately.

The best 10 designs, with respect to the total annualised cost, resulting from the conceptual design methodology are presented in Table 4.13. The configurations obtained are based on the top-section reactive hybrid configuration, as MTBE is a heavy component and it will be a bottom product, and a non-reactive section is needed in the stripping section for pure MTBE to be obtained.
Figure 4.22 Stage composition lines and middle composition profiles from intersection points of non-reactive SCLs with the reactive surface for MTBE synthesis.

Table 4.13 Feasible designs for MTBE production, ranked based on total annualised cost.

<table>
<thead>
<tr>
<th>No</th>
<th>Type</th>
<th>NR [-]</th>
<th>NMR [-]</th>
<th>NMS [-]</th>
<th>NS [-]</th>
<th>N_{TOT} [-]</th>
<th>R [-]</th>
<th>S [-]</th>
<th>q [-]</th>
<th>Cond. Duty [kW]</th>
<th>Reb. Duty [kW]</th>
<th>Total Cost [M$/yr]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>II(T)</td>
<td>9</td>
<td>0</td>
<td>0</td>
<td>5.87</td>
<td>14.87</td>
<td>1.31</td>
<td>3.01</td>
<td>0.17</td>
<td>511</td>
<td>562</td>
<td>0.265</td>
</tr>
<tr>
<td>2</td>
<td>I(T)</td>
<td>7</td>
<td>0</td>
<td>1.1</td>
<td>6</td>
<td>14.1</td>
<td>1.36</td>
<td>2.78</td>
<td>0.08</td>
<td>523</td>
<td>518</td>
<td>0.285</td>
</tr>
<tr>
<td>3</td>
<td>II(T)</td>
<td>8</td>
<td>0</td>
<td>0</td>
<td>6.07</td>
<td>14.07</td>
<td>1.39</td>
<td>2.74</td>
<td>0.06</td>
<td>529</td>
<td>511</td>
<td>0.286</td>
</tr>
<tr>
<td>4</td>
<td>II(T)</td>
<td>7</td>
<td>0</td>
<td>0</td>
<td>5.97</td>
<td>12.97</td>
<td>1.85</td>
<td>2.82</td>
<td>-0.07</td>
<td>630</td>
<td>527</td>
<td>0.293</td>
</tr>
<tr>
<td>5</td>
<td>FR</td>
<td>6</td>
<td>0</td>
<td>3.75</td>
<td>5</td>
<td>14.75</td>
<td>0.67</td>
<td>4.52</td>
<td>0.81</td>
<td>369</td>
<td>842</td>
<td>0.333</td>
</tr>
<tr>
<td>6</td>
<td>FR</td>
<td>5</td>
<td>0</td>
<td>3.73</td>
<td>5</td>
<td>13.73</td>
<td>0.79</td>
<td>4.52</td>
<td>0.77</td>
<td>397</td>
<td>842</td>
<td>0.333</td>
</tr>
<tr>
<td>7</td>
<td>FR</td>
<td>4</td>
<td>0</td>
<td>3.54</td>
<td>5</td>
<td>12.54</td>
<td>1.28</td>
<td>4.52</td>
<td>0.60</td>
<td>505</td>
<td>842</td>
<td>0.334</td>
</tr>
<tr>
<td>8</td>
<td>FR</td>
<td>5</td>
<td>0</td>
<td>1.2</td>
<td>6</td>
<td>12.2</td>
<td>2.52</td>
<td>2.78</td>
<td>-0.31</td>
<td>778</td>
<td>518</td>
<td>0.359</td>
</tr>
<tr>
<td>9</td>
<td>FR</td>
<td>6</td>
<td>0</td>
<td>0</td>
<td>6.15</td>
<td>12.15</td>
<td>2.69</td>
<td>2.70</td>
<td>-0.39</td>
<td>817</td>
<td>504</td>
<td>0.370</td>
</tr>
<tr>
<td>10</td>
<td>FR</td>
<td>10</td>
<td>0</td>
<td>0</td>
<td>5.69</td>
<td>15.69</td>
<td>1.27</td>
<td>3.31</td>
<td>0.26</td>
<td>502</td>
<td>617</td>
<td>0.433</td>
</tr>
</tbody>
</table>
Design 1 from Table 4.13 was used to initialise a rigorous simulation using HYSYS v2.4, using 9 stages in the rectifying section (including the condenser) and 6 stages in the stripping section (including the reboiler). The results of the conceptual design method were used to specify the reactive column: a reflux ratio of 1.3, a reboil ratio of 3.0 and a feed condition 0.17. The product compositions predicted by simulation are compared to those specified in the conceptual design method in Table 4.14. The simulation shows good agreement with the conceptual design method.

Table 4.14 Product compositions obtained by simulation, based on the results from the conceptual design procedure (Design 1 in Table 4.13)

<table>
<thead>
<tr>
<th>Component</th>
<th>Simulation results</th>
<th>Conceptual design specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$x_F$</td>
<td>$x_D$</td>
</tr>
<tr>
<td>Butene</td>
<td>0.317†</td>
<td>0.0789</td>
</tr>
<tr>
<td>MeOH</td>
<td>0.283†</td>
<td>0.0000</td>
</tr>
<tr>
<td>MTBE</td>
<td>0.0†</td>
<td>0.0001</td>
</tr>
<tr>
<td>n-Butane</td>
<td>0.4†</td>
<td>0.9210</td>
</tr>
</tbody>
</table>

*Specified values

4.6.3. Diethyl - Carbonate system

Diethyl-carbonate (DEC) is obtained from a trans-esterification reaction from dimethyl-carbonate and ethanol (Eqs. 4.37 and 4.38). The reaction is a two-step reaction, with an intermediate component (methyl-ethyl-carbonate) being formed in the first step. Both reactions are equilibrium reactions, and assuming that the equilibrium is reached in the column, the global reaction (Eq. 4.39) can be used.

\[
\begin{align*}
DMC + EtOH & \rightleftharpoons MEC + MeOH \\
MEC + EtOH & \rightleftharpoons DEC + MeOH \\
DMC + 2EtOH & \rightleftharpoons DEC + 2MeOH
\end{align*}
\] (4.37)  (4.38)  (4.39)
For the global reaction, $K_{eq}$ is calculated from $K_{eq1}$ and $K_{eq2}$, as in Eq. 4.40.

$$K_{eq} = K_{eq1} \cdot K_{eq2}$$  \hspace{1cm} (4.40)

The kinetic and thermodynamic data for DEC system are listed in Appendix E.3.

The system is a non-ideal system. A maximum boiling reactive azeotrope is formed at 75.76 °C, with the composition of 0.085 DMC and 0.9145 MeOH (mole fractions), as can be observed in the residue curve map in Figure 4.23(b).

![Figure 4.23](image)

Figure 4.23 Residue curve map in transformed composition space for DEC system. (a) transformed composition space; (b) Residue curve map at 1 bar (algorithm from Barbosa and Doherty, 1988a). A reactive azeotrope is formed at 0.085 DMC and 0.9145 MeOH

The shape of transformed composition space depends on the type of reaction and stoichiometric coefficients (Appendix A). For the reaction above, if the reference component is DEC, then the transformed composition space will be a trapezoid as in Figure 4.23, resulting from overlapping feasible transformed composition intervals for all components. The feasible transformed composition
intervals for the components present in the system are (Appendix A): DMC: [0, 1], Ethanol: [0, 2], DEC: [-1, 1], Methanol: [-2, 1]. Figure 4.23 shows the transformed limits for dimethyl-carbonate system (a) and the residue curve map (b) for the system described by reaction 4.39.

The product composition for the distillate was chosen close to the reactive azeotrope, and for the bottom product near pure DEC (Table 4.15); reaction conversion for the specified product compositions is 99%. Both products are located on the reactive surface, so for this case both fully reactive and hybrid configurations are possible. To generate stage composition lines, the same ranges as in examples before were chosen for reflux/reboil ratios.

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Stoichiometry</th>
<th>Boiling temp. at 1 bar [°C]</th>
<th>Distillate</th>
<th>Bottoms</th>
<th>Feed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$X_D$, mole fr.</td>
<td>$x_D$</td>
<td>$X_B$, mole fr.</td>
</tr>
<tr>
<td>DMC</td>
<td>-1</td>
<td>61.4</td>
<td>0.006</td>
<td>0.004*</td>
<td>0.986</td>
</tr>
<tr>
<td>Ethanol</td>
<td>-2</td>
<td>128.0</td>
<td>0.008</td>
<td>0.004*</td>
<td>1.97</td>
</tr>
<tr>
<td>DEC</td>
<td>1</td>
<td>136.4</td>
<td>0</td>
<td>0.002*</td>
<td>0</td>
</tr>
<tr>
<td>Methanol</td>
<td>2</td>
<td>69.4</td>
<td>0.986</td>
<td>0.990*</td>
<td>-1.956</td>
</tr>
</tbody>
</table>

*Specified values

Flowrates [kmol/h]: 64.872, 35.1, 100

A study on the effect of constant molar overflow assumption for this system shows that in the rectifying section the assumption has no influence on composition profiles, but for a stripping section the assumption affects the profiles for both reactive and non-reactive stripping sections (Figure 4.24). Based on this observation, heat balances were used in the calculation of both reactive and non-reactive composition profiles.
Many feasible designs are possible for this system, including fully reactive and hybrid configurations. Because the number of feasible designs in this case is high (more than 400), a constraint was applied to restrict the feed condition between 0 and 1.2. The best 10 designs with respect to the total annualised cost, satisfying the constraint, are listed in Table 4.16.

Table 4.16 Best 10 designs ranked based on total annualised cost obtained for DEC system, for $q_F = [0;1.2]$

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>II(T)</td>
<td>4</td>
<td>-</td>
<td>1.9</td>
<td>18</td>
<td>23.9</td>
<td>2.24</td>
<td>3.04</td>
<td>0.11</td>
<td>1591</td>
<td>1235</td>
<td>0.370</td>
</tr>
<tr>
<td>2</td>
<td>I(T)</td>
<td>5</td>
<td>-</td>
<td>-</td>
<td>17.4</td>
<td>22.4</td>
<td>2.04</td>
<td>3.54</td>
<td>0.41</td>
<td>1494</td>
<td>1435</td>
<td>0.389</td>
</tr>
<tr>
<td>3</td>
<td>II(T)</td>
<td>5</td>
<td>-</td>
<td>5.9</td>
<td>18</td>
<td>28.9</td>
<td>0.90</td>
<td>3.04</td>
<td>0.80</td>
<td>932</td>
<td>1235</td>
<td>0.456</td>
</tr>
<tr>
<td>4</td>
<td>II(T)</td>
<td>5</td>
<td>-</td>
<td>2.3</td>
<td>17</td>
<td>24.3</td>
<td>0.76</td>
<td>3.88</td>
<td>1.20</td>
<td>866</td>
<td>1571</td>
<td>0.459</td>
</tr>
<tr>
<td>5</td>
<td>F</td>
<td>4</td>
<td>-</td>
<td>-</td>
<td>16</td>
<td>20</td>
<td>2.28</td>
<td>3.10</td>
<td>0.11</td>
<td>1612</td>
<td>1257</td>
<td>0.616</td>
</tr>
<tr>
<td>6</td>
<td>F</td>
<td>4</td>
<td>-</td>
<td>-</td>
<td>15</td>
<td>19</td>
<td>1.99</td>
<td>3.74</td>
<td>0.52</td>
<td>1469</td>
<td>1516</td>
<td>0.629</td>
</tr>
<tr>
<td>7</td>
<td>F</td>
<td>5</td>
<td>-</td>
<td>-</td>
<td>20</td>
<td>25</td>
<td>0.96</td>
<td>2.90</td>
<td>0.71</td>
<td>963</td>
<td>1179</td>
<td>0.633</td>
</tr>
<tr>
<td>8</td>
<td>F</td>
<td>5</td>
<td>-</td>
<td>-</td>
<td>19</td>
<td>24</td>
<td>0.92</td>
<td>3.06</td>
<td>0.79</td>
<td>945</td>
<td>1241</td>
<td>0.634</td>
</tr>
<tr>
<td>9</td>
<td>F</td>
<td>5</td>
<td>-</td>
<td>-</td>
<td>21</td>
<td>26</td>
<td>0.99</td>
<td>2.79</td>
<td>0.65</td>
<td>976</td>
<td>1135</td>
<td>0.635</td>
</tr>
<tr>
<td>10</td>
<td>F</td>
<td>5</td>
<td>-</td>
<td>-</td>
<td>18</td>
<td>23</td>
<td>0.87</td>
<td>3.27</td>
<td>0.90</td>
<td>920</td>
<td>1326</td>
<td>1.354</td>
</tr>
</tbody>
</table>

F – fully reactive column

Figure 4.24. Influence of constant molar overflow assumption on composition profiles. (a) Non-reactive stripping section; (b) Reactive stripping section
As it was expected, the hybrid configurations are preferred, due to a lower total cost. Even though the total number of stages for hybrid configurations is the same or even higher than for fully reactive columns, a lower number of reactive stages will lead to a lower total cost, as reactive stages are much more expensive than the non-reactive stages. For example, Design 1 in Table 4.16 (a hybrid column Type II(T)) is similar, in terms of number of stages and operating parameters (reflux and reboil ratio and feed condition), to Design 5 (a fully reactive column). Because in single-feed columns the reaction is concentrated around the feed stage, most of the reactive stages from the stripping section of the fully reactive column in Figure 4.25a can be replaced with non-reactive stages (Figure 4.25b), without affecting the overall performance. This will lead to a capital cost with 40% lower.

Figure 4.25 Reaction distribution in a single-feed reactive distillation column  (a) Fully reactive column (Design 5 in Table 4.16); (b) Hybrid column Type II(T) (Design 1 in Table 4.16).
Table 4.17 Product compositions obtained by simulation, based on the results from the conceptual design procedure (Design 1 in Table 4.16)

<table>
<thead>
<tr>
<th>Component</th>
<th>Simulation results</th>
<th>Conceptual design specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$x_F$</td>
<td>$x_D$</td>
</tr>
<tr>
<td>DMC</td>
<td>0.334</td>
<td>0.0072</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.666</td>
<td>0.0046</td>
</tr>
<tr>
<td>DEC</td>
<td>0.0</td>
<td>0.0023</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.0</td>
<td>0.9859</td>
</tr>
</tbody>
</table>

*Specified values

Design 1 from Table 4.16 was used to initialise a rigorous simulation using HYSYS v2.4. A column with 6 reactive stages and 18 non-reactive stages (including the condenser and the reboiler) was used, with the feed placed on stage 5. A reflux ratio of 2.24 and a reboil ratio of 3.04 were specified, together with feed specifications: composition and flowrate according to Table 4.15 and a feed condition of 0.11. The rigorous simulation results presented in Table 4.17 show very good agreement with the conceptual design method.

4.7. Conclusions

In this chapter, the graphical design methodology developed for non-hybrid columns (Groemping, 2002) has been extended to accommodate hybrid columns. The methodology developed can be applied to assess feasibility and design columns for reactive systems with two degrees of freedom according to the Gibbs phase rule (Eq. 2.2). It is assumed that equilibrium reactions take place in the liquid phase only. Further assumptions of constant molar overflow in the vapour phase and no pressure drop in the column are not fundamental to the approach. A preliminary test for the influence of constant molar overflow assumption was performed in all cases and if necessary, heat balances were included to calculate the internal flows.

Two approaches for the methodology were presented: In a first approach, intersection of SCLs in transformed variables, together with an additional
feasibility criterion, were used to assess feasibility. The method offers good initialisation for rigorous simulation, but is time consuming as exhaustive search for intersection of all SCL segments must be performed, and then the additional feasibility criterion must be applied.

To overcome these inconveniences, the method was improved by applying some insights and incorporating some features specific to hybrid reactive columns. Intersections of non-reactive SCLs with the reactive surface were used in the search routine allowing a more rapid screening for feasible designs. Also, the use of intersection of non-reactive SCLs with the reactive surface allows a wider range of hybrid configurations and feed arrangements to be analysed: top or bottom section reactive columns, columns with a reactive core, with the feed at either the interface between the reactive and the non-reactive sections or within the reactive section.

The methodology can be easily automated and typically generates multiple designs. The approach does not require iteration to obtain column profiles, and is efficient in the way the information obtained from composition profiles is used. For synthesis purposes, both fully reactive (method developed by Groemping, 2002) and hybrid configurations were introduced in the same framework. Multiple designs of various configurations can be obtained for a given system, which can be ranked using more or less sophisticated cost models. This allows the design engineer a fast evaluation of which configurations are most appropriate for the defined reactive separation task.

Three case studies were discussed, showing that the methodology can apply successfully to both ideal (the ideal A, B, C, D system) and highly non-ideal systems (MTBE production). The benefit of including both fully reactive and hybrid columns in the same framework was shown in the case of DEC production, showing that hybrid configurations are usually preferred over fully reactive columns due to a lower total cost. In all cases, the results obtained from the design methodology provided good initialisation for rigorous simulation.
The concepts developed in this chapter for the synthesis and design of single-feed reactive distillation columns, can be used to analyse more complex configurations, such as double-feed fully reactive and hybrid reactive distillation columns, presented in the following chapter.
5. CONCEPTUAL DESIGN OF DOUBLE-FEED REACTIVE DISTILLATION COLUMNS

5.1. Introduction

Double-feed columns are widely used for reactive systems (e.g. methyl-acetate and ethylene-glycol production), with most industrial applications featuring double or multiple feed columns. Usually the reactants have very different boiling points, and a double (or multiple) feed configuration will improve the contact between them. Therefore, in a double-feed reactive column the reaction extent will be uniformly distributed between the two feed stages, not concentrated around feed stage as in single-feed columns. Also, by introducing a second feed, distillation boundaries can be crossed, and the feasibility region extended (Thong, 2000). Moreover, we can use the extra degree of freedom introduced by the second feed to control some of the operating parameters resulting from the design procedure, as it will be presented in the case studies. Overall, including double-feed configurations in column synthesis and design is an important step, allowing the extension of column design alternatives.

In this chapter, a systematic conceptual design methodology able to assess feasibility and obtain multiple designs for a double-feed column separating two products will be presented. The method, based on the design methodologies developed for single-feed columns, generates multiple column configurations, either fully reactive or hybrid. The feasible designs obtained can be ranked using more or less sophisticated cost models, providing the best few double-feed reactive column configurations.
5.2. Previous work

Very few studies are available for double-feed reactive distillation columns. Generally, optimisation methods can easily accommodate multiple feed configurations, as presented in Ciric and Gu (1995) and in Jackson and Grossman (2001). However, for the design of a single column, the optimisation methods are very time consuming, being more appropriate for analysing a large variety of flowsheet structures.

A design method based on the visualisation of the lever rule has been developed by Lee et al. (2000, 2001), but is not systematic and it is based on the specification of reaction extent on each tray. For equilibrium reactions the reaction extent cannot be arbitrarily chosen, being dependent on the liquid composition at each tray, in reactive and thermodynamic equilibrium.

The only published work on conceptual design of double-feed reactive distillation columns is by Barbosa and Doherty (1988d), who developed a method based on BVM to assess feasibility and to obtain feasible designs for double-feed reactive columns. It addresses only fully reactive columns and, as all BV methods, it is more focused on feasibility of proposed products and finding one design which will satisfy the specifications, and not on general reactive column synthesis. Also, it considers fixed feed condition, therefore there is only one remaining degree of freedom, chosen as either the reflux or the reboil ratio. However, the method establishes the basic concepts for two-feed reactive columns, which, together with the concepts presented in Chapter 4 for single-feed columns, can be easily included in a more general methodology for design and synthesis of double-feed reactive columns.
5.3. Calculation of composition profiles and stage composition lines for double-feed columns

For the general mass balance in transformed variables (Eqs. 5.1 and 5.2), if the transformed product compositions $X_D$ and $X_B$ are fully specified, there are $2C-2R+1$ unknowns for the $C-R$ equations, leaving $C-R+1$ degrees of freedom (Appendix B.2).

$$\bar{E} + 1 = \bar{U} \cdot \bar{E} + \bar{L} \quad (5.1)$$

$$\bar{E} \cdot X_{FU,i} + X_{FL,i} = \bar{U} \cdot \bar{E} \cdot X_{D,i} + \bar{L} \cdot X_{B,i} \quad i = 1, \ldots, C-R-1 \quad (5.2)$$

For double-feed columns, the transformed composition for one of the two feeds must also be specified ($C-R-1$ compositions), leaving 2 degrees of freedom for the general mass balance. The feed for which the composition is fully specified will be referred to in this chapter as the specified feed. The remaining 2 specifications can be chosen between transformed ratios $\bar{U}$, $\bar{L}$, $\bar{E}$ and the transformed mole fraction for one component for the second feed. After solving the general and component mass balances, the total reaction extent in the column is calculated from the overall mass balance for the reference component (Appendix B.2). Here is worth mentioning that for a fully reactive column the composition of the reference component in the product streams can be calculated from a reactive bubble point (or a reactive dew point if the product is in the vapour phase). For non-reactive streams (e.g. feed streams or products obtained from a non-reactive section), the compositions of the reference component have to be specified for the total reaction extent calculation.

A double-feed column features three sections: a rectifying section, a stripping section and a middle section, placed between the two feeds. Each section can be reactive or non-reactive, resulting in fully reactive or hybrid column configurations. The equations for calculating composition profiles for reactive rectifying and stripping sections are not affected by the presence of a second feed: we can use the same equations as for single-feed columns (Appendix
B.3). The operating lines for the rectifying and stripping section in transformed variables are:

- rectifying section

\[
Y_{n+1,i} = \frac{R_n}{R_n + 1} \cdot X_{n,i} + \frac{1}{R_n + 1} \cdot X_{D,i}, \quad \forall \ i = 1, \ldots, C - R - 1
\] (5.3)

- stripping section

\[
X_{m+1,i} = \frac{S_m}{S_m + 1} \cdot Y_{m,i} + \frac{1}{S_m + 1} \cdot X_{B,i}, \quad \forall \ i = 1, \ldots, C - R - 1
\] (5.4)

Middle section profiles are calculated starting from the specified feed stage. For fully reactive columns, either of the two feeds can be chosen as the specified feed, with similar results. For hybrid reactive columns, the specified feed will be chosen depending on the arrangement of the two feeds. In Chapter 4, the situations when a hybrid column is beneficial were discussed, which are valid also for two-feed columns. This leads to special considerations in the arrangement of the two feeds. For example, for a system where a hybrid configuration is used to obtain a pure product which is not located on the reactive surface (e.g. systems type \( A + B \leftrightarrow C \) with inert D), one of the feeds should be always situated on the interface between the reactive and non-reactive sections. The reason for this is that on all trays below the lower feed (for top section reactive columns and C obtained as the bottom product) or above the upper feed (for bottom section reactive columns and C obtained as the top product) a decomposition of the product C into the reactants A and B will occur (reverse reaction), leading to a decrease in total reaction conversion.

For systems type \( A + B \leftrightarrow C + D \), when a fully reactive column can be used to obtain pure products C and D (Chapter 4) and the use of hybrid columns is only advisable for economic reasons (replacing reactive stages with low reaction extent with non-reactive ones to reduce the capital cost), there are no
restrictions of the two feeds placement. However, in this work, for consistency and simplicity of the algorithms used, one of the feeds was always considered to be situated at the interface between the reactive and non-reactive sections. Based on this assumption, the methodology developed requires that the feed situated at the interface to be the specified feed, e.g. the lower feed stage will be specified for a top reactive column and the upper feed stage for a bottom reactive column. If the column has a reactive core, then two arrangements are possible, e.g. one of the feeds situated at the interface and the other within the reactive section, or both feeds situated at the interface (one at the top and one at the bottom of the reactive core). However, in both situations one of the feeds will always be situated at the interface, and this will be fully specified. If both feeds are at the interface, then any of them can be specified, with similar results.

Intersections of non-reactive SCLs with the reactive surface are calculated first (as described in Section 4.5.1, to obtain the composition of the liquid leaving the interface stage (the specified feed stage) and then a mass and energy balance

Figure 5.1 Middle reactive sections for hybrid columns. (a) Upper feed specified; (b) Lower feed specified

(a)  
(b)
around the interface stage is used to obtain internal reflux/reboil ratios and initial compositions for the middle section (envelope 1 in Figure 5.1a and b).

For the upper feed specified, the middle rectifying operating line (Eq. 5.5) will calculate the composition of the vapour top-down in the middle rectifying reactive section using a mass balance around envelope 2 in Figure 5.1a. The lower feed stage is considered to be the last stripping stage. Stages in the stripping section are numbered from the bottom of the column towards the lower feed stage.

\[
Y_{p+1,j} = \frac{A_p}{A_p + 1} \cdot X_{p,j} + \frac{A_0 + 1}{A_p + 1} \cdot Y_{1,j} - \frac{A_0}{A_p + 1} \cdot X_{0,j}
\]

\[\forall \; j = 1, \ldots, C - R - 1\]  \hspace{1cm} (5.5)

where the ratios \(A_0\) and \(A_p\) are defined by Eqs 5.6 and 5.7.

\[
\overline{A}_p = \frac{L_p}{V_{out} - L_{in}} \quad \hspace{1cm} (5.6)
\]

\[
\overline{A}_0 = \frac{L_{in}}{V_{out} - L_{in}} \quad \hspace{1cm} (5.7)
\]

For the lower feed specified, the middle stripping operating line (Eq. 5.10) will be used to calculate the liquid composition bottom-up in the middle section, using a mass balance around envelope 2 in Figure 5.1b. In this case, the upper feed stage is considered to be the last middle stripping stage (stages numbered from the lower feed stage upwards in the column).

\[
X_{p,i} = \frac{B_{p-1}}{B_{p-1} + 1} \cdot Y_{p-1,i} + \frac{B_0 + 1}{B_{p-1} + 1} \cdot X_{out,i} - \frac{B_0}{B_{p-1} + 1} \cdot Y_{in,i}
\]

\[\forall \; i = 1, \ldots, C - R - 1\]  \hspace{1cm} (5.8)

where the ratios \(B_0\) and \(B_{p-1}\) are defined by Eqs 5.9 and 5.10.

\[
\overline{B}_{p-1} = \frac{V_{p-1}}{L_{out} - V_{in}} \quad \hspace{1cm} (5.9)
\]
\[
\overline{B}_0 = \frac{\overline{V}_{in}}{L_{out} - \overline{V}_{in}} \tag{5.10}
\]

If the assumption of constant molar overflow in transformed variables holds, then the local ratios \( \overline{A}_p \) and \( \overline{B}_{p-1} \) are the same as initial ratios \( \overline{A}_0 \) and \( \overline{B}_0 \) and Eqs. 5.5 and 5.10 become:

\[
Y_{p+1,j} = Y_{out,j} + \frac{\overline{A}_0}{\overline{A}_0 + 1} \cdot (X_{p,j} - X_{in,j}) \tag{5.11}
\]
\[
\forall \ i = 1, \ldots, C - R - 1
\]

\[
X_{p,j} = X_{out,j} + \frac{\overline{B}_0}{\overline{B}_0 + 1} \cdot (Y_{p-1,j} - Y_{in,j}) \tag{5.12}
\]
\[
\forall \ i = 1, \ldots, C - R - 1
\]

A detailed derivation of the equations can be found in Appendix B.3.

Alternate application of the rectifying or middle rectifying operating line and the dew point calculation or the reactive dew point, if the rectifying section is a reactive section, will give the rectifying composition profile. Similar, the stripping profile is obtained by alternate application of the stripping or middle stripping operating line and the bubble point calculation, or reactive bubble point if the stripping section is a reactive section. SCLs are obtained by calculating the composition profiles for a set of reflux and reboil ratios and rearranging the information obtained.

Rectifying and stripping SCLs are used in conjunction with middle section SCLs, CPs or intersections of non-reactive SCLs with the reactive surface to analyse the possibility of using different types of double-feed configurations to perform a specified reactive distillation task.
5.4. Design methodology for fully reactive double-feed distillation columns

5.4.1. Feasibility criterion for double-feed fully reactive columns

For the design procedure, the two product compositions are fully specified, together with the composition and flowrate of one of the two feeds. For the general and component overall mass balance in transformed variables (Eqs. 5.1 and 5.2), there are two degrees of freedom remaining. If the flowrate of the second feed (or the ratio $E$) is specified, there is only one degree of freedom remaining, which can be chosen between $X_{i_{\text{ref}}}$, $U$ and $L$. For a feasible design, not only do the overall mass balances have to be satisfied, but also a continuous profile should be possible in the column. Previous section presented the equations used to calculate the profiles in a double-feed fully reactive column, for rectifying section, stripping section and middle sections (rectifying or stripping). Depending on which one of the two feeds has been specified (upper or lower feed), the feasibility criterion will check for a continuous profile in the column by looking for intersections between a rectifying SCL and a middle stripping SCL for the lower feed specified, or between a stripping SCL and a middle rectifying SCL for the upper feed specified.

D. Upper feed specified

The feasibility criterion in this case is that the transformed composition of the liquid leaving the lower feed stage $m$ must be the same as the composition of the liquid leaving the middle rectifying stage $p+1$ (Figure 5.1a).

$$X_{p+1} = X_m$$  \hspace{1cm} (5.13)

E. Lower feed specified

The feasibility criterion in this case will verify if the composition of the liquid leaving rectifying stage $n+1$ coincides with the liquid leaving upper feed stage $p$ (Figure 5.1b).
\[ X_{n+1} = X_p \]  \hfill (5.14)

For a fully reactive column all composition profiles (rectifying, middle and stripping) are situated on the reactive surface, so the feasibility criterion in transformed variables, defined by either Eq. 5.13 or 5.14, is necessary and sufficient to guarantee a continuous profile in the column.

### 5.4.2. Design methodology for fully reactive double-feed columns

The feasibility criterion for double-feed fully reactive columns is based on intersections of liquid composition profiles in transformed variables (Section 5.4.1). Depending on the specified feed (upper or lower) the liquid composition can be a point on a reactive rectifying, stripping or middle section SCL.

A graphical visualisation of the feasibility criterion in the two cases is presented in Figure 5.2. A segment [AB] on a rectifying (or middle rectifying) SCL will represent all possible liquid transformed compositions for reflux ratios between \( R_A \) and \( R_B \). Similarly, a segment [CD] on a stripping (or middle stripping) SCL will represent all possible liquid compositions (in transformed variables) for reboil ratios between \( S_C \) and \( S_D \). Feasible designs are obtained by performing a 2D line-line intersection between the two segments [AB] and [CD]. The intersection is characterised by composition \( X_{\text{int}} \). Two linear parameters, \( \alpha \) and \( \beta \), can be calculated using the composition at the intersection (Appendix G). For a feasible design to exist, the two parameters \( \alpha \) and \( \beta \) should have values within the interval \([0, 1]\), meaning that the intersection occurs within the segments [AB] and [CD]. The design parameters at the intersection are:

- No. of stages for the rectifying section: \( NR \) (or \( NMR \) for a middle rectifying section)
- No. of stages for the stripping section: \( NS \) (or \( NMS \) for a middle stripping section)
- Reflux ratio: \( R_{\text{int}} \)
- Reboil ratio: \( S_{\text{int}} \).
If the chosen intervals for reflux and reboil ratios are small enough, the composition on each tray can be considered linearly dependent on the reflux or reboil ratio. Therefore, the reflux or reboil ratios at the intersection point, $R_{\text{int}}$ and $S_{\text{int}}$, can be obtained by linear interpolation using the two parameters $\alpha$ and $\beta$ (Eqs. 5.15 and 5.16). Alternatively, a root search algorithm can be used to calculate the reflux or reboil ratios at the intersection, but a linear interpolation usually provides a very good approximation.

$$R_{\text{int}} = R_A + \alpha(R_B - R_A)$$

$$S_{\text{int}} = S_C + \beta(S_D - S_C)$$

For a fully reactive column, the second feed stage is always considered as the first stripping (or middle stripping) stage. The design details, obtained from the intersection, for a double-feed column in the two cases – upper and lower feed specified – are presented in Table 5.1.

<table>
<thead>
<tr>
<th>Specified feed</th>
<th>No. of rectifying stages</th>
<th>No. of middle stages</th>
<th>No. of stripping stages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper feed</td>
<td>NR*</td>
<td>NMR-1</td>
<td>NS</td>
</tr>
<tr>
<td>Lower feed</td>
<td>NR-1</td>
<td>NMS</td>
<td>NS*</td>
</tr>
</tbody>
</table>

* Specified feed stage
Based on the results of the design procedure, the remaining parameters can then be calculated: feed condition, condenser and reboiler duties, column diameter and column cost. Feed condition is obtained from an overall energy balance (Appendix B.5). Condenser and reboiler duties are direct functions of reflux and reboil ratios. From the condenser and reboiler duties, utility cost can then be calculated. Column diameter and column capital cost are calculated based on the correlation given in Appendix F. The feasible designs can then be ranked according to any of these parameters (number of stages, energy requirement or total cost) to obtain the best few designs.

5.5. Design methodology for double-feed hybrid reactive distillation columns

5.5.1. Feasibility criteria for hybrid double-feed reactive columns

Chapter 4 established the principles for conceptual design of single-feed hybrid reactive distillation columns, for systems with two degrees of freedom. For a specified pair of product compositions, a non-reactive SCL must intersect the reactive surface for a hybrid configuration to be possible. The intersection will represent the composition leaving the reactive interface stage (Figure 4.9). For synthesis and design of hybrid double-feed columns, the same concepts are valid, and we can easily extend the methodology developed for single-feed hybrid columns to accommodate double-feed configurations. For the simplification of the design procedure, one of the feeds will always be assumed to be situated at the interface between a reactive and a non-reactive section.

Three types of double-feed hybrid configurations can be identified, depending on the second feed location and on the general type of the reactive system (Figure 5.3):

- Type I – top/bottom section reactive double-feed column
- Type II – reactive core configuration with both feeds at interfaces of
the reactive core
- Type III – reactive core configuration with one feed at the interface and one feed within the reactive core

Figure 5.3 Possible hybrid configurations for a double-feed reactive column. U – the upper feed is specified; L – the lower feed is specified

Table 5.2 summarises the types of configurations for hybrid reactive column configurations. A hybrid column Type I has three sections: two reactive sections (a rectifying or stripping section and a middle reactive section between the two feeds) and a non-reactive section. The non-reactive section can be either stripping or rectifying, depending on the column type: top section reactive or bottom section reactive. A reactive core column Type II also features three sections: a reactive section situated between the two feeds, and two non-reactive sections (a rectifying and a stripping section). A reactive core configuration Type III features 4 sections: two reactive sections (one between the two feeds and one middle rectifying or stripping section) and two non-reactive sections (a rectifying and a stripping section).

For a feasible design, a continuous profile must exist between the top and bottom product compositions. For double-feed columns, if the upper feed is specified, this means that the liquid composition leaving the lower feed stage should coincide with the liquid composition entering the last stripping stage (where stages are numbered from column ends towards the lower feed). In the
case that the lower feed is specified, a continuous profile will be guaranteed if the composition of the liquid leaving the upper feed stage coincides with that of the liquid entering the first middle stage (where stages are numbered starting from column ends towards the upper feed stage).

Table 5.2 Types of sections for various hybrid two-feed column configurations.

<table>
<thead>
<tr>
<th>Section</th>
<th>Type I</th>
<th>Type II</th>
<th>Type III</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(a)</td>
<td>(b)</td>
<td>(a)</td>
</tr>
<tr>
<td>Rectifying</td>
<td>R</td>
<td>Non-R</td>
<td>Non-R</td>
</tr>
<tr>
<td>Middle Rectifying</td>
<td>-</td>
<td>-</td>
<td>R</td>
</tr>
<tr>
<td>Middle between the two feeds</td>
<td>R</td>
<td>R</td>
<td>R</td>
</tr>
<tr>
<td>Middle Stripping</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Stripping</td>
<td>Non-R</td>
<td>R</td>
<td>Non-R</td>
</tr>
</tbody>
</table>

*R*: Reactive; *Non-R*: non-reactive

Taking into account the particularities of hybrid two-feed reactive distillation columns, the general feasibility criterion changes depending on the column configuration. Three feasibility criteria can be formulated for the configurations analysed in this chapter.

A. **Second feed stage within the reactive section – upper feed specified**

![Diagram](image)

*Figure 5.4 Feed stage arrangement for a column with the feed within the reactive section. (a) Upper feed specified; (b) Lower feed specified*
This arrangement is characteristic of configurations of Types I (U) and III (U) (see Figure 5.3). In this case, if the lower feed stage is considered to be the last stripping stage (Figure 5.4), the general feasibility criterion is similar to the general feasibility criterion for fully reactive columns: the liquid composition leaving middle rectifying stage $p+1$ should coincide with the liquid composition leaving lower feed stage $m$. As all liquid compositions are located on the reactive surface, transformed variables can be used. The feasibility criterion in transformed variables for a column with the lower feed within the reactive section can be written as:

$$X_{p+1} = X_m$$  \hspace{1cm} (5.17)

B. **Second feed stage within the reactive section – lower feed specified**

This arrangement is characteristic of configurations of Types I (L) and III (L). In this case, the upper feed stage is taken to be the last middle stripping stage (Figure 5.4b). Stages are numbered from column ends towards the second feed stage. The general feasibility criterion is similar to the general feasibility criterion for fully reactive columns: the liquid composition leaving feed stage $n+1$ should coincide with the liquid composition leaving upper feed stage $p$. The feasibility criterion in transformed variables for a column with the upper feed within the reactive section is:

$$X_{n+1} = X_p$$  \hspace{1cm} (5.18)

C. **Second feed at the interface between the reactive and the non-reactive sections**

This arrangement is characteristic of the Type II configuration. Because in this case both feeds are located at the interface, we can specify either of them, with similar results. For hybrid configurations, the interface stage will be always considered as a middle stage (Figure 5.5a). A continuous profile will be
guaranteed in the column if the composition of the liquid leaving middle stage \( p \) coincides with the liquid composition at the intersection of the non-reactive SCLs with the reactive surface \( (X_{\text{intersect}}) \). Using the intersection of non-reactive SCLs with the reactive surface to formulate the feasibility criterion will allow the use of transformed variables for visualisation and column design, as all liquid composition points of interest will be located on the reactive surface. The feasibility criterion for the Type II hybrid configuration can be written in transformed variables as:

\[
X_p = X_{\text{intersect}}
\]  

(5.19)

Figure 5.5 Feed stage arrangements for Type II configuration. (a) Upper feed specified; (b) Lower feed specified

No additional feasibility conditions are necessary, the criteria presented above being not only necessary, but also sufficient for the feasibility of the proposed product compositions. The feasibility criteria for the design of hybrid two-feed columns are summarised for easy reference in Table 5.3.
### Table 5.3. Feasibility criteria for the hybrid column configurations shown in Figure 5.3

<table>
<thead>
<tr>
<th>Hybrid configuration</th>
<th>Feasibility criterion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type I (U)</td>
<td>$X_m = X_{p-1}$</td>
</tr>
<tr>
<td>Type I (L)</td>
<td>$X_p = X_{n+1}$</td>
</tr>
<tr>
<td>Type II (U)</td>
<td>$X_p = X_{\text{intersect}}$</td>
</tr>
<tr>
<td>Type II (L)</td>
<td>$X_p = X_{\text{intersect}}$</td>
</tr>
<tr>
<td>Type III (U)</td>
<td>$X_m = X_{p-1}$</td>
</tr>
<tr>
<td>Type III (L)</td>
<td>$X_p = X_{n+1}$</td>
</tr>
</tbody>
</table>

#### 5.5.2. Design methodology for double-feed hybrid reactive distillation columns

For double-feed hybrid configurations, as for single-feed configurations, the feasibility criteria (presented in Table 5.3) are based on liquid compositions represented in transformed variables. Depending on the configuration type, the liquid composition can be a point on a reactive SCL, a point of intersection of a non-reactive SCL with the reactive surface or a point on a middle composition profile.

Reactive SCLs are calculated using Eqs. 5.3 and 5.4 for a range of reflux and reboil ratios. Middle section profiles are calculated using Eqs. 5.11 and 5.12 starting from intersections of non-reactive SCLs with the reactive surface. A mass and energy balance is used at the interface stage to obtain initial points for calculating middle composition profiles. If the interface stage also contains one of the feeds, then a mass and energy balance including the feed is used to generate initial points for calculating the middle composition profiles (e.g. for configurations of Types II and III). Figure 5.6 shows middle section profiles calculated from intersection points for the system $A + B \leftrightarrow C$ (inert D). Intersections of non-reactive stripping SCLs with the reactive surface were
calculated, resulting in a set of 6 points. In this case the lower feed is specified. A mass and energy balance including lower feed is used at each intersection point to initialise the calculation of middle composition profiles.

Each intersection of a non-reactive SCL with the reactive surface is characterised by a specific reflux or reboil ratio, as described in Section 4.3, e.g. for stripping stage no. 12, the corresponding reboil ratio is 3.7 (Figure 5.6). The specific reflux or reboil ratio is used to calculate the internal liquid and vapour flows at the interface between the reactive and the non-reactive sections.

To obtain feasible designs, a search for intersections between different combinations of segments - of reactive SCLs, middle composition profiles, or between two adjacent points of intersection of non-reactive SCLs with the reactive surface – is performed, depending on the hybrid configuration type.
Table 5.4 summarises the types of intersections checked to obtain feasible designs for various double-feed hybrid configurations.

### Table 5.4 Intersections checked for feasible double-feed hybrid column designs.

<table>
<thead>
<tr>
<th>Hybrid Configuration</th>
<th>Intersection Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type I</td>
<td>(U) Middle rectifying CPs(**) + Stripping SCLs</td>
</tr>
<tr>
<td></td>
<td>(L) Rectifying SCLs + Middle stripping CPs(**)</td>
</tr>
<tr>
<td>Type II</td>
<td>(U) Middle rectifying CPs(**) + Stripping SCLs-RS points(*)</td>
</tr>
<tr>
<td></td>
<td>(L) Rectifying SCLs-RS points(*) + Middle stripping CPs(**)</td>
</tr>
<tr>
<td>Type III</td>
<td>(U) Middle rectifying CPs(<strong>) + Middle stripping CPs(</strong>)</td>
</tr>
<tr>
<td></td>
<td>(L) Middle rectifying CPs(<strong>) + Middle stripping CPs(</strong>)</td>
</tr>
</tbody>
</table>

(*) Intersections of non-reactive SCLs with the reactive surface  
(**) Composition profiles calculated from specified feed stage  
(***) Composition profiles calculated from intersections of non-reactive SCLs with the reactive surface

A general representation of the feasibility test is presented in Figure 5.7. [AB] can represent a segment between two reflux ratios from a rectifying SCL, a segment between two consecutive stages from a middle rectifying CP or a segment between two adjacent points of intersection of non-reactive rectifying SCLs with the reactive surface. Similarly, [CD] can represent a segment between two reboil ratios on a stripping SCL, a segment between two consecutive stages on a middle stripping CP or a segment between two adjacent points of intersection of non-reactive stripping SCLs with the reactive surface.

![Figure 5.7 Graphical visualisation of the feasibility test for hybrid reactive distillation columns.](image)
For example, for a hybrid column Type I (L), \([AB]\) will represent a segment of a reactive SCL containing all possible compositions of stage NR for reflux ratios between \(R_A\) and \(R_B\), and \([CD]\) will represent a segment between two adjacent stages from a middle composition profile (dashed line). A 2D line-line intersection is performed between the two segments \([AB]\) and \([CD]\), the resulting intersection point \(I\) being characterized by \(X_{int}, NR, R_{int}, NMS_{int}\) and \(S_{intersect}\). \(X_{int}\) represents the transformed liquid composition at intersection, \(NR\) represents the number of rectifying stages and \(S_{intersect}\) the reboil ratio resulting from the intersection of non-reactive stripping stage composition line \(NS\) with the reactive surface. This value of reboil ratio is used to calculate the initial point for the middle stripping composition profile, to obtain internal liquid and vapour flows at the interface stage. \(R_{int}\) and \(NMS_{int}\) are calculated by linear interpolation, using the two linear parameters \(\alpha\) and \(\beta\) resulting from the line-line intersection (Appendix G). For a feasible design to exist, the two parameters \(\alpha\) and \(\beta\) should have values within the interval [0, 1], meaning that the segments intersect. Even though the composition on a stage is not linearly dependent on the reflux ratio, a linear interpolation gives a good approximation if the reflux ratio intervals are close enough. Alternatively, a root search algorithm can be applied to find the reboil ratio giving a composition \(X_{int}\) at stage \(NR\). To obtain the number of middle stages \(NMS_{int}\) we use linear interpolation between the two consecutive stages \(NMS_C\) and \(NMS_D\). Using the operating lines for the middle section (Eqs. 5.9 and 5.10), only an integer number of stages can be used. However, even though a fractional number of stages will result from the linear interpolation, this offers a good initialisation for rigorous simulation, as will be shown in the case studies.

For other types of configurations, intersections between segments on SCLs, middle CPs or between two adjacent non-reactive interface points are checked (as presented in Table 5.4). Similarly, the design details at intersection point are estimated using linear interpolation (Eqs. 5.20 to 5.27):
1) Segments from SCLs

\[ R_{\text{int}} = R_A + \alpha (R_B - R_A) \]  \hspace{1cm} (5.20)

\[ S_{\text{int}} = S_C + \beta (S_D - S_C) \]  \hspace{1cm} (5.21)

2) Segments from middle CPs

\[ NR_{\text{int}} = NR_A + \beta (NR_B - NR_A) \]  \hspace{1cm} (5.22)

\[ NS_{\text{int}} = NS_C + \beta (NS_D - NS_C) \]  \hspace{1cm} (5.23)

3) Segments between two adjacent points of intersection of non-reactive SCLs with the reactive surface

\[ R_{\text{int}} = R_A + \alpha (R_B - R_A) \]  \hspace{1cm} (5.24)

\[ NR_{\text{int}} = NR_A + \beta (NR_B - NR_A) \]  \hspace{1cm} (5.25)

\[ S_{\text{int}} = S_C + \beta (S_D - S_C) \]  \hspace{1cm} (5.26)

\[ NS_{\text{int}} = NS_C + \beta (NS_D - NS_C) \]  \hspace{1cm} (5.27)

Using the information available from the intersection, the design details for various double-feed column configurations can then be estimated (Table 5.5). For each feasible design found, based on the design details resulting from the design procedure, the remaining parameters can then be estimated: feed condition, condenser and reboiler duties, column diameter and column total cost.

Feed condition is calculated using an overall energy balance (Appendix B.5). The condenser and reboiler duties are direct functions of reflux and reboil ratios (Appendix B), and they can be easily calculated from an energy balance around the condenser or reboiler. Based on the information obtained, the utility cost can be calculated, as can be the capital cost of the heat exchangers. The capital cost of the column will take into account different prices for reactive and non-reactive stages (Appendix F). Thus, we can rank the feasible designs to obtain
the best few designs with respect to the parameters above: number of stages, energy requirement or total cost.

Table 5.5 Design details for double-feed configurations shown in Figure 5.3.

<table>
<thead>
<tr>
<th>Rectifying section</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Configuration type</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Type I</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(L)</td>
<td>$R_{int}$</td>
<td>NR-1</td>
<td>-</td>
</tr>
<tr>
<td>(U)</td>
<td>$R_{intersect(NR_{non-R})}$</td>
<td>NR$_{non-R}$</td>
<td>NMR$_{int-1}$ (*)</td>
</tr>
<tr>
<td>Type II</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(L)</td>
<td>$R_{int}$</td>
<td>NR$_{int}$</td>
<td>-</td>
</tr>
<tr>
<td>(U)</td>
<td>$R_{intersect(NR_{non-R})}$</td>
<td>NR$_{non-R}$</td>
<td>NMR$_{int}$ (*)</td>
</tr>
<tr>
<td>Type III</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(L)</td>
<td>$R_{intersect(NR_{non-R})}$</td>
<td>NR$_{non-R}$</td>
<td>NMR$_{int-1}$ (***)</td>
</tr>
<tr>
<td>(U)</td>
<td>$R_{intersect(NR_{non-R})}$</td>
<td>NR$_{non-R}$</td>
<td>NMR$_{int-1}$ (***)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Stripping section</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Configuration type</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Type I</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(L)</td>
<td>$S_{intersect(NS_{non-R})}$</td>
<td>NS$_{non-R}$</td>
<td>NMS$_{int}$ (*)</td>
</tr>
<tr>
<td>(U)</td>
<td>$S_{int}$</td>
<td>NS</td>
<td>-</td>
</tr>
<tr>
<td>Type II</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(L)</td>
<td>$S_{intersect(NS_{non-R})}$</td>
<td>NS$_{non-R}$</td>
<td>NMS$_{int}$ (*)</td>
</tr>
<tr>
<td>(U)</td>
<td>$S_{int}$</td>
<td>NS</td>
<td>-</td>
</tr>
<tr>
<td>Type III</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(L)</td>
<td>$S_{intersect(NS_{non-R})}$</td>
<td>NS$_{non-R}$</td>
<td>NMS$_{int}$ (*)</td>
</tr>
<tr>
<td>(U)</td>
<td>$S_{intersect(NS_{non-R})}$</td>
<td>NS$_{non-R}$</td>
<td>NMS$_{int}$ (*)</td>
</tr>
</tbody>
</table>

(*) Middle composition profiles calculated from specified feed stage  
(**) Middle composition profiles calculated from intersections of non-reactive SCLs with the reactive surface  
$NR_{non-R}$ or $NS_{non-R}$ – No. of stages in the non-reactive rectifying or stripping section  
$R_{intersect(NR_{non-R})}$ – Specific reflux ratio at intersection of non-reactive stage $NR_{non-R}$ with the reactive surface  
$S_{intersect(NS_{non-R})}$ – Specific reboil ratio at intersection of non-reactive stage $NS_{non-R}$ with the reactive surface

5.5.3. Synthesis and design procedure for double-feed reactive distillation columns

The previous sections described the conceptual design methodology for fully reactive and hybrid double-feed configurations. From the synthesis point of view it is important to decide not only between various designs within a specified
structure, but between various column structures as well, e.g. fully reactive vs. hybrid configurations. Therefore, the methodologies presented in this chapter are included in a more general framework, including both fully reactive and hybrid configurations. The general procedure for the design methodology is as follows:

1. Set two fully specified product compositions for the top and bottom products. Also, set reflux and reboil ratios ranges (to calculate SCLs), and the flowrate, composition and feed condition for the specified feed. For the second feed, set the flowrate and the reference component(s) composition(s) \( x_{i,\text{ref}} \). For the overall mass balance, in order to satisfy the number of degrees of freedom only one more parameter is needed, chosen from \( U, L \) and \( x_{f, i,\text{ref}} \).

2. Calculate the remaining variables (remaining feed compositions, \( D \) and \( B \) flowrates and the reaction extent in the column) from the overall mass balance (Eqs. 5.1 and 5.2).

3. Check whether the constant molar overflow assumption holds, for both reactive and non-reactive sections. If the assumption does not hold, use energy balances in the calculation of composition profiles.

4. Calculate reactive and non-reactive SCLs for both rectifying and stripping sections using the specified ranges for the reflux and reboil ratios.

5. Calculate intersections of non-reactive SCLs with the reactive surface for both rectifying and stripping section.

6. If any intersections are found in Step 5, calculate for each of them middle composition profiles. Two sets of middle composition profiles are calculated for each point: one set is calculated considering the interface stage a feed stage (for configuration Types I, II and III), and one set is calculated considering the interface stage not a feed stage (for configuration Type III). The initial points for the calculation of middle composition profiles are obtained from a mass and energy balance around the interface stage. If the interface stage is a feed stage, the
specified feed is included in the mass and energy balance at the interface.

7. Search for feasible designs for all types of configurations: fully reactive double-feed columns and all types of double-feed hybrid configurations.

8. Rank the feasible designs obtained based on total cost (or any other parameter e.g. number of stages, energy requirement)

9. Narrow the results to meet the constraints if necessary, e.g. feed condition, maximum number of stages, maximum total cost.

The design procedure can be easily automated, and offers a fast tool to generate various double-feed configurations (useful in the synthesis step) and to obtain feasible designs for reactive distillation columns. To generate feasible designs it will take less than 5 min for an ideal system and less than 30 min for a highly non-ideal system, using a PIII 1.5 GHz personal computer.

5.6. Case studies

5.6.1. Ideal system

The first case-study to illustrate the synthesis and design procedure for double-feed columns is the ideal system presented in Chapter 4 (Section 4.6.1). The specified product compositions can be obtained in a hybrid single-feed column, either with the top section reactive (configuration Types I(T) or II(T)) or with a reactive core (configuration Type V), as shown in Table 4.7. In this chapter we will investigate whether a double-feed configuration will achieve the specified reactive separation task more economically.

We have described in Section 4.6.1 the necessity of using a hybrid column for this system. C, a heavy product, is obtained at the bottom of the column. In Table 5.6 the top and bottom product compositions are listed, together with upper and lower feed compositions. Pure C is obtained as the bottom product,
and near pure inert D as top product. Because for the ideal system, component C is not located on the reactive surface, a non-reactive stripping section is needed in the column. C is obtained as the bottom product; therefore a hybrid top section reactive column is expected to be feasible. For hybrid columns with the top section reactive, the lower feed will be fully specified. For the upper feed, only the mole fraction of the reference component (C) and of component A are specified, together with upper feed flowrate. The remaining specifications – the remaining feed compositions and the feed condition – will be calculated from the overall mass and energy balances (Appendix B.2). Product compositions were chosen to be the same as for single-feed columns. Table 5.7 lists the specifications necessary to calculate stage composition lines and composition profiles for double-feed columns. The constant molar overflow assumption is valid for this system, as has been discussed in Section 4.6.1 (Figure 4.17).

Table 5.6 Products and feed compositions for the ideal example

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Stoichiom.</th>
<th>( T_B ) 5 bar</th>
<th>Distillate</th>
<th>Bottoms</th>
<th>Upper Feed</th>
<th>Lower Feed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( v )</td>
<td>( T_B )</td>
<td>( X_D )</td>
<td>( x_D )</td>
<td>( X_B )</td>
<td>( x_B )</td>
</tr>
<tr>
<td></td>
<td>([\text{-}])</td>
<td>([\degree C])</td>
<td>([\text{transf. mole fr.}])</td>
<td>([\text{transf. mole fr.}])</td>
<td>([\text{transf. mole fr.}])</td>
<td>([\text{transf. mole fr.}])</td>
</tr>
<tr>
<td>A</td>
<td>-1</td>
<td>1.7</td>
<td>0.003</td>
<td>0.003(^#)</td>
<td>0.4992</td>
<td>1.E-07(^#)</td>
</tr>
<tr>
<td>B</td>
<td>-1</td>
<td>50.3</td>
<td>0.047</td>
<td>0.047(^#)</td>
<td>0.5003</td>
<td>0.002(^#)</td>
</tr>
<tr>
<td>C</td>
<td>1</td>
<td>156.9</td>
<td>0</td>
<td>1.E-5(^#)</td>
<td>0.0</td>
<td>0.997(^#)</td>
</tr>
<tr>
<td>D</td>
<td>0</td>
<td>37.9</td>
<td>0.95</td>
<td>0.95(^#)</td>
<td>0.0005</td>
<td>0.001(^#)</td>
</tr>
</tbody>
</table>

\(^\#\) specified values

Table 5.7 Specifications for generating stage composition lines

<table>
<thead>
<tr>
<th>Distillate flowrate</th>
<th>Bottoms flowrate</th>
<th>Upper Feed flowrate</th>
<th>Lower Feed flowrate</th>
<th>Upper Feed quality</th>
<th>Lower Feed quality</th>
<th>Reflux ratio range</th>
<th>Reboil ratio range</th>
<th>Maximum number of stages in each section</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D ) ([\text{kmol/h}])</td>
<td>( B ) ([\text{kmol/h}])</td>
<td>( F_U ) ([\text{kmol/h}])</td>
<td>( F_L ) ([\text{kmol/h}])</td>
<td>( q_{FU} )</td>
<td>( q_{FL} )</td>
<td>( r )</td>
<td>( s )</td>
<td>( m, n, p )</td>
</tr>
<tr>
<td>36.12</td>
<td>31.99</td>
<td>68</td>
<td>32</td>
<td>Eq. B.104</td>
<td>1</td>
<td>0.2 – 20</td>
<td>0.2 – 20</td>
<td>30</td>
</tr>
</tbody>
</table>
Figure 5.8 Rectifying reactive SCLs and middle composition profiles calculated from the lower feed stage for the ideal system $A + B ⇔ C$ (with inert $D$); $K_{eq} = 20$.

Table 5.8 First 10 feasible double-feed column designs obtained for the ideal system $A + B ⇔ C$ (inert $D$), listed in order of increasing total cost.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>III(L)</td>
<td>2</td>
<td>10.5</td>
<td>1.8</td>
<td>7</td>
<td>21.3</td>
<td>3.7</td>
<td>7.5</td>
<td>1.27</td>
<td>866</td>
<td>1872</td>
<td>0.497</td>
</tr>
<tr>
<td>2</td>
<td>I(L)</td>
<td>12</td>
<td>-</td>
<td>1.6</td>
<td>7</td>
<td>20.6</td>
<td>3.9</td>
<td>7.5</td>
<td>1.17</td>
<td>902</td>
<td>1872</td>
<td>0.498</td>
</tr>
<tr>
<td>3</td>
<td>I(L)</td>
<td>11</td>
<td>-</td>
<td>1.8</td>
<td>7</td>
<td>19.8</td>
<td>4.5</td>
<td>7.5</td>
<td>0.86</td>
<td>1011</td>
<td>1872</td>
<td>0.521</td>
</tr>
<tr>
<td>4</td>
<td>I(L)</td>
<td>10</td>
<td>-</td>
<td>2.0</td>
<td>7</td>
<td>19.0</td>
<td>5.7</td>
<td>7.5</td>
<td>0.27</td>
<td>1224</td>
<td>1872</td>
<td>0.566</td>
</tr>
<tr>
<td>5</td>
<td>I(L)</td>
<td>19</td>
<td>-</td>
<td>1.1</td>
<td>7</td>
<td>27.1</td>
<td>2.3</td>
<td>7.5</td>
<td>2.01</td>
<td>598</td>
<td>1872</td>
<td>0.596</td>
</tr>
<tr>
<td>6</td>
<td>I(L)</td>
<td>18</td>
<td>-</td>
<td>1.2</td>
<td>7</td>
<td>26.2</td>
<td>2.4</td>
<td>7.5</td>
<td>1.95</td>
<td>622</td>
<td>1872</td>
<td>0.601</td>
</tr>
<tr>
<td>7</td>
<td>I(L)</td>
<td>17</td>
<td>-</td>
<td>1.4</td>
<td>7</td>
<td>25.4</td>
<td>2.6</td>
<td>7.5</td>
<td>1.86</td>
<td>653</td>
<td>1872</td>
<td>0.608</td>
</tr>
<tr>
<td>8</td>
<td>I(L)</td>
<td>16</td>
<td>-</td>
<td>1.5</td>
<td>7</td>
<td>24.5</td>
<td>2.8</td>
<td>7.5</td>
<td>1.72</td>
<td>701</td>
<td>1872</td>
<td>0.618</td>
</tr>
<tr>
<td>9</td>
<td>I(L)</td>
<td>15</td>
<td>-</td>
<td>1.4</td>
<td>7</td>
<td>23.4</td>
<td>3.1</td>
<td>7.5</td>
<td>1.59</td>
<td>749</td>
<td>1872</td>
<td>0.628</td>
</tr>
<tr>
<td>10</td>
<td>I(L)</td>
<td>14</td>
<td>-</td>
<td>1.4</td>
<td>7</td>
<td>22.4</td>
<td>3.3</td>
<td>7.5</td>
<td>1.48</td>
<td>789</td>
<td>1872</td>
<td>0.637</td>
</tr>
</tbody>
</table>
In Figure 5.8, the rectifying SCLs and the middle composition profiles calculated from the lower feed stage are shown. For this system, both top section reactive and reactive core configurations are possible. Table 5.8 lists the design details for the best 10 double-feed column designs, based on total annualised cost. Compared to single-feed configurations (Table 4.7), the double-feed configurations have a lower cost, since fewer reactive stages are required.

For double-feed hybrid configurations with a reactive top section, the feed stages are included in the middle stripping section. The upper feed stage will be located at the uppermost middle stripping stage, and the lower feed at the lowest middle stripping stage. As can be observed in Table 5.8, some of the designs have only one or two middle stages. In the case of 2 middle stripping stages, the feeds will be located on adjacent stages (as for the middle reactive core configuration in Figure 5.9b). For configurations which have 1 middle stripping stage, both feeds are located on the same stage, and this is the same as a single-feed configuration (for example, Design 5 in Table 5.8).

![Figure 5.9](image)

**Figure 5.9** (a) Composition profiles and (b) Design details for a reactive core configuration Type III(L)
To verify the results obtained from the design procedure, a rigorous simulation using Hysys v2.4 was performed for the reactive core design in Figure 5.9 (Design 1 in Table 5.8). The column features 2 non-reactive rectifying stages (including the condenser), 7 stripping stages (including the reboiler) and a reactive core with 13 stages. A reflux ratio of 3.7 and a reboil ratio of 7.5 were specified for the rigorous simulation. The feed condition is 1.27, corresponding to an upper feed (mixture of B and D) to subcooled to approx. 5 °C. The product compositions obtained from the rigorous simulation are in very good agreement with the conceptual design specifications (Table 5.9).

<table>
<thead>
<tr>
<th>Component</th>
<th>Simulation results</th>
<th>Conceptual design specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0(^#) 1 0.0002 3.1E-09 0(^#) 1 # 0.003 # 1.E-07#</td>
<td>0(^#) 0 # 0.003 # 1.E-07#</td>
</tr>
<tr>
<td>B</td>
<td>0.4949# 0 0.0448 0.0015 0.4949 0# 0.047 # 0.002 #</td>
<td>0.4949# 0 # 0.047 # 0.002 #</td>
</tr>
<tr>
<td>C</td>
<td>0# 0 8.4E-11 0.9982 0# 0 # 1.E-5# 0.997#</td>
<td>0# 0 # 1.E-5# 0.997#</td>
</tr>
<tr>
<td>D</td>
<td>0.5051# 0 0.9550 0.0002 0.5051 0# 0.95# 0.001#</td>
<td>0.5051# 0 # 0.95# 0.001#</td>
</tr>
</tbody>
</table>

\(^\#\) Specified values

However, a feed temperature of 5 °C is not very practical. Double-feed columns have one extra degree of freedom, compared to single-feed columns, chosen between the ratios \(E, U\) and \(L\) (Section 5.3). For the case study discussed above, the ratio \(E\) was fixed (by setting the flowrate for both feeds). This ratio influences, through the overall mass balance, the ratios \(U\) and \(L\), and ultimately, through the overall energy balance, the upper feed condition. We can adjust the feed condition of the upper feed by adjusting the upper feed flowrate. This is similar to a change in the feed composition for a single-feed column, as analysed in Section 4.6.1. Table 5.10 and Table 5.11 show the results obtained for the reactive core design, for various upper feed flowrates. It is important to note that, as shown in Table 5.10, the column design (number of stages in each section) does not change with the change in the upper feed flowrate. This result is not surprising, if we analyse the impact of the change in the upper feed flowrate on the number of stages in each section of the reactive core column:
• The numbers of stages in the non-reactive rectifying and stripping sections (Sections I and IV of the reactive core column in Figure 5.9b) are obtained from the intersections of non-reactive SCLs with the reactive surface. Constant molar overflow proved to be a valid assumption for this system, therefore the non-reactive SCLs are functions of product compositions and reflux and reboil ratios only (Appendix B). As the product compositions and the reflux and reboil ratios do not change during the analysis, the number of stages in each of these two sections is also constant (Table 5.11).

• The composition profiles for Section II of the column in Figure 5.9b are calculated from the intersections of non-reactive rectifying SCLs with the reactive surface. A mass and energy balance around the interface stage to obtain initial points for the calculation of middle composition profiles is used. As the non-reactive rectifying SCLs for Section I are not affected, the intersections points are the same, therefore the only influence in the middle composition profiles is caused by the mass and energy balance at the interface stage. The distillate flowrate change (Table 5.11); for a fixed reflux ratio this affects the internal liquid and vapour flows at the interface. Therefore, a change in the number of stages in Section II is expected. However, for ideal systems the energy balance at the interface stage has shown very little or no effect on composition profiles, leading in this case to no change in the number of stages in Section II (Table 5.11).

• The composition profiles for the middle stripping section (Section III in Figure 5.9b) are calculated from the intersections of non-reactive stripping SCLs with the reactive surface. In this case a mass and energy balance around the interface stage containing the lower feed is used to obtain initial points for the calculation of middle composition profiles. As shown in Table 5.10, the bottom flowrate changes very little with the change in the upper feed flowrate, therefore the number of stages in Section III is practically constant (Table 5.11).
Overall, the design details – number of stages and reflux and reboil ratios – are almost the same for all cases. The upper feed flowrate will significantly affect only the product flowrates and the upper feed composition, through the overall mass balance, and the upper feed condition through the overall heat balance. As shown in Table 5.11, a feed condition of saturated liquid can be achieved for an upper feed flowrate of 72 kmol/h.

Table 5.10 Influence of upper feed flowrate on product flowrates and upper feed composition.

<table>
<thead>
<tr>
<th>$F_U$</th>
<th>$F_L$</th>
<th>$D$</th>
<th>$B$</th>
<th>$E$</th>
<th>$U$</th>
<th>$L$</th>
<th>$x_{FU}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[kmol/h]</td>
<td>[kmol/h]</td>
<td>[kmol/h]</td>
<td>[-]</td>
<td>[-]</td>
<td>[-]</td>
<td>$x_{FU,B}$</td>
<td>$x_{FU,D}$</td>
</tr>
<tr>
<td>60</td>
<td>32</td>
<td>28.1</td>
<td>32.01</td>
<td>1.875</td>
<td>0.4678</td>
<td>1.0003</td>
<td>0.5550</td>
</tr>
<tr>
<td>65</td>
<td>32</td>
<td>33.1</td>
<td>32</td>
<td>2.031</td>
<td>0.5092</td>
<td>1.0000</td>
<td>0.5157</td>
</tr>
<tr>
<td>70</td>
<td>32</td>
<td>38.1</td>
<td>31.98</td>
<td>2.188</td>
<td>0.5447</td>
<td>0.9994</td>
<td>0.4820</td>
</tr>
<tr>
<td>72</td>
<td>32</td>
<td>40.1</td>
<td>31.98</td>
<td>2.250</td>
<td>0.5575</td>
<td>0.9994</td>
<td>0.4699</td>
</tr>
<tr>
<td>75</td>
<td>32</td>
<td>28.1</td>
<td>32.01</td>
<td>2.344</td>
<td>0.5754</td>
<td>0.9991</td>
<td>0.4528</td>
</tr>
</tbody>
</table>

Table 5.11 Influence of upper feed flowrate on design details and upper feed condition.

<table>
<thead>
<tr>
<th>$F_U$</th>
<th>$NR$ (Section I)</th>
<th>$NMR$ (Section II)</th>
<th>$NMS$ (Section III)</th>
<th>$NS$ (Section IV)</th>
<th>$N_{TOT}$</th>
<th>Reflux ratio</th>
<th>Reboil ratio</th>
<th>$q_{FU}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[kmol/s]</td>
<td>[-]</td>
<td>[-]</td>
<td>[-]</td>
<td>[-]</td>
<td>[-]</td>
<td>[-]</td>
<td>[-]</td>
<td>[-]</td>
</tr>
<tr>
<td>60</td>
<td>3</td>
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<td>1.80</td>
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<td>3.71</td>
<td>7.52</td>
<td>1.49</td>
</tr>
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<td>11.56</td>
<td>1.79</td>
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<td>3.71</td>
<td>7.52</td>
<td>1.13</td>
</tr>
<tr>
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<td>3</td>
<td>11.56</td>
<td>1.79</td>
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<td>3.71</td>
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<td>24.35</td>
<td>3.71</td>
<td>7.52</td>
<td>0.82</td>
</tr>
</tbody>
</table>

Generally, double-feed columns offer not only lower cost designs, but also more flexibility, which is very useful, especially in retrofit studies. For example, if one wants to re-use a standard existing column as a reactive column, this can be achieved by replacing the internals with catalytic packing, and determining which operating conditions will lead to a desired product. If the conceptual design methodology will lead to columns with similar numbers of stages, but with infeasible operating parameters (e.g. feed condition), these parameters can
be adjusted by adjusting the ratio between the two feeds, $E$, as illustrated in this case study.

### 5.6.2. Methyl-acetate production

The second example to illustrate the procedure for double-feed reactive columns is the methyl-acetate formation. Methyl-acetate is obtained from a reaction between methanol and acetic-acid, according to Eq. 5.28. The reactive equilibrium constant data was taken from Chen et al. (2000) (Appendix E.4). For the VLE calculations, a HYSYS v2.4 real time interface was used, with the NRTL model for the liquid phase and the virial model for the vapour phase (to model the dimerisation of acetic-acid) (HYSYS v2.4 Users Guide).

\[
\text{Methanol} + \text{Acetic Acid} \rightleftharpoons \text{Methyl Acetate} + \text{Water} \\
(\text{MeOH}) \quad (\text{AAC}) \quad (\text{MeAc}) \quad (W)
\]  

(5.28)

The system is a non-ideal system, with an unstable minimum-boiling non-reactive azeotrope (53.8 °C) at 31.7 mol% methanol and 68.2 mol% methyl-acetate, and a saddle reactive azeotrope (98.9 °C) at 4.2 mol% acetic acid and 95.8 mole% water. A second non-reactive azeotrope, predicted by the model at 92.5 mole% methyl-acetate and 7.4 mole% water, is not present in the reactive mixture. Figure 5.10 shows the residue curve map for the reactive system at 1 bar, in transformed variables. A distillation boundary is formed between the non-reactive and reactive azeotropes, which makes impossible the separation of pure methyl-acetate and pure water in a single-feed reactive column. Even if we choose a purity for water near the saddle point, the separation in a single-feed column is very hard to achieve, as the operating leaves for the stripping and the rectifying section will be very far from each other. However, by using a double-feed column, the middle section profiles will be able to connect the two operating leaves, even across the distillation boundary, making the separation possible (Thong, 2002).
A purity of 95 mole% methyl-acetate and 95 mole% water was proposed for the distillate and bottom products, respectively (Table 5.12). The specifications needed for generating SCLs are listed in Table 5.13. The proposed product compositions cannot be obtained from a single-feed column, as they lead to operating leaves situated in different distillation regions (Figure 5.12). It is interesting to note that, even though the bottom product composition was chosen near the reactive saddle azeotrope, in Region I, all stripping SCLs are located in Region II (Figure 5.12). This is because the azeotrope appears only in reactive systems and the reboiler is considered to be non-reactive, therefore a bubble point calculation for the bottom product composition: 5 mole% acetic-
acid and 95% water, will lead to a vapour composition situated in Region II: 3.6 mole% acetic-acid and 96.4 mole% water. Considering a reboil ratio between 0.2 and 20 (Table 5.13), from a mass balance around the reboiler, the composition of the liquid leaving the first bottom reactive stage will be between 3.6 and 4.06 mole% water (96.4 and 95.94 mole% acetic-acid, respectively), situated in Region II. This will lead to SCLs for the stripping section situated in Region II. Therefore, the proposed product compositions are not feasible for a single-feed column, as they lead to SCLs located in different distillation regions. In this case study we will investigate the possibility of using a double-feed configuration to obtain the proposed products.

Table 5.13 Specifications for generating stage composition lines

<table>
<thead>
<tr>
<th>Distillate flowrate</th>
<th>Bottoms flowrate</th>
<th>Upper Feed flowrate</th>
<th>Lower Feed flowrate</th>
<th>Upper Feed quality</th>
<th>Lower Feed quality</th>
<th>Reflux ratio range</th>
<th>Reboil ratio range</th>
<th>Rectif. stages range</th>
<th>Stripp. stages range</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>B</td>
<td>$F_U$</td>
<td>$F_L$</td>
<td>$q_{FU}$</td>
<td>$q_{FL}$</td>
<td>$r$</td>
<td>$s$</td>
<td>$n$</td>
<td>$m$</td>
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<tr>
<td>[kmol/h]</td>
<td>[kmol/h]</td>
<td>[kmol/h]</td>
<td>[kmol/h]</td>
<td>[-]</td>
<td>[-]</td>
<td>[-]</td>
<td>[-]</td>
<td>[-]</td>
<td>[-]</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>Eq. B.104</td>
<td>1</td>
<td>0.2 – 20</td>
<td>0.2 – 20</td>
<td>1 – 30</td>
<td>1 - 30</td>
</tr>
</tbody>
</table>

Figure 5.11 Influence of energy balances on reactive composition profiles for methyl acetate system. (a) Rectifying section composition profiles for $R = 2.0$; (b) Stripping section composition profiles for $S = 2.0$
The first step in the design procedure is to check whether the constant molar overflow assumption holds. As shown in Figure 5.11a, the constant molar overflow assumption holds for the rectifying section; for the stripping section, the influence of energy balances on composition profiles is more accentuated after stage 12, when a sharp change in the relative volatilities occurs. However, in this case study, the lower feed stage was chosen to be the 11th stripping stage numbered from the bottom, and as we can see from Figure 5.11b, we can safely consider a constant molar overflow for the stripping section, too.

Figure 5.12 Rectifying and middle SCLs for methyl-acetate system. Specified lower feed stage is 11.

Figure 5.12 represents the SCLs for the rectifying and stripping sections, together with the middle SCLs calculated starting from lower feed stage. No intersections of the non-reactive SCLs with the reactive surface were found, so for the proposed product compositions, only fully reactive double-feed columns are possible. As it can be observed, for the proposed bottom product composition, all stripping SCLs are located in Region II, but choosing an appropriate lower feed stage (11 in this case) will ensure that all middle SCLs will lie in Region I, making the proposed separation possible. By intersecting the
middle SCLs with the rectifying SCLs, feasible designs for fully reactive double-feed reactive columns can be obtained. Table 4.16 lists the first 10 designs matching feed condition between 0 and 1.5, that is between saturated vapour and a liquid (acetic acid) subcooled to approx. 30 °C.

Table 5.14 Best 10 designs obtained for methyl-acetate system for \( q = [0;1.5] \)

<table>
<thead>
<tr>
<th></th>
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<td>1</td>
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<td>29</td>
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<td>46</td>
<td>1.74</td>
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<td>3278</td>
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<td>19</td>
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<td>11</td>
<td>36</td>
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<td>3.21</td>
<td>0.30</td>
<td>3798</td>
<td>3458</td>
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</tr>
<tr>
<td>8</td>
<td>F</td>
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<tr>
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<td>15</td>
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<td>11</td>
<td>34</td>
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<td>5.11</td>
<td>0.75</td>
<td>5552</td>
<td>5509</td>
<td>2.63</td>
</tr>
</tbody>
</table>

*F – fully reactive column*

Table 5.15 Product compositions obtained by simulation, for the best design based on the total annualised cost (Design 1 in Table 5.14)

<table>
<thead>
<tr>
<th>Component</th>
<th>Simulation results</th>
<th>Conceptual design specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( x_{FU} )</td>
<td>( x_{FL} )</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.0*</td>
<td>1.0*</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>1.0*</td>
<td>0.0*</td>
</tr>
<tr>
<td>M-Acetate</td>
<td>0.0*</td>
<td>0.0*</td>
</tr>
<tr>
<td>Water</td>
<td>0.0*</td>
<td>0.0*</td>
</tr>
</tbody>
</table>

*Specified values*

The best design based on total cost features 46 stages, with 29 rectifying stages (including the condenser), 6 middle stages and 11 stripping stages, (including the reboiler). A reflux ratio of 1.74 and a reboil ratio of 2.55 were obtained from the design procedure. The thermal condition of the upper feed (acetic acid) is 1.45, corresponding to a temperature of the feed of 39 °C. The
above design and operating parameters were used as specifications for a rigorous simulation, using Hysys v2.4. As can be seen in Table 5.15, the product compositions obtained from simulation are in good agreement with the compositions specified for conceptual design.

![Graph showing multiplicity in a reactive distillation column.](image)

**Figure 5.13** Multiplicity in a reactive distillation column. Two sets of operating conditions leading to the same product compositions, with the same column configuration.

The conceptual design methodology presented in this work can also identify the presence of multiple steady states for a system. Multiplicity is a very common phenomenon in reactive distillation, as discussed widely in the open literature (Jacobs and Krishna, 1993; Nijhuit et al., 1993; Guttinger and Morari, 1999a and 1999b; Blagov et al., 2000). Multiplicity appears in reactive distillation due to non-idealities of the system and/or non-linearity of the kinetic model. For non-ideal systems, the stage composition lines are more curved compared to ideal systems, where they are quasi-linear. Sometimes, the projection of an operation leaf in transformed variables looks folded, with the pinch curve crossing the distillation line (Groemping, 2002). Because of the curvature of the stage composition lines, there are situations when they intersect more than once, as can be observed in Figure 5.13. Therefore, for the same column configuration
and same product compositions, different sets of operating conditions can be found to be feasible. For example, for a column featuring 28 rectifying stages, 6 middle stages and 11 stripping stages, the proposed product compositions can be obtained using either a reflux ratio of 1.48 and a reboil ratio of 3.67 with an upper feed condition of -0.3 (superheated vapour), or using a reflux ratio of 1.85 and a reboil ratio of 2.5, with a subcooled upper feed \( q_{FU} = 1.2 \) (Design 2 in Table 4.16). The possibility of identifying input multiplicities can be useful in retrofit studies, if there are constraints on internal flows: we can choose, for example, a lower reflux or reboil ratio, with some penalty in the feed condition.

5.7. Conclusions

In this chapter, the graphical design methodology developed for single-feed reactive columns and systems with two degrees of freedom has been extended to accommodate double-feed columns. Both fully reactive and hybrid configurations have been discussed.

As presented in the case studies, double-feed configurations offer a higher flexibility in column design, on the one hand by extending the feasible domain (by crossing distillation boundaries, as shown in methyl-acetate example), and on the other by the possibility of manipulating the extra degree of freedom to obtain more practical results. A better reaction distribution can be obtained in some cases, leading to a lower column cost, compared to single-feed columns. Overall, investigating double-feed configurations for reactive distillation is a very important step in reactive column design.

For a proposed pair of products, the new methodology developed can be applied to assess feasibility and to design double-feed columns. Multiple configurations can be obtained, either fully reactive, top or bottom section reactive or reactive-core configurations. It is worth mentioning here that fully reactive columns have an extra degree of freedom compared to hybrid double-feed and single-feed columns: the location of the specified feed. The location of
the specified feed can be optimised to give the minimum number of stages in
the column (or minimum total cost). However, as pointed out by Levy (1986)
and Barbosa and Doherty (1988d), this is a very insensitive optimisation
problem, as by moving the feed stage location two or three stages away from
the optimal location, the total number of stages changes only by one. For
hybrid double-feed columns, because of the assumption that the specified feed
will be located at the interface between a reactive and a non-reactive section,
the actual location of the specified feed is known, resulting from the intersection
of non-reactive SCLs with the reactive surface.

The methodology proved to be a fast method to assess feasibility of double-
feed reactive distillation columns and to identify promising designs, even though
it is restricted by the graphical representation only to systems with two degrees
of freedom and equilibrium reactions. Both ideal and non-ideal systems can be
analysed, by including appropriate VLE models in the calculation of composition
profiles.

The methodology is easily automated and typically generates multiple designs.
For a more complete design methodology, single-feed configurations can be
implemented in the same framework, offering a much higher flexibility in
reactive distillation column design. A design engineer can obtain, using the
methodologies developed in Chapters 3 and 4, multiple designs of various types
of configurations, making easier the comparison between various design
options: hybrid vs. fully reactive columns, single- vs. double-feed configurations,
or even between different sets of operating parameters for the same column
configuration.

Overall, the methodologies developed in Chapters 3 and 4 fill a significant gap
in conceptual design of reactive systems. They offer a systematic tool for
synthesis and design of reactive distillation columns for systems with two
degrees of freedom and equilibrium reactions, which represents a very
important group of reactive systems.
6. CONCEPTUAL DESIGN OF KINETICALLY-CONTROLLED
REACTIVE DISTILLATION COLUMNS

6.1. Introduction

Previous chapters assumed that reactive equilibrium is achieved on every reactive stage in the column, but in real columns this is not always the case. Unless the reaction is very fast, or a very high holdup (or residence time) exists on column trays, reactive equilibrium cannot be achieved in a reactive column. Assuming reactive equilibrium will not provide a realistic prediction of column performance; for realistic prediction we need to incorporate kinetic models in reaction extent calculation. Kinetic models take into account the type of reaction (fast or slow), the holdup on each reactive stage (i.e. the amount of liquid or vapour on each stage, where reaction takes place) and also the residence time, influenced by the internal liquid and vapour flowrates.

This chapter will describe the influence of kinetically-controlled reactions on the synthesis and design of reactive distillation columns. The methods developed for equilibrium reactions will not be valid for kinetically-controlled reactions, as the liquid and vapour on a stage will be in thermodynamic equilibrium only, and not in chemical equilibrium. This will not restrict the composition profiles to lie on the reactive surface; therefore the transformed variables cannot be used for synthesis and design. Moreover, for kinetically-controlled reactive distillation, the feasibility condition of intersection of composition profiles is only a necessary, but not a sufficient condition. An additional feasibility criterion is needed to guarantee feasibility, namely that the sum of reaction extents for rectifying and stripping section at the intersection point must match the overall reaction extent from the overall mass balance. This will further limit the feasible region for a specified pair of product compositions. This aspect will be discussed in more detail in the following sections.
Overall, kinetically-controlled reactions introduce further restrictions to the already challenging problem of synthesis and conceptual design of reactive distillation columns. This chapter will try to solve some of the problems arising when accounting for reaction kinetics in reactive distillation modelling. A conceptual design methodology will be presented, that is able to assess the feasibility of a proposed pair of products and to obtain column designs for both ternary and quaternary mixtures. The method, extended from the methodologies developed in Chapters 4 and 5, will take into account the particularities of kinetically-controlled reactive distillation processes, and by adjusting some of the method’s representative steps will be able to overcome some of the challenges introduced by kinetically-controlled reactions.

6.2. Kinetically-controlled reactive distillation column design.

Previous work

Due to the challenges and difficulties arising from introducing kinetic models in the reactive column design, there are very few studies in the open literature for the design of kinetically-controlled reactive distillation columns. Optimisation methods, either MINLP (e.g. Ciric & Gu, 1994) or local optimisation methods (e.g. Pekkanen, 1995), can generally accommodate various types of kinetic model, multicomponent mixtures and complex column configurations. However, for the design of a single reactive distillation column, optimisation methods proved to be very time consuming; they are more appropriate for analysing a wide variety of structures and flowsheet alternatives than for column design.

For the conceptual design of a single reactive distillation column, there are very few studies available. Lee (2000) developed a methodology based on the visualisation of the lever rule, able to assess feasibility and obtain column designs for mixture containing up to four components. The main drawback of the method is that it is based on the specification of reaction extent at each stage. For kinetically-controlled reaction this assumption is more realistic than for equilibrium reactions, as we can adjust the amount of reaction taking place
on a particular stage by adjusting the holdup. However, in practice this is very
difficult to achieve. Moreover, the method is not systematic, several trials being
needed to obtain a feasible design.

Another approach for the conceptual design of a kinetically-controlled reactive
distillation column is based on the BVM (Buzad and Doherty, 1994 and 1995;
Okasinski and Doherty, 1998; Mahajani, 1996, 1999). In BVMs, feasible designs
are obtained by intersecting rectifying and stripping composition profiles for fully
specified product compositions and feed condition. For kinetically-controlled
reactive distillation, at each intersection point an additional constraint has to be
satisfied, i.e. the sum of the reaction extent in the rectifying section and the
reaction extent in the stripping section is equal to the total reaction extent
obtained from overall mass balance. Therefore, kinetically-controlled reactive
distillation is a highly constrained process and sometimes there are very few
designs satisfying the additional constraint. Moreover, because in kinetically-
controlled reactive systems the concept of transformed compositions can be
used only as a representation tool, but not as a design tool, it is very difficult to
address more than three components. Therefore, the literature available for the
conceptual design generally addresses ternary mixtures (Buzad and Doherty,
1994 and 1995; Okasinski and Doherty, 1998; Mahajani, 1996) with very few
attempts to extend the methodology to four components (Mahajani, 1999).
However, the extension is not very straightforward and requires iteration on
several parameters in order to satisfy the constraints and reach a solution.

BVMs are generally focused more on feasibility of the proposed products and
finding one design which satisfies the specifications, and not on column
synthesis and finding alternative configurations for a given separation task. For
kinetically-controlled reactive systems, available BVMs assume constant holdup
in the column and a fixed feed condition. This will further limit the solution
space, resulting in a highly iterative procedure to obtain feasible designs.
However, the method offers insights about the behaviour of kinetically-
controlled reactive systems and also offers a good basis for developing a
systematic and efficient method for column design. This chapter will present a methodology based on the BVM, which will be able to assess feasibility and obtain feasible designs for fully reactive and hybrid kinetically-controlled reactive distillation columns. The applicability of the method is restricted by the graphical representation to ternary and quaternary mixtures. However, this will represent an important contribution to the conceptual design of reactive distillation columns, as no systematic methods are available at the moment for the synthesis and design of kinetically-controlled columns, able to provide multiple designs of various configurations.

6.3. Implications and limitations of kinetically-controlled reactions in the design of reactive distillation columns

In kinetically-controlled reactive distillation, the reactive equilibrium is not achieved in the column, although it may be realistic to assume that thermodynamic vapour-liquid equilibrium is achieved on each tray. The departure from reactive equilibrium can be evaluated at each stage (Figure 6.1), given the internal flows, holdup and kinetic parameters of the reaction. For example, for a reaction $2A \rightarrow B + C$ (Okasinski and Doherty, 1998), the departure from the reactive equilibrium on a stage can be evaluated as the difference between the composition of the liquid (or the vapour if the reaction is in the vapour phase) leaving the stage (e.g. $x_M$, composition of point M in Figure 6.1) and the composition of the same stream if reactive equilibrium would be achieved on that tray (e.g. $x_N$, the composition of point N in Figure 6.1). Using a vectorial representation of the reactive process, as described in Hauan et al. (2000a), the composition change from $x_M$ to $x_N$, can be represented by a vector with origin in $M$, pointing towards the reaction difference point $\delta_R$ (Chapter 3). The reaction difference point (Eq. 6.1), is an important parameter in reactive systems; it acts as a focus for chemical reaction vectors (Hauan et al., 2000a, b). A particular case is when there is no change in the number of moles due to reaction, leading to a difference point located at infinity. In this case the
reaction vectors will be parallel to the vector of stoichiometric coefficients. The case analysed in Figure 6.1 is such a case; the reaction vectors will be parallel to the vector of stoichiometric coefficients \( \mathbf{v}^T = [-2, 1, 1] \).

\[
\delta_R = \sum_i \mathbf{v}_i \mathbf{v}^T
\]  

(6.1)

**Figure 6.1 Evaluation of the departure from equilibrium for a kinetically-controlled reactive system. System \( 2A \rightarrow B + C \) (Okasinski and Doherty, 1998)**

The composition of a reactive tray (e.g. \( x_M \)) depends on reaction kinetics, internal flows and tray holdup, which all interact to result in a specific reaction extent (Eq. 6.2).

\[
\xi_{j,n} = \frac{1}{n_{ref,j}} \cdot r_{ref,j,n} \cdot H_n
\]  

(6.2)

where:

- \( \xi_{j,n} \) - reaction extent of reaction \( j \) on stage \( n \);

- \( r_{ref,j,n} \) - rate of reaction \( j \) on stage \( n \) based on a reference component
\( \nu_{\text{ref}, j} \) - stoichiometric coefficient of the reference component

\( H_n \) - holdup on stage \( n \) (liquid or vapour holdup, depending in which phase the reaction takes place)

The difference compared to equilibrium reactions resides in the fact that for kinetically-controlled reactions, the reaction extent is a function not only of tray composition and temperature (through the reaction rate) but also of tray holdup. For equilibrium reactions, the reaction extent is calculated from a mass balance around the stage, under the condition that both thermodynamic and chemical equilibrium are achieved. Therefore, the reaction extent will be a function only of tray composition (in reactive and thermodynamic equilibrium) and temperature, but not of liquid holdup.

![Figure 6.2 Most common catalytic packings for reactive distillation. (a) KATAPAK-S (Sulzer); (b) Monolithic structures (Corning Inc.); (c) Multipak (Julius Montz Gmbh) (d) Internal layout for Multipak catalytic packing.](image)

For kinetically-controlled reaction there is one more design parameter than for equilibrium reactions, that is the liquid holdup (or vapour holdup if the reaction takes place in the vapour phase) on each tray. The reaction extent on each tray
could be controlled by controlling the amount of holdup. For homogeneous or autocatalytic reactions, standard trays are usually used as internals in the columns, and the liquid holdup can be adjusted by modifying geometrical parameters of the tray, such as the diameter of the column or the weir length or height. For heterogeneously catalysed reactions, special catalytic internals are usually used, having both separation and catalytic functions. The most common commercial catalytic packings are presented in Figure 6.2. For catalytic internals, the holdup depends on the internal geometry of the packing, such as diameter of catalyst particles, void fraction, corrugation angle, corrugation step and height (for internals based on corrugated sheets such as Katapak-S and Multipak) or any other geometric parameter of the packing. Liquid and vapour flows have also an influence on the holdup in a structured packing (Moritz and Hasse, 1999; van Hasselt et al., 1999). Therefore is very difficult to adjust the holdup internally.

For synthesis and design purposes, if constant internal flows are assumed in a column section, is more practical to assume a uniform holdup in that section (i.e. the same holdup on all stages in a section). In the case of non-constant internal flows (as it is usually the case in reactive distillation), the variation of the holdup with the internal flows can be considered, on the expense of computational time. However, a constant holdup is a good approximation for the synthesis and conceptual design steps. In this work, a constant holdup was considered in each reactive column section, but different holdups for different sections were allowed in order to extend the applicability of the design procedure.

The dependence of liquid or vapour holdup on internal flows, and hence on reflux and reboil ratios, introduce an extra limitation in the design of kinetically-controlled reactive distillation. However, for the synthesis and design step, it is more convenient to consider the holdup independent of reflux and reboil ratios. This assumption is realistic in the case of staged columns, where the holdup is controlled by the tray geometry. For packed columns, the results obtained from
the conceptual design procedure are only an approximation of the real behaviour; they can be approximately converted for packed column by using the concept of HETP. Further simulations and CFD calculations are needed for a realistic representation of packed reactive distillation columns.

Reflux and reboil ratios, as well as the holdup, affect the column performance by affecting the residence time. For a fixed holdup, very high reflux/reboil ratios will lead to a very short residence time and hence a very small reaction extent; the composition profiles will be similar to the profiles for simple distillation. If a very small reflux/reboil ratio is used in the column, this will lead to a very high residence time, allowing the reaction to approach equilibrium. The profiles in this case will be similar to the profiles obtained for equilibrium reactions. In Figure 6.3 the composition profiles for various reflux ratios are shown, obtained from a rigorous simulation using Hysys v2.4 (Figure 6.3a) and using BVM (Figure 6.3b). A column with 40 stages was used for the rigorous simulation (feed stage 15), and the product purities were specified. The BVM profiles were calculated from a fully specified top product composition. The same trend is observed in both cases, the composition profiles moving away from the equilibrium line with the increase in the reflux ratio.

Let us analyse now the influence of holdup on the composition profiles, for a fixed reflux or reboil ratio. At a very high holdup the residence time will be very high; therefore the reaction will approach equilibrium. For a very low holdup, the residence time will become very short, and practically no reaction will take place in the column. The profiles in this case will be similar to the profiles obtained in a non-reactive column. Figure 6.4 presents the composition profiles obtained for a fixed reflux ratio \( R = 5 \) and various holdup values. As can be observed in Figure 6.4 (a) the rigorous simulation results confirm the expected trend. The profiles for high holdup approach equilibrium, even though the product composition obtained in each case is different (as a fixed number of stages \( N=40 \) were used for the column and the reflux and reboil ratio were constant).
Figure 6.3 Influence of reflux ratio on composition profiles for kinetically-controlled reactive distillation. (a) Profiles resulted from rigorous simulation. (b) Rectifying profiles, calculated using BVM. System $2C \leftrightarrow A + B$. Kinetic data from Okasinski and Doherty (1998) (Appendix E5).

Figure 6.4 Influence of holdup on composition profiles for kinetically-controlled reactive distillation. (a) Profiles resulted from rigorous simulation. (b) Rectifying profiles, calculated using BVM. System $2C \leftrightarrow A + B$. Kinetic data from Okasinski and Doherty (1998) (Appendix E5).
For the BVM (Figure 6.4b), the composition profiles show a different trend. We can see that with the increase in holdup, the profiles move away from the equilibrium line. This behaviour is caused by the approach used in BVM, where the composition profiles are calculated from fixed product. Eq. 6.3 is used to obtain the composition of the vapour leaving stage \( n+1 \), and a dew point calculation to obtain the liquid composition \( x_{n+1} \) in VLE with \( y_{n+1} \) (Appendix B).

\[
y_{n+1} = \frac{L_n}{V_{n+1}} \cdot x_n + \left(1 - \frac{L_n}{V_{n+1}}\right) \cdot \left(x_D - \frac{V \cdot \xi_n}{D}\right)
\]  

(6.3)

Figure 6.5 shows the composition of the liquid leaving the rectifying reactive stage 2 (stage 1 is the condenser, assumed non-reactive), calculated for various holdups. No matter where the starting product composition is situated, on the left side of the reactive equilibrium curve (forward reaction), or on the right side (reverse reaction), the profiles always move away from the reactive equilibrium curve as holdup increases.

![Figure 6.5 Influence of holdup on composition profiles for the direct and reverse reaction. System 2C ↔ A + B. Kinetic data from Okasinski and Doherty (1998) (Appendix E5).](image)

Figure 6.5 Influence of holdup on composition profiles for the direct and reverse reaction. System 2C ↔ A + B. Kinetic data from Okasinski and Doherty (1998) (Appendix E5).
The above behaviour becomes much easier to understand if the interactions between the reaction and the separation are addressed through the use of difference points. For a reactive cascade (a succession of counter-current reactive stages), at stage $n$, the composition difference between the vapour stream entering from below and the liquid composition leaving the stage is equivalent to the composition of the difference point (Hauan et al., 2000b). This difference point for a reactive cascade is denoted, for a rectifying section, with $\delta_R'$. Geometrically, this means that for a rectifying stage, the compositions $x_n$, $y_{n+1}$ and $\delta_{R,n}'$ are all found on a straight line, with the relative length of the line segments given by the lever-arm rule. For a rectifying reactive cascade, the reactive difference point is given by (Hauan et al., 2000b):

$$\delta_{R,n}' = x_D - \frac{y \cdot \xi_n}{D}$$  \hspace{1cm} (6.4)

The value of the reaction difference point for the rectifying cascade is, for a given system, a function of reaction extent (Eq. 6.4), hence of liquid holdup and tray composition. For a fixed incoming liquid composition ($x_n$), the resulting vapour composition ($y_{n+1}$) will therefore depend only on the position of the reactive difference point for the rectifying cascade.

Figure 6.6 represents the vapour compositions for rectifying stage $n+1$ calculated using Eq. 6.3, for different values of holdup. The liquid compositions for stage $n+1$, in thermodynamic equilibrium with the vapours, are also represented. The reactive difference point for the rectifying cascade ($\delta_R'$) will be a point on a line going through $x_D$ towards the reaction difference point ($\delta_R$), defined by Eq. 6.1. For a fixed liquid composition $x_n$ and forward reaction (positive reaction extent $\xi_n$), an increase in the holdup will cause $\delta_R'$ to move away from the reactive equilibrium line (Figure 6.6). If the reaction extent is negative (reverse reaction), $\delta_R'$ will move in the opposite direction, again away from the reactive equilibrium line. This analysis explains why the composition profiles calculated using the BVM will have an opposite trend compared to the rigorous simulation, the profiles moving further away from the equilibrium curve.
as holdup increases. The analysis was illustrated for a rectifying section; but similar considerations apply for a stripping reactive section.

![Figure 6.6 Vapour and liquid compositions for a rectifying reactive cascade, calculated for different holdup values. System $2C \leftrightarrow A + B$. Kinetic data from Okasinski and Doherty (1998) (Appendix E5).](image)

The opposite trend of composition profiles calculated using the BVM compared to simulation results, does not prevent the method to be valid for feasibility analysis. An intersection of a rectifying with a stripping rectifying profile will still represent a feasible design, if the reaction extent constraint is satisfied. The feasibility conditions for a kinetically-controlled reactive distillation column will be discussed in detail in one of the following sections of this chapter.

Another important characteristic of kinetically-controlled reactive profiles, which can be easily identified based on the results in Figure 6.6, is that they are not confined to the feasible composition space, as are profiles for equilibrium
reactive columns. For example, in Figure 6.6, the vapour composition for stage $n+1$ ($y_{n+1}$) will be located in the feasible composition space only for holdup values smaller than 14.6 m$^3$. Composition profiles can extend outside the composition space, but a feasible design will be found only if the continuous profile linking the top and bottom product compositions is situated entirely in the feasible composition space. Therefore, in the design methodology presented in this chapter, only those parts of the profiles located inside the composition space were used in the feasibility test. The design procedure will calculate composition profiles (or SCLs) for a range of holdup values, reflux and reboil ratios, and check for intersections only for the segments located inside the feasible composition space.

Based on the discussions and analysis presented in this section, a few key observations result, with implications in the design methodology of kinetically-controlled reactive distillation columns developed in this chapter:

a. Tray holdup is a very important parameter for kinetically-controlled reactive distillation columns. It directly affects the reaction extent, and using a constant holdup in the column will significantly reduce the feasible solution space. Therefore, all BVMs published, where a constant holdup is used in the column, are highly iterative, and many trials are needed to find the right combination of product compositions, operating parameters (reflux or reboil ratios and feed condition) and holdup leading to a feasible design.

b. Kinetically-controlled reactive distillation process is highly constrained, and the available conceptual design methods are not sufficiently developed to provide fast and reliable tools for column synthesis and design.

c. BVMs offer good insights of the kinetically-controlled reactive distillation process, and can be used as a basis for developing a more systematic methodology, able to assess the feasibility of a specified reactive separation task and provide alternative configurations (i.e. fully reactive columns vs. hybrid columns) and multiple designs.
Based on above considerations, an extension of the BVM (Buzad and Doherty, 1994, 1995) is considered in this work. The feasible solution space for the specified kinetically-controlled separation task has been extended in this work, on one hand by introducing SCLs in column design, which allows the operating conditions (i.e. reflux and reboil ratios) to be varied independently. The advantage of using SCLs in the feasibility and design of equilibrium reactive distillation columns was discussed extensively in the previous chapters. The same considerations apply for the design of kinetically-controlled reactive distillation columns. On the other hand, the assumption of constant holdup in the column is relaxed, firstly by considering different hold-ups in the rectifying and stripping section, and secondly by allowing the holdup for each section to vary within a specified range. SCLs calculated for a range of hold-ups will form Stage Composition Surfaces (SCSs). Similar to SCLs, a SCS will represent the locus of all possible compositions on a reactive stage, for all possible reflux (or reboil) ratios and all holdup values. The use of SCLs and SCSs offers a much higher flexibility in the synthesis and design of kinetically-controlled reactive distillation columns, as will be shown in the following sections of this chapter.

6.4. Calculation of composition profiles and stage composition lines for kinetically-controlled reactive distillation columns

In kinetically-controlled reactions, the reactive equilibrium is not achieved in the column, therefore the composition profiles will not be restricted to lie on the reactive surface. The reaction extent for kinetically-controlled reactions is an explicit function of reaction rate and holdup (Eq. 6.2), therefore the composition profiles can be easily calculated in real composition space, similar to non-reactive systems. Transformed compositions can be, however, obtained for kinetically-controlled reactions, as it does not matter how the reaction extent is calculated (implicitly by using reactive equilibrium constraint or explicitly by
using a kinetic model) (Chapter 2). However, because the composition profiles for kinetically-controlled reactions are not constrained on the reactive surface, the back transformation does not provide a singular solution; therefore transformed variables can be used for visualisation purposes, but not for column design.

The overall general and component mass balances for a kinetically-controlled reactive column are (Envelope 1 in Figure 6.7):

\[ F = D + B - \sum_{j=1}^{R} v_{j,tot} \cdot \xi_{j,tot} \quad (6.5) \]

\[ F \cdot x_{F,j} = D \cdot x_{F,j} + B \cdot x_{F,j} - \sum_{j=1}^{R} v_{i,j} \cdot \xi_{j,tot} \quad \forall j = 1, \ldots, C - 1 \quad (6.6) \]

where \( \xi_{j,tot} \) is the total reaction extent in the column, for reaction \( j \).

For fully specified product compositions \( (x_D \text{ and } x_B) \) and feed flowrate \( (F) \), there are \( R+1 \) degrees of freedom remaining for the \( C \) overall mass balance.
equations. The remaining specifications can be chosen between the feed composition for any component \((x_{F,i})\), the product flowrates \((D\) and \(B)) or the reaction extents for any reaction \(j\), \(\xi_{\text{tot},j}\). A common practice is to set the reaction extents for all \(R\) reactions, together with the feed composition for the reference component, which for kinetically-controlled reactions can be assumed to be the base component for the main reaction rate \((i.e.\) the component used to define the reaction rate). Alternatively, any combination of the above parameters can be specified to satisfy the degrees of freedom for the overall mass balances.

The conceptual design methodology presented in this chapter can accommodate two types of kinetically-controlled reactive distillation columns: fully reactive columns and hybrid columns with a top or bottom section reactive. The methodology is applied only to single-feed columns, but double-feed configurations can be introduced in the future work.

The composition profiles for the non-reactive sections of the column are calculated using Eqs. 6.7 and 6.8 (Thong, 2000). SCLs are obtained by calculating the composition profiles for a range of reflux and reboil ratios, and rearranging the information obtained.

- **Rectifying section:**

\[
y_{n+1,i} = \frac{R_n}{R_n + 1} \cdot x_{n,i} + \frac{1}{R_n + 1} \cdot x_{D,i} \quad \forall \; i = 1, \ldots, C - 1
\]  

(6.7)

- **Stripping section:**

\[
x_{m+1,i} = \frac{S_m}{S_m + 1} \cdot y_{m,i} + \frac{1}{S_m + 1} \cdot x_{B,i} \quad \forall \; i = 1, \ldots, C - 1
\]  

(6.8)

For the reactive sections of the column, the equations for the operating lines are obtained from the general and component mass balances around the rectifying and the stripping sections (Appendix B.3).
- Rectifying section:
\[
y_{n+1,i} = \frac{R_n}{R_n + 1 - \Delta_r} \cdot x_{n,i} + \frac{1}{R_n + 1 - \Delta_r} \cdot \left( x_{D,i} - v_i \cdot v_{ad} \Delta_r \right) \quad \forall \ i = 1, \ldots, C - 1
\]  
(6.9)

- Stripping section:
\[
x_{m+1,i} = \frac{S_m}{S_m + 1 - \Delta_s} \cdot y_{m,i} + \frac{1}{S_m + 1 - \Delta_s} \cdot \left( x_{B,i} - v_i \cdot v_d^{-1} \Delta_s \right) \quad \forall \ i = 1, \ldots, C - 1
\]  
(6.10)

where \( R_n \) and \( S_m \) represent the local reflux and reboil ratios defined by Eqs. 6.11 and 6.12, and \( \Delta_r \) and \( \Delta_s \) are dimensionless reaction terms defined by Eqs. 6.13 and 6.14.

\[
R_n = \frac{L_n}{D} \quad (6.11)
\]
\[
S_m = \frac{V_m}{B} \quad (6.12)
\]
\[
\Delta_r = \frac{1}{D} \cdot v_{ld} \cdot \xi_r \quad (6.13)
\]
\[
\Delta_s = \frac{1}{B} \cdot v_{ld} \cdot \xi_s \quad (6.14)
\]

For constant molar overflow in the non-reactive sections, Eqs. 6.7 and 6.8 become:

- Non-reactive rectifying section:
\[
y_{n+1,i} = \frac{R}{R + 1} \cdot x_{n,i} + \frac{1}{R + 1} \cdot x_{D,i} \quad \forall \ i = 1, \ldots, C - 1
\]  
(6.15)

- Non-reactive stripping section:
\[
x_{m+1,i} = \frac{S}{S + 1} \cdot y_{m,i} + \frac{1}{S + 1} \cdot x_{B,i} \quad \forall \ i = 1, \ldots, C - 1
\]  
(6.16)
For the reactive sections, in order to account for the change in the number of moles due to reactions, the constant molar overflow assumption for equilibrium reaction was expressed in terms of transformed variables. As mentioned earlier, the mass balances in transformed variables hold for both equilibrium and kinetically-controlled reactive columns, therefore the same concept can be used for kinetically-controlled reactive columns. Using the non-dimensional parameters $k_r$ and $k_s$, defined in Appendix B.3, Eqs. 6.8 and 6.10 become:

- Reactive rectifying section:

$$y_{n+1j} = \frac{R \cdot k_{r,n} \cdot k_{r,D}}{R \cdot k_{r,n} \cdot k_{r,D} + 1 - \Delta_r} \cdot x_{n,i} + \frac{1}{R \cdot k_{r,n} \cdot k_{r,D} + 1 - \Delta_r} \cdot \left( x_{D,j} - \frac{v_i}{v_{tot}} \cdot \Delta_r \right) \quad \forall \ i = 1, ..., C - 1$$

- Reactive stripping section:

$$x_{m+1j} = \frac{S \cdot k_{s,m} \cdot k_{s,B}}{S \cdot k_{s,m} \cdot k_{s,B} + 1 - \Delta_s} \cdot x_{n,i} + \frac{1}{S \cdot k_{s,m} \cdot k_{s,B} + 1 - \Delta_s} \cdot \left( x_{B,j} - \frac{v_i}{v_{tot}} \cdot \Delta_s \right) \quad \forall \ i = 1, ..., C - 1$$

where $R$ and $S$ represent the external reflux and reboil ratios (Eqs. 6.19 and 6.20), and the reaction extent terms for single reactions are defined as in Eqs. 6.21 and 6.22.

$$R = \frac{L_g}{D}$$

$$S = \frac{V_g}{B}$$

$$\Delta_r = \frac{1}{D} \cdot v_{tot} \cdot \xi_r$$

$$\Delta_s = \frac{1}{D} \cdot v_{tot} \cdot \xi_s$$

The reaction extent in each section is calculated as a sum of reaction extents for all stages up to the current stage (stages numbered from column ends towards the feed stage).
The reaction extent at each stage is a direct function of the stage composition and temperature (Appendix B.3) and stage holdup (Eq. 6.2).

A detailed derivation of the operating line equations for kinetically-controlled reactive distillation can be found in Appendix B.3.

The rectifying SCLs are obtained from a consecutive application of the rectifying operating line (Eq. 6.7 or 6.9), followed by VLE calculations, for a range of reflux ratios and holdup values. Similar, stripping SCLs are obtained from a successive application of the stripping operating line (Eq. 6.8 or 6.10) and a bubble point calculation, for a range of reboil ratios and holdup values. By repeating the calculations for SCLs for a range of holdups, Stage Composition Surfaces can be obtained (SCSs).

The next section will describe a systematic methodology for assessing feasibility and obtaining column designs for kinetically-controlled reactive distillation columns, using intersection of rectifying and stripping SCLs or SCSs.

6.5. Design methodology for kinetically-controlled reactive distillation columns

6.5.1. Feasibility criterion for kinetically-controlled reactive columns

For kinetically-controlled reactive systems, composition profiles and SCLs can be calculated using a range of reflux or reboil ratios and a fixed holdup value for each section. The approach is similar to the design methodologies based on intersection of SCLs, developed for non-reactive systems (Thong, 2000). The
underlying premise is that for a feasible design to exist, a continuous profile between the top and the bottom product compositions must also exist, meaning that an intersection between a rectifying and a stripping SCL exist.

For fully reactive columns, considering that the feed stage is the first stripping stage, the first feasibility condition, the intersection of the rectifying and stripping SCLs, can be written as:

\[ x_{n+1} = x_m \]  \hfill (6.25)

For hybrid reactive columns, the feed stage will be considered to be the last reactive stage, i.e. the feed stage will be the last rectifying stage for a top section reactive column and the last stripping stage for a bottom section reactive column. The feasibility criterion for a top section reactive column can be written as in Eq. 6.26. For a bottom section reactive column, the feasibility criterion is the same as for fully reactive columns (Eq. 6.25).

\[ x_{n+1} = x_m \]  \hfill (6.26)

The first feasibility condition (Eq. 6.25 or 6.26) is necessary, but not sufficient to guarantee the feasibility of the proposed products for a kinetically-controlled reactive distillation column. The second feasibility condition is derived from the mass balance at the feed stage. The feed stage location is determined from the intersection of rectifying and stripping SCLs (first feasibility criterion), as the first stripping stage \( m \). A mass balance around the feed stage will give (Envelope 4 in Figure 6.7):

\[
F \cdot x_{F,j} = V_{n+1,i} \cdot y_{n+1,i} - L_n \cdot x_{n+1,i} + L_m \cdot x_{m,j} - V_{m-1,i} \cdot y_{m-1,i} - \sum_{j=1}^{R} v_j \cdot \xi_{F,j} \quad \forall \ i = 1, \ldots, C - 1
\]  \hfill (6.27)
For the rectifying section, a mass balance around envelope 2 in Figure 6.7 will give:

\[ V_{n-1} \cdot y_{n-1,i} - L_n \cdot x_{n-1,i} = D \cdot x_{D,i} - \sum_{j=1}^{R} v_j \cdot \bar{\xi}_{r,j} \quad \forall \; i = 1, \ldots, C - 1 \quad (6.28) \]

Similarly, for the stripping section, a mass balance around envelope 3 in Figure 6.7 will give:

\[ L_m \cdot x_{m,i} - V_{m-1} \cdot y_{m-1,i} = B \cdot x_{B,i} - \sum_{j=1}^{R} v_j \cdot \bar{\xi}_{s,j} \quad \forall \; i = 1, \ldots, C - 1 \quad (6.29) \]

Substituting Eqs. 6.28 and 6.29 into Eq.6.27 will give:

\[ F \cdot x_{F,i} = D \cdot x_{D,i} - \sum_{j=1}^{R} v_j \cdot \bar{\xi}_{r,j} + B \cdot x_{B,i} - \sum_{j=1}^{R} v_j \cdot \bar{\xi}_{s,j} - \sum_{j=1}^{R} v_j \cdot \bar{\xi}_{F,j} \quad \forall \; i = 1, \ldots, C - 1 \quad (6.30) \]

Eq. 6.30 will be identical to the overall mass balance (Eq. 6.6) if and only if the sum of the reaction extents for the reactive column sections is the same as the total reaction extent in the column. This gives the second feasibility criterion for kinetically-controlled reactive distillation columns:

\[ \sum_{j=1}^{R} \bar{\xi}_{tot,j} = \sum_{j=1}^{R} \bar{\xi}_{r,j} + \sum_{j=1}^{R} \bar{\xi}_{s,j} + \sum_{j=1}^{R} \bar{\xi}_{F,j} \quad (6.31) \]

The two feasibility criteria represented by Eqs. 6.24 (or 6.25) and 6.31, are valid for both fully reactive and hybrid columns, as for a hybrid column the reaction extent for that section will be zero.

The design methodology searches for feasible designs by identifying first intersections between rectifying and stripping SCLs, and then applying the second feasibility criterion for each intersection point found. For a fixed holdup value for each section (even though different holdup values can be used in different sections of the column), there will not be many feasible intersection
points satisfying the total reaction extent constraint. One way to avoid the difficulty in obtaining feasible results usually encountered in kinetically-controlled reactive distillation systems is to relax the feasibility constraint, that is:

\[ 0.8 \sum_{j=1}^{R} \xi_{\text{tot},j} \leq \sum_{j=1}^{R} \xi_{r,j} + \sum_{j=1}^{R} \xi_{F,j} + \sum_{j=1}^{R} \xi_{s,j} \leq 1.2 \sum_{j=1}^{R} \xi_{\text{tot},j} \quad (6.32) \]

Another way to improve the results is to consider a range of holdups for each section. SCLs calculated for a range of holdup values will form surfaces (SCSs), as mentioned in the previous section. Using SCSs in the design methodology, combined with a reasonable relaxation of the reaction extent constraint, will significantly increase the probability of obtaining feasible designs for a specified pair of product compositions.

Next sections will describe a systematic methodology for the conceptual design of kinetically-controlled reactive distillation columns that is able to accommodate both ternary and quaternary mixtures. Intersections of SCSs with SCLs will be used for ternary mixtures, and intersections of SCSs for quaternary mixtures. Multiple designs will be generated, ranked based on the total annualised cost (or any other column design parameter) to give the best few column configurations able to perform the specified task.

6.5.2. Design methodology for kinetically-controlled reactive distillation columns separating ternary mixtures

For ternary mixtures, in the case of a fully reactive column, SCSs for the rectifying and stripping sections can be calculated using Eqs. 6.17 and 6.18 for a range of reflux and reboil ratios and a range of holdups. The resulting surfaces will be two-dimensional, and an intersection between two surfaces in a two-dimensional space is also a surface, representing the area of potentially feasible designs. In Figure 6.8, a ‘patch’ \( ABCD \) on a rectifying SCS will represent all possible liquid compositions for reflux ratios between \( R_A \) and \( R_B \),
and between rectifying holdup values $H_A$ and $H_D$. Similarly, MNOP represents a ‘patch’ on a stripping SCS containing all liquid compositions for reboil ratios between $S_M$ and $S_N$ and between stripping holdup values $H_M$ and $H_P$. The resulting area of intersection of the two patches, limited by the intersection points $I_1$, $I_2$, $I_3$, and $I_4$, represents the area of potentially feasible designs for the specified intervals of reflux and reboil ratios and rectifying and stripping holdups.

Figure 6.8 Two-dimensional intersection of rectifying and stripping SCSs for a fully reactive kinetically-controlled reactive distillation column

For a design to be feasible, the reaction extent constraint has to be satisfied as well, (section 6.5.3). Considering the dependency of the reaction extent in a rectifying section ($\xi_R$) on combined reflux ratio and holdup (Figure 6.9), the reaction extent values for the rectifying section will be points located on a surface. The locus of all points satisfying a specific constraint for the reaction extent is a curve, resulting from the intersection of the surface with a horizontal plane at $\xi_R = \text{constant}$. Therefore, there are an infinite number of combinations between reflux ratio and holdup which lead to a specific value for the reaction extent. Considering the influence of reboil ratio and stripping holdup on total reaction extent as well, the complexity of the problem will be increased even further. Therefore, inside the potentially feasible space limited by the
intersection points $I_1$, $I_2$, $I_3$, and $I_4$ is very difficult to identify the locus of constant total reaction extent, which will guarantee the feasibility of the proposed products.

Figure 6.9 Rectifying reaction extent dependency on reflux ratio and holdup, for a rectifying section containing 5 stages. System $2C \leftrightarrow A + B$. Kinetic data from Okasinski and Doherty (1998) (Appendix E.5).

Figure 6.10 Line of potentially feasible designs resulting by considering a continuous holdup parameter for the stripping section and a constant value for the rectifying section.
To simplify the problem, the holdup will be considered as a continuous variable only in one of column sections; for the other a constant value (or a number of discrete values) will be assumed. This assumption will restrict the potentially feasible space to lines instead of surfaces, therefore the identification of the points satisfying the total reaction extent constraint will be much easier.

Using a constant value (or several discrete values) for the holdup in the rectifying section a line (or a series of lines) will result (see Figure 6.10), limited by the intersection points $I_1$ and $I_2$, representing the locus of potentially feasible designs for the specified conditions. The design details at each intersection point are calculated using the linear parameters: $\alpha$ – for the rectifying section and $\beta$ – for the stripping section (Appendix G.2). For the two intersection points in Figure 6.10, the design details are:

\[
\begin{align*}
R_1 &= R_A + \alpha_1 \cdot (R_B - R_A) \\
S_1 &= S_M + \beta_1 \cdot (S_N - S_M) \\
R_2 &= R_A + \alpha_2 \cdot (R_B - R_A) \\
S_2 &= S_P + \beta_2 \cdot (S_O - S_P)
\end{align*}
\]

If small enough intervals are used for the reflux and reboil ratios and for the holdup, then a linear dependency of reaction extent can be assumed, and the reaction extent for each section at intersection points can be calculated by linear interpolation (Eqs. 6.37 to 6.40)

\[
\begin{align*}
\xi_{R,1} &= \xi_A + \alpha_1 \cdot (\xi_B - \xi_A) \\
\xi_{S,1} &= \xi_M + \beta_1 \cdot (\xi_N - \xi_M) \\
\xi_{R,2} &= \xi_A + \alpha_2 \cdot (\xi_B - \xi_A) \\
\xi_{S,2} &= \xi_P + \beta_2 \cdot (\xi_O - \xi_P)
\end{align*}
\]
The total reaction extent will result from the sum of the reaction extents for the rectifying and for the stripping section (which also contains the feed stage):

\[ \xi_{\text{tot,1}} = \xi_{R,1} + \xi_{S,1} \]  
\[ \xi_{\text{tot,2}} = \xi_{R,2} + \xi_{S,2} \]  

(6.41)  
(6.42)

The second feasibility criterion (Eq. 6.31) is then applied to both intersection points \( I_1 \) and \( I_2 \). If the total reaction extent calculated from the overall mass balance (Eq. 6.6) has a value between the values calculated for the points \( I_1 \) and \( I_2 \), that is \( \xi_1 < \xi_{\text{tot}} < \xi_2 \) or \( \xi_1 > \xi_{\text{tot}} > \xi_2 \), then the conditions satisfying the second feasibility criterion can be obtained by interpolation between the conditions of intersection points \( I_1 \) and \( I_2 \). If the point satisfying the second feasibility criterion is outside the potentially feasible space (segment \( I_1I_2 \)), and the above interpolation strategy cannot be applied, then the relaxed feasibility criterion for the reaction extent can be used (Eq. 6.32). The design details obtained by applying the relaxed feasibility criterion can be used for interpolation between relaxed designs, i.e. interpolation between column designs with different number of stages, as well as various reflux and reboil ratios and holdup values. Using the above methodology, multiple designs can be generated. Even if considering discrete values for one of the column sections will restrict the solution space, the methodology typically generates many feasible designs.

Also, the methodology can directly accommodate hybrid columns. For the non-reactive section the holdup is fixed to zero. A range of holdups can be used for the reactive section, in the same manner as for fully reactive columns. An intersection between the non-reactive SCLs and reactive SCSs will also generate a line. The procedure to identify the points satisfying the second feasibility criterion is the same; the total reaction extent will represent the reaction extent for the reactive section of the hybrid column, as for the non-reactive section the reaction extent is zero. Because the same methodology can be used for both fully reactive and hybrid columns, the two configurations can be analysed in a single design framework. The synthesis and design procedure...
for kinetically-controlled reactive distillation columns separating a ternary mixture can be described in the following steps:

1. Set two fully specified product compositions for the top and bottom products and the feed flowrate. The remaining $R+1$ specifications needed to satisfy the number of degrees of freedom can be chosen between the feed composition for any component ($x_{F,i}$), the product flowrates ($D$ and $B$) and the reaction extents for any reaction $j$, ($\xi_{tot,j}$, $j = 1,\ldots,R$). Alternatively, if the feed composition is given, specify fully the composition of one of the two products; the other $R+1$ specifications will be chosen between $D$, $B$, $\xi_{tot,j}$ ($j = 1,\ldots,R$) and the composition of the other product.

2. Calculate the remaining variables (e.g. remaining feed compositions, $D$ and $B$ flowrates and the reaction extents in the column) from the overall mass balance (Eqs. 6.5 and 6.6)

3. Set a range of reflux and reboil ratios. Fix a holdup value (or discrete values) for one of the sections. If the section is non-reactive, set the holdup value to zero. Set a range of holdups for the other section.

4. Check if constant molar overflow assumption holds, for both reactive and non-reactive sections. If the assumption does not hold, use energy balances in composition profiles calculation.

5. Calculate reactive SCLs for the section with fixed holdup, and SCSs for the other section.

6. Calculate intersections of SCLs and SCSs and evaluate reaction extent at intersection points.

7. Compare reaction extents at intersection points with total reaction extent from overall mass balance (Eq. 6.31). Interpolate between designs with the same number of stages but different operating parameters to satisfy the constraint if possible.

8. Apply the relaxed reaction extent constraint (Eq. 6.32) to all intersection points and store the details at points which satisfy the condition.
Interpolate between designs with different numbers of stages and different operating conditions to satisfy the total reaction extent constraint.

9. Rank all feasible design obtained at steps 7 and 8 based on total annualised cost (or any other parameter e.g. number of stages, energy requirement)

10. Narrow the results to meet user specifications if necessary, e.g. feed condition, maximum number of stages, maximum total cost.

Using the design methodology described in this section, multiple designs can be obtained, either fully reactive or hybrid, which will give the user the possibility to compare efficiently between designs, and to choose whether a hybrid configuration will be preferable to a fully reactive column, for the defined reactive separation task. The design procedure can be easily automated, and offers a fast tool to generate feasible designs for kinetically-controlled reactive distillation columns. To generate multiple feasible designs it will take less than 20 min for an ideal system and less than 1 h for a highly non-ideal system, using a PIII 1.5 GHz PC. The computational time is directly dependent on the number of intervals used for the reflux and reboil ratios and for the holdup. Therefore, there is a trade-off between the number of intervals used to allow the linear interpolation between intersection points, and the computational time spent on searching for intersections. A couple of pre-runs to analyse the influence of reflux and reboil ratios and holdup on composition profiles will generally give good information about the minimum number of intervals needed for a good linear approximation.
6.5.3. Design methodology for kinetically-controlled reactive distillation columns separating quaternary mixtures

Fully reactive kinetically-controlled columns

For quaternary mixtures, the same approach as for ternary mixtures can be used. SCSs for the rectifying and stripping sections can be calculated using Eqs. 6.17 and 6.18 for a range of reflux and reboil ratios and a range of holdups; they will be surfaces in the three-dimensional composition space. The intersection between two surfaces in 3-D is a line (or curve). As described in the previous section, it is not difficult to identify the points satisfying the total extent constraint if the potentially feasible space is a curve (or line segments approximating the curve). Therefore, for quaternary mixtures it is possible to use the intersection of the rectifying and stripping SCSs for testing the feasibility of the proposed product; the intersection of the two surfaces will be a curve, representing the potentially feasible solution space. Assuming that the intervals for reflux and reboil ratios and for the holdup in the rectifying and stripping section are small enough to assume linear dependence of the reaction extent on the four parameters \( R, S, H_R \) and \( H_S \), then the curve can be approximated by linear segments. The search for points satisfying the reaction extent feasibility criterion (Eq. 6.31 ) can be performed along each segment, and if a point satisfying the constraint is found, a linear interpolation can be used to obtain the design details.

In Figure 6.11 \( ABCD \) represents a ‘patch’ on a rectifying SCS between reflux ratios \( R_A \) and \( R_B \), and between rectifying holdup values \( H_A \) and \( H_D \). Similarly, \( MNOP \) represents a ‘patch’ on a stripping SCS between reboil ratios \( S_M \) and \( S_N \), and between stripping holdup values \( H_M \) and \( H_P \). In three-dimensional space, four points will define a surface. As is very difficult to define analytically the surface limited by the four points, in order to calculate the intersection between them, each surface patch will be approximated by two triangles. The main advantage of approximating each ‘patch’ by triangles is that the intersection
between two triangles in 3-D can be calculated analytically (Appendix G.4). Therefore, the intersection between the two patches \(ABCD\) and \(MNOP\) can be approximated by the intersection of triangles \(ABD\) and \(BCD\) from the rectifying SCS patch with triangles \(MNP\) and \(NOP\) from the stripping SCS patch.

![Diagram of potentially feasible designs resulting from the intersection of SCSs for the rectifying and stripping sections.](image)

Figure 6.11 Locus of potentially feasible designs resulting from the intersection of SCSs for the rectifying and stripping sections.

From the intersection of all pairs of rectifying and stripping triangles, a maximum of three line segments defined by four points of intersection can be obtained. For each intersection point, the design details can be calculated, using the four surface parameters: \(\alpha\) and \(\beta\) for triangles from the rectifying SCS patch and \(\gamma\) and \(\delta\) for triangles from the stripping SCS patch. The parameters are defined such as \(\alpha\) and \(\beta\) are directly related to the reflux ratio and rectifying holdup, and \(\gamma\) and \(\delta\) are directly related to the reboil ratio and stripping holdup (Appendix G.4). The details at each intersection point can then be estimated by
interpolation using the above parameters. For example the details at intersection point \( I_2 \) in Figure 6.11 can be estimated using Eqs. 6.43 to 6.49:

\[
R_2 = R_A + \alpha \cdot (R_B - R_A) \\
H_{R,2} = H_A + \beta \cdot (H_D - H_A) \\
\xi_{R,2} = \xi_A + \alpha \cdot (\xi_B - \xi_A) + \beta \cdot (\xi_D - \xi_A) \\
S_2 = S_M + \gamma \cdot (S_N - S_M) \\
H_{S,2} = H_M + \delta \cdot (H_P - H_M) \\
\xi_{S,2} = \xi_M + \gamma \cdot (\xi_P - \xi_M) + \delta \cdot (\xi_N - \xi_M) \\
\xi_{\text{tot},2} = \xi_{R,2} + \xi_{S,2}
\]

Using similar equations, the total reaction extent can be calculated at all intersection points. The point(s) satisfying the total reaction extent constraint (Eq. 6.31) can then be searched along the potentially feasible design line \( I_1I_2I_3I_4 \). If between two adjacent points of intersection the total reaction extent satisfies the condition:

\[
\forall i \in [\xi_{i,i}, \xi_{i,i+1}] 
\]

then the conditions satisfying the second feasibility criterion can be obtained by interpolation between the conditions of intersection points \( I_i \) and \( I_{i+1} \). If there is no point, along the potentially feasible design line \( I_1I_2I_3I_4 \), satisfying the second feasibility criterion (Eq. 6.31), then the relaxed feasibility criterion is applied (Eq. 6.32) at each intersection point. If the criterion is satisfied, the design details corresponding to that point are used for interpolation between relaxed designs, i.e. interpolation between column designs with different number of stages, as well as various reflux and reboil ratios and holdup values. For example, considering the hypothetical situation in Figure 6.12, there are two lines resulting from the intersection of SCS for rectifying stage 5 and SCSs for stripping stages 7 and 8.
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Figure 6.12 Strategies for interpolation to satisfy the total reaction extent constraint: (a) Interpolation between designs with different operation conditions, but same number of stages – points E1, E2 and E3; (b) Interpolation between designs with different operation conditions and different number of stages – points E4 and E5.

Along the line defined by points $I_1', I_2', I_3'$ and $I_4'$, there is only one point, $E_1$, satisfying the total reaction extent $\xi_{\text{tot}} = 44 \text{ kmol/h}$. Similarly, for the line defined by points $I_1'', I_2'', I_3''$ and $I_4''$, the total reaction extent is satisfied at points $E_2$ and $E_3$. Also, points $I_2', I_1'$ and $I_2''$ satisfy the relaxed reaction extent criterion (Eq. 6.32). The designs corresponding to these points are also considered feasible, as they can offer a good initialisation for the rigorous simulation. Also, they can be used for interpolation between designs, e.g. the conditions at point $E_4$, obtained from interpolation between points $I_2'$ and $I_1''$, will satisfy the total reaction extent constraint, but fractional stages will be obtained for the stripping section. However, as proven in several case studies in Chapters 4 and 5, fractional stages offer very good initialisation for the rigorous simulation, as one stage more or less in one column section does not affect dramatically the column performance.

The design details at points obtained from interpolation between relaxed designs are calculated using a linear parameter $\omega$, e.g. for point $E_4$ $\omega$ is defined as in Eq. 6.50.
\[ \omega = \frac{\xi_{\text{tot}} - \xi_{\text{f}}} {\xi_{\text{f}} - \xi_{\text{i}}} \]  

(6.50)

The design details for the column are obtained using Eqs. 6.51 to 6.54.

\[ R_{E_{i}} = R_{E_{i}} + \omega \left( R_{E_{i}} - R_{E_{i}} \right) \]  

(6.51)

\[ S_{E_{i}} = S_{E_{i}} + \omega \left( S_{E_{i}} - S_{E_{i}} \right) \]  

(6.52)

\[ NR_{E_{i}} = NR_{E_{i}} + \omega \left( NR_{E_{i}} - NR_{E_{i}} \right) \]  

(6.53)

\[ NS_{E_{i}} = NS_{E_{i}} + \omega \left( NS_{E_{i}} - NS_{E_{i}} \right) \]  

(6.54)

**Hybrid kinetically-controlled reactive columns**

The methodology described above for fully reactive columns cannot give satisfactory results for hybrid configurations, even though the intersection between non-reactive SCLs and reactive SCSs can be calculated in three-dimensional space. The result of the intersection will be a point, not a line, as is the case for fully reactive columns. Apart from the fact that very few intersections are usually found between the non-reactive SCLs and reactive SCSs, the intersection points are very unlikely to satisfy the reaction extent constraint, even if the relaxed condition is used. This behaviour is caused mainly by the fact that fully specifying both product compositions, together with the reaction extent feasibility test, is too restrictive for hybrid kinetically-controlled reactive distillation columns.

However, as discussed in Section 6.5.2, the dependency of the reaction extent at a specific stage on reflux (or reboil) ratio and section holdup shows, for small enough intervals, a quasi-linear behaviour. A series of lines will be obtained for a section of the column, each representing the locus of constant reaction extent for a specific stage. In Figure 6.13 the lines of constant reaction extent for a rectifying section for the ideal system \( A \rightarrow B + C \) (inert D) is shown. As, for hybrid columns, only one of the sections will be reactive, these lines will also represent
the locus of feasible feed points for the column. Knowing this locus is very useful in design analysis, as it offers the possibility to identify feasible designs by calculating, starting from the feed stage, the number of stages needed in the non-reactive section in order to achieve a certain purity of the product. Therefore, the composition of the product resulting from the non-reactive section will not be fully specified, which increases the number of degrees of freedom for the system. Using this approach, a significant increase in the number of feasible designs was obtained, even for situation where extra constraints were applied, e.g. the feed condition set to saturated liquid.

Figure 6.13 Lines of constant total reaction extent for an ideal system \( A \rightarrow B + C \) (inert D). Transformed variables are used for visualisation.

For a hybrid column, the design details at the intersection point between a non-reactive SCL and a reactive SCS are calculated depending on the type of each section: reactive or non-reactive. For the situation in Figure 6.13, when the rectifying section is non-reactive and the stripping section is reactive, the design details for point \( I_1 \) will be:
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\[ R_1 = R_A + \alpha \cdot (R_B - R_A) \]  \( \text{(6.55)} \)

\[ S_1 = S_M + \gamma \cdot (S_N - S_M) \]  \( \text{(6.56)} \)

\[ H_{s1} = H_M + \delta \cdot (H_p - H_M) \]  \( \text{(6.57)} \)

\[ \xi_{s1} = \xi_M + \gamma \cdot (\xi_p - \xi_M) + \delta \cdot (\xi_N - \xi_M) \]  \( \text{(6.58)} \)

\[ \xi_{ref,1} = \xi_{s1} \]  \( \text{(6.59)} \)

where \( \alpha \) is the linear parameter used for the non-reactive SCL and \( \gamma \) and \( \delta \) are the surface parameters used for the SCS (Appendix G3).

Based on the column details resulting from the design procedure, for each feasible design found, the remaining parameters can then be estimated: feed condition, column condenser and reboiler duties, column diameter and column total cost. Feed condition is calculated using an overall energy balance (Appendix B.5). The condenser and reboiler duties are direct functions of reflux and reboil ratios (Appendix B), and they can be easily calculated from energy balances around the condenser and reboiler. Based on the information obtained, the utility cost can be calculated, as well as the capital cost for the heat exchangers. The capital cost of the column will take into account different prices for the reactive and non-reactive stages (Appendix F). Thus, the feasible designs can be ranked to obtain the best few designs based on total annualised cost or any other operating or design parameter: reflux or reboil ratio, number of stages, energy requirement (condenser or reboiler duties).

The synthesis and design procedure for kinetically-controlled reactive distillation columns separating quaternary mixtures can be described as follows:

1. Set two fully specified product compositions for the top and bottom products and the feed flowrate. The remaining \( R+1 \) specifications needed to satisfy the number of degrees of freedom can be chosen between the feed composition for any component \( (x_{f,i}) \), the product
1. Calculate the remaining variables (remaining feed compositions, \( D \) and \( B \) flowrates and the reaction extents in the column) from the overall mass balance (Eqs. 6.5 and 6.6)

3. Set a range of reflux and reboil ratios. Set a range of holdup values for the rectifying and stripping sections.

4. Check if constant molar overflow assumption holds, for both reactive and non-reactive sections. If the assumption does not hold, use energy balances in composition profiles calculation.

5. Calculate reactive SCSs and the line of constant total reaction extent for both rectifying and stripping sections.

6. Calculate intersections of rectifying and stripping SCSs for fully reactive columns.

7. Apply the reaction extent constraint at each intersection point (Eq. 6.31). For fully reactive columns, interpolate between designs with same number of stages but different operating parameters to satisfy the constraint if possible (type (a) in Figure 6.12)

8. Apply the relaxed reaction extent constraint (Eq. 6.32) to all intersection points and store the details at points which satisfy the condition. Interpolate between designs with different number of stages and different operating condition to satisfy the total reaction extent constraint (type (b) in Figure 6.12). This step is valid for both fully reactive and hybrid configurations.

9. Calculate both rectifying and stripping composition profiles starting from the feed stage for hybrid columns. Store feasible designs satisfying the product purity constraint.

10. Rank all feasible design obtained at steps 7, 8 and 9 based on total annualised cost (or any other performance indicator, e.g. number of stages, reflux or reboil ratio, energy requirement)

11. Narrow the results to meet user specifications if necessary, e.g. feed condition, maximum number of stages, maximum total cost.
The design methodologies described in this section for fully reactive and hybrid configurations can be included in a single framework, which will allow comparison between designs. The design procedure described above can be easily automated, offering a fast tool to generate feasible designs for kinetically-controlled reactive distillation columns separating quaternary mixtures. To generate feasible designs takes around 30 min for an ideal system and around 2 h for a highly non-ideal system, using a PIII 1.5 GHz. The computational time is directly dependent on the number of intervals used for the reflux and reboil ratios and for the holdup. Using pre-runs to analyse the influence of reflux and reboil ratios and holdup on composition profiles will offer some guidance about the number of intervals we can use for the reflux and reboil ratios and for the holdup, in order to assume a linear dependency of composition on a specific tray with the operating parameters.

6.6. Case studies

6.6.1. Olefin metathesis

Olefin metathesis (converting an olefin into lower and higher molecular weight olefins) is a class of reaction very well suited for reactive distillation (Okasinski and Doherty, 1998). One of the main reasons for considering olefin metathesis in reactive distillation applications is their reaction conditions: most of the reactions take place at moderate temperature and pressure. Also, olefins have an ideal thermodynamic behaviour, as the reactants and the products are similar chemicals. Details about thermodynamics and kinetics of metathesis reactions are covered in Ivin (1983) and Dragutan et al. (1985).

The conceptual design methodology developed in this chapter will be used to design a reactive distillation column for the metathesis of 2-pentene to 2-butene and 2-hexene (Eq. 6.60).
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\[
2C_5H_{10} \leftrightarrow C_4H_8 + C_6H_4
\]  

(6.60)

The reaction equilibrium constant is \( K_{eq} = 0.25 \), and the rate of \( C_6 \) formation is described by Eq. 6.61 (Okasinski and Doherty, 1998).

\[
r_{C_6} = 0.5 \cdot k_f \left( x_{C_5}^2 \cdot \frac{x_{C_4} \cdot x_{C_6}}{K_{eq}} \right)
\]  

(6.61)

where:

\[
k_f = 3553.6 \cdot \exp\left( -\frac{6.6 [kcal/gmol]}{RT} \right) \text{ min}^{-1}
\]  

(6.62)

The thermodynamic parameters used to model this system are listed in Appendix E.5.

**Table 6.1 Feed and product compositions for the olefin metathesis**

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Stoichiometry</th>
<th>Boiling points (3 bar)</th>
<th>Distillate</th>
<th>Bottom</th>
<th>Feed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ν</td>
<td>T_B [°C]</td>
<td>x_D</td>
<td>x_B</td>
<td>x_F</td>
</tr>
<tr>
<td>C_5</td>
<td>-2</td>
<td>72.7</td>
<td>0.0495*</td>
<td>0.0497*</td>
<td>1.0*</td>
</tr>
<tr>
<td>C_4</td>
<td>1</td>
<td>36.0</td>
<td>0.95*</td>
<td>3.E-4*</td>
<td>0.0*</td>
</tr>
<tr>
<td>C_6</td>
<td>1</td>
<td>105.2</td>
<td>5.E-4*</td>
<td>0.95*</td>
<td>0.0</td>
</tr>
</tbody>
</table>

*Specified values

For the design procedure, the product compositions were fully specified, as shown in Table 6.1. The feed specifications included the feed flowrate and feed mole fraction for 2-pentene. To satisfy the degrees of freedom for the mass balance, one other parameter needs to be specified, between D/F, B/F, feed composition for a component other than the base component and reaction extent. As in this case the feed contains pure 2-pentene, the mole fraction for 2-butene in the feed was specified to be zero (Table 6.1). The remaining variables
are calculated from the overall mass balance. For the specified product compositions, the reaction conversion will be 95.04%.

To generate the stage composition lines, the ranges for reflux and reboil ratios and for the holdup, and the maximum number of stages in each section were specified (Table 6.2)

Table 6.2 Specifications for generating stage composition lines

<table>
<thead>
<tr>
<th>Distillate flowrate</th>
<th>Bottoms flowrate</th>
<th>Feed flowrate</th>
<th>Reflux ratio range</th>
<th>Reboil ratio range</th>
<th>Rectifying stages range</th>
<th>Stripping stages range</th>
<th>Holdup range</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D$ [kmol/h] 50</td>
<td>$B$ [kmol/h] 50</td>
<td>$F$ [kmol/h] 100</td>
<td>$r$ [-] 0.5 – 20</td>
<td>$s$ [-] 0.5 – 20</td>
<td>$n$ [-] 1 – 20</td>
<td>$M$ [-] 1 – 20</td>
<td>$q$ [m$^3$] 0.05-0.5</td>
</tr>
</tbody>
</table>

The first step in the design procedure is to check whether the constant molar overflow assumption is valid for this system. The system has an ideal behaviour, and the heat of reaction is very small compared to the heat of vaporisation, therefore the constant molar overflow assumption is expected to be valid, for both reactive and non-reactive sections. Figure 6.14 confirms that there is very little influence of energy balances on reactive composition profiles, therefore we can use Eqs. 6.17 and 6.18 to calculate the composition profiles and SCFs.

Using the reflux and reboil ratios and the holdup ranges listed in Table 6.2, stage composition surfaces are calculated for the rectifying section. For the stripping section, SCLs are calculated for discrete values of holdup; 10 discrete values at equal intervals were chosen within the specified holdup range.
Figure 6.14 Influence of constant molar overflow on reactive composition profiles. (a) Rectifying profiles for R = 5; (b) Stripping profiles for S = 5.

Figure 6.15 Rectifying SCS for rectifying stage NR = 8 and stripping SCLs for HS = 0.5 m$^3$. Kinetic and thermodynamic data listed in Appendix E.5.

Figure 6.15 shows the rectifying SCS for rectifying stage 8 and the stripping SCLs for a stripping holdup of 0.5 m$^3$. For this value of the stripping holdup, only the first 10 SCLs can be represented, as for NS greater than 10 the SCLs will lie
outside the feasible composition space. A line resulting from the intersection of a rectifying SCS with a stripping SCL will indicate the locus of potentially feasible designs. To satisfy the reaction extent constraint, a search along the line is performed; the design parameters for the point satisfying the reaction extent constraint are obtained by interpolation, as described in Section 6.5.2.

For example, Figure 6.16 shows a segment on a SCL containing all compositions on stripping stage 5 between $S_1 = 4.83$ and $S_2 = 7$, for a stripping holdup $H_S = 0.6 \text{ m}^3$, together with a patch on a rectifying SCS containing all compositions for stage $NR = 9$, between reflux ratios $R_1 = 4.83$ and $R_2 = 7$, and rectifying holdup values $H_R,1 = 0.6 \text{ m}^3$ and $H_R,2 = 0.7 \text{ m}^3$. The details at the two intersection points $I_1$ and $I_2$ are listed in Table 6.3. The point satisfying the total reaction extent constraint $\xi_{tot} = 47.4 \text{ kmol/h}$ is situated between points $I_1$ and $I_2$, as for point $I_1$ $\xi_{tot}$ is 47.99 and for point $I_2$ is 37.53 (Table 6.3). Using a linear interpolation between points $I_1$ and $I_2$, the design details for the feasible column are: $NR = 8$ (the feed stage is the first stripping stage, therefore the number of rectifying stages is $NR-1$), $NS = 5$, $R = 5.35$, $S = 5.31$, $H_R = 0.697 \text{ m}^3$ and $HR = \ldots$
0.6 m³ (Design 8 in Table 6.5). The condenser and reboiler are included in the number of stages for the rectifying and stripping sections, respectively.

Table 6.3 Design details at intersection points $I_1$ and $I_2$

<table>
<thead>
<tr>
<th>Point</th>
<th>Reflux ratio</th>
<th>Reboil ratio</th>
<th>Rectifying holdup</th>
<th>Stripping holdup</th>
<th>Total reaction extent</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_1$</td>
<td>5.86</td>
<td>5.64</td>
<td>0.7</td>
<td>0.6</td>
<td>47.99</td>
</tr>
<tr>
<td>$I_2$</td>
<td>4.83</td>
<td>6.57</td>
<td>0.657</td>
<td>0.6</td>
<td>37.5</td>
</tr>
</tbody>
</table>

Applying the same procedure to all rectifying SCSs patches and to all stripping SCLs, several designs satisfying the total reaction extent can be obtained. For the specifications in Table 6.1 and Table 6.2, 38 feasible designs were found, the design details for the first 10 design, ranked based on total annualised cost, are listed in Table 6.4.

Table 6.4 Ten feasible column designs for the metathesis reaction, satisfying the total reaction extent constraint. Designs are ranked based on the total annualised cost.

<table>
<thead>
<tr>
<th>No</th>
<th>NR</th>
<th>NS</th>
<th>$N_{TOT}$</th>
<th>R</th>
<th>S</th>
<th>$H_R$</th>
<th>$H_S$</th>
<th>$q$</th>
<th>Cond. Duty</th>
<th>Reb. Duty</th>
<th>Total Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8</td>
<td>5</td>
<td>13</td>
<td>5.80</td>
<td>5.70</td>
<td>0.697</td>
<td>0.6</td>
<td>0.91</td>
<td>2055</td>
<td>2102</td>
<td>1.34</td>
</tr>
<tr>
<td>2</td>
<td>7</td>
<td>5</td>
<td>12</td>
<td>6.83</td>
<td>6.27</td>
<td>0.782</td>
<td>0.6</td>
<td>0.76</td>
<td>2367</td>
<td>2314</td>
<td>1.35</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>6</td>
<td>12</td>
<td>6.40</td>
<td>6.45</td>
<td>0.828</td>
<td>0.6</td>
<td>1.06</td>
<td>2234</td>
<td>2381</td>
<td>1.36</td>
</tr>
<tr>
<td>4</td>
<td>7</td>
<td>5</td>
<td>12</td>
<td>7.18</td>
<td>6.67</td>
<td>0.824</td>
<td>0.7</td>
<td>0.82</td>
<td>2471</td>
<td>2463</td>
<td>1.38</td>
</tr>
<tr>
<td>5</td>
<td>7</td>
<td>5</td>
<td>12</td>
<td>7.91</td>
<td>5.58</td>
<td>0.850</td>
<td>0.6</td>
<td>-0.11</td>
<td>2692</td>
<td>2061</td>
<td>1.41</td>
</tr>
<tr>
<td>6</td>
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<td>5</td>
<td>13</td>
<td>5.34</td>
<td>6.79</td>
<td>0.682</td>
<td>0.7</td>
<td>1.72</td>
<td>1917</td>
<td>2506</td>
<td>1.41</td>
</tr>
<tr>
<td>7</td>
<td>7</td>
<td>5</td>
<td>12</td>
<td>6.53</td>
<td>7.43</td>
<td>0.761</td>
<td>0.7</td>
<td>1.54</td>
<td>2275</td>
<td>2743</td>
<td>1.42</td>
</tr>
<tr>
<td>8</td>
<td>9</td>
<td>4</td>
<td>13</td>
<td>7.37</td>
<td>6.89</td>
<td>0.771</td>
<td>0.9</td>
<td>0.85</td>
<td>2529</td>
<td>2541</td>
<td>1.42</td>
</tr>
<tr>
<td>9</td>
<td>9</td>
<td>4</td>
<td>13</td>
<td>7.55</td>
<td>6.29</td>
<td>0.777</td>
<td>0.8</td>
<td>0.44</td>
<td>2584</td>
<td>2320</td>
<td>1.42</td>
</tr>
<tr>
<td>10</td>
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<td>4</td>
<td>13</td>
<td>7.79</td>
<td>5.55</td>
<td>0.783</td>
<td>0.7</td>
<td>-0.07</td>
<td>2656</td>
<td>2049</td>
<td>1.43</td>
</tr>
</tbody>
</table>

The number of feasible designs can be increased significantly if the reaction extent constraint is relaxed, as discussed in Section 6.5.2. For example, the total number of designs found, satisfying both the exact and the relaxed
constraint for the total reaction extent is greater than 600. Because some of the
designs have an infeasible feed condition, only the designs with a feed
condition between 0 and 1.2 were considered, leading to 50 feasible designs.
The first 10 designs ranked based on total annualised cost are listed in Table
6.5. It is worth mentioning that from the 38 designs found to satisfy exactly the
total reaction extent only 6 designs have the feed condition between 0 and 1.2;
therefore considering the relaxed reaction extent constraint will improved the
results significantly.

Table 6.5 Ten feasible column designs, ranked by total annualised cost, for the
metathesis reaction, satisfying the relaxed reaction extent constraint, with the
feed condition between 0-1.2

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7</td>
<td>6</td>
<td>13</td>
<td>4.86</td>
<td>4.83</td>
<td>0.696</td>
<td>0.5</td>
<td>0.86</td>
<td>41.8</td>
<td>1770</td>
<td>1783</td>
<td>1.28</td>
</tr>
<tr>
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<td>7</td>
<td>6</td>
<td>13</td>
<td>4.83</td>
<td>4.84</td>
<td>0.695</td>
<td>0.5</td>
<td>0.87</td>
<td>41.6</td>
<td>1762</td>
<td>1787</td>
<td>1.28</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>7</td>
<td>13</td>
<td>4.83</td>
<td>5.06</td>
<td>0.761</td>
<td>0.5</td>
<td>0.99</td>
<td>48.7</td>
<td>1762</td>
<td>1867</td>
<td>1.29</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>7</td>
<td>13</td>
<td>5.37</td>
<td>4.96</td>
<td>0.800</td>
<td>0.5</td>
<td>0.70</td>
<td>50.9</td>
<td>1924</td>
<td>1832</td>
<td>1.30</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>8</td>
<td>13</td>
<td>4.98</td>
<td>5.49</td>
<td>0.900</td>
<td>0.5</td>
<td>1.16</td>
<td>52.6</td>
<td>1807</td>
<td>2026</td>
<td>1.32</td>
</tr>
<tr>
<td>6</td>
<td>8</td>
<td>5</td>
<td>13</td>
<td>5.84</td>
<td>4.83</td>
<td>0.687</td>
<td>0.5</td>
<td>0.41</td>
<td>41.1</td>
<td>2067</td>
<td>1783</td>
<td>1.32</td>
</tr>
<tr>
<td>7</td>
<td>8</td>
<td>5</td>
<td>13</td>
<td>5.86</td>
<td>5.64</td>
<td>0.700</td>
<td>0.6</td>
<td>0.85</td>
<td>48.0</td>
<td>2074</td>
<td>2082</td>
<td>1.33</td>
</tr>
<tr>
<td>8</td>
<td>5</td>
<td>8</td>
<td>13</td>
<td>5.80</td>
<td>5.70</td>
<td>0.697</td>
<td>0.6</td>
<td>0.91</td>
<td>47.4</td>
<td>2055</td>
<td>2102</td>
<td>1.34</td>
</tr>
<tr>
<td>9</td>
<td>6</td>
<td>7</td>
<td>13</td>
<td>6.08</td>
<td>4.83</td>
<td>0.855</td>
<td>0.5</td>
<td>0.30</td>
<td>56.3</td>
<td>2140</td>
<td>1783</td>
<td>1.34</td>
</tr>
<tr>
<td>10</td>
<td>6</td>
<td>6</td>
<td>12</td>
<td>6.62</td>
<td>5.30</td>
<td>0.800</td>
<td>0.5</td>
<td>0.32</td>
<td>39.1</td>
<td>2303</td>
<td>1955</td>
<td>1.34</td>
</tr>
</tbody>
</table>

Some of the designs obtained using a relaxed reaction extent constraint can be
used directly to initialise a rigorous simulation, if the calculated value for the
reaction extent is close to ξ_tot. An example is Design 3 in Table 6.5, for which
the calculated reaction extent, 48.7 kmol/h, is very close to ξ_tot (47.4 kmol/h). In
other situations, the values are quite far, but we can use an interpolation
between designs, e.g. between designs 2 and 3 or between designs 5 and 6.
Also, some feasible designs for intermediate stripping holdup values can be
found by interpolation; this compensates for the restriction of discrete stripping
holdup values imposed by the design methodology. In Table 6.5, designs 7 and
8 represent such a situation, where the number of stages for the rectifying and stripping sections is the same for both designs, but the stripping holdup values are different. Interpolating between the two designs will lead to a column with 8 rectifying stages, 5 stripping stages, a reflux ratio of 5.86 and a reboil ratio of 5.57, a rectifying holdup of 0.699 m$^3$ and a stripping holdup of 0.591 m$^3$. Overall, the use of a relaxed constraint for the total reaction extent is very useful in increasing the number of feasible designs obtained for a kinetically-controlled reactive distillation column.

Design 8 from Table 6.5 is used to initialise a rigorous simulation using HYSYS v2.4, using 8 rectifying stages and 5 stripping stages (including the condenser and reboiler). The results of the conceptual design method were used to specify the reactive column: reflux ratio 5.8, reboil ratio 5.7 and feed condition 0.91. The stage holdup in the rectifying section was specified to 0.697 m$^3$ and for the stripping section to 0.6 m$^3$. The product compositions predicted by simulation are compared to those specified in the conceptual design method (Table 6.6). The simulation results show good agreement with the conceptual design method.

Table 6.6 Product compositions obtained by simulation, based on the results from the conceptual design procedure

<table>
<thead>
<tr>
<th></th>
<th>Simulation results</th>
<th>Conceptual design specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Composition</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Component</td>
<td>$x_F$</td>
<td>$x_D$</td>
</tr>
<tr>
<td>C$_5$</td>
<td>1.0*</td>
<td>0.05768</td>
</tr>
<tr>
<td>C$_4$</td>
<td>0.0*</td>
<td>0.94164</td>
</tr>
<tr>
<td>C$_6$</td>
<td>0.0*</td>
<td>0.00068</td>
</tr>
<tr>
<td><strong>Flowrates</strong></td>
<td>[kmol/h]</td>
<td>100*</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Total reaction extent</strong></td>
<td>[kmol/h]</td>
<td>47.15</td>
</tr>
</tbody>
</table>

* Specified values

Hybrid configurations were also investigated for this system; Table 6.7 lists three configurations with the top section reactive, satisfying the relaxed reaction extent constraint and the feed condition between 0 and 1.2. Because this
system is better suited to fully reactive columns, the hybrid configurations obtained have very few non-reactive stripping stages. Also, all the designs found satisfy only the relaxed reaction extent constraint. Therefore, using any hybrid configuration from Table 6.7 to initialise a rigorous simulation (e.g. Design 3) will lead to a lower composition in the top of the column than the distillate composition specified in the conceptual design method, due to a lower total reaction extent (Table 6.8).

Table 6.7 Hybrid reactive column designs for the metathesis reaction, satisfying the relaxed reaction extent constraint, with the feed condition between 0-1.2.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>3</td>
<td>13</td>
<td>11.56</td>
<td>11.33</td>
<td>0.889</td>
<td>0</td>
<td>0.39</td>
<td>37.9</td>
<td>3795</td>
<td>4182</td>
<td>3.41</td>
</tr>
<tr>
<td>2</td>
<td>14</td>
<td>2</td>
<td>16</td>
<td>16.44</td>
<td>17.53</td>
<td>1.000</td>
<td>0</td>
<td>1.04</td>
<td>45.3</td>
<td>5269</td>
<td>6467</td>
<td>8.56</td>
</tr>
<tr>
<td>3</td>
<td>14</td>
<td>2</td>
<td>16</td>
<td>16.43</td>
<td>17.83</td>
<td>1.000</td>
<td>0</td>
<td>1.20</td>
<td>46.1</td>
<td>5266</td>
<td>6580</td>
<td>8.64</td>
</tr>
</tbody>
</table>

*Reactive stages

Table 6.8 Product compositions obtained by simulation, using a top section reactive column (Design 3 Table 6.7)

<table>
<thead>
<tr>
<th>Component</th>
<th>Simulation results</th>
<th>Conceptual design specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Feed</td>
<td>Distillate</td>
</tr>
<tr>
<td>C_5</td>
<td>x_F</td>
<td>x_D</td>
</tr>
<tr>
<td></td>
<td>1.0*</td>
<td>0.13940</td>
</tr>
<tr>
<td>C_4</td>
<td>0.0*</td>
<td>0.85643</td>
</tr>
<tr>
<td>C_6</td>
<td>0.0*</td>
<td>0.00417</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Flowrates</th>
<th>[kmol/h]</th>
<th>100*</th>
<th>53.30</th>
<th>46.70</th>
<th>100</th>
<th>50</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total reaction extent</td>
<td>[kmol/h]</td>
<td>45.65</td>
<td>47.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Specified values
6.6.2. MTBE synthesis

The second example to illustrate the automated feasibility and design procedure for kinetically-controlled hybrid columns is methyl tertiary butyl ether (MTBE) production. The conceptual design of the equilibrium reactive distillation process for this system was presented in Section 4.6.2. In this section we will analyse the influence of non-equilibrium reactive conditions on column design.

\[
\text{IB} + \text{MeOH} \xleftrightarrow{\text{Cat.}} \text{MTBE}
\]  
(Eq. 6.63)

MTBE results from the reaction between iso-butene (IB) and methanol (MeOH) (Eq. 6.63) The reactive mixture contains n-butane as an inert component. MTBE is a heavy product and it will be obtained as a bottom product. The thermodynamic and kinetic data are listed in Appendix E.2. For this example, the kinetic model proposed by Chen et al. (2002) was used (Eq. 6.64).

\[-r_{IB} = k_i \left( a_{IB} a_{\text{MeOH}} - \frac{a_{\text{MTBE}}}{K_{eq}} \right)\]  
(Eq. 6.64)

where:

\[K_{eq} = 8.33 \cdot 10^{-8} \exp \left( \frac{6820}{T} \right)\]  
(Eq. 6.65)

\[K_i = 4464 \exp \left( -\frac{3187}{T} \right) \text{ h}^{-1}\]  
(Eq. 6.66)

The thermodynamic parameters used to model this system are listed in Appendix E.2.

For the design procedure, both fully reactive and hybrid configurations were considered in analysis, as the composition profiles are not confined to the reactive surface. However, MTBE decomposes into reactants on reactive stages below the feed stage (i.e. the reaction extent has a negative value); therefore only hybrid configurations with the top section reactive are possible. The product compositions were fully specified, along with feed specification: feed flowrate and feed composition for the reaction base component i-Butene.
However, because the design procedure for hybrid kinetically-controlled columns does not require a fully specified product composition for the non-reactive section (in this case MTBE), the specifications in Table 6.9 are used only for mass balance calculation. To satisfy the degrees of freedom for the mass balance, one other parameter needs to be specified, between D/F, B/F, the feed composition for a component other than the base component and reaction extent. The composition (mole fraction) for i-Butene in the feed was specified to 0.32. The remaining variables are calculated from the overall mass balance. For the specified product compositions, the reaction conversion will be 97%.

Table 6.9 Feed and product compositions for MTBE system

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Stoichiometry</th>
<th>Boiling points (8 bar)</th>
<th>Distillate</th>
<th>Bottom</th>
<th>Feed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ν</td>
<td>T_B [°C]</td>
<td>X_D</td>
<td>X_B</td>
<td>X_F</td>
</tr>
<tr>
<td>i-Butene</td>
<td>-1</td>
<td>61.4</td>
<td>0.025#</td>
<td>0.0006#</td>
<td>0.32#</td>
</tr>
<tr>
<td>Methanol</td>
<td>-1</td>
<td>128.0</td>
<td>0.005#</td>
<td>0.004#</td>
<td>0.3136</td>
</tr>
<tr>
<td>MTBE</td>
<td>1</td>
<td>136.4</td>
<td>1.E-6#</td>
<td>0.98#</td>
<td>0.0#</td>
</tr>
<tr>
<td>n-Butane</td>
<td>0</td>
<td>69.4</td>
<td>0.97#</td>
<td>0.0154#</td>
<td>0.3664</td>
</tr>
</tbody>
</table>

# Specified values

To generate the stage composition surfaces, the ranges for reflux and reboil ratios and for the holdup were specified, as well as the maximum number of stages in each section (Table 6.10)

Table 6.10 Specifications for generating stage composition lines

<table>
<thead>
<tr>
<th>Distillate flowrate</th>
<th>Bottoms flowrate</th>
<th>Feed flowrate</th>
<th>Reflux ratio range</th>
<th>Reboil ratio range</th>
<th>Rectifying stages range</th>
<th>Stripping stages range</th>
<th>Holdup range</th>
</tr>
</thead>
<tbody>
<tr>
<td>D [kmol/h]</td>
<td>B [kmol/h]</td>
<td>F [kmol/h]</td>
<td>r [-]</td>
<td>s [-]</td>
<td>n [-]</td>
<td>M [-]</td>
<td>q [m^3]</td>
</tr>
<tr>
<td>37.26</td>
<td>31.68</td>
<td>100</td>
<td>0.5 – 20</td>
<td>0.5 – 20</td>
<td>1 – 20</td>
<td>1 – 20</td>
<td>0.05-0.5</td>
</tr>
</tbody>
</table>

The first step in the design procedure is to check if the constant molar overflow assumption is valid for this system. Figure 4.21 shows that the constant molar
overflow is not an appropriate assumption for the reactive section; energy balances were included in the calculation of reactive composition profiles. For the non-reactive system the assumption of constant molar overflow holds, therefore we can use Eq. 6.7 and 6.8 to calculate the composition profiles.

![Graph showing composition profiles](image)

**Figure 6.17 Influence of constant molar overflow on composition profiles calculated using BVM, for the MTBE system. (a) Rectifying reactive section; (b) Stripping non-reactive section**

Using the reflux and reboil ratios and the holdup ranges listed in Table 6.10, stage composition surfaces are calculated for the rectifying section. The line of constant reaction extent is then computed as a series of points, and the non-reactive stripping composition profiles are calculated top-down from the feed stage. The feed condition was specified as saturated liquid. An energy balance is used at the feed stage to obtain starting points for the calculation of composition profiles in the stripping section, and to calculate the reboil ratio. Figure 6.18 shows the line of constant reaction extent and the stripping composition profiles calculated downwards from the feed stage; transformed variables were used for visualisation.

The first 10 designs ranked by total annualised cost, obtained using on the procedure described in this chapter, are listed in Table 6.11.
Figure 6.18 One line of constant reaction extent and stripping composition profiles in transformed variables, calculated from the feed stage. Kinetic and thermodynamic data for the MTBE system are listed in Appendix E.2.

Table 6.11 Ten feasible column designs, ranked by total annualised cost, for the MTBE system, satisfying the total reaction extent constraint

<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
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<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>7</td>
<td>17</td>
<td>4.79</td>
<td>5.49</td>
<td>0.05</td>
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<td>1161</td>
<td>1232</td>
<td>0.503</td>
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<td>2</td>
<td>9</td>
<td>5</td>
<td>14</td>
<td>5.46</td>
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<td>0.07</td>
<td>-</td>
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<td>1297</td>
<td>1590</td>
<td>0.512</td>
</tr>
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<td>9</td>
<td>5</td>
<td>14</td>
<td>5.56</td>
<td>7.14</td>
<td>0.06</td>
<td>-</td>
<td>1</td>
<td>1316</td>
<td>1601</td>
<td>0.513</td>
</tr>
<tr>
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<td>5</td>
<td>14</td>
<td>5.51</td>
<td>7.17</td>
<td>0.08</td>
<td>-</td>
<td>1</td>
<td>1307</td>
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<td>5</td>
<td>9</td>
<td>5</td>
<td>14</td>
<td>5.64</td>
<td>7.30</td>
<td>0.09</td>
<td>-</td>
<td>1</td>
<td>1332</td>
<td>1638</td>
<td>0.518</td>
</tr>
<tr>
<td>6</td>
<td>9</td>
<td>5</td>
<td>14</td>
<td>5.74</td>
<td>7.36</td>
<td>0.09</td>
<td>-</td>
<td>1</td>
<td>1352</td>
<td>1650</td>
<td>0.520</td>
</tr>
<tr>
<td>7</td>
<td>9</td>
<td>5</td>
<td>14</td>
<td>6.00</td>
<td>7.48</td>
<td>0.05</td>
<td>-</td>
<td>1</td>
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<td>1677</td>
<td>0.524</td>
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<tr>
<td>8</td>
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<td>15</td>
<td>3.71</td>
<td>4.74</td>
<td>0.02</td>
<td>-</td>
<td>1</td>
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<td>0.593</td>
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<td>15</td>
<td>3.84</td>
<td>4.57</td>
<td>0.01</td>
<td>-</td>
<td>1</td>
<td>971</td>
<td>1026</td>
<td>0.604</td>
</tr>
<tr>
<td>10</td>
<td>11</td>
<td>4</td>
<td>15</td>
<td>4.32</td>
<td>5.13</td>
<td>0.01</td>
<td>-</td>
<td>1</td>
<td>1066</td>
<td>1151</td>
<td>0.653</td>
</tr>
</tbody>
</table>

Reactive stages
Design 1 from Table 6.11 is used to initialise a rigorous simulation using HYSYS v2.4, using 10 rectifying stages and 7 stripping stages (including the condenser and reboiler). The results of the conceptual design method were used to specify the reactive column: reflux ratio 4.8, reboil ratio 5.5 and feed condition 1. The stage holdup in the rectifying section was specified to be 0.05 m³.

Table 6.12 Product compositions obtained by simulation for the MTBE process, based on the results from the conceptual design procedure

<table>
<thead>
<tr>
<th>Component</th>
<th>$x_F$</th>
<th>$x_D$</th>
<th>$x_B$</th>
<th>$x_F$</th>
<th>$x_D$</th>
<th>$x_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>i-Butene</td>
<td>0.3200</td>
<td>0.0182</td>
<td>0.0001</td>
<td>0.32</td>
<td>0.025</td>
<td>0.0006</td>
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<tr>
<td>Methanol</td>
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<td>0.004</td>
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<tr>
<td>MTBE</td>
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<td>2.6E-06</td>
<td>0.9232</td>
<td>0.0</td>
<td>1.E-6</td>
<td>0.98</td>
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<tr>
<td>n-Butane</td>
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<td>0.9817</td>
<td>0.0766</td>
<td>0.3664</td>
<td>0.97</td>
<td>0.0154</td>
</tr>
</tbody>
</table>

Flowrates

| [kmol/h] | 100.00 | 34.67  | 33.97  | 100    | 37.26  | 31.68  |

Total reaction extent

| [kmol/h] | 31.36  | 31.04  |

The results in Table 6.11 show that using the conceptual design specification to initialise the rigorous simulation, the purity of MTBE in the bottom product is lower than 98%. This is mainly caused by the errors introduced by the linear interpolation in the calculation of the constant reaction extent line. To improve the results, a better approach will be to introduce a root search algorithm at this step, at the expense of computational time, to calculate the exact reflux ratio or holdup necessary to obtain the desired reaction extent on a certain stage. However, the results obtained by interpolation offer good starting point for rigorous simulation. In this case, by reducing the reflux ratio from 4.7 to 3.5 the specified purity of MTBE in the bottom product will be met.
6.7. Conclusions

In this chapter, a design methodology for kinetically-controlled reactive distillation columns has been developed. The assumption of equilibrium reaction on each stage was eliminated by considering kinetic models in the calculation of reaction extent. For kinetically-controlled reactive columns, a supplementary feasibility criterion has to be satisfied, verifying the total reaction extent in the column. This introduces a limitation in obtaining feasible design using BVMs, as typically very few feasible points are found to satisfy the additional constraint. In this work, this limitation has been relaxed by considering a range of holdups for the rectifying and stripping sections. SCLs for a range of holdups form surfaces; intersection of these surfaces forms a line of potentially feasible designs. The feasible designs are obtained by performing a search along this line for points satisfying the total reaction extent.

The methodology developed in this chapter fills in a significant gap in conceptual design of kinetically-controlled reactive systems. The available conceptual design methods (Buzad and Doherty, 1994, 1995; Mahajani, 1999) generally consider fully reactive columns, fixed holdup and fixed feed condition, and they are highly iterative. Also, they are based on the intersection of composition profiles, which restricts their applicability to three components only. By considering SCLs and SCSs in the conceptual design methodology, the feasible solution space has been extended significantly, and the probability of obtaining feasible designs increased. Most importantly, the use of SCSs in the column synthesis and design allowed the extension to quaternary systems, which have not been addressed so far in a systematic framework. Also, the methodology developed in this chapter can accommodate both fully reactive and hybrid columns (top or bottom section reactive), which have not been addressed so far in the open literature in a systematic approach.
The applicability of the methodology is restricted by the graphical representation to maximum four components. However, most of the reactive systems of interest (Sharma, 2001) are systems with one reaction and maximum four components (esterification, etherification, hydrolysis or isomerisation reactions). The two case-studies presented showed that the methodology can be successfully applied, by including appropriate VLE models in the composition profiles calculation, to both ideal (olefin metathesis) and highly non-ideal systems (MTBE system). The results obtained from the design procedure provided very good initialisation for rigorous simulation.

The methodology, for both ternary and quaternary mixtures, offers a systematic tool for synthesis and design of kinetically-controlled reactive distillation columns. The methodology is easily automated and typically generates multiple designs. A general design framework has been developed, including both fully reactive and hybrid configurations, allowing the design engineer to efficiently compare between various design options.
7. CONCLUSIONS AND FUTURE WORK

7.1. Conclusions

In the past decades, combining reaction with distillation in a single unit has proved to be very effective; production of fuel ethers (MTBE, ETBE and TAME) and methyl-acetate are only a few of the most successful industrial applications (Sundmacher and Kienle, 2003). The challenge, in the context of growing interest in developing new reactive distillation applications, is to develop fast and effective tools for assessing the feasibility and designing such processes. Conceptual design methods proved to be very helpful in understanding the underlying phenomena of reactive distillation process and providing insights into the behaviour of the reactive systems. However, their development is limited by the complexity of the problem, on one hand caused by the phase non-idealities of reactive systems, and on the other by the restrictions imposed by the chemical reaction (reactive equilibrium constraints or holdup requirements). Further difficulties are encountered when hybrid configurations are considered. During the conceptual design steps, promising column configurations and column design parameters (number of stages, reflux and reboil ratios, feed condition) need to be identified and compared, for a cost effective reactive distillation process. Therefore, there is a need for improving the existing methods or finding new approaches to facilitate an efficient comparison between various design options.

The methodologies developed in this work facilitate a step change in conceptual design practice, offering a systematic and easy to use tool for the synthesis and design of reactive distillation columns. The major contributions of this work can be summarised as follows:

- A systematic methodology for the synthesis and design of equilibrium hybrid reactive distillation columns has been developed. The methodology, based on the intersection of SCLs and/or composition
profiles in transformed space, takes full advantage of some insight and specific features of hybrid reactive distillation columns. By introducing the intersections of non-reactive SCLs with the reactive surface in column design allowed a wider range of hybrid configurations and feed arrangements to be analysed: top or bottom section reactive columns, columns with a reactive core, with the feed at either the interface between the reactive and the non-reactive sections or within the reactive section. For synthesis purposes, both fully reactive (method developed by Groemping, 2002) and hybrid configurations were introduced in the same framework, allowing a more efficient evaluation of design alternatives; case studies showed that hybrid configurations are usually preferred over fully reactive columns due to a lower total cost.

- Based on the concepts developed for single-feed columns, the methodology was extended to accommodate double-feed columns. Both fully reactive and hybrid double-feed configurations have been addressed. Case studies showed that double-feed configurations offer a higher flexibility in the synthesis and design of reactive distillation columns, mainly by extending the feasible domain (e.g. by allowing distillation boundaries to be crossed), and by improving the contact between the reactants, thus leading to a lower total cost compared to single-feed columns.

- The assumption of equilibrium reaction on each stage was eliminated, and a design methodology for kinetically-controlled reactive distillation columns has been developed. By considering SCLs and SCSs in the conceptual design methodology, the feasible solution space has been extended significantly, and the probability of obtaining feasible designs increased. Also, the methodology developed in this chapter can accommodate both fully reactive and hybrid columns (top or bottom section reactive), which have not been addressed so far in the open literature in a systematic approach.
The main benefit of the methodologies developed in this work is given by the systematic approach; various configurations are addressed in the same framework, thus allowing a more rapid screening for feasible designs. Also, the use of stage composition lines (SCLs) and stage composition surfaces (SCSs, for kinetically-controlled reactions), offer a higher flexibility in assessing the feasibility of a proposed separation task. The constant molar overflow assumption, common in available conceptual design methods, was eliminated in this work. A preliminary test for the validity of the assumption of constant molar overflow was performed in all cases, and heat balances were included in the calculation of the composition profiles if necessary.

The applicability of the methodologies is restricted by the graphical representation to systems with two degrees of freedom (according to the Gibbs Phase Rule) for equilibrium reactions and maximum four components for kinetically-controlled reactions. However, as mentioned previously in this work, most of the reactive systems of interest (Sharma, 2001) are systems with one reaction and maximum four components (esterification, etherification, hydrolysis or isomerisation reactions).

All methodologies presented in this work can be easily automated and typically generate multiple designs. The methodologies developed offer a systematic tool for synthesis and design of reactive distillation columns; the general design framework including various column configurations – fully reactive and hybrid configurations, single and double-feed columns – allowing the design engineer to efficiently compare between various design options.

7.2. Future work

The methodologies presented in this work offer a very good basis for developing a more generalised framework, including more complex reactive column configurations. Columns with a side rectifier, a side stripper or a side reactor can prove efficient in overcoming some of the separation limitations that
often occur in reactive systems. Also, columns with a side draw or dividing wall columns may prove to be the solution for eliminating some intermediate boiling component which affects the selectivity of a desired reaction.

This work assumed that phase equilibrium is achieved on all trays. This assumption can be eliminated by introducing rate-based models. Even though introducing rate based models will increase the dimensionality of the composition profiles (from a series of discrete point to a continuous line), thus making difficult the use of SCLs, the applicability of the methodologies developed in this work is still possible if some practical considerations are taken into account. Commercial catalytic packings (such as Katapak-S, Mellapak, etc.) are usually built in stacks (Chapter 6); therefore the concept of SCLs can be redefined as representing all possible compositions at a certain *height* in a packed reactive column, for all reflux or reboil ratios. Using this definition, the methodologies developed in this work can be applied directly to accommodate non-equilibrium mass transfer.

Another area worth investigating is the extension of the methodologies to accommodate multicomponent systems. Unfortunately, due to the limitations of the methodologies caused by the graphical representation, the direct application of the methodologies to multicomponent systems is not very straightforward. However, the concepts developed in this work, combined with the method of Groemping (2002) for multicomponent systems, could be applied to investigate a wider variety of configurations, such as columns with a reactive core or double-feed configurations.
**NOTATIONS**

Vectors and matrices are printed bold.

**Latin symbols**

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<thead>
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<th>Symbol</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
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<td>$B$</td>
<td>bottoms molar flowrate</td>
<td>kmol/h</td>
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<tr>
<td>$C$</td>
<td>number of components</td>
<td>-</td>
</tr>
<tr>
<td>$D$</td>
<td>distillate molar flowrate</td>
<td>kmol/h</td>
</tr>
<tr>
<td>$Da$</td>
<td>Damköhler number</td>
<td>-</td>
</tr>
<tr>
<td>$DOF$</td>
<td>degrees of freedom</td>
<td>-</td>
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<td>$F$</td>
<td>feed molar flowrate</td>
<td>kmol/h</td>
</tr>
<tr>
<td>$F'$</td>
<td>transformed feed flowrate</td>
<td>kmol/h</td>
</tr>
<tr>
<td>$h$</td>
<td>specific enthalpy</td>
<td>kJ/kmol</td>
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<tr>
<td>$H$</td>
<td>reactive holdup</td>
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<tr>
<td>$K_{eq}$</td>
<td>thermodynamic equilibrium constant</td>
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<td>$L$</td>
<td>liquid molar flowrate</td>
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</tr>
<tr>
<td>$L'$</td>
<td>transformed liquid molar flowrate</td>
<td>kmol/h</td>
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<td>$N_{MR}$</td>
<td>number of stages in the rectifying middle section</td>
<td>-</td>
</tr>
<tr>
<td>$N_{MS}$</td>
<td>number of stages in the stripping middle section</td>
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</tr>
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<td>number of stages above the feed (rectifying section) for a column design (including condenser)</td>
<td>-</td>
</tr>
<tr>
<td>$N_{S}$</td>
<td>number of stages below the feed (stripping section) for a column design (including reboiler)</td>
<td>-</td>
</tr>
<tr>
<td>$N_{TOT}$</td>
<td>total number of stages in the column (including condenser and reboiler)</td>
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<td>$P$</td>
<td>pressure</td>
<td>bar</td>
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<td>$P_{i,sat}$</td>
<td>saturation pressure of component i</td>
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<tr>
<td>$q$</td>
<td>feed quality ($q = 0$: saturated vapour, $q = 1$: saturated liquid)</td>
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</tr>
<tr>
<td>$Q$</td>
<td>heat duty</td>
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<td>$\bar{R}_n$</td>
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</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
<td>K</td>
</tr>
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<td>$V$</td>
<td>vapour molar flowrate</td>
<td>kmol/h</td>
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<td>$x$</td>
<td>liquid mole fraction</td>
<td>kmol/kmol</td>
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<td>$x_{n,ref}$</td>
<td>column vector of R reference component liquid mole fractions leaving stage n</td>
<td>kmol/kmol</td>
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<td>transformed vapour composition (A.2)</td>
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<td>$y$</td>
<td>vapour mole fraction</td>
<td>kmol/kmol</td>
</tr>
<tr>
<td>$y_{n,ref}$</td>
<td>column vector of R reference component vapour mole fractions leaving stage n</td>
<td>kmol/kmol</td>
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**Greek symbols**

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<tr>
<td>$\alpha$</td>
<td>relative volatility</td>
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<tr>
<td>$\xi$</td>
<td>column vector of R molar extents of reaction</td>
<td>Kmol/h</td>
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<td>$\gamma_{ref}$</td>
<td>square matrix of dimension $(R, R)$ of stoichiometric coefficients for the R reference components in the R reactions</td>
<td>-</td>
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<tr>
<td>$\phi$</td>
<td>diameter</td>
<td>m</td>
</tr>
<tr>
<td>$\Pi$</td>
<td>number of phases</td>
<td>-</td>
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<tr>
<td>$\nu_i$</td>
<td>column vector of R stoichiometric coefficient of component $i$</td>
<td>-</td>
</tr>
<tr>
<td>$\nu_{tot}$</td>
<td>column vector of R sums of stoichiometric coefficients</td>
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**Sub- and Superscripts**

<table>
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<tr>
<td>$V$</td>
<td>vapour</td>
</tr>
<tr>
<td>$L$</td>
<td>liquid</td>
</tr>
<tr>
<td>$B$</td>
<td>bottoms</td>
</tr>
<tr>
<td>$D$</td>
<td>distillate</td>
</tr>
<tr>
<td>$F$</td>
<td>feed</td>
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### Notations

<table>
<thead>
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<th>Symbol</th>
<th>Description</th>
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<tr>
<td>$i$</td>
<td>counter for components ($i = 1, \ldots, C$)</td>
</tr>
<tr>
<td>$j$</td>
<td>counter for components ($j = 1, \ldots, C$)</td>
</tr>
<tr>
<td>$m$</td>
<td>counter for stages in stripping section (including reboiler), ($m = 1, \ldots, NS$)</td>
</tr>
<tr>
<td>$n$</td>
<td>counter for stages in rectifying section (including condenser), ($n = 1, \ldots, NR$)</td>
</tr>
<tr>
<td>$r$</td>
<td>counter for reactions ($r = 1, \ldots, R$)</td>
</tr>
<tr>
<td>$r$</td>
<td>rectifying section</td>
</tr>
<tr>
<td>$s$</td>
<td>stripping section</td>
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### Abbreviations

<table>
<thead>
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<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>AAc</td>
<td>acetic acid</td>
</tr>
<tr>
<td>A, B, C, D</td>
<td>component species</td>
</tr>
<tr>
<td>BVM</td>
<td>boundary value method</td>
</tr>
<tr>
<td>CSTR</td>
<td>continuously stirred tank reactor</td>
</tr>
<tr>
<td>DEC</td>
<td>diethyl carbonate</td>
</tr>
<tr>
<td>DMC</td>
<td>dimethyl carbonate</td>
</tr>
<tr>
<td>EtOH</td>
<td>ethanol</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>water</td>
</tr>
<tr>
<td>IB</td>
<td>iso-butene</td>
</tr>
<tr>
<td>MeAc</td>
<td>methyl acetate</td>
</tr>
<tr>
<td>MeOH</td>
<td>methanol</td>
</tr>
<tr>
<td>MTBE</td>
<td>methyl tertiary butyl ether</td>
</tr>
<tr>
<td>nB</td>
<td>n-butane</td>
</tr>
<tr>
<td>SCL</td>
<td>stage composition line</td>
</tr>
<tr>
<td>SCS</td>
<td>stage composition surface</td>
</tr>
<tr>
<td>RCM</td>
<td>residue curve map</td>
</tr>
<tr>
<td>TAC</td>
<td>total annualised cost</td>
</tr>
<tr>
<td>VLE</td>
<td>vapour-liquid equilibrium</td>
</tr>
<tr>
<td>W</td>
<td>water</td>
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APPENDICES

Appendix A. Reaction Space and Transformed Compositions

For systems with equilibrium reactions, any feasible composition in a reactive section of a column will always lie on the reactive equilibrium surface (or reaction space (Bessling, 1997). According to the Gibbs phase rule for isobaric systems (Wales, 1985) mixtures with two degrees of freedom, even those with more than three components, will have a two-dimensional reaction space; this space can be mapped onto a two-dimensional plane in transformed composition space [Ung and Doherty, 1995; Espinosa et. al., 1995] (Chapter 2).

\[ \text{DOF} = 1 + C - \pi - R \] (A.1)

Figure A.1 Chemical equilibrium surface (grid of thinner lines) and reactive distillation line map (thicker lines lying on surface) (a) in real space and (b) in transformed variables. Decomposition reaction \( c \leftrightarrow a + b \) with inert component \( d \) (Espinosa et. al., 1995a).

The transformed compositions and flowrates are given by Eqs. A.2 and A.3, according to Ung and Doherty (1995a):
\[ X_i = \frac{X_i - v_i^T Y_{ref} x_{ref}}{1 - v_{tot}^T Y_{ref} x_{ref}} \quad \forall \ i = 1, \ldots, C - R - 1, \]  
(A.2)

\[ \bar{F} = F(1 - v_{tot}^T Y_{ref} x_{F,ref}) \]  
(A.3)

where:

\[ v_i = [v_{i,1}, \ldots, v_{i,R}]^T \] - column vector of stoichiometric coefficients of component \( i \) in reaction \( j \);

\[ Y_{ref} = \begin{bmatrix} v_{(C-R+1),1} & \cdots & v_{(C-R+1),R} \\ \vdots & \ddots & \vdots \\ v_{C,1} & \cdots & v_{C,R} \end{bmatrix} \] - matrix of stoichiometric coefficients of reference component \( i \) in reaction \( j \);

\[ x_{ref} = [x_{C-R+1}, \ldots, x_C]^T \] - column vector of \( R \) reference components liquid mole fractions.

Mapping transformed composition back to mole fraction space requires calculation of reactive bubble and dew points for the combined chemical and phase equilibrium condition. In this work, we used the algorithm proposed by Ung and Doherty (1995).

The transformed reaction space depends on the type of reaction and the stoichiometric coefficients. Because the limits of transformed composition space are not 0 and 1, as in real space, the transformed composition space will have various shapes, i.e. for a four component system and one reaction it can be a triangle, a square or a trapezoid. The bounds of the transformed space can be calculated by overlapping the feasible intervals of transformed compositions for each component. The feasible composition intervals for each component are obtained from the equation defining transformed variables (Eq. A.2), by setting the compositions of component \( i \) and the reference component to 0 and 1:

- for \( x_i = 0, \ x_{ref} = 1 \) : \[ X_i = \frac{-v_i^T Y_{ref}}{1 - v_{tot}^T Y_{ref}} \]
- for \( x_i = 1, \ x_{ref} = 0 \) : \[ X_i = 1 \]
- for \( x_i = 0, \ x_{ref} = 0 \) : \[ X_i = 0 \]
Therefore, the minimum and maximum limits will be set by:

\[
X_{i,\text{min}} = \min \left( 0, \frac{-v_i^T \gamma_{\text{ref}}^{-1}}{1 - v_{\text{tot}}^T \gamma_{\text{ref}}^{-1}} \right)
\]

\[
X_{i,\text{max}} = \max \left( 1, \frac{-v_i^T \gamma_{\text{ref}}^{-1}}{1 - v_{\text{tot}}^T \gamma_{\text{ref}}^{-1}} \right)
\]

For example, for a system \( A + B \leftrightarrow C \) (inert \( D \)), taking component \( C \) as the reference component, the feasible intervals for each component are: \( X_A = [0, 1] \), \( X_B = [0, 1] \) and \( X_D = [0, 1] \), the same as in a non-reactive ternary mixture, with the point corresponding to \( x_{\text{ref}} = 1 \) at \( X_A = 0.5 \) and \( X_B = 0.5 \) (Figure A.2(a)).

If component \( D \) participates in the reaction, as in reaction \( A + B \leftrightarrow C + D \), then the feasible intervals for the transformed composition space will be \( X_A = [0, 1] \), \( X_B = [0, 1] \) and \( X_D = [-1, 1] \), resulting in a square, with the point corresponding to \( x_{\text{ref}} = 1 \) being at \( X_A = 1 \) and \( X_B = 1 \) (Figure A.2(b))

Figure A.2 Transformed composition space. (a) reaction \( A + B \leftrightarrow C \) (inert \( D \)); (b) \( A + B \leftrightarrow C + D \)
Appendix B. Composition profiles and internal flows for reactive columns

B.1. Mass and energy balances in single-feed columns

**General mass balance**

\[ F = B + D - \sum_{j=1}^{R} v_{j, tot} \xi_{j, tot} \]  \hspace{1cm} (B.1)

**Component mass balances**

\[ F \cdot x_{F,i} = B \cdot x_{B,i} + D \cdot x_{B,i} - \sum_{j=1}^{R} v_{i,j} \xi_{j, tot} \]  \hspace{1cm} (B.2)

\[ i = 1, \ldots, C - R - 1 \]

**Energy balance**

\[ F \cdot h_{F,i} = B \cdot h_{B,i} + D \cdot h_{B,i} + Q_c - Q_r - \sum_{j=1}^{R} \xi_{j, tot} \cdot \Delta H_{react,j} \]  \hspace{1cm} \( i = 1, \ldots, C - R - 1 \)

\[ h_F = f(T_F, x_F, P, \text{phase}) \]

\[ h_D = f(T_D, x_D, P, \text{liquid}) \]  \hspace{1cm} (B.3)

\[ h_B = f(T_B, x_B, P, \text{liquid}) \]

**General mass balance in transformed variables**

\[ \tilde{F} = \tilde{B} + \tilde{D} \]  \hspace{1cm} (B.4)

**Component mass balances in transformed variables**

\[ \tilde{F} \cdot x_{F,i} = \tilde{B} \cdot x_{B,i} + \tilde{D} \cdot x_{B,i} \]  \hspace{1cm} \( i = 1, \ldots, C - R - 1 \)  \hspace{1cm} (B.5)
There are C - R equations for the mass balances, and 3(C - R - 1)+3 unknowns. Setting a set of fully specified transformed product compositions, and the feed flowrate, there is \( [3 \cdot (C - R - 1) + 3] - (C - R) - [2 \cdot (C - R - 1) + 1] = 1 \) degree of freedom remaining. For the remaining degree of freedom, either \( \bar{D} \), \( \bar{B} \) or the feed composition for a component other than the reference component can be specified. The remaining variables will be calculated from the mass balances (Eqs. B.4 and B.5).

For the calculation of the R reaction extents, the compositions of the R reference components in all streams are needed. The total reaction extents will be:

\[
\begin{bmatrix}
\xi_{\text{tot},1} \\
\vdots \\
\xi_{\text{tot},R}
\end{bmatrix} =
\begin{bmatrix}
v_{(C-R+1),1} & \cdots & v_{(C-R+1),R}
\vdots & \ddots & \vdots \\
v_{C,1} & \cdots & v_{C,R}
\end{bmatrix}
\begin{bmatrix}
x_{D,\text{ref},1} \\
\vdots \\
x_{D,\text{ref},R}
\end{bmatrix} +
\begin{bmatrix}
x_{B,\text{ref},1} \\
\vdots \\
x_{B,\text{ref},R}
\end{bmatrix} -
\begin{bmatrix}
x_{F,\text{ref},1} \\
\vdots \\
x_{F,\text{ref},R}
\end{bmatrix}
\]

(B.6)

Using the following vector definitions:
- column vector of reaction extents for the R reactions

\[
\xi_{\text{tot}} = \begin{bmatrix}
\xi_{\text{tot},1} \\
\vdots \\
\xi_{\text{tot},R}
\end{bmatrix}
\] (B.7)

- matrix of stoichiometric coefficients of reference component \( i \) in reaction \( j \).

\[
\gamma_{\text{ref}} = \begin{bmatrix}
v_{(C-R+1),1} & \cdots & v_{(C-R+1),R} \\
\vdots & \ddots & \vdots \\
v_{C,1} & \cdots & v_{C,R}
\end{bmatrix}
\] (B.8)

- column vector of mole fractions for the R reference components.

\[
x_{\text{ref}} = \begin{bmatrix}
x_{\text{ref},1} \\
\vdots \\
x_{\text{ref},R}
\end{bmatrix}
\] (B.9)

Eq. B.6 can be written as:
Condenser and Reboiler Duties

Heat Balance around condenser (non-reactive total condenser)

Mass balance:

\[ V_2 = D + L_1; \quad R_{\text{ext}} = \frac{L_1}{D} \] (B.11)

Heat balance:

\[ Q_c = V_2 h_2 - D h_0 - L_1 h_0 \]
\[ Q_c = V_2 h_2 - h_0 (D + L_1) \] (B.13)

using Eq. B.8:

\[ Q_c = (R_{\text{ext}} + 1)(h_2 - h_0)D = D(R_{\text{ext}} + 1)\dot{x}_D \] (B.14)

Where

\[ h_D \] - specific enthalpy of distillate, kJ/kmol
\[ h_2 \] - specific enthalpy of the vapour leaving stage 2, kJ/kmol
\[ Q_C \] - condenser duty, kJ/s
\[ P \] - pressure in the condenser, bar
\[ T_2 \] - temperature of vapour leaving tray 2, K
\[ T_D \] - temperature of liquid leaving condenser (tray 1), K
\[ \lambda_D \] - latent heat of vaporisation for the distillate, kJ/kmol

Heat Balance around reboiler (kettle reboiler)

Mass balance:

\[ L_2 = B + V_1; \quad S_{\text{ext}} = \frac{V_1}{B}; \] (B.15)
\[ L_2 = (S_{\text{ext}} + 1)B \] (B.16)

Heat balance:

\[ Q_r = B h_B + V_1 h_1 - L_2 h_2 \] (B.17)
using Eq. B.8:

\[ Q_r = B \cdot S_{ext} \cdot h_1 + B \cdot h_B - (S_{ext} + 1) \cdot B \cdot h_2 \]  

\[ Q_r = B \cdot [(h_B - h_2) + S_{ext} (h_1 - h_2)] \]  

(B.18)

Where:

- \( h_B \) - specific enthalpy of bottom product, kJ/kmol
- \( h_1 \) - specific enthalpy of the vapours leaving reboiler (stage 1), kJ/kmol
- \( h_2 \) - specific enthalpy of the liquid leaving stage 2, kJ/kmol
- \( Q_r \) - reboiler duty, kJ/s
- \( P \) - pressure in the reboiler, bar
- \( T_2 \) - temperature of liquid leaving tray 2, K
- \( T_B \) - temperature of reboiler (tray 1), K

B.2. Mass and energy balances in double-feed columns

**General mass balance**

\[ F = B + D - \sum_{j=1}^{R} v_{tot,j} \xi_{tot,j} \]  

(B.19)

**Component mass balances**

\[ F_U \cdot x_{FU,j} + F_L \cdot x_{FL,i} = B \cdot x_{B,j} + D \cdot x_{B,i} - \sum_{j=1}^{R} v_{i,j} \xi_{tot,j} \]  

\[ i = 1, \ldots, C - R - 1 \]  

(B.20)

**Energy balance**

\[ F_U \cdot h_{FU,i} + F_L \cdot h_{FL,i} = B \cdot h_{B,j} + D \cdot h_{B,i} + Q_{cond} - Q_{reb} - \sum_{j=1}^{R} \xi_{tot,j} \cdot \Delta H_{react,j} \]  

\[ i = 1, \ldots, C - R - 1 \]

\[ h_{FU} = f(T_{FU}, x_{FU}, P, \text{phase}) \]

\[ h_{FL} = f(T_{FL}, x_{FL}, P, \text{phase}) \]

\[ h_D = f(T_D, x_D, P, \text{liquid}) \]  

\[ h_B = f(T_B, x_B, P, \text{liquid}) \]  

(B.21)
By choosing a set of R reference components, eliminating the reaction extent from the R corresponding component mass balances and using the definition of transformed compositions (Eq. A.2) and transformed flowrates (Eq. A.3), the mass balances in Eq. B.19 and B.20 become (Ung and Doherty, 1997):

**General mass balance in transformed variables**

\[
F_u + F_L = B + D \tag{B.22}
\]

**Component mass balances in transformed variables**

\[
F_u \cdot X_{FU,i} + F_L \cdot X_{FL,i} = B \cdot X_{B,i} + D \cdot X_{B,i} \quad \text{for } i = 1, \ldots, C - R - 1 \tag{B.23}
\]

Using the ratios \( U, E \) and \( L \), Eqs. B.10 and B.11 become:

\[
E + 1 = U \cdot E + L \tag{B.24}
\]

\[
E \cdot X_{FU,i} + X_{FL,i} = U \cdot E \cdot X_{D,i} + L \cdot X_{B,i} \quad \text{for } i = 1, \ldots, C - R - 1 \tag{B.25}
\]

There are C-R equations for the transformed mass balances, and 4(C-R-1) + 3 unknowns. Fully specifying a set of transformed product compositions and the composition for one of the feeds (the specified feed), there are [4(C-R-1) + 3] - (C-R) - [3(C-R-1)] = 2 degrees of freedom remaining. If the mole fraction for one component other than the reference component for the second feed is specified, there is one degree of freedom remaining, which can be specified between any of the ratios \( U, E, L \). The remaining variables will be calculated from the mass balances (Eqs. B.22 and B.23).

For the calculation of the R reaction extents, the compositions of the R reference components in all streams involved are needed. The total reaction extents will be:

\[
\begin{bmatrix}
\xi_{ref,1}^f \\
\vdots \\
\xi_{ref,R}^f
\end{bmatrix} = \begin{bmatrix}
\nu_{(C-R)+1,1} \\
\vdots \\
\nu_{j,j} \\
\vdots \\
\nu_{C,1} \\
\vdots \\
\nu_{C,R}
\end{bmatrix} \cdot \begin{bmatrix}
D \\
\vdots \\
B
\end{bmatrix} \cdot \begin{bmatrix}
X_{D,ref,1} \\
\vdots \\
X_{D,ref,R} \\
X_{B,ref,1} \\
\vdots \\
X_{B,ref,R} \\
X_{FU,ref,1} \\
\vdots \\
X_{FU,ref,R} \\
X_{FL,ref,1} \\
\vdots \\
X_{FL,ref,R}
\end{bmatrix} + \begin{bmatrix}
F_U \\
\vdots \\
F_L
\end{bmatrix} \tag{B.26}
\]
Using the vectors defined by Eqs. B.7 to B.9, Eq. B.26 can be written as:

\[
\xi_{\text{tot}} = \gamma_{\text{ref}}^{-1} \cdot \left( B \cdot x_{\text{ref}} + D \cdot x_{\text{D,ref}} - F_U \cdot x_{\text{U,ref}} - F_L \cdot x_{\text{L,ref}} \right)
\]  

(B.27)

The condenser and reboiler duties are calculated with equations derived for single-feed columns (Eqs. B.14 and B.17), as they are not affected by the presence of the second feed.

**B.3. Calculation of profiles in a reactive column under the assumption of constant molar overflow in transformed variables**

**B.3.1. Equilibrium reaction**

**Rectifying section**

A mass balance around the rectifying section of the column (Figure B.1(a)) will give:

\[
V_{r,n+1}, y_{r,n+1} \rightarrow L_{r,n}, x_{r,n} \rightarrow V_{r,t}, y_{r,1,t} \\
L_{s,n+1}, x_{s,n+1} \rightarrow D, x_{D,n} \rightarrow L_{s,0}, x_{s,0,n} \\
V_{s,m}, y_{s,m} \rightarrow V_{s,0}, y_{s,0} \rightarrow V_{s,0,1} \\
R_{\text{ext}} = L_{r,0} / D
\]

(a)

\[
S_{\text{ext}} = V_{s,0} / B \rightarrow B, x_{b,1} \\
L_{r,0}, x_{r,0} \rightarrow V_{r,0}, y_{r,0,1} \rightarrow V_{r,0,1} \\
V_{r,t}, y_{r,1,t} \rightarrow L_{r,0}, x_{r,0} \rightarrow V_{r,0}, y_{r,0,1} \rightarrow V_{r,0,1}
\]

(b)

Figure B.1 (a) Rectifying and (b) stripping sections for generating composition profiles

**General mass balance:**

\[
V_{r,n+1} = L_{r,n} + D - \sum_{j=1}^{R} V_{\text{tot},j} \xi_{r,n,j}
\]  

(B.28)
Component mass balance

\[ V_{r,n+1}Y_{r,n+1} = L_{r,n}x_{r,n,j} + Dx_{D,j} - \sum_{j=1}^{R} v_{i,j}z_{r,n,j} \quad i = 1, \ldots, C - 1 \]  \hspace{1cm} (B.29)

By choosing a set of \( R \) reference components \( x_{ref,j} \), eliminating the reaction extent \( \xi_{r,n,j} \) from \( R \) component mass balances and rearranging the equations using the defined transformed variables (Eqs. A.2 and A.3), the mass balances become (Ung and Doherty, 1997):

General mass balance in transformed variables:

\[ \bar{V}_{r,n+1} = \bar{L}_{r,n} + \bar{D} \]  \hspace{1cm} (B.30)

Component mass balance in transformed variables

\[ \bar{V}_{r,n+1}Y_{r,n+1,j} = \bar{L}_{r,n}x_{r,n,j} + \bar{D}x_{D,j} \quad i = 1, \ldots, C - 1 \]  \hspace{1cm} (B.31)

Using transformed variables the mass balances have the same form as for non-reactive systems.

The operating line for a reactive rectifying section using transformed variables will be:

\[ Y_{r,n+1,j} = \frac{\bar{L}_{r,n}x_{r,n,j}}{\bar{V}_{r,n+1}} + \frac{\bar{D}}{\bar{V}_{r,n+1}}x_{D,j} \quad i = 1, \ldots, C - R - 1 \]  \hspace{1cm} (B.32)

Using the local transformed reflux ratio \( \bar{R}_{n} = \frac{\bar{L}_{n}}{\bar{D}} \), the operation line for the rectifying section is:

\[ Y_{r,n+1,j} = \frac{\bar{R}_{n}}{\bar{R}_{n} + 1}x_{r,n,j} + \frac{1}{\bar{R}_{n} + 1}x_{D,j} \quad i = 1, \ldots, C - R - 1 \]  \hspace{1cm} (B.33)

If the constant molar overflow in transformed variables is valid (Eq. B.34), then the local reflux ratio, \( R_{n} \), is related to the external reflux ratio, \( r_{ext} \), by Eq. B.35.

\[ \bar{L}_{n} = \bar{L}_{0} = \text{constant} \]  \hspace{1cm} (B.34)
\[
\overline{R}_n = \frac{\overline{L}_n}{D} = \frac{\overline{L}_0}{D} = \overline{R}_0 = R_{\text{ext}} \cdot \frac{1 - \nu_{\text{tot}}^T \nu_{\text{tot}}^{-1} \mathbf{x}_{\text{ref},0}}{1 - \nu_{\text{tot}}^T \nu_{\text{tot}}^{-1} \mathbf{x}_{\text{ref},D}} \quad (B.35)
\]

If total condenser is used at the top of the column, then \( \mathbf{x}_{\text{ref},0} = \mathbf{x}_{\text{ref},D} \) and \( \overline{R}_n = R_{\text{ext}} \).

**Stripping section**

A mass balance around the stripping section of the column (Figure B.1 (b)) will give:

**General mass balance:**

\[
L_{s,m+1} = V_{s,m} + B - \sum_{j=1}^{R} \nu_{\text{tot},j} \xi_{s,m,j} \quad (B.36)
\]

**Component mass balance**

\[
L_{s,m+1} \mathbf{x}_{s,m+1,j} = V_{s,m} \mathbf{y}_{s,m,j} + B \mathbf{x}_{B,j} - \sum_{j=1}^{R} \nu_{i,j} \xi_{s,m,j} \quad i = 1, \ldots, C - 1 \quad (B.37)
\]

As with the rectifying section, by choosing a set of reference components \( \mathbf{x}_{\text{ref},j} \) and eliminating the reaction extent \( \xi_{s,m,j} \) from \( R \) component mass balances and rearranging:

**General mass balance in transformed variables:**

\[
\overline{L}_{s,m+1} = \overline{V}_{s,m} + \overline{B} \quad (B.38)
\]

**Component mass balance in transformed variables**

\[
\overline{L}_{s,m+1} \mathbf{X}_{s,m+1,j} = \overline{V}_{s,m} \mathbf{Y}_{s,m,j} + \overline{B} \mathbf{X}_{B,j} \quad i = 1, \ldots, C - 1 \quad (B.39)
\]

The operating line for a reactive stripping section using transformed variables will be:

\[
\mathbf{X}_{s,m+1,j} = \frac{\overline{V}_{s,m}}{\overline{L}_{s,m+1}} \mathbf{Y}_{s,m,j} + \frac{\overline{B}}{\overline{L}_{s,m+1}} \mathbf{X}_{B,j} \quad i = 1, \ldots, C - R - 1 \quad (B.40)
\]
Using the local transformed reboil ratio $\bar{S}_n = \frac{\bar{V}_m}{\bar{B}}$, the operation line for the stripping section is:

$$X_{s,m+1,i} = \frac{\bar{S}_m}{\bar{S}_m + Y_{s,m,i}} + \frac{1}{\bar{S}_m + 1} X_{B,i} \quad i = 1, \ldots, C - R - 1$$ (B.41)

If the constant molar overflow in transformed variables is valid (Eq. B.42), then the local reflux ratio $\bar{S}_m$ is related to the external reflux ratio $s_{\text{ext}}$ by Eq. B.43.

$$\bar{V}_m = \bar{V}_0 = \text{constant}$$ (B.42)

$$\bar{S}_m = \frac{\bar{V}_m}{\bar{B}} = \frac{\bar{V}_0}{\bar{B}} = \bar{S}_0 = \frac{s_{\text{ext}}}{1 - \bar{v}_t \gamma^{-1} Y_{\text{ref,0}}} \quad \text{Eq. B.43}$$

**Middle section**

![Middle section](image)

Figure B.2 (a) Middle rectifying and (b) middle stripping sections for generating middle composition profiles

A middle section can be treated either as a rectifying section, when the profiles are calculated from a defined point (stage) downwards in the column, or as a stripping section, when they are calculated from a defined stage upwards in the column.
**Middle rectifying section**

A mass balance around the middle rectifying section of the column (Figure B.2(a)) will give:

**General mass balance:**

\[
V_{p+1} = L_p + V_1 - L_0 - \sum_{j=1}^{R} V_{i,j} \xi_{j,p,j} 
\]  \(\text{(B.44)}\)

**Component mass balance**

\[
V_{p+1} y_{p+1,i} = L_p x_{p,i} + V_1 y_1 - L_0 x_0 - \sum_{j=1}^{R} V_{i,j} \xi_{p,j} \quad i = 1, \ldots, C - 1 
\]  \(\text{(B.45)}\)

By choosing a set of reference components \(x_{ref,i}\), eliminating the reaction extent \(\xi_{r,n,j}\) from \(R\) component mass balances and rearranging the equations using the defined transformed variables (Eqs. A.2 and A.3), the mass balances become:

**General mass balance in transformed variables:**

\[
\bar{V}_{p+1} = \bar{L}_p + \bar{V}_1 - \bar{L}_0 
\]  \(\text{(B.46)}\)

**Component mass balance in transformed variables**

\[
\bar{V}_{p+1} \cdot y_{p+1,i} = \bar{L}_p \cdot x_{p,i} + \bar{V}_1 \cdot y_1 - \bar{L}_0 \cdot x_0 - i = 1, \ldots, C - R - 1
\]  \(\text{(B.47)}\)

The operating line for a reactive rectifying section using transformed variables will be:

\[
y_{p+1,i} = \frac{\bar{L}_p}{\bar{V}_{p+1}} x_{p,i} + \frac{\bar{V}_1}{\bar{V}_{p+1}} y_1 - \frac{\bar{L}_0}{\bar{V}_{p+1}} x_0 - i = 1, \ldots, C - R - 1
\]  \(\text{(B.48)}\)

Using the local transformed reflux ratios \(\bar{A}_p = \frac{\bar{L}_p}{\bar{V}_1 - \bar{L}_0}\) and \(\bar{A}_0 = \frac{\bar{L}_0}{\bar{V}_1 - \bar{L}_0}\), the operation line for the middle rectifying section becomes:
\[ Y_{p+1,j} = \frac{\bar{A}_p}{\bar{A}_p + 1} \cdot X_{p,j} + \frac{\bar{A}_0 + 1}{\bar{A}_p + 1} \cdot Y_{t,j} - \frac{\bar{A}_0}{\bar{A}_p + 1} \cdot X_{0,j}; \quad \forall j = 1, \ldots, C - R - 1 \]  

(B.49)

\( \bar{V}_1 - \bar{L}_0 \) represents the net product rate (in transformed variables) obtained from the middle rectifying section.

If the assumption of constant molar overflow in transformed variables is valid, then the local reflux ratio, \( \bar{A}_n \), is related to the initial reflux ratio, \( \bar{A}_0 \), by Eq. B.51.

\[ \bar{L}_p = \bar{L}_0 = \text{constant} \]  

(B.50)

\[ \bar{A}_n = \frac{\bar{L}_p}{\bar{V}_1 - \bar{L}_0} = \frac{\bar{L}_0}{\bar{V}_1 - \bar{L}_0} = \bar{A}_0 \]  

(B.51)

and the middle operating line becomes:

\[ Y_{p+1,j} = Y_{t,j} + \frac{\bar{A}_0}{\bar{A}_0 + 1} \cdot (X_{p,j} - X_{0,j}); \quad \forall j = 1, \ldots, C - R - 1 \]  

(B.52)

**Middle stripping section**

A mass balance around the middle stripping section of the column (Figure B.1 (b)) will give:

**General mass balance:**

\[ L_{p+1} = V_p + L_1 - V_0 - \sum_{j=1}^{R} v_{tot,j} \xi_{p,j} \]  

(B.53)

**Component mass balance:**

\[ L_{p+1} x_{p+1,i} = V_p y_{p,i} + L_1 x_1 - V_0 y_{0,i} - \sum_{j=1}^{R} v_{i,j} \xi_{p,j} \quad i = 1, \ldots, C - R - 1 \]  

(B.54)

By choosing a set of reference components \( x_{ref,j} \), eliminating the reaction extent \( \xi_{r,n,j} \) from \( R \) component mass balances and rearranging the equations
using the defined transformed variables (Eqs. A.2 and A.3), the mass balances become:

**General mass balance in transformed variables:**

\[ \bar{L}_{p+1} = \bar{V}_p + \bar{L}_1 - \bar{V}_0 \]  \hspace{1cm} (B.55)

**Component mass balance in transformed variables**

\[ L_{p+1} \cdot X_{p+1,i} = \bar{V}_p \cdot Y_{p,i} + \bar{L}_1 \cdot X_1 \cdot \bar{V}_0 \cdot Y_{0,i} \hspace{1cm} i = 1, \ldots, C - R - 1 \]  \hspace{1cm} (B.56)

The operating line for a reactive middle stripping section using transformed variables will be:

\[ X_{p+1,j} = \frac{\bar{V}_p}{L_{p+1}} \cdot Y_{p,j} + \frac{\bar{L}_1}{L_{p+1}} \cdot L_1 - \frac{\bar{V}_0}{L_{p+1}} \cdot Y_{0,j} \hspace{1cm} i = 1, \ldots, C - R - 1 \]  \hspace{1cm} (B.57)

Using the local transformed reboil ratios \( \bar{B}_p = \frac{\bar{V}_p}{\bar{L}_1 - \bar{V}_0} \) and \( \bar{B}_0 = \frac{\bar{V}_0}{\bar{L}_1 - \bar{V}_0} \), where \( \bar{L}_1 - \bar{V}_0 \) represents the net transformed product rate resulting from the middle stripping section, the operation line Eq. B.57 becomes:

\[ X_{p+1,j} = \frac{\bar{B}_p}{\bar{B}_p + 1} \cdot Y_{p,j} + \frac{\bar{B}_0 + 1}{\bar{B}_p + 1} \cdot X_{t,j} - \frac{\bar{B}_0}{\bar{B}_p + 1} \cdot Y_{0,j} \hspace{1cm} \forall \ j = 1, \ldots, C - R - 1 \]  \hspace{1cm} (B.58)

If the assumption of constant molar overflow in transformed variables is valid, then the local reflux ratio, \( \bar{B}_p \), is related to the initial reflux ratio, \( \bar{B}_0 \), by Eq. B.60.

\[ \bar{V}_p = \bar{V}_0 = \text{constant} \]  \hspace{1cm} (B.59)

\[ \bar{B}_p = \frac{\bar{V}_p}{\bar{L}_1 - \bar{V}_0} = \frac{\bar{V}_0}{\bar{L}_1 - \bar{V}_0} = \bar{B}_0 \]  \hspace{1cm} (B.60)

and the middle operating line becomes:

\[ X_{p+1,j} = X_{t,j} + \frac{\bar{B}_0}{\bar{B}_0 + 1} \cdot (Y_{p,j} - Y_{0,j}) \hspace{1cm} \forall \ j = 1, \ldots, C - R - 1 \]  \hspace{1cm} (B.61)
B.3.2. Kinetically-controlled reactions

Rectifying section

For kinetically controlled reactions, the overall and component mass balances around the rectifying section of the column (Figure B.1(a)) are the same as for equilibrium reactions (Eqs. B.28 and B.29).

\[
V_{r,n+1} = L_{r,n} + D - \sum_{j=1}^{R} v_{j,n}^\text{tot} \xi_{r,n,j} \tag{B.62}
\]

\[
V_{r,n+1} y_{r,n+1} = L_{r,n} x_{r,n} + Dx_{D,i} - \sum_{j=1}^{R} v_{i,j}^\text{tot} \xi_{r,n,j} \quad i = 1,...,NC - 1 \tag{B.63}
\]

Dividing by \( V_{r,n+1} \) in Eq. B.63 leads to:

\[
y_{r,n+1} = \frac{L_{r,n}}{V_{r,n+1}} x_{r,n} + \frac{D}{V_{r,n+1}} x_{D,i} - \frac{1}{V_{r,n+1}} \sum_{j=1}^{R} v_{i,j}^\text{tot} \xi_{r,n,j} \tag{B.64}
\]

The operating line for the rectifying section can be written as:

\[
y_{r,n+1} = \frac{R_n}{R_n + 1 - \Delta_r} x_{r,n} + \frac{1}{R_n + 1 - \Delta_r} \left( x_{D,i} - v_i^\text{tot} \cdot \Delta_r \right) \quad i = 1,...,NC - 1 \tag{B.65}
\]

where \( R_n \) represents the local reflux ratio defined by Eq. B.66 and \( \Delta_r \) represents the reaction extent term defined by Eq. B.67.

\[
R_n = \frac{L_n}{D} \tag{B.66}
\]

\[
\Delta_r = \frac{1}{D} v_i^\text{tot} \cdot \xi_r \tag{B.67}
\]

If the constant molar overflow in transformed variables is valid (Eq. B.68), then the local reflux ratio \( R_n \) is related to the external reflux ratio \( R_{\text{ext}} \) by Eq. B.69.

\[
\bar{L}_n = \bar{L}_0 = \text{constant} \tag{B.68}
\]

\[
R_n = \frac{L_n}{D} = \frac{\bar{L}_n}{D} \cdot \frac{1 - v_i^\text{tot} \gamma_i^{-1} x_{\text{ref},D}}{1 - v_i^\text{tot} \gamma_i^{-1} x_{\text{ref},n}} = \frac{\bar{L}_0}{D} \cdot K_{r,n} = \frac{L_0}{D} \cdot \frac{1 - v_i^\text{tot} \gamma_i^{-1} x_{\text{ref},D}}{1 - v_i^\text{tot} \gamma_i^{-1} x_{\text{ref},n}} \cdot k_{r,n} = R_{\text{ext}} \cdot k_{r,D} \cdot k_{r,n} \tag{B.69}
\]
In Eq. B.69, $k_{r,n}$ and $k_{r,D}$ are defined as:

$$k_{r,n} = \frac{1 - \frac{T_{tot}^T\gamma Y^{-1}x_{ref,D}}{1 - \frac{T_{tot}^T\gamma Y^{-1}x_{ref,n}}}}{k_{r,D}} = \frac{1 - \frac{T_{tot}^T\gamma Y^{-1}x_{ref,D}}{1 - \frac{T_{tot}^T\gamma Y^{-1}x_{ref,D}}}}{1 - \frac{T_{tot}^T\gamma Y^{-1}x_{ref,D}}{1 - \frac{T_{tot}^T\gamma Y^{-1}x_{ref,D}}}}$$ 

(B.70)

$$k_{r,D} = \frac{1 - \frac{T_{tot}^T\gamma Y^{-1}x_{ref,D}}{1 - \frac{T_{tot}^T\gamma Y^{-1}x_{ref,D}}}}{1 - \frac{T_{tot}^T\gamma Y^{-1}x_{ref,D}}{1 - \frac{T_{tot}^T\gamma Y^{-1}x_{ref,D}}}}$$ 

(B.71)

Using Eq. B.69, the operating line for the rectifying section becomes:

$$y_{r,n+1,j} = \frac{R_{ext} \cdot k_{r,n} \cdot k_{r,D}}{R_{ext} \cdot k_{r,n} \cdot k_{r,D} + 1 - \Delta_r} x_{r,n,j} + \frac{1}{R_{ext} \cdot k_{r,n} \cdot k_{r,D} + 1 - \Delta_r} \left( x_{D,j} - v_i \cdot v_{tot}^{-1} \cdot \Delta_r \right)$$

\(i = 1, \ldots, N_{C} - 1\)

(B.72)

**Stripping section**

The general and the component mass balances for a stripping section (Figure B.1(b)) are:

$$L_{s,m+1} = v_{s,m} + B - \sum_{j=1}^{R} y_{tot,i} z_{s,m,j}$$

(B.73)

$$L_{s,m+1} x_{s,m+1,j} = V_{s,m} y_{s,m,i} + B x_{B,j} - \sum_{j=1}^{R} v_{i,j} z_{s,m,j}$$ \(i = 1, \ldots, N_{C} - 1\)

(B.74)

Dividing by $L_{s,m+1}$ in Eq. B.74 leads to:

$$x_{s,m+1,j} = \frac{V_{s,m}}{L_{s,m+1}} y_{s,m,i} + \frac{B}{L_{s,m+1}} x_{B,j} - \frac{1}{L_{s,m+1}} \sum_{j=1}^{R} v_{i,j} z_{s,m,j}$$ \(i = 1, \ldots, N_{C} - 1\)

(B.75)

The operating line for the rectifying section can be written as:

$$x_{s,m+1,j} = \frac{S_m}{S_m + 1 - \Delta_s} y_{s,m,i} + \frac{1}{S_m + 1 - \Delta_s} \left( x_{B,j} - v_i \cdot v_{tot}^{-1} \cdot \Delta_s \right)$$

\(i = 1, \ldots, N_{C} - 1\)

(B.76)

where $s_m$ represents the local reboil ratio defined by Eq. B.77 and $\Delta_s$ represent the reaction extent term defined by Eq. B.78.
If the constant molar overflow in transformed variables is valid (Eq. B.79), then the local reflux ratio \( r_n \) is related to the external reflux ratio \( r_{ext} \) by Eq. B.80.

\[
\bar{V}_m = \bar{V}_0 = \text{constant} \tag{B.79}
\]

\[
S_m = \frac{V_m}{B} = \frac{\bar{V}_m}{B} \cdot \frac{1 - \psi_{tot}^{-1} y_{ref,B}}{1 - \psi_{tot}^{-1} y_{ref,m}} = \frac{\bar{V}_m}{B} \cdot k_{s,m} = \frac{V_m}{B} \cdot \frac{1 - \psi_{tot}^{-1} y_{ref,0}}{1 - \psi_{tot}^{-1} x_{ref,B}} \cdot k_{s,m} = S_{ext} \cdot k_{s,B} \cdot k_{s,m} \tag{B.80}
\]

In Eq. B.80, \( k_{s,m} \) and \( k_{s,B} \) are defined as:

\[
k_{s,m} = \frac{1 - \psi_{tot}^{-1} y_{ref,B}}{1 - \psi_{tot}^{-1} y_{ref,m}} \tag{B.81}
\]

\[
k_{s,B} = \frac{1 - \psi_{tot}^{-1} y_{ref,0}}{1 - \psi_{tot}^{-1} x_{ref,B}} \tag{B.82}
\]

Using Eq. B.80, the operating line for the stripping section becomes:

\[
x_{s,m+1,i} = \frac{S_{ext} \cdot k_{s,m} \cdot k_{s,B}}{S_{ext} \cdot k_{s,m} \cdot k_{s,B} + 1 - \Delta_s} y_{s,m,i} + \frac{1}{S_{ext} \cdot k_{s,m} \cdot k_{s,B} + 1 - \Delta_s} \left( x_{s,i} - \psi_i \cdot \psi_{tot}^{-1} \cdot \Delta_s \right)
\]

\[i = 1, \ldots, \text{NC} - 1 \tag{B.83}\]
B.4. Calculation of profiles in a reactive column using energy balances

In classical distillation, constant molar overflow is a valid assumption for most systems for conceptual design purposes. An extension of the assumption to reactive systems led to the assumption of constant molar overflow in transformed variables. This assumption takes into account the change in internal flows caused only by the change in the number of moles due to reaction. For reactive systems with no change in the number of moles, the assumption reduces to the normal constant molar overflow in real variables.

The heat of reaction changes the stage temperature, hence the vapour-liquid equilibrium, sometimes causing a sharp change in composition from one stage to another. The heat of reaction has a significant effect, especially if the reaction extent is unevenly distributed in the column (as is the case of single-feed reactive columns, where the reaction is concentrated around the feed stage). Therefore, a sharp change in liquid and vapour flows will be expected around the feed stage for reactive columns with the reaction concentrated around feed stage and for the stages near an interface between a reactive and a non-reactive section (hybrid columns).

Overall, a complex process takes place on a reactive stage, and constant molar overflow (even if transformed variables are used) is not always a good assumption, even for reactions with no change in the number of moles.

Some published work (Pekkanen, 1995; Melles, 2000) estimated the change in the liquid and vapour flows by considering the heat of reaction effect, without considering the change in internal flows due to the change in the composition. To estimate the change in internal flows in a distillation column (reactive or not), heat balances need to be considered in the calculation of composition profiles.
Heat balance equations can be added to Eqs. B.28 and B.29 (for the rectifying section), or Eqs. B.36 and B.37 (for the stripping section), leading to a set of nonlinear equations, which can be solved simultaneously for composition and liquid and vapour flows.

In the calculation of composition profiles using energy balances, for better convergence good initial estimates of internal flows are necessary. Instead of using balances around the top or bottom of the column, as is usual for calculation of composition profiles calculation, a stage-by-stage approach is preferable. In this approach, the energy balance around each stage is calculated individually; the results of one stage are taken as initial estimates for the next stage.

![Diagram of reactive rectifying and stripping stages](image)

Figure B.3. Reactive rectifying and stripping stages used in calculation of profiles with energy balances.

Mass and energy balances around a stage $n$ (either rectifying, middle or stripping) will give (Figure B.3):

$$V_{n+1} + L_{n-1} = L_n + V_n - \sum_{j=1}^{R} v_{tot,j} \xi_{n,j}$$  \hspace{1cm} (B.84)

$$V_{n+1} x_{n+1,j} + L_{n-1} x_{n-1,j} = L_n x_{n,j} + V_n y_{n,j} - \sum_{j=1}^{R} v_{i,j} \xi_{n,j} \hspace{1cm} i = 1, \ldots, C$$  \hspace{1cm} (B.85)
\[ V_{n+1} h_{n+1}^V + L_{n-1} h_{n-1}^L = L_n h_{n,j}^L + V_n h_{n,j}^V - \sum_{j=1}^{R} \xi_{n,j} \cdot \Delta H_{\text{react},j} \]  \hspace{1cm} (B.86)

\[ \xi_n = \begin{cases} 0 & \text{if stage is non-reactive} \\ K_{\text{eq}}(x_{r,n}) = K_{\text{eq}}(T) & \text{for equilibrium reactions} \\ r_{\text{ref}} \cdot H_n & \text{for kinetically controlled reactions} \end{cases} \]  \hspace{1cm} (B.87)

The system of equations B17 – B20 are solved for \( y_{n+1,j} \) (\( i = 1, \ldots, C \)), \( L_n \), \( V_{n+1} \) and \( \xi_n \) for a rectifying stage and for \( x_{n-1,j} \) (\( i = 1, \ldots, C \)), \( V_n \), \( L_{n-1} \) and \( \xi_n \) for a stripping stage (e.g. using a modification of Powell’s dogleg method, as implemented in IMSL routine DNEQLU).

The general approach presented above has reasonably fast convergence for non reactive systems, but is quite slow for reactive systems, and it often fails for highly non-ideal reactive systems. A new approach was proposed in this work, based on a sequential algorithm, which takes full advantage of the pseudo-linear characteristic of the system of equations.

This new approach decouples the mass balance from the energy balance and solves it separately to obtain liquid or vapour compositions. The energy balance equation will only be used in a non-linear root search (outer loop) to correct the results. It can be applied for both reactive and non-reactive systems, transformed variables being used for equilibrium reactive systems.

We assume that, for a non-reactive stage \( n \) (Figure B.3), we know \( x_{n-1}, y_n, L_{n-1} \) and \( V_n \) (stage \( n \) is a rectifying stage). From VLE relationships, the composition of the liquid leaving the stage, \( x_n \), can also be determined. By setting an arbitrary value for the vapour flowrate \( V_{n+1} \), the flowrate of the liquid leaving the stage, \( L_n \), can be calculated from the general mass balance (Eq. B.84). The composition of the vapour entering the stage, \( y_{n+1} \), can then be calculated using the lever rule, as shown in Figure B.3 (Eq. B.84).
At this point, all flowrates and compositions of the streams entering and leaving stage $n$ are known. Now, we can use the heat balance (Eq B.85) to check if the assumed value for the vapour flowrate, $V_{n+1}$, was correct. If the heat balance is not satisfied, a new value for the vapour flowrate will be chosen, and the above sequence of calculation repeated. In this way, the algorithm will reduce to a root search for $V_{n+1}$, using heat balance as a test function. The procedure is similar for a stripping stage (where the search will look for a value of the liquid flowrate $L_{n-1}$). For reactive systems the procedure is similar, only that transformed variables are used.

The algorithm for calculating composition profiles with heat balances in a reactive rectifying section using the sequential approach is:

1. Specify the product composition $X_D$
2. Calculate transformed internal flows for the first stage: $\tilde{L}_0 = \tilde{D} \cdot R$ and $\tilde{V}_1 = \tilde{D} \cdot (R + 1)$
3. Calculate liquid and vapour compositions at the top of the column: $x_0$ and $y_1$ and transformed compositions $X_0$ and $Y_f$.
4. Start stage by stage calculations for $n = 1, \ldots NR_{max}$
   4.1. Calculate composition of the liquid leaving stage $n$, $x_n$: use a reactive bubble point calculations for equilibrium reactions and a simple bubble
point calculation for kinetically-controlled reactions. Calculate $X_n$ (Eq. A.2).

4.2. Calculate $y_{n+1}$ and liquid and vapour flows $L_n$ and $V_{n+1}$.

4.2.1. Choose a value for $\overline{V}_{n+1}$. A good initial value is $\overline{V}_n$.

4.2.2. Calculate $\overline{L}_n$ and $Y_{n+1}$ from general and component mass balances in transformed variables.

4.2.3. Calculate all real vapour and liquid compositions: use reactive dew or bubble point calculations for equilibrium reactions. For kinetically-controlled reactions first calculate the reaction extent (Eq. B.87) and then use Eq. B.85. to obtain the real vapour composition.

4.2.4. Calculate all real liquid and vapour flows (Eq A.3)

4.2.5. If equilibrium reaction, calculate the reaction extent from a mass balance for the reference component (Eq. B.85 for $i = \text{ref}$)

4.2.6. Calculate enthalpies for all streams

4.2.7. Calculate energy balance

4.2.8. If energy balance holds, then continue, else repeat from step 4.2.1

4.3. Take the results from stage $n$ as input for stage $n+1$

5. Return to step 4 and repeat procedure for all rectifying stages

For a stripping section the algorithm is similar, except that the calculation in this case is performed from the bottom stage upwards:

1. Specify the product composition $X_B$

2. Calculate transformed internal flows for the first stage: $\overline{L}_1 = \overline{B} \cdot (S + 1)$ and $\overline{V}_0 = \overline{B} \cdot S$

3. Calculate liquid and vapour compositions at the bottom stage of the column: $y_0$ and $x_1$ and transformed compositions $Y_0$ and $X_1$.

4. Start stage by stage calculations for $m = 1, \ldots NS_{\text{max}}$
4.1. Calculate composition of the vapour leaving stage \( m \), \( y_m \), using a reactive bubble point calculation for equilibrium reactions and simple bubble point for kinetically-controlled reactions. Calculate \( Y_m \) (Eq. A.2).

4.2. Calculate \( x_{m+1} \) and liquid and vapour flows \( L_{m+1} \) and \( V_m \).

4.2.1. Choose a value for \( \bar{L}_{m+1} \). A good initial value is \( \bar{L}_m \).

4.2.2. Calculate \( \bar{V}_m \) and \( X_{m+1} \) from general and component mass balances in transformed variables.

4.2.3. Calculate all real vapour and liquid compositions using reactive dew point or bubble point calculations for equilibrium reaction. For kinetically-controlled reactions first calculate the reaction extent (Eq. B.87) and then use Eq. B.85 to obtain the real liquid composition (\( x_{m+1} \)).

4.2.4. Calculate all real liquid and vapour flows (Eq A.3)

4.2.5. Calculate reaction extent for equilibrium reactions from a mass balance for the reference component (Eq. B.85 for \( i = \text{ref} \))

4.2.6. Calculate enthalpies for all streams

4.2.7. Calculate energy balance

4.2.8. If energy balance holds, then continue, else repeat from step 4.2.1

4.3. Take the results from stage \( m \) as input for stage \( m+1 \)

5. Return to step 4 and repeat procedure for all stripping stages

The inner loop from step 4.2.1 was solved using a non-linear root search routine (Brent, 1971), searching for the liquid or vapour flowrate and using heat balance as test function. The sequential algorithm offers a faster convergence than the simultaneous algorithms solving the system of equations B.84-B.86, even for highly non-ideal systems and it can accommodate both reactive and non-reactive stages. In Figure B. 5 the composition profiles for a reactive stripping section, resulted from the sequential procedure and from a rigorous simulation are presented. The system used was DMC, for which the constant molar overflow is not a valid assumption (Chapter 4). As it can be seen, up to stage 20, the profiles are practically identical.
B.5. Feed condition calculation in reactive systems

In a distillation column, reactive or non-reactive, there is a close relationship between the reflux ratio, \( R \), the reboil ratio, \( S \), and the feed condition. Only two of the three parameters can be specified independently, the third parameter will be dependent on the other two; e.g. we can specify the feed condition and the reflux ratio, and calculate the reboil ratio using Eq. B.99. In practice feed condition (i.e. feed temperature) is specified, together with either the reflux or reboil ratio. However, for all the design methodologies presented in this work, reflux and reboil ratios were considered independent parameters, leaving the feed condition as the dependent parameter.

For reactive systems, feed condition can be easily calculated if constant molar overflow (in transformed variables) is assumed. For example, for the feed stage in Figure B.4a, the internal liquid and vapour flows can be calculated based on
from external reflux and reboil ratios \((R_{ext} \text{ and } S_{ext})(\text{Eqs. B.88 to B.91}).\)

\[
L_r = R_{ext} \cdot k_{0,x} \cdot D \tag{B.88}
\]

\[
V_r = (R_{ext} \cdot k_{0,D} + 1) \cdot D \cdot k_{r,y} \tag{B.89}
\]

\[
L_s = (S_{ext} \cdot k_{0,B} + 1) \cdot B \cdot k_{s,x} \tag{B.90}
\]

\[
V_s = S_{ext} \cdot k_{0,y} \cdot B \tag{B.91}
\]

where:

\[
k_{0,x} = \frac{1 - \gamma \frac{1}{Y} x_{ref,0}}{1 - \gamma \frac{1}{Y} x_{ref,r}} \tag{B.92}
\]

\[
k_{0,D} = \frac{1 - \gamma \frac{1}{Y} x_{ref,0}}{1 - \gamma \frac{1}{Y} x_{ref,D}} \tag{B.93}
\]

\[
k_{r,y} = \frac{1 - \gamma \frac{1}{Y} x_{ref,D}}{1 - \gamma \frac{1}{Y} y_{ref,r}} \tag{B.94}
\]

\[
k_{0,y} = \frac{1 - \gamma \frac{1}{Y} y_{ref,0}}{1 - \gamma \frac{1}{Y} y_{ref,s}} \tag{B.95}
\]

\[
k_{0,B} = \frac{1 - \gamma \frac{1}{Y} y_{ref,0}}{1 - \gamma \frac{1}{Y} x_{ref,B}} \tag{B.96}
\]

\[
k_{s,x} = \frac{1 - \gamma \frac{1}{Y} x_{ref,B}}{1 - \gamma \frac{1}{Y} x_{ref,s}} \tag{B.97}
\]

If we further assume that the reaction takes place in the liquid phase only, then the vapour flows can be considered to be affected only by the feed (Marek, 1954) (Figure B.6). Based on the vapour phase balance, feed condition can be calculated from local reflux or reboil ratios.

\[
V_r = V_s + (1 - q) \cdot F \tag{B.98}
\]

\[
q = 1 - \left[ (R_{ext} \cdot k_{0,D} + 1) \cdot k_{r,y} \cdot D/F - S_{ext} \cdot k_{0,y} \cdot B/F \right] \tag{B.99}
\]
For highly non-ideal reactive systems, even if constant molar overflow assumption (in transformed variables) is valid, the reaction affects both liquid and vapour flows, even for the situation where the reaction is confined in the liquid phase only. This is on one hand caused by the change in composition and flows in the liquid phase due to reaction which will induce, through VLE, a change in the composition and flowrate in the vapour phase, as well. On the other hand the heat of reaction can have an important effect, especially if the molar reaction turn-over (reaction extent) on the feed stage is significant. This effect is more accentuated for hybrid columns. Because of the reaction at feed stage (and for single feed equilibrium reactions the reaction extent at feed stage is usually considerable), there is a sharp change in the flowrates from one section to the other. Therefore, for these systems the general assumption that the reaction affects only the liquid internal flow is not valid. Instead, a heat balance at the feed stage can be used to evaluate the feed enthalpy, hence the feed temperature, for specified reflux and reboil ratios.

Considering the envelope from Figure B.7a, the feed enthalpy can be evaluated from the feed stage energy balance (Eq. B.100):

$$h_F = \frac{1}{F} \left( \sum_{i=1}^{R} \xi_{F,i} \cdot \Delta H_{\text{react},i} - L_s h_s - L_r h_r + V_r H_r - V_s H_s - \xi_F \cdot (F_L + L_r - \nu_{\text{tot}}) \right)$$  \hspace{1cm} (B.100)
The internal liquid and vapour flows are calculated depending on the type of the column section: if the section is reactive, then Eqs B.35 and B.43 need to be used. The reaction extent for each reaction at the feed stage is calculated from the mass balance for each reference component around the feed stage.

\[
\Delta H_{\text{react}} \cdot \phi_{F} - \sum_{i=1}^{R} \Delta H_{\text{react},i} \cdot \phi_{\text{tot},i} = Q_{\text{cond}} - Q_{\text{reb}}
\]  

Figure B.7 Heat balances for a reactive distillation column (a) Feed stage; (b) Single-feed reactive distillation column; (c) Double-feed reactive distillation column

A simpler and a more general approach which will avoid the use of different equations for calculating internal flows at the interface (e.g. reactive or non-reactive) is based on the overall heat balance (Figure B.7b and c). The total reaction extent for each reaction is calculated from an overall mass balance for each reference component. For single-feed columns, feed enthalpy is calculated using Eq. B.101, valid no matter where the reaction stages are placed in the column. The overall enthalpy balance can be used for top/bottom reactive columns, columns with a reactive core or fully reactive columns, as well as for non-reactive columns, where the total reaction extent is zero.

\[
h_{F} = \frac{1}{F} \left( D h_{D} + B h_{B} + Q_{\text{cond}} - Q_{\text{reb}} - \sum_{i=1}^{R} \phi_{\text{tot},i} \cdot \Delta H_{\text{react},i} \right)
\]  

Generally, the condenser and the reboiler are non-reactive (especially for
heterogeneously catalysed reactions) therefore their duties are direct functions of external reflux and reboil ratios. Even for homogeneously catalysed or autocatalytic reactions, the condenser and reboiler duties can be considered non-reactive, as reaction extent is usually very small at the ends of the column. If this assumption is not valid then the heat of reaction should be considered during the calculation of condenser and reboiler duties.

For double-feed columns, Eq. B.101 is modified to include the specified feed. For example, if lower feed is specified, the upper feed enthalpy will be calculated based on Eq. B.102. A similar equation is used if upper feed is specified (Eq. B.103)

\[
h_{FU} = \frac{1}{F_U} \left(Dh_D + Bh_B - F_U h_{FL} + Q_{\text{cond}} - Q_{\text{reb}} - \sum_{i=1}^{R} \xi_{\text{tot},i} \cdot \Delta H_{\text{react},i}\right) \quad (B.102)
\]

\[
h_{FL} = \frac{1}{F_L} \left(Dh_D + Bh_B - F_L h_{FU} + Q_{\text{cond}} - Q_{\text{reb}} - \sum_{i=1}^{R} \xi_{\text{tot},i} \cdot \Delta H_{\text{react},i}\right) \quad (B.103)
\]

The feed enthalpy (\(h_F\) for single-feed columns, or \(h_{FL}\) (or \(h_{FU}\) for double-feed columns) can then be used to calculate either feed temperature or feed condition (Eq. B.104):

\[
q = \frac{H_F - h_F}{\lambda_F} \quad (B.104)
\]

where \(H_F\) represents the specific enthalpy of the feed as saturated vapours and \(\lambda_F\) is the latent heat of vaporisation for the feed.
Appendix C. Calculation of the intersection of non-reactive SCLs with the reactive surface

The intersections of non-reactive SCLs with the reactive surface are calculated using a non-linear root search routine, which calculates the value of the reflux or reboil ratio, for which the liquid (or vapour) leaving a certain stage will be in reactive equilibrium.

For a stripping non-reactive section, the routine takes two liquid compositions $x_A(S_A)$ and $x_B(S_B)$ on a SCL (Figure C.1) and compares the values of $K_{eq}(T)$ with $K_{eq}(x)$. If the difference $K_{eq}(T) - K_{eq}(x)$ changes its sign from point A to point B, then there will be a value $S_{intersect}$ between $S_A$ and $S_B$ for which the equality condition $K_{eq}(T) = K_{eq}(x)$ will be satisfied. A non-linear root search routine (Brent) is used to calculate the reboil ratio value $s_{int}$ at the intersection point.

![Figure C.1 Intersection of a non-reactive stripping SCL with the reactive surface](image)

For a non-reactive rectifying SCL, the routine takes two vapour composition points $y_A(R_A)$ and $y_B(R_B)$ on a stage composition line $m$ and calculates the liquid composition in thermodynamic equilibrium $x_A$ and $x_B$. If the difference $K_{eq}(T) - K_{eq}(x)$ changes signs from point A to B, then there is a reflux ratio $R_{intersect}$ for which the liquid composition leaving stage $m$ is in reactive equilibrium, i.e. satisfies the condition $K_{eq}(T) = K_{eq}(x_{intersect})$. A non-linear root search routine (Brent) is used to calculate the reflux ratio value $r_{intersect}$ at the intersection point.
Appendix D. Physical property models

Models for physical properties calculations are presented below. The coefficients and interaction parameters for these models are presented in Appendix E.

D.1. Vapour pressure

A modified Antoine equation is used to calculate vapour pressure:

\[
\ln(P_{i}^{\text{sat}}) = a_i - \frac{b_i}{T + c_i} + d_i \ln T + e_i T^f
\]  

(D.1)

where saturation pressure \( P_{i}^{\text{sat}} \) is given in [kPa] and temperature \( T \) in [K] (HYSYS v2.4 Users Guide).

D.2. Activity coefficients

NRTL-model

\[
\ln \gamma_i = \frac{\sum x_j \tau_{ij} G_{ij}}{\sum x_k G_{ki}} + \sum_{j} \left[ \frac{x_j G_{ji}}{\sum_k x_k G_{kj}} \left( \tau_{ij} - \frac{\sum_m x_m \tau_{mj} G_{mj}}{\sum_k x_k G_{kj}} \right) \right]
\]  

(D.2)

\[ G_{ij} = e^{-a_{ij} \tau_{ij}} \quad \forall \ i \neq j \]

\[ G_{ii} = 1 \quad \forall \ i = j \]

\[ \tau_{ij} = A_{ij} + B_{ij} \quad \forall \ i \neq j \]

\[ \tau_{ii} = 0 \quad \forall \ i = j \]

\[ \alpha_{ij} = C_{ij} = 0.3 \quad \forall \ i, j \]

where \( T \) is the temperature in K, \( x_i \) is the mole fraction of component \( i \) and \( \gamma_i \) is the resulting activity coefficient of component \( i \). \( A_{ij}, B_{ij}, \) and \( C_{ij} \) are the binary interaction parameters of the NRTL-model (HYSYS v2.4 Users Guide).
Wilson-model

\[
\ln \gamma_i = 1 - \ln \left( \sum_j x_j \cdot \Lambda_{ij} \right) - \sum_k \left[ \frac{x_k \cdot \Lambda_{ki}}{\sum_j x_j \cdot \Lambda_{kj}} \right]
\]

\[
\Lambda_{ij} = \frac{v_{L,i,j}}{v_{L,j}} \cdot \exp \left( -\frac{a_{ij}}{R_G \cdot T} \right)
\]  \hspace{1cm} (D.3)

\[
a_{ij} = A_{ij}
\]

where \( T \) is the temperature in K, \( x_i \) is the mole fraction of component \( i \), \( R_G \) is the gas constant, \( A_{ij} \) is the binary interaction parameter of the Wilson-model and \( \gamma_i \) is the resulting activity coefficient of component \( i \) (HYSYS v2.4 Users Guide).

**D.3. Specific Enthalpy**

To speed up the convergence of energy balances, for enthalpy calculations a polynomial equation was used; the parameters for both liquid and vapour enthalpies were obtained from HYSYS v2.4. using the Tabular Properties option.

\[
h_{\text{liq}} = H_{\text{H Liq}}A + H_{\text{H LiqB}} \cdot T + H_{\text{H LiqC}} \cdot T^2 + H_{\text{H LiqD}} \cdot T^3 + H_{\text{H LiqE}} \cdot T^4
\]  \hspace{1cm} (D.4)

\[
h_{\text{vap}} = H_{\text{V Apa}}A + H_{\text{V Apb}} \cdot T + H_{\text{V ApC}} \cdot T^2 + H_{\text{V ApD}} \cdot T^3 + H_{\text{V ApE}} \cdot T^4
\]  \hspace{1cm} (D.5)

where the specific enthalpy \( h_i \) of component \( i \) is given in [kJ/kmol] and the temperature \( T \) in [K].

**D.4. Heat of reaction**

Since the elemental reference state is used for enthalpy calculations, the heat of reaction \( \Delta H_{\text{rxn}} \) can be calculated from the standard enthalpies of formation \( h_i^\text{form} \) and the stoichiometry (HYSYS v2.4 Users Guide):

\[
\Delta H_{\text{rxn}}^0 = \sum_{i=1,C} v_i \cdot h_i^\text{form,0}
\]  \hspace{1cm} (D.6)

where \( \Delta H_{\text{rxn}}^0 \) is the standard heat of reaction at \( T^\text{form} = 0 \) K and \( P^\text{form} = 1 \) bar.
Appendix E. Thermodynamic and kinetic data

The models to which the parameters and coefficients presented below apply are presented in Appendix D. Unless otherwise stated, all parameters and coefficients in this section were obtained from Hysys v2.4 database.

E1. Ideal A, B, C, D system

Reaction

\[ A + B \rightleftharpoons C \quad (\text{inert } D) \]  \hspace{1cm} (E.1)

Critical data

<table>
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<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
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Antoine parameters

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<th>ANTc</th>
<th>ANTD</th>
<th>ANTE</th>
<th>ANTF</th>
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<tbody>
<tr>
<td>A</td>
<td>52.38</td>
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<td>1.12E-05</td>
<td>0.0</td>
</tr>
<tr>
<td>B</td>
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<td>-10.56</td>
<td>1.36E-05</td>
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<tr>
<td>C</td>
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<td>6.30E-06</td>
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</tr>
<tr>
<td>D</td>
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<td>0.0</td>
<td>-7.017</td>
<td>1.04E-05</td>
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Enthalpy coefficients

Liquid enthalpy

<table>
<thead>
<tr>
<th>Component</th>
<th>HLIQA</th>
<th>HLIQB</th>
<th>HLIQC</th>
<th>HLIQD</th>
<th>HLIQE</th>
<th>HLIQA</th>
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<tr>
<td>A</td>
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<td>-3491</td>
<td>0.0</td>
<td>-6.109</td>
<td>1.12E-05</td>
<td>0.0</td>
</tr>
<tr>
<td>B</td>
<td>82.16</td>
<td>-5279</td>
<td>0.0</td>
<td>-10.56</td>
<td>1.36E-05</td>
<td>0.0</td>
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<tr>
<td>C</td>
<td>74.79</td>
<td>-6650</td>
<td>0.0</td>
<td>-8.95</td>
<td>6.30E-06</td>
<td>0.0</td>
</tr>
<tr>
<td>D</td>
<td>58.78</td>
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<td>0.0</td>
<td>-7.017</td>
<td>1.04E-05</td>
<td>0.0</td>
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</table>
Vapour enthalpy

<table>
<thead>
<tr>
<th>Component</th>
<th>HVAPA</th>
<th>HVAPB</th>
<th>HVAPC</th>
<th>HVAPD</th>
<th>HVAPE</th>
<th>HVAPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>52.38</td>
<td>-3491</td>
<td>0.0</td>
<td>-6.109</td>
<td>1.12E-05</td>
<td>0.0</td>
</tr>
<tr>
<td>B</td>
<td>82.16</td>
<td>-5279</td>
<td>0.0</td>
<td>-10.56</td>
<td>1.36E-05</td>
<td>0.0</td>
</tr>
<tr>
<td>C</td>
<td>74.79</td>
<td>-6650</td>
<td>0.0</td>
<td>-8.95</td>
<td>6.30E-06</td>
<td>0.0</td>
</tr>
<tr>
<td>D</td>
<td>58.78</td>
<td>-4137</td>
<td>0.0</td>
<td>-7.017</td>
<td>1.04E-05</td>
<td>0.0</td>
</tr>
</tbody>
</table>

**Kinetic data**

For the hypothetical ideal system A, B, C, D the value for the reaction equilibrium constant was considered to be:

\[ K_{eq} = 20 \]  

(E.2)

**E2. MTBE System**

Components: iso-butene (IB; i-C\(_4\)H\(_8\)), methanol (MeOH; CH\(_3\)OH), methyl tertiary butyl ether (MTBE; (CH\(_3\))\(_3\)COCH\(_3\)), and the inert component n-butane (n-B; n-C\(_4\)H\(_{10}\)).

\[ \text{IB + MeOH} \xrightarrow{\text{Cat.}} \text{MTBE} \]  

(E.3)

The NRTL model is used to calculate activity coefficients in the liquid phase. HYSYS v2.4 is used to calculate all properties of the reactive mixture. All thermodynamic data listed below were obtained from HYSYS v2.4 database.

**Critical data**

<table>
<thead>
<tr>
<th>Component</th>
<th>Mol. Weight</th>
<th>Boiling point</th>
<th>T(_C)</th>
<th>P(_C)</th>
<th>V(_C)</th>
<th>Omega</th>
<th>Dipole Moment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[kg/kmol]</td>
<td>[K]</td>
<td>[K]</td>
<td>[bar]</td>
<td>[m(^3)/kmol]</td>
<td>[-]</td>
<td>[Debye]</td>
</tr>
<tr>
<td>i-Butene</td>
<td>56.11</td>
<td>266.3</td>
<td>417.9</td>
<td>40</td>
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<td>0.5</td>
</tr>
<tr>
<td>Methanol</td>
<td>32.04</td>
<td>337.8</td>
<td>512.6</td>
<td>73.8</td>
<td>0.1</td>
<td>0.557</td>
<td>1.7</td>
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<tr>
<td>MTBE</td>
<td>88.15</td>
<td>328.3</td>
<td>496.4</td>
<td>33.7</td>
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<td>0.269</td>
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<tr>
<td>n-Butane</td>
<td>58.123</td>
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</table>
## Antoine parameters

<table>
<thead>
<tr>
<th>Component</th>
<th>ANTA</th>
<th>ANTB</th>
<th>ANTC</th>
<th>ANTD</th>
<th>ANTE</th>
<th>ANTF</th>
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<tr>
<td>i-Butene</td>
<td>57.8859</td>
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</table>

## NRTL Binary interaction parameters

<table>
<thead>
<tr>
<th>Component</th>
<th>i-Butene</th>
<th>Methanol</th>
<th>MTBE</th>
<th>n-Butane</th>
</tr>
</thead>
<tbody>
<tr>
<td>i-Butene</td>
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## Enthalpy coefficients

### Liquid enthalpy

<table>
<thead>
<tr>
<th>Component</th>
<th>HLIQA</th>
<th>HLIQB</th>
<th>HLIQC</th>
<th>HLIQD</th>
<th>HLIQE</th>
</tr>
</thead>
<tbody>
<tr>
<td>i-Butene</td>
<td>0</td>
<td>87.68001</td>
<td>0.10855</td>
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<td>Methanol</td>
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### Vapour enthalpy

<table>
<thead>
<tr>
<th>Component</th>
<th>HVAPA</th>
<th>HVAPB</th>
<th>HVAPC</th>
<th>HVAPD</th>
<th>HVAPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>i-Butene</td>
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<td>3.18E-04</td>
<td>-4.06E-07</td>
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<tr>
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<td>93.976</td>
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<td>-6.27E-07</td>
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<tr>
<td>MTBE</td>
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<td>146.9121</td>
<td>-0.44409</td>
<td>1.18E-03</td>
<td>-1.12E-06</td>
</tr>
</tbody>
</table>

## Kinetic data

In Chen et al. (2002) the following kinetic model is:

\[ -r_{IB} = k_f \left( a_{IB} a_{MeOH} - \frac{a_{MTBE}}{K_{eq}} \right) \]  

(E.4)

where:
\[ K_{eq} = 8.33 \cdot 10^{-8} \exp\left(\frac{6820}{T}\right) \quad (E.5) \]

\[ K_f = 4464 \exp\left(-\frac{3187}{T}\right) \ h^{-1} \quad (E.6) \]

where \( T \) is temperature in K.

### E3. DEC System

#### Reaction

\[ DMC + EtOH \leftrightarrow MEC + MeOH \]

\[ MEC + EtOH \leftrightarrow DEC + MeOH \]

\[ DMC + 2EtOH \leftrightarrow DEC + 2MeOH \quad (E.7) \]

where:

- DMC – dimethyl carbonate
- EtOH – ethanol
- MEC – methyl ethyl carbonate
- MeOH – Methanol
- DEC – diethyl carbonate

### Critical data

<table>
<thead>
<tr>
<th>Component</th>
<th>Mol. Weight [kg/kmol]</th>
<th>Boiling point [K]</th>
<th>( T_C )</th>
<th>( P_C ) [bar]</th>
<th>( V_C ) [m³]</th>
<th>Omega [-]</th>
<th>Dipole Moment [Debye]</th>
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<td>DMC</td>
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<td>250</td>
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</table>
### Antoine parameters

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<td>DEC</td>
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### NRTL Binary interaction parameters

<table>
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<th>Methanol</th>
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<tr>
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<tr>
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<td>411.055</td>
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### Enthalpy coefficients

#### Liquid enthalpy

<table>
<thead>
<tr>
<th>Component</th>
<th>HLIQA</th>
<th>HLIQB</th>
<th>HLIQC</th>
<th>HLIQD</th>
<th>HLIQE</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.2721</td>
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<td>-5.55E-16</td>
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<td>3.13E-04</td>
<td>-2.78E-16</td>
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</tbody>
</table>

#### Vapour enthalpy

<table>
<thead>
<tr>
<th>Component</th>
<th>HVAPA</th>
<th>HVAPB</th>
<th>HVAPC</th>
<th>HVAPD</th>
<th>HVAPE</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1.80E-03</td>
<td>-1.04E-06</td>
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<tr>
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<td>3.94E-09</td>
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<tr>
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<td>84934</td>
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<td>0.29969</td>
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<td>1.97E-08</td>
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<tr>
<td>Methanol</td>
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<td>-2.06E-09</td>
</tr>
</tbody>
</table>

### Kinetic data

For DEC system, the kinetic model was taken from Luo et al. (2001)

\[
\dot{r}_1 = k_1 \cdot \left[ C_1 C_2 - C_3 C_4 / k_{eq1} \right] \tag{E.8}
\]
\( r_2 = k_2 \cdot \left[ C_3 C_2 - C_5 C_4 / k_{eq2} \right] \) \hspace{1cm} (E.9)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate ( [s^{-1}] )</th>
<th>( K_{eq} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( 2.148 \times 10^4 \exp[-12454.9/RT] )</td>
<td>( 145.95 \exp \left[ -\frac{628.44}{RT} \right] )</td>
</tr>
<tr>
<td>2</td>
<td>( 3.076 \times 10^3 \exp[-12210.2/RT] )</td>
<td>( 33.222 \exp \left[ -\frac{593.87}{RT} \right] )</td>
</tr>
</tbody>
</table>

**E.4. Methyl Acetate system**

Methyl-acetate is obtained from a catalytic reaction between Methanol (MeOH; \( \text{CH}_3\text{OH} \)) and Acetic Acid (AAc, \( \text{CH}_3\text{COOH} \)) according to Eq. E.10. Water (W, \( \text{H}_2\text{O} \)) is obtained as by-product. The catalytic reaction can be either homogeneous (e.g. sulphuric acid), as discussed in Sawistowski and Pilavakis (1979) and Popken \textit{et al.} (2000), or heterogeneous (e.g. ion exchange resins in structured reactive packings), discussed in Song \textit{et al.} (1998) and Popken \textit{et al.} (2000, 2001). In this work, the model proposed by Popken \textit{et al.} (2000) was used.

\[ \text{MeOH} + \text{AAc} \xrightleftharpoons[\text{Cat.}]{\text{MMeAc} + \text{W}} \] \hspace{1cm} (E.10)

For VLE calculations, a HYSYS (v2.4) real time interface was used, with NRTL model for the liquid phase and virial equation for the vapour phase (to model the dimerisation of AAc in the vapour phase). All thermodynamic data listed below were obtained from HYSYS v2.4 database.

**Critical data**

<table>
<thead>
<tr>
<th>Component</th>
<th>Mol. Weight</th>
<th>Boiling point ( [K] )</th>
<th>( T_C )</th>
<th>( P_C )</th>
<th>( V_C )</th>
<th>Omega</th>
<th>Dipole Moment ( [\text{Debye}] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>32.04</td>
<td>337.8</td>
<td>512.6</td>
<td>73.8</td>
<td>0.127</td>
<td>0.557</td>
<td>1.7</td>
</tr>
<tr>
<td>B</td>
<td>60.05</td>
<td>391.1</td>
<td>592.8</td>
<td>57.7</td>
<td>0.171</td>
<td>0.447</td>
<td>1.3</td>
</tr>
<tr>
<td>C</td>
<td>74.08</td>
<td>330.4</td>
<td>506.8</td>
<td>46.9</td>
<td>0.228</td>
<td>0.326</td>
<td>1.7</td>
</tr>
<tr>
<td>D</td>
<td>18.02</td>
<td>373.1</td>
<td>647.3</td>
<td>221</td>
<td>0.057</td>
<td>0.344</td>
<td>1.8</td>
</tr>
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</table>
Antoine parameters

<table>
<thead>
<tr>
<th>Component</th>
<th>ANTA</th>
<th>ANTB</th>
<th>ANTC</th>
<th>ANTD</th>
<th>ANTE</th>
<th>ANTF</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>59.84</td>
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<td>-6.379</td>
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<tr>
<td>B</td>
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<td>-6769</td>
<td>0.00E+00</td>
<td>-6.727</td>
<td>4.84E-06</td>
<td>2</td>
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<tr>
<td>C</td>
<td>96.52</td>
<td>-7050</td>
<td>0.00E+00</td>
<td>-12.38</td>
<td>1.14E-05</td>
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<tr>
<td>D</td>
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<td>-7227.53</td>
<td>0.00E+00</td>
<td>-7.17695</td>
<td>4.01E-06</td>
<td>2</td>
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Enthalpy coefficients

Liquid enthalpy

<table>
<thead>
<tr>
<th>Component</th>
<th>HLIQA</th>
<th>HLIQB</th>
<th>HLIQC</th>
<th>HLIQD</th>
<th>HLIQE</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.0</td>
<td>105.8</td>
<td>-0.1811</td>
<td>3.13E-04</td>
<td>-3.64E-13</td>
</tr>
<tr>
<td>B</td>
<td>0.0</td>
<td>139.6</td>
<td>-0.1604</td>
<td>3.00E-04</td>
<td>2.02E-11</td>
</tr>
<tr>
<td>C</td>
<td>0.0</td>
<td>61.26</td>
<td>0.1355</td>
<td>-4.03E-09</td>
<td>3.36E-12</td>
</tr>
<tr>
<td>D</td>
<td>0.0</td>
<td>76.28</td>
<td>2.57E-02</td>
<td>-1.13E-04</td>
<td>1.33E-07</td>
</tr>
</tbody>
</table>

Vapour enthalpy

<table>
<thead>
<tr>
<th>Component</th>
<th>HVAPA</th>
<th>HVAPB</th>
<th>HVAPC</th>
<th>HVAPD</th>
<th>HVAPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>50920</td>
<td>93.98</td>
<td>-0.3743</td>
<td>7.94E-04</td>
<td>-6.27E-07</td>
</tr>
<tr>
<td>B</td>
<td>18430</td>
<td>169.1</td>
<td>-0.2972</td>
<td>8.18E-04</td>
<td>-6.90E-07</td>
</tr>
<tr>
<td>C</td>
<td>44670</td>
<td>33.83</td>
<td>7.34E-02</td>
<td>1.31E-04</td>
<td>-2.62E-07</td>
</tr>
<tr>
<td>D</td>
<td>47300</td>
<td>107.6</td>
<td>-0.2203</td>
<td>3.66E-04</td>
<td>-3.23E-07</td>
</tr>
</tbody>
</table>

Kinetic data

The kinetic data for methyl-acetate formation was taken from Song et al. (1998).

The reaction equilibrium constant is:

\[ K_{eq} = 2.32 \exp\left(\frac{782.98}{T}\right) \]  \hspace{1cm} (E.11)

E.5. Olefin metathesis: 2-Pentene, 2-Butene, 2-Hexene system

The conversion of 2-Pentene into lower and higher molecular weight olefins, i.e. 2-butene and 2-hexene, is a representative reaction for olefin metathesis (Eq. E.12).
The olefins mixture has an ideal thermodynamic behaviour, as the components are similar chemicals. The critical and thermodynamic data, listed below, were obtained from HYSYS v2.4 database.

### Critical data

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Pentene</td>
<td>70.14</td>
<td>310</td>
<td>475.9</td>
<td>36.5</td>
<td>302.1</td>
<td>0.241</td>
<td>0</td>
</tr>
<tr>
<td>2-Butene</td>
<td>56.11</td>
<td>276.9</td>
<td>435.6</td>
<td>42.1</td>
<td>233.9</td>
<td>0.203</td>
<td>0.3</td>
</tr>
<tr>
<td>2-Hexene</td>
<td>84.16</td>
<td>342</td>
<td>517.5</td>
<td>32.8</td>
<td>35.1</td>
<td>0.256</td>
<td>0</td>
</tr>
</tbody>
</table>

### Antoine parameters

<table>
<thead>
<tr>
<th>Component</th>
<th>ANTA</th>
<th>ANTB</th>
<th>ANTC</th>
<th>ANTD</th>
<th>ANTE</th>
<th>ANTF</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Pentene</td>
<td>62.0945</td>
<td>-5128.93</td>
<td>0.00E+00</td>
<td>-7.25505</td>
<td>7.12E-06</td>
<td>0.0</td>
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<tr>
<td>2-Butene</td>
<td>66.2488</td>
<td>-4720.75</td>
<td>0.00E+00</td>
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<td>0.0</td>
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<tr>
<td>2-Hexene</td>
<td>13.8231</td>
<td>-2680.52</td>
<td>-48.2</td>
<td>0.00E+00</td>
<td>0.00E+00</td>
<td>0.0</td>
</tr>
</tbody>
</table>

### Enthalpy coefficients

#### Liquid enthalpy

<table>
<thead>
<tr>
<th>Component</th>
<th>HLIQA</th>
<th>HLIQB</th>
<th>HLIQC</th>
<th>HLIQD</th>
<th>HLIQE</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Pentene</td>
<td>0.00E+00</td>
<td>179</td>
<td>-0.3101</td>
<td>7.62E-04</td>
<td>-4.30E-07</td>
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<tr>
<td>2-Butene</td>
<td>0.00E+00</td>
<td>126.7</td>
<td>-3.27E-02</td>
<td>-2.13E-04</td>
<td>7.28E-07</td>
</tr>
<tr>
<td>2-Hexene</td>
<td>0.00E+00</td>
<td>269.3</td>
<td>-0.4451</td>
<td>6.52E-04</td>
<td>8.45E-13</td>
</tr>
</tbody>
</table>

#### Vapour enthalpy

<table>
<thead>
<tr>
<th>Component</th>
<th>HVAPA</th>
<th>HVAPB</th>
<th>HVAPC</th>
<th>HVAPD</th>
<th>HVAPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Pentene</td>
<td>39530</td>
<td>150.5</td>
<td>-0.3646</td>
<td>8.82E-04</td>
<td>-7.09E-07</td>
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<tr>
<td>2-Butene</td>
<td>33360</td>
<td>115</td>
<td>-0.1963</td>
<td>2.73E-04</td>
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<td>2-Hexene</td>
<td>43550</td>
<td>238.9</td>
<td>-0.4808</td>
<td>7.04E-04</td>
<td>-1.60E-07</td>
</tr>
</tbody>
</table>
**Kinetic data**

Kinetic data are taken from Okasinski and Doherty, 1998.

- **Equilibrium constant:**
  \[ K_{eq} = 0.25 \]  
  (E.13)

- **Rate of C₆ formation**
  \[
  r_{C₆} = 0.5 \cdot k_f \cdot \left( x_{C₅}^2 - \frac{x_{C₄} x_{C₆}}{K_{eq}} \right)
  \]  
  (E.14)

where:

\[
  k_f = 3553.6 \cdot \exp\left( -\frac{6.6 \text{ [kcal/gmol]}}{RT} \right) \text{ min}^{-1}
  \]  
  (E.15)
Appendix F. Column Cost Correlations

F.1. Column Diameter

Calculation of the diameter of the column is based on the vapour velocity at the bottom of the column. The vapour velocity is for normal column operation between 70 to 90 percent of the flooding velocity (Sinnot, 1993).

Volumetric flowrate:
\[ Q = \frac{V \cdot M_W}{\rho_G} \]  
(F.1)

Maximum velocity (flooding) is calculated using equation (Sinnot, 1993):
\[ v = K \sqrt{\frac{\rho_L - \rho_G}{\rho_G}} \]  
(F.2)

where:
\[ K = f \left( \text{tray spacing, } \frac{L}{G} \sqrt{\frac{\rho_G}{\rho_L}} \right) \]  
(F.3)

For 80% flooding:
\[ A_r = \frac{Q}{0.8v} \]  
\[ \phi = \sqrt{\frac{4A_r}{\pi}} \]  
(F.4)

where:
- \( A_r \) - active area, m\(^2\)
- \( L \) - mass flowrate of the liquid, kg/s
- \( G \) - mass flowrate of the vapour, kg/s
- \( Q \) - volumetric flow rate, m\(^3\)/s
- \( M_W \) - molecular weight, kg/kmol
- \( v \) - linear velocity, m/s
- \( \rho_G, \rho_L \) - vapour and liquid density, kg/m\(^3\)
- \( \phi \) - column diameter, m
F.2. Cost Estimation

The equipment and operating costs are based on the costs in 1990 (Cost index in 1990 = 357.6). Costs for 2002 are estimated using relative cost index to the cost index in 1990 (Peters and Timmerhaus, 1991):

\[
Cost_{2002} = \frac{Cost\ Index_{2002}}{Cost\ Index_{1990}} \times Cost_{1990}
\]  

(F.5)

![Chemical Engineering Equipment Cost Index](image)

Figure F.1 Chemical Engineering Equipment Cost Index (Chemical Engineering, 1993, Chemical Engineering, 1999)

Cost index 2002 = 402

F.2.1. Steam and Cooling Water Cost

Data taken from Peters and Timmerhaus (1991); Sinnot (1993):

Cost of steam and cooling water (cost in 1990):

<table>
<thead>
<tr>
<th>Steam Type</th>
<th>Cost, $/1000 kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>High pressure</td>
<td>7.938</td>
</tr>
<tr>
<td>Medium pressure</td>
<td>5.292</td>
</tr>
<tr>
<td>Exhaust</td>
<td>2.425</td>
</tr>
</tbody>
</table>

Cooling Water = $ 0.066/ m³
F.2.2. Capital Cost

The equations to calculate the column cost, heat exchanger cost and reboiler cost are derived from graph and table (Peters and Timmerhaus, 1980; Sinnott, 1993). The costs of the equipment in the current year are obtained using equation (F.5):

Column cost:

\[ C_{\text{col}} = N \cdot \exp(0.958 \ln(\phi) + 4.44)F_c C_i \]  

The capital column cost takes into account reactive and non-reactive stages. As no exact cost correlations were found in open literature for the reactive stages, based on the information provided by reactive packing manufacturers (e.g. Sulzer), the reactive stages were considered to be 5 times more expensive than the non-reactive stages.

Reboiler cost

\[ C_r = (18982 + 176.05A)C_i \]  

Condenser cost:

\[ C_C = (9599 + 137.25A)C_i \]  

Area of heat exchanger:

\[ A = \frac{Q}{U\Delta T_{LM}} \]  

where:

- \( A \) - heat transfer area, m\(^2\)
- \( C_i \) - Cost Index \(_{2002}\) / Cost Index \(_{1990}\)
- \( F_c \) - pressure factor
- \( N \) - number of stages
- \( Q \) - heat duty, J/s
- \( C_c \) - cost of condenser or feed pre-heat exchanger, $
Appendices

$C_r$ - cost of reboiler, $\
$C_{col}$ - cost of column, $\
$U$ - overall heat transfer coefficient, J/(m$^2$s K)
$\Delta T_{LM}$ - mean logarithmic temperature difference for a heat exchanger
$\phi$ - column diameter (m)

**Capital cost**
Capital cost includes all equipment costs for the column, the condenser and the reboiler. Total installed cost is calculated using factor $F_{cap}$:

$$Cap = (C_{col} + C_r + C_c) \cdot F_{cap} \quad (F.10)$$

**Operating cost:**

$$Op = C_{steam} + C_{CW} \quad (F.11)$$

where:

$F_{cap}$ - total installed cost factor, i.e., ratio of total installed cost to equipment cost.
$C_{steam}$ - cost of steam
$C_{CW}$ - cost of cooling water

**F.2.3. Total Annualised Cost**

The capital cost expressed on an annual basis is (Smith, 1995):

$$AC = \frac{T_{cap} i(1+i)^n}{(1+i)^{n-1}} \quad (F.12)$$

$$TAC = \frac{T_{cap} i(1+i)^n}{(1+i)^{n-1}} + Opr \quad (F.13)$$

where

$AC$ - annual capital cost, $/yr
$TAC$ - total annual cost, $/yr
$i$ - interest rate
$n$ - number of years
Appendix G. Graphical Algorithms

G.1. Intersection of two line segments in 2-D

Considering two lines in 2-D space, containing the segments AB and CD defined by the points A(x_A,y_A); B(x_B,y_B); A(x_C,y_C); A(x_D,y_D), where x represents the horizontal coordinate, and y the vertical coordinate (Figure G1.1), their intersection will be a point, I(x_i,y_i) (http://www.faqs.org/faqs/graphics/algorithms-faq/).

![Figure G.1 Intersection of two segments [AB] and [CD] in 2-D](image)

The parametric equation of line 1 (the line going through points A and B) is:

\[ x = x_A + \alpha(x_B - x_A) \]
\[ y = y_B + \alpha(y_B - y_A) \]  \hspace{1cm} (G.1)

where the linear parameter \( \alpha \) defines the relative position between A and B of the point defined by coordinates \( x \) and \( y \). Similar, the parametric equation for line 2 can be written as:
\[
x = x_c + \beta(x_D - x_C) \tag{G.2}
\]
\[
y = y_c + \beta(y_D - y_C)
\]

where the linear parameter \( \beta \) defines the relative position between C and D of the point defined by coordinates \( x \) and \( y \).

An intersection occurs between the two lines when they have one common point. If the lines have more than one point in common, then the two lines coincide. The intersection point is obtained by solving for \( \alpha \) and \( \beta \) the system of the two parametric equations:

\[
\begin{align*}
\alpha &= \frac{(y_A - y_C)(x_D - x_C) - (x_A - x_C)(y_D - y_C)}{(x_B - x_A)(y_D - y_C) - (y_B - y_A)(x_D - x_C)} \tag{G.4} \\
\beta &= \frac{(y_A - y_C)(x_B - x_A) - (x_A - x_C)(y_B - y_A)}{(x_B - x_A)(y_D - y_C) - (y_B - y_A)(x_D - x_C)} \tag{G.5}
\end{align*}
\]

The coordinates at the intersection point \( I(x_I, y_I) \) can be then calculated from either Eqs. G.1 or G.2. For an intersection between the two segment \([AB]\) and \([CD]\) to be feasible, point \( I(x_I, y_I) \) should be within the common intervals defined by the points A, B and C, D, that is:

\[
x_I \in [x_A, x_B] \cap [x_C, x_D] \tag{G.6}
\]
\[
y_I \in [y_A, y_B] \cap [y_C, y_D] \tag{G.7}
\]

The conditions defined by Eqs. G.6 and G.7 will lead to both values of \( \alpha \) and \( \beta \) within the interval \([0,1]\). Therefore, the feasibility test for intersection of the defined segments \([AB]\) and \([CD]\) can be written as:

\[
0 \leq \alpha \leq 1 \tag{G.8}
\]
\[
0 \leq \beta \leq 1
\]
G.2. Intersection of a tetragon (patch) and a line segment in 2-D

Considering in 2-D space a patch (tetragon) $ABCD$ defined by the points $A(x_A, y_A)$, $B(x_B, y_B)$, $C(x_C, y_C)$, $D(x_D, y_D)$, and a line containing the segment $MN$ defined by the points $M(x_M, y_M)$ and $N(x_N, y_N)$, where $x$ represents the horizontal coordinate, and $y$ the vertical coordinate (Figure G2.1), their intersection will be a segment contained on $MN$, delimited by points $I_1(x_{I1}, y_{I1})$ and $I_2(x_{I2}, y_{I2})$.

![Figure G.2 Intersection of a patch ABCD with a segment MN in 2-D](image)

For the tetragon $ABCD$, using an equally distributed grid as in Figure G2.2, two linear parameters can be defined: $\alpha$ along the lines $AB$ and $DC$, and $\beta$ along the lines $AD$ and $BC$. Using this grid representation, the values for the two parameters will be 0 at point $A$ and 1 at point $C$. The coordinates of a point inside the tetragon can be expressed the following parametric equations:
\[ x = x_A + \alpha(x_B - x_A) + \beta(x_D - x_A) \]
\[ y = y_A + \alpha(y_B - y_A) + \beta(y_D - y_A) \]  \hspace{1cm} (G.9)

or:
\[ x = x_C + (1-\alpha)(x_D - x_C) + (1-\beta)(x_B - x_C) \]
\[ y = y_C + (1-\alpha)(y_D - y_C) + (1-\beta)(y_B - y_C) \]  \hspace{1cm} (G.10)

where parameters \( \alpha \) and \( \beta \) define the relative position of a point \( I(x,y) \).

Similarly, for the line \( MN \), a linear parameter \( \gamma \) will define the relative position between A and B of a point \( I(x,y) \). The parametric equation for line \( MN \) can be written as:
\[ x = x_M + \gamma(x_N - x_M) \]
\[ y = y_M + \gamma(y_N - y_M) \]  \hspace{1cm} (G.11)

To calculate the coordinates of the two points of intersection \( I_1 \) and \( I_2 \), a check for intersection has to be performed for the segment \( MN \) with all four edges of the tetragon: \( AB \), \( BC \), \( CD \) and \( DA \). The algorithm for intersection of two segments was described in Appendix G.1.

Knowing the coordinates of intersection points \( I_1 \) and \( I_2 \), the parameters \( \alpha \) and \( \beta \) can then be calculated. For the situation in Figure G2.1, the parameters \( \alpha_{1,2} \) and \( \beta_{1,2} \) will be:
\[ \alpha_1 = 1 \]
\[ \beta_1 = \frac{x_{i1} - x_B}{x_C - x_B} \]  \hspace{1cm} (G.12)
\[ \alpha_2 = \frac{x_{i2} - x_D}{x_C - x_D} \]
\[ \beta_2 = 1 \]  \hspace{1cm} (G.13)

If an intersection point is not located on the edge, as in the case of intersection of segment \( M'N' \) with the tetragon ABCD in Figure G.2, then the calculation of the parameters \( \alpha \) and \( \beta \) is not as straightforward as it is for a point situated on the edge.
For example, to calculate the parameters $\alpha$ and $\beta$ for point $N'$, first we need to establish which of the points is located inside the tetragon. The intersection procedure can identify when such a situation occurs, as there will be only one valid point of intersection (point $I_{1}'$ in Figure G.1), but no information will be obtained about which one of the points $M'$ or $N'$ is situated inside the area $ABCD$. An algorithm useful in such situations is based on ray intersection (described at http://www.faqs.org/faqs/graphics/algorithms-faq/). The procedure will count the number of intersection found between each segments $M'O$ and $N'O$ with the tetragon, where $O$ is a point which is known to be outside the area (e.g. the origin). If an odd number of intersections is found, then the point is inside and if an even number is found then the point is outside. For example, in Figure G.3 case (a), two intersections were found, indicating that the point is outside the defined area, and in case (b) three points were found, meaning that the point is inside.

![Figure G.3 Identifying the position of point M relative to area defined by points ABCD (a) Point outside the area; (b) Point inside the area](image)

After identifying which of the two points is situated inside, then the parameters $\alpha$ and $\beta$ for that point can be calculated using the coordinates of points $P_1$, $P_2$ and $R_1$, $R_2$ (Figure G.3):
\[ \alpha_2 = \frac{x_{R2} - x_{R1}}{x_{R2} - x_{R1}} \]
\[ \beta_2 = \frac{x_{R2} - x_{P1}}{x_{P2} - x_{P1}} \]

The coordinates of points \( P_1, P_2 \) and \( R_1, R_2 \) (Figure G.4) can also be expressed in terms of parameters \( \alpha \) and \( \beta \) and coordinates of points \( A, B, C \) and \( D \) (Eqs.G2.7).

\[ x_{P1} = x_A + \alpha(x_B - x_A) \]
\[ y_{P1} = y_A + \alpha(y_B - y_A) \]
\[ x_{P2} = x_D + \alpha(x_C - x_D) \]
\[ y_{P2} = y_D + \alpha(y_C - y_D) \]

Figure G.4 Intersection of a patch \( ABCD \) with a segment \( MN \) in 2-D. Point \( N \) is inside the area defined by points \( A, B, C \) and \( D \).
Point \( I_2 \) is situated at the intersection between lines \( P_1P_2 \) and \( R_1R_2 \). Therefore point \( I_2 \) will verify the equation of any of the two lines, e.g. for line \( P_1P_2 \) we can write:

\[
y = a_p \cdot x + b_p
\]  

(G.17)

By expressing \( a_p \) and \( b_p \) explicitly, Eq. G.17 becomes:

\[
y = \frac{y_{P2} - y_{P1}}{x_{P2} - x_{P1}} \cdot x + \frac{y_{P1} \cdot x_{P2} - y_{P2} \cdot x_{P1}}{x_{P2} - x_{P1}}
\]  

(G.18)

Using Eq. G.2.7 in Eq. G.2.10 will lead to a second order equation:

\[
\alpha^2 + m \cdot \alpha + n = 0
\]  

(G.19)

where:

\[
m = \frac{y_{I2}(x_{CD} - x_{BA}) - x_{I2}(y_{CD} - y_{BA}) - x_{CD}y_A + x_Ay_{CD} - x_Dy_{BA} + y_Dx_{BA}}{y_{CD}x_{BA} - y_{BA}x_{CD}}
\]  

(G.20)

\[
n = \frac{y_{I2}(x_D - x_A) - x_{I2}(y_D - y_A) - x_Dy_A + x_Ay_D}{y_{CD}x_{BA} - y_{BA}x_{CD}}
\]  

(G.21)

\[
x_{CD} = x_C - x_D; \quad y_{CD} = y_C - y_D
\]

\[
x_{BA} = x_B - x_A; \quad y_{BA} = y_B - y_A
\]  

(G.22)

Solving Eq. G.19 will provide two roots for \( \alpha \), one within the interval \([0,1]\).

For the parameter \( \beta \), the coordinates of points \( P_1 \) and \( P_2 \) need to be calculated first (Eq. G.15). Then, the parameter \( \beta \) can be obtained using Eq. G.17.

The two parameters \( \alpha, \beta \) for the patch \( ABCD \), and the line parameter \( \gamma \) for the segment \( MN \) calculated using the procedure described above, can then be used
G.3. Intersection of a line with a plane in 3-D

Considering in 3-D space a plane $P1$ defined by the points $A(x_A, y_A, z_A)$, $B(x_B, y_B, z_B)$, $C(x_C, y_C, z_C)$, and a line containing the segment $MN$ defined by the points $M(x_M, y_M, z_M)$ and $N(x_N, y_N, z_N)$ (Figure G.5), their intersection will be a point $I_1(x_{I1}, y_{I1}, z_{I1})$ [http://www.faqs.org/faqs/graphics/algorithms-faq/].

The general equation of the plane $P1$ is:

$$Ax + By + Cz + D = 0$$  \hspace{1cm} (G.23)

where $A$, $B$, $C$ and $D$ are calculating using the following determinants:
The parametric equations of line 1 (the line going through points A and B) are:

\[ x = x_M + \alpha(x_M - x_N) \]
\[ y = y_M + \alpha(y_M - y_N) \]
\[ z = z_M + \alpha(z_M - z_N) \]  \hspace{1cm} (G.28)

Substituting x, y, z into the plane equation (Eq. G.23) and solving for \( \alpha \) will give:

\[ \alpha = \frac{Ax_M + By_M + Cz_M + D}{A(x_N - x_M) + B(y_N - y_M) + C(z_N - z_M)} \]  \hspace{1cm} (G.29)

The coordinates of point I_1 can then be calculated using either Eqs. G.23 or G.28.

**G.4. Intersection of a two triangles in 3-D**

Considering in 3-D space two triangles, ABC defined by the points \( A(x_A,y_A,z_A) \), \( B(x_B,y_B,z_B) \), \( C(x_C,y_C,z_C) \) and MNO defined by the points \( M(x_M,y_M,z_M) \), \( N(x_N,y_N,z_N) \) and \( O(x_O,y_O,z_O) \), where x,y,z represents the three coordinates (
Figure G.6), their intersection will be a segment \( I_1I_2 \), delimited by points \( I_1(x_{I1}, y_{I1}) \) and \( I_2(x_{I2}, y_{I2}) \).

![Figure G.6 Intersection of two triangles, ABC and MNO in 3-D](image)

The intersection points are located on the line of the intersection of the planes containing the two triangles: plane \( P1 \) containing triangle \( ABC \) and plane \( P2 \) containing triangle \( MNO \). The parametric equations for the two planes \( P1 \) and \( P2 \) are:

\[
\begin{align*}
  x &= x_A + \alpha(x_B - x_A) + \beta(x_C - x_A) \\
  y &= y_A + \alpha(y_B - y_A) + \beta(y_C - y_A) \\
  z &= z_A + \alpha(z_B - z_A) + \beta(z_C - z_A) \\
  x &= x_A + \gamma(x_N - x_M) + \delta(x_O - x_M) \\
  y &= y_A + \gamma(y_N - y_M) + \delta(y_O - y_M) \\
  z &= z_A + \gamma(z_N - z_M) + \delta(z_O - z_M)
\end{align*}
\]

(G.30) (G.31)

To calculate the coordinates of intersection points, first the intersection of the edges with the second plane need to be calculated for each triangle, e.g. the
The intersection of lines $MN$ and $MO$ with $P1$ will provide points $I_1$ and $I_4$ and the intersection of lines $AB$ and $AC$ with $P2$ will provide point $I_2$ and $I_3$. However, only two of the four points are common points to both triangles $ABC$ and $MNO$; for the case presented in Figure G.6 the valid points are $I_1$ and $I_2$. The coordinates of the intersection points are calculated as described in Appendix G.3.

Knowing the coordinates of the intersection points, the parameters $\alpha$, $\beta$ for plane $P1$ can be calculated using two of the three parametric equations, e.g. equation for $x$ and $y$ in Eq. G.30.

For example, for point $I_1(x_{I1}, y_{I1}, z_{I1})$, Eq. G.30 gives:

\[
\begin{align*}
    x_{I1} &= x_A + \alpha(x_B - x_A) + \beta(x_C - x_A) \\
    y_{I1} &= y_A + \alpha(y_B - y_A) + \beta(y_C - y_A)
\end{align*}
\]

Solving for $\alpha$ and $\beta$ will lead to:

\[
\begin{align*}
    \alpha &= \frac{(x_{I1} - x_A)(y_C - y_A) - (y_{I1} - y_A)(x_C - x_A)}{(x_B - x_A)(y_C - y_A) - (y_B - y_A)(x_C - x_A)} \quad \text{(G.33)} \\
    \beta &= \frac{(x_{I1} - x_A)}{(x_C - x_A)} - \alpha \frac{(x_B - x_A)}{(x_C - x_A)} \quad \text{(G.34)}
\end{align*}
\]

In a similar fashion, for plane $P2$ we can use the equations for $x$ and $y$ in Eq. G.31, leading to:

\[
\begin{align*}
    \gamma &= \frac{(x_{I1} - x_M)(y_O - y_M) - (y_{I1} - y_M)(x_O - x_M)}{(x_N - x_M)(y_O - y_M) - (y_N - y_M)(x_O - x_M)} \quad \text{(G.35)} \\
    \delta &= \frac{(x_{I1} - x_M)}{(x_N - x_M)} - \alpha \frac{(x_N - x_M)}{(x_O - x_M)} \quad \text{(G.36)}
\end{align*}
\]

The four parameters, $\alpha$ and $\beta$ for the triangle $ABC$, and $\gamma$ and $\delta$ for the triangle $MNO$ calculated using the procedure described above, can then be used in the linear interpolation for calculating the value of different operating parameters (reflux ratio, reboil ratio, holdup, etc.) at intersection points.