Methodologies for the optimisation, control and consideration of uncertainty of reactive distillation

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DOCTOR OF PHILOSOPHY

by

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I, Aikaterini Tsatse confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the thesis.
Abstract

The work presented in this thesis is motivated by the current obstacles hindering the implementation of reactive distillation in industry, mainly related to the complexities of its design and control, as well as the impact of uncertainties thereupon. This work presents a rigorous methodology for the optimal design and control under uncertainty of reactive distillation. The methodology can also be used to identify and investigate mitigation strategies for process failures arising due to design and/or operation deficiencies under changed processing conditions, based on the evaluation of different design and/or control alternatives.

The first step of the methodology is the simultaneous (MINLP) optimisation of the design and operation of a reactive distillation process superstructure, used to explore the possible steady-state design alternatives available, including ancillary equipment such as pre- and side-reactors, side-strippers and additional distillation columns, based on product-related constraints and a detailed objective cost function. The next step is the investigation of the dynamic control performance of this optimal system, where conventional and advanced process control strategies are considered in order to investigate how robust the system is towards operational disturbances, or whether revising the optimal steady-state design is required. As the optimisation depends heavily on accurate data for reaction kinetics and separation performance, the final step of the methodology is the evaluation of the impact of parameter uncertainty on the performance of the optimal controlled system, including redesigning the controlled system if required.

The methodology is demonstrated using a number of industrially relevant case studies with different reaction and separation characteristics in order to investigate how these determine the design and control of an economically attractive and rigorous reactive distillation process. It is demonstrated that the process characteristics have a significant impact on the design of the system, and that auxiliary equipment may be required to meet production specifications and/or to ensure robust controlled behaviour. It is also shown that, under parameter uncertainty, an optimal controlled system may nevertheless face performance issues, and revising the design and/or operation of the process may be required in order to mitigate such situations.
Impact statement

The main goal of this work was the development of mitigation strategies for reactive distillation systems in order to tackle production failure issues due to operational disturbances and/or modelling uncertainties. A framework was therefore developed based on a systematic evaluation of optimal design and control alternatives. The methodology offers the possibility of revising the design and/or operation of the process in order to minimise the risk of production failures and to increase the flexibility of the process considered. In addition to the overall methodology developed, additional insight was obtained through the investigation of the design, control and consideration of uncertainty for reactive distillation systems individually, and this is discussed below.

With regards to the optimal design of the process, this work has for the first time considered the simultaneous determination of the optimal design and operation of a complex reactive distillation process considering a wide range of process alternatives. This novel methodology was applied to a number of industrially relevant case studies varying in the key system characteristics, i.e. reaction kinetics and separation parameters. The methodology indicated that the system characteristics do indeed impact on the optimal design and operation, and that the extent of the impact depends on the relative contributions from separation performance and from kinetics. A 3-D figure representing the optimal results was presented that illustrates the relative contributions of key parameters to the optimal design, in particular, in relation to the number of units required. This figure can be used as a guide for future investigations to indicate the most likely optimal design for different combinations of key parameters.

With regards to the controllability of the process, the evaluation of case studies with different key parameters provided insight into how reaction and separation phenomena interact within the column, the relative importance of these phenomena and what the corresponding impact is of their interaction on process controllability. In addition, the methodology developed provided insight into how the presence of the reaction affects the controllability of the distillation column compared to distillation alone, and how design variables can be taken into consideration in order to improve controllability and process performance towards typical operational disturbances often encountered in industry.
The final factor considered in addition to the design and control, but which is equally important for the wider implementation of reactive distillation, is uncertainty in parameter values for e.g. the reaction or the separation characteristics. Using a systematic methodology developed in this work, it was shown how, and to what extent, this uncertainty impacts on the performance of the overall process and how the uncertainty can be considered in order to mitigate production failure issues depending on the separation and reaction characteristics of the process considered. The mitigation strategies considered in this work include applications of tighter process control, enhancement of process flexibility by revising its design and operational parameters, as well as addition of ancillary equipment. The findings indicate that careful consideration of the impact of uncertainty is required, as neglecting this may have a significant impact on the performance and economics of the process, and may even mean that the specifications cannot be met.

Overall, this work presents a framework for the optimal design of economically attractive and flexible reactive distillation processes, offering potential economic and sustainability benefits (e.g. energy savings, process performance improvements etc.). In addition, insight into the design and control of reactive distillation is provided so that R&D resources can be better prioritised towards a potential industrial implementation. Finally, the development of mitigation strategies can reduce the inherent risk (from an economic and product quality perspective) to uncertainty of this intensified process and pave the way for its wider industrial acceptance.
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# Abbreviations

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<th>Description</th>
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<tbody>
<tr>
<td>BDF</td>
<td>Backward Differentiation Formulae</td>
</tr>
<tr>
<td>BLAS</td>
<td>Basic Linear Algebra System</td>
</tr>
<tr>
<td>CEPCI</td>
<td>Chemical Engineering Plant Cost Index</td>
</tr>
<tr>
<td>CFD</td>
<td>Computational Fluid Dynamics</td>
</tr>
<tr>
<td>CPU</td>
<td>Central Processing Unit</td>
</tr>
<tr>
<td>CRF</td>
<td>Capital Recovery Factor</td>
</tr>
<tr>
<td>CSTR</td>
<td>Continuous Stirred Tank Reactor</td>
</tr>
<tr>
<td>CVP</td>
<td>Control Vector Parameterisation</td>
</tr>
<tr>
<td>DAE</td>
<td>Differential Algebraic Equations</td>
</tr>
<tr>
<td>DEA</td>
<td>Diethanolamine</td>
</tr>
<tr>
<td>DIPE</td>
<td>Diisopropyl ether</td>
</tr>
<tr>
<td>DIPPR</td>
<td>Design Institute for Physical Properties</td>
</tr>
<tr>
<td>DLS</td>
<td>Design Limiting Step dimensionless number</td>
</tr>
<tr>
<td>EG</td>
<td>Ethylene Glycol</td>
</tr>
<tr>
<td>ETBE</td>
<td>Ethyl tert-butyl ether</td>
</tr>
<tr>
<td>GBD</td>
<td>Generalised Benders Decomposition</td>
</tr>
<tr>
<td>GMF</td>
<td>Generalised Modular Representation Framework</td>
</tr>
<tr>
<td>GSA</td>
<td>Global System Analysis</td>
</tr>
<tr>
<td>HEN</td>
<td>Heat Exchanger Network</td>
</tr>
<tr>
<td>IAE</td>
<td>Integral Absolute Error</td>
</tr>
<tr>
<td>KPI</td>
<td>Key Performance Indicators</td>
</tr>
<tr>
<td>LU</td>
<td>Lower-Upper (decomposition/factorisation)</td>
</tr>
<tr>
<td>MA</td>
<td>Methyl Acetate</td>
</tr>
<tr>
<td>MIBK</td>
<td>Methyl isobutyl ketone</td>
</tr>
<tr>
<td>MIDO</td>
<td>Mixed-Integer Dynamic Optimisation</td>
</tr>
<tr>
<td>MILP</td>
<td>Mixed-Integer Linear Programming</td>
</tr>
<tr>
<td>MINLP</td>
<td>Mixed-Integer Non-Linear Programming</td>
</tr>
<tr>
<td>MPC</td>
<td>Model Predictive Control</td>
</tr>
<tr>
<td>MTBE</td>
<td>Methyl tert-butyl ether</td>
</tr>
<tr>
<td>NEQ</td>
<td>Non-Equilibrium dimensionless number</td>
</tr>
<tr>
<td>NF</td>
<td>Nelson-Farrar Refinery Construction Cost</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>NLP</td>
<td>Non-Linear Programming</td>
</tr>
<tr>
<td>OAERAP</td>
<td>Outer Approximation Equality Relaxation Augmented Penalty</td>
</tr>
<tr>
<td>OCFE</td>
<td>Orthogonal Collocation on Finite Elements</td>
</tr>
<tr>
<td>P</td>
<td>Proportional (controller)</td>
</tr>
<tr>
<td>PI</td>
<td>Process Intensification</td>
</tr>
<tr>
<td>PID</td>
<td>Proportional-Integral (controller)</td>
</tr>
<tr>
<td>RD</td>
<td>Reactive Distillation</td>
</tr>
<tr>
<td>SP</td>
<td>Set Point</td>
</tr>
<tr>
<td>SVS</td>
<td>Saved Variable Set</td>
</tr>
<tr>
<td>TAC</td>
<td>Total Annualised Cost</td>
</tr>
<tr>
<td>TAME</td>
<td>Tert-amyl methyl ether</td>
</tr>
<tr>
<td>VLE</td>
<td>Vapour-Liquid Equilibrium</td>
</tr>
<tr>
<td>VLLE</td>
<td>Vapour-Liquid-Liquid Equilibrium</td>
</tr>
<tr>
<td>ZSM</td>
<td>Zeolite Socony Mobil</td>
</tr>
</tbody>
</table>
Notation

The following list presents all notation included in this work. Additional symbols related to the superstructure variables are presented in Chapter 3.

A
- Heat exchange area (m$^2$)

$a_{\text{Lang}}$
- Lang factor (-)

annual. CAPEX
- Capital (annualised) cost (€/yr)

annual. OPEX
- Operating (annualised) cost (€/yr)

C
- Concentration of component i (mol/m$^3$)

CAPEX
- Capital cost (including purchase and installation) (€)

CAPEX 2019
- Capital cost (incl. purchase and installation) brought up to 2019 (€)

C$_C$
- Condenser purchase cost ($)

C$_{DC}$
- Distillation column purchase cost ($)

C$_{\text{main}}$
- Plant maintenance operating cost (€/s)

C$_{OF}$
- Feed cost (€/s)

C$_{OS}$
- Steam cost (€/s)

C$_{OW}$
- Waste treatment cost (€/s)

C$_R$
- Reboiler purchase cost ($) (€)

C$_{RC}$
- Reactor purchase cost ($)

C$_{RD}$
- Reflux drum purchase cost ($) (€)

CRF
- Interest rate and depreciation factor (1/yr)

C$_S$
- Stripper purchase cost ($) (€)

C$_{ST}$
- Sieve trays purchase cost ($) (€)

C$_T$
- Total purchase cost ($) (€)

d
- Density of column construction material (0.284 lb/in$^3$)

D$_A$
- Diffusivity (m$^2$/s)

Da
- Damköhler number (-)

D$_i$
- Internal column diameter (in)

D$_o$
- External column diameter (in)

D$_{\text{tray}}$
- Tray diameter (m)

E
- Fractional weld efficiency (85%)

F$_{\text{OW}}$
- Organic waste flow rate (kg/s)

F$_T$
- Total feed flow rate (kg/s)

H$_0$
- Tray liquid holdup (mol)

Ha
- Hatta number (-)
$k_b$  Backward reaction rate constant ($m^3/(kmol\cdot s)$)

$K_{eq}$  Reaction chemical equilibrium (-)

$k_f$  Forward reaction rate constant ($m^3/(kmol\cdot s)$)

$k_L$  Mass transfer coefficient (m/s)

$L$  Tangent-to-tangent column height (in)

$n$  Reaction order (-)

$N_i$  Number of equipment units (-)

$OPEX$  Total operating cost ($\€/s$)

$P_d$  Internal design gauge pressure (psig)

$Q_{condenser}$  Condenser heat duty (W)

$Q_{reboiler}$  Reboiler heat duty (W)

$rate_{exch}$  Dollars to euros exchange rate ($\€$/\$)

$r_b$  Backward reaction rate (kmol/(m$^3$ hr))

$R_C$  Reaction rate of component C (kmol/(m$^3$ hr))

$r_f$  Forward reaction rate (kmol/(m$^3$ hr))

$S$  Maximum allowable stress (15000 lbf/in$^2$)

$TAC$  Total Annualised Cost ($\€$/yr)

$t_p$  Internal pressure thickness (in)

$t_s$  Column head and shell thickness (in)

$t_w$  Thickness to withstand wind at the bottom (in)

$V$  Reflux drum capacity (m$^3$)

$V_R$  Reactor volume (m$^3$)

$V_t$  Tray vapour rate (mol/s)

$V_{total}$  Total tray liquid volume (m$^3$)

$W$  Stripper shell weight (kg)

$W_{shell}$  Column shell weight (kg)

$x$  Liquid mole fraction of component i

$y$  Vapour mole fraction of component i

$\phi$  Total vapour flow at stage i (kmol/hr)
List of publications resulting from this work

Journal papers:

Tsatse, A., Oudenhoven, S.R.G., ten Kate, A.J.B. and Sorensen, E. (2021b). "A methodology to evaluate the controllability of reactive distillation." To be submitted. (Relates to Chapter 4)


Conference contributions:


**Educational papers:**

Chapter 1. Introduction

The aim of this chapter is to present the general background of the project. The significance of Process Intensification (PI) towards greener, more sustainable, as well as more cost-effective technologies is highlighted. Reactive distillation is presented as an excellent representative example of PI as it combines reaction and separation into a single unit, offering great process performance improvements as well as potential cost and energy savings. Fundamental knowledge on reactive distillation is presented, related to its history and numerous applications. An insight into the advantages of reactive distillation is provided, related to how improvements in the overall process, its cost and energy requirements can be achieved comparing to the conventional, multi-unit process. Information on the limitations and constraints of the process, caused by the intensified nature of it, are provided, along with existing feasibility evaluation methodologies aimed at indicating whether reactive distillation is an economically attractive alternative for the given reaction and separation tasks. In addition, the aims and structure of the thesis are outlined and briefly described.
1.1 The importance of Process Intensification

Over the last decades, there has been a growing environmental awareness of the negative impact of energy consumption and production of undesired reaction by-products within the process industry. In addition, legislation has requested industry to reduce gas emissions and improve energy efficiency. In an effort to reduce this environmental impact, whilst still maintaining or improving their competitiveness in the global market, the process industry has focused on the development of “greener”, more sustainable, eco-efficient and cheaper technologies and operations (processes and/or units) (Boodhoo and Harvey 2013). Process Intensification (PI) can contribute to this innovation, and according to Stankiewicz and Moulijn (2000): “Process Intensification consists of the development of novel apparatuses and techniques that, compared to those commonly used today, are expected to bring dramatic improvements in manufacturing and processing, substantially decreasing equipment-size/production-capacity ratio, energy consumption, or waste production, and ultimately resulting in cheaper, sustainable technologies”.

The PI concept was first established at Imperial Chemical Industries during the late 1970’s and since then, great developments have taken place. Today, many processes and types of equipment belong to this field and PI can now be divided into two main areas (although obviously some overlap can exist) (Boodhoo and Harvey 2013):

- **Process-intensifying equipment**, such as novel reactors and intensive mixing; and
- **Process-intensifying methods**, such as hybrid separations, integration of reaction and separation, techniques using alternative energy sources (light, ultrasound, etc.), and new process-control methods (such as intentional unsteady-state operation).

New methods may require new types of equipment to be developed, and vice versa, existing equipment may use novel or unconventional processing methods. In Figure 1.1, a classification of PI equipment and methods is presented. Intensified equipment may or may not include chemical reactions. Intensified methods can be divided into multifunctional reactors, hybrid separations, alternative energy sources and other methods. The potential benefits offered by the concept of PI are numerous and related
to the process itself as well as industrial and environmental considerations as categorised and summarised in Figure 1.2.

Figure 1.1: Classification of PI equipment and methods (Stankiewicz and Moulijn 2000).

Figure 1.2: Potential benefits of Process Intensification (Boodhoo and Harvey 2013).
Reactive separations, which belong to the “multi-functional reactors” category according to Figure 1.1, is an important category of intensified processes as they combine reaction and separation into a single unit. Reactive separation processes can be categorised according to Figure 1.3, based on the phases involved in the process. The focus of this work is on the gas/vapour reactive separation process, or reactive distillation (RD) using either homogeneous or heterogeneous catalysts. When no catalyst is required for reaction to take place, the process is considered homogeneously auto-catalysed.

![Figure 1.3: Reactive separation processes (Lutze and Sudhoff 2016).](image)

1.2 Reactive distillation process description

Most chemical plants include reaction and separation processes. Reaction can take place in a variety of reactor types (e.g. CSTRs, plug-flow or batch) whilst separation exists in various forms such as distillation, crystallisation, adsorption etc. From the latter, distillation is the most common (Luyben and Yu 2008). Reactive distillation (RD) is an integrated operation that combines reaction and distillation into a single unit, allowing the simultaneous production, separation and removal of the products. As reactants enter the column, they form the products in the reactive zone within the column which are subsequently separated and removed in the product streams. The unused reactants can be recycled and returned to the column to improve reaction conversion and yield. A reactive distillation column can have single or multiple feeds, and the main product can
be isolated either from the top or bottom stream, depending on the relative volatilities of all participating compounds. A conventional reactive distillation column is presented in Figure 1.4. It has to be noted that in Figure 1.4 the flowsheet includes two reactant feeds, however, this is one of several possible feed configurations as reactants can be fed together at the same stage or split into several feed streams if this is beneficial in terms of process performance.

In a reactive distillation process, the reactants enter the column and react throughout the reactive zone. The reactive zone can be either a part of the column or the entire column depending on the conditions or the location of the catalyst, if any. As reaction progresses, usually in the liquid phase, the lightest components are separated at the top of the column (rectifying section) due to the heat provided by the reboiler and the evaporation of the most volatile components that takes place, whilst the heaviest components are driven to the bottom of the column (stripping section). As in a conventional distillation column, vapour/liquid equilibrium (VLE) exists and operation is adjusted to enhance the purity of the product stream. In the ideal scenario, the relative volatilities are such that the unreacted feed (if any) and the by-products are removed in one product stream of the column while the desired product is removed in the other outlet stream. However, this is not always the case and further separation steps may be required when unfavourable relative volatilities and/or unfavourable kinetics are present.
Reactive distillation processes can be divided into homogeneous (both auto-catalysed and homogeneously catalysed) processes and heterogeneous processes that are catalysed by a solid catalyst (catalytic distillation) as illustrated in Table 1.1. The rate of autocatalytic reactions can only be influenced by the temperature or pressure of the reactive distillation equipment, while homogeneously catalysed reactions can be influenced also by changing the concentration of catalyst and, thus, the reaction rate can be adapted over a wide range to the needs of the reactive distillation equipment. While homogeneous catalysis is more flexible, it normally requires expensive additional separation steps for the catalyst to recover. Heterogeneous catalysis on the other hand, requires a special construction to accommodate the catalyst. The catalyst can be packed in “tea bags” on trays, or sandwiched in structured packing, such as Sulzer Katapak, in order to fix the catalytic particles in the reactive zone, thus limiting the catalyst concentration which can be achieved. Nevertheless, the packings used in conventional and reactive columns are very similar (Kiss 2013).
Table 1.1: Applications of reactive distillation along with their catalysts and/or internals (Kiss 2013).

<table>
<thead>
<tr>
<th>Reaction type</th>
<th>Catalyst/internals</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Alkylation</strong></td>
<td></td>
</tr>
<tr>
<td>Alkyl benzene from ethylene/propylene and benzene</td>
<td>Zeolite β, molecular sieves</td>
</tr>
<tr>
<td><strong>Amination</strong></td>
<td></td>
</tr>
<tr>
<td>Amines from ammonia and alcohols</td>
<td>H₂ and hydrogenation catalyst</td>
</tr>
<tr>
<td><strong>Carbonylation</strong></td>
<td></td>
</tr>
<tr>
<td>Acetic acid from CO and methanol/dimethyl ether</td>
<td>Homogeneous</td>
</tr>
<tr>
<td><strong>Condensation</strong></td>
<td></td>
</tr>
<tr>
<td>Diacetone alcohol from acetone</td>
<td>Heterogeneous</td>
</tr>
<tr>
<td>Bisphenol-A from phenol and acetone</td>
<td>N/A</td>
</tr>
<tr>
<td>Trioxane from formaldehyde</td>
<td>Strong acid catalyst, zeolite ZSM-5</td>
</tr>
<tr>
<td><strong>Esterification</strong></td>
<td></td>
</tr>
<tr>
<td>Methyl acetate from methanol and acetic acid</td>
<td>H₂SO₄, dowex 50, amberlyst-15</td>
</tr>
<tr>
<td>Ethyl acetate from ethanol and acetic acid</td>
<td>N/A</td>
</tr>
<tr>
<td>2-methyl propyl acetate from 2-methyl propanol and acid</td>
<td>Katapak-S</td>
</tr>
<tr>
<td>Butyl acetate from butanol and acetic acid</td>
<td>Cation exchange resin</td>
</tr>
<tr>
<td>Fatty acid methyl esters from fatty acids and methanol</td>
<td>H₂SO₄, amberlyst-15, metal oxides</td>
</tr>
<tr>
<td>Fatty acid alkyl esters from fatty acids and alkyl alcohols</td>
<td>H₂SO₄, amberlyst-15, metal oxides</td>
</tr>
<tr>
<td>Cyclohexyl carboxylate from cyclohexene and acids</td>
<td>Ion-exchange resin bags</td>
</tr>
<tr>
<td><strong>Etherification</strong></td>
<td></td>
</tr>
<tr>
<td>MTBE from isobutene and methanol</td>
<td>Amberlyst-15</td>
</tr>
<tr>
<td>ETBE from isobutene and ethanol</td>
<td>Amberlyst-15/pellets, structured</td>
</tr>
<tr>
<td>TAME from isoamylene and methanol</td>
<td>Ion-exchange resin</td>
</tr>
<tr>
<td>DIPE from isopropanol and propylene</td>
<td>ZSM 12, amberlyst-36, zeolite</td>
</tr>
<tr>
<td><strong>Hydration/dehydration</strong></td>
<td></td>
</tr>
<tr>
<td>Mono ethylene glycol from ethylene oxide and water</td>
<td>Homogeneous</td>
</tr>
<tr>
<td><strong>Hydrogenation/dehydrogenation</strong></td>
<td></td>
</tr>
<tr>
<td>Cyclohexane from benzene</td>
<td>Alumina supported Ni catalyst</td>
</tr>
<tr>
<td>MIBK from benzene</td>
<td>Cation-exchange resin with Pd/Ni</td>
</tr>
<tr>
<td><strong>Hydrolysis</strong></td>
<td></td>
</tr>
<tr>
<td>Acetic acid and methanol from methyl acetate and water</td>
<td>Ion-exchange resin bags</td>
</tr>
<tr>
<td>Acrylamide from acrylonitrile</td>
<td>Cation exchanger, copper oxide</td>
</tr>
<tr>
<td><strong>Isomerization</strong></td>
<td></td>
</tr>
<tr>
<td>Iso-parafins from n-parafins</td>
<td>Chlorinated alumina and H₂</td>
</tr>
<tr>
<td><strong>Nitratation</strong></td>
<td></td>
</tr>
<tr>
<td>4-nitrochlorobenzene from chlorobenzene and nitric acid</td>
<td>Azeotropic removal of water</td>
</tr>
<tr>
<td><strong>Transesterification</strong></td>
<td></td>
</tr>
<tr>
<td>Ethyl acetate from ethanol and butyl acetate</td>
<td>Homogeneous</td>
</tr>
<tr>
<td>Diethyl carbonate from ethanol and dimethyl carbonate</td>
<td>Heterogeneous</td>
</tr>
<tr>
<td>Vinyl acetate from vinyl stearate and acetic acid</td>
<td>N/A</td>
</tr>
<tr>
<td><strong>Unclassified reactions</strong></td>
<td></td>
</tr>
<tr>
<td>Monosilane from trichlorosilane</td>
<td>Heterogeneous</td>
</tr>
<tr>
<td>Methanol from syngas</td>
<td>Cu/Zn/Al₂O₃ and inert solvent</td>
</tr>
<tr>
<td>DEA from monoethanolamine and ethylene oxide</td>
<td>N/A</td>
</tr>
</tbody>
</table>
1.3 Reactive distillation: History and Applications

The reactive distillation process was invented in 1921 when the first patents appeared (Backhaus 1921, Backhaus 1922, Backhaus 1923a, Backhaus 1923b). Early journal articles were published by various authors including Keyes (1932), Schniepp et al. (1945), Leyes and Othmer (1945a, 1945b) and Berman et al. (1948a, 1948b) (Taylor and Krishna 2000). The first publications dealt mainly with homogeneous, auto-catalysed reactions such as esterifications, trans-esterifications and hydrolysis (Kiss 2013). The first experimental application of reactive distillation was reported in 1948 by the Othmer group (Berman 1948a) and referred to the esterification of dibutyl phthalate from butanol and phthalic acid.

One of the earliest industrial applications of reactive distillation was a DuPont process in which dimethyl terephthalate reacted with ethylene glycol in a distillation column to produce methanol (removed from the top of the column) and ethylene terephthalate used for polyester production (removed from the bottom) (Luyben and Yu 2008). However, the most well-known industrial application of reactive distillation belongs to the Eastman Chemical Co. The publication of a ground-breaking paper by engineers from Eastman Chemical Co. in 1990 (Agreda et al. 1990), drew the attention towards the potential of reactive distillation in both industry and academia. The Eastman reactive distillation column described in the influential manuscript (Figure 1.5), produced methyl acetate (removed from the top) and water (removed from the bottom), with methanol fed into the lower part of the column and acetic acid fed into the upper part. It was reported that this single reactive column replaced a conventional multi-unit process that consumed five times more energy and whose capital investment was five times that of the reactive column (Luyben and Yu 2008). These benefits were achieved as the acid-catalysed reaction was traditionally carried out using a processing scheme which consists of one reactor and a train of nine distillation columns (Taylor and Krishna 2000). This provides an outstanding example of innovative chemical engineering and Process Intensification.
Another representative example of the importance of reactive distillation, and possibly the most important from the standpoint of the number of installations and production capacity, is the production of methyl tertiary butyl ether (MTBE). A mixed C4 hydrocarbon stream from a refinery debutanizer column containing isobutene and other inert C4 components (isobutane, n-butane, and n-butene) is fed into a reactive distillation column along with methanol. Isobutene reacts with methanol in the reactive column towards MTBE, which is removed from the bottom whilst the chemically inert C4s are removed from the top of the column. MTBE is mainly used in gasoline blending although its use is now being substituted due to environmental awareness, along with other similar esters such as ethyl tertiary butyl ether (ETBE) and tert amyl methyl ether (TAME), also produced using reactive distillation (Luyben and Yu 2008).

In addition to the applications mentioned above, various other large-scale reactive distillation processes within the petrochemical industry have been around for many decades (since 1953), although have not been disclosed to the public until recently. Today, reactive distillation processes can reach capacities of 3000 ktn/yr (Harmsen 2007). Some of those applications are presented in Table 1.1 (Kiss 2013), however, the current total number of commercial applications of reactive distillation exceeds 150 and
Luyben and Yu (2008) listed 236 reactive distillation systems that have been considered in the open literature, classified by reaction types.

Luyben and Yu (2008) also presented the number of publications (patents and papers) of reactive distillation from 1971 to 2007 (Figure 1.6). In an effort to bring those numbers up to date, currently 2800 patents can be found according to the US Patent Office, using as keywords either "reactive distillation" or "catalytic distillation". It can therefore be seen that there has been a significant increase in numbers through the years. However, the implementation of reactive distillation can be further accelerated when some of the limitations of the process, described in the next section, are overcome.

![Figure 1.6: Publications or U.S. patents of reactive distillation for the period 1971-2007 as listed in the Engineering Index and U.S. Patent Office (Luyben and Yu 2008).](image)

1.4 Advantages, Limitations and Feasibility challenges of reactive distillation

As mentioned, reactive distillation is a prime PI example, offering a number of benefits as will be outlined in this section. However, general industrial acceptance is currently limited by a number of drawbacks, which are also outlined along with the associated feasibility challenges.

1.4.1 Advantages

The advantages of the reactive distillation process are multiple and are mainly related to process performance, cost and sustainability (Malone and Doherty 2000, Malone et al. 2003). First of all, reactive distillation ensures higher reactant conversion through the
simultaneous removal of the products from the column, and can therefore overcome reaction equilibrium which would not be possible in a conventional reactor (Taylor and Krishna 2000). Similarly, reactive distillation can also achieve higher product selectivity as it often eliminates side reactions by continuously removing the desired product (Schmidt-Traub and Górak 2006). Furthermore, the interaction between reaction and separation can improve process performance through various ways such as by overcoming azeotropes, removing catalyst poisons and reducing catalyst requirements (Taylor and Krishna 2000), reacting away contaminants and enhancing overall rates (Kiss 2013). Separation of close-boiling components is also possible in reactive distillation columns since a reactive entrainer can be used to react with one of the components to form an intermediate product whose boiling point facilitates separation (Keller 2014). For example, Kumar et al. (Kumar et al. 2011) described a process where reaction between cyclohexene and formic acid takes place in a catalytic column to form cyclohexyl formate which in turn reacts with water in a subsequent catalytic column, to produce cyclohexanol. In this study, formic acid successfully works as a reactive entrainer in the first catalytic column to separate cyclohexene and cyclohexane.

Reactive distillation, as already explained, can lead to the reduction of units in the plant. In addition, the integration of reaction and separation into a single apparatus can lead to lower energy consumption. When exothermic reactions are present, the heat of the reaction can be used for separation, thus reducing the column energy requirements (i.e. reboiler heat duty). Furthermore, reactive distillation has the potential of reducing water and solvent consumption due to higher reaction conversion/selectivity or formation of azeotropes in cases when extraction is needed to obtain high product purity. Overall, the reactive distillation process can lead to reduced investment (capital) and operating costs as well as to the development of a greener, more sustainable process. Many of the above-mentioned advantages are evident in the Eastman process mentioned in the previous section.

The aspects of reactive distillation as a sustainable process are very well summarised by Malone et al. (Malone et al. 2003). The authors recognise that reactive distillation promotes prevention instead of treatment by reducing solvent requirements, overcoming unfavourable chemical equilibrium and improving selectivity, as well as design for separation, i.e. avoiding difficult separations. Reactive distillation also maximizes efficiency and minimizes excess (i.e. enhances overall reaction rates),
conserves complexity and supports design for a commercial afterlife through the reduction in the number of units, and integrates local material and energy flows through the use of more specialised equipment by reducing energy demands. However, the authors mention that the use of more specialised equipment increases the complexity, affecting the design and control of the process, as explained in the next section.

1.4.2 Limitations
Having mentioned the advantages of reactive distillation, one should not ignore the constraints which may limit reactive distillation applications (Keller 2014). The first limitation is related to the need for the conditions of reaction, separation and apparatus to overlap (Figure 1.7). In a conventional, multi-unit process, reactors can operate at the optimum conditions (temperature and pressure) that are selected to favour the given chemical kinetics. Similarly, distillation columns can operate at their optimum conditions, selected to be the most favourable for the given VLE properties. However, in the reactive distillation column, reaction and separation are performed under the same pressure and under the column temperature determined by the tray compositions. In turn, these process conditions must match the conditions that the apparatus can meet. As a consequence, the conditions under which reactive distillation can successfully operate are usually limited and a potential mismatch may even render the process infeasible.

There are additional volatility constraints which may sometimes restrict the application of reactive distillation. The desired product should be lighter or heavier than the reactants, so that the latter can be contained in the column and the product can be easily removed from the top or from the bottom of the reactive column. Additionally, residence time constraints limit reactive distillation applications as the residence time must be adequate for reaction to take place but short enough to allow efficient separation. Similarly, reasonably high reaction rates are required, as for slow reactions, the required tray holdups and number of reactive trays would be too large leading to a less cost-effective process.

In addition to the above, multiple steady states often exist in reactive distillation processes (Keller 2014), making them too complex, from an operation perspective, to be applied. Multiple steady states have been studied theoretically using, for instance, singularity analysis for the production of methyl tert-butyl ether (Güttinger and Morari 1997). The authors demonstrated that multiple steady states exist due to the interaction of the reactive and non-reactive sections of the column but can be avoided when the
right specifications are given to the system. Later, Mohl et al. (1999) experimentally demonstrated the existence of multiple steady states (different steady state profiles for the same operating conditions) for the synthesis of tert-amyl methyl ether. Finally, some of the limitations of reactive distillation include the fact that it is limited to liquid-phase reactions as there is very little holdup in the vapour phase; that the heats of reaction must be modest to prevent large changes in vapour and liquid rates through the reactive zone; that a highly exothermic reaction could potentially dry up the trays (Luyben and Yu 2008); and finally, that the creation of reactive azeotropes is possible (Song et al. 1997).

![Figure 1.7: Reactive distillation operating window for two operating parameters (pressure, temperature) (Keller 2014).](image)

1.4.3 Feasibility challenges

As already mentioned, even though reactive distillation offers significant advantages when it can be applied, the operational window constraints, as well as the interactions between reaction and separation, do not always make reactive distillation feasible, or even an attractive choice. A proper understanding of the process in terms of its reaction, separation and overall process conditions is necessary in order to evaluate its feasibility. Various methods have been described to provide a systematic way to evaluate reactive distillation feasibility (e.g. Thery et al. 2005), and Kiss et al. (2011) proposed a framework for checking whether a reactive distillation process is economically attractive (Figure 1.8). For the framework to be used, preliminary data is required, such as vapour–liquid
equilibrium (VLE data), stoichiometry of reactions, kinetics, and enthalpy of reactions. Based on this data, the framework identifies whether reactive distillation may be feasible, assuming that the preliminary data is known within a small uncertainty range. The framework indicates that even the evaluation of the feasibility of the process is a demanding task, which potentially discourages its implementation in industry.

Figure 1.8: Framework for checking whether reactive distillation is an attractive option, as suggested by Kiss et al. (2011).
1.5 The implications of complexity on process design, control and uncertainty considerations

From the previous section it can be seen that reactive distillation can offer a number of benefits, given that certain conditions are met for the process to be feasible. However, the limitations, including but not limited to the potential operating window mismatch, and the requirement of relatively fast kinetics etc., indicate that the design and operation of the reactive distillation process can be challenging (Harmsen 2007).

This is supported by the fact that although the design of reactive distillation processes has been studied for many decades, the extension of conventional distillation design techniques to reactive systems is still a challenge due to the integration of reaction and distillation in a single unit. In addition, for relatively slow reactions, the process requires a significant liquid holdup, whilst the liquid holdup is normally minimized in conventional distillation equipment. Moreover, it has been shown that the introduction of an in-situ separation function within the reaction zone can hinder process controllability (e.g. through the existence of multiple steady states) (Gütinger and Morari 1997, Mohl 1999), making the control of the process a more demanding task.

When also facing parameter uncertainties, the design challenge is amplified. In addition, due to the integration of different process functions, the effect of the combined uncertainty, for instance reaction kinetics and VLE, is intensified and may become disastrous for the integrated operation. Although several aspects of reactive distillation have been elucidated, its design and control under uncertainty, stand as a barrier towards wider industrialisation. A systematic and rigorous methodology for the design of reactive distillation processes under uncertainty, including an evaluation of the associated controllability, has not yet been fully established (Wang et al. 2010), but could possibly increase the acceptance of the technology and accelerate its industrial implementation.

1.6 Summary

In an effort to reduce environmental impact whilst still maintaining or improving competitiveness in the global market, the process industry has focused on the development of “greener”, more sustainable, eco-efficient and cheaper technologies and operations. As a result, Process Intensification (PI) and its potential benefits has attracted the interest of scientists and engineers. Reactive distillation is an excellent PI
example as it combines reaction and separation into a single unit, replacing the corresponding conventional multi-unit flowsheet. Although reactive distillation can offer multiple benefits, including but not limited to overcoming chemical equilibrium, improving reaction selectivity and yield, reducing capital and operating cost etc., it is also restricted by a number of factors.

It is clear that the benefits of reactive distillation are significant, however, its limitations which impact on the design, control and consideration of uncertainty still hinder its industrial acceptance. Despite the continuous research on many aspects of reactive distillation, the findings have not sufficiently encouraged a widespread industrial implementation and further work is needed.

1.7 Aim of thesis

The work presented in this thesis is motivated by the current obstacles hindering the implementation of reactive distillation in industry, mainly related to the complexities of its design and control, as well as the impact of uncertainties thereupon. The aim of this thesis is the development of rigorous methodologies for the optimal design and control under uncertainty of reactive distillation. The framework can also be used to identify and investigate mitigation strategies for process failures arising due to design and/or operation deficiencies under changed processing conditions. The combined work can hopefully pave the way for greater industrial acceptance of reactive distillation technology in the future.

1.8 Structure of thesis

The thesis consists of six chapters and five appendices. This chapter focused on general information about Process Intensification and more specifically, reactive distillation as an intensified process. Its history, applications, advantages and limitations, feasibility constraints, as well as the aim of the thesis, have been presented.

Chapter 2 includes the literature review related to the work conducted. Existing literature on the design of reactive distillation processes, including modelling approaches, is presented. The main focus is on optimisation, and more specifically superstructure optimisation, which is the methodology used in this work. Literature related to the control of reactive distillation processes, as well as the consideration of the impact of uncertainty, is also included. At the end of this chapter, a more detailed insight into the aim of the thesis, organised by chapter, is provided.
Chapter 3, the first chapter of the main work, focuses on the optimal design and operation of reactive distillation systems. Although feasibility assessment and design methods exist in the literature, the methods are either based on a set of preliminary data or they consider a small number of process alternatives, without being able to indicate the global optimum amongst alternative solutions. The objective in this chapter is therefore to develop a rigorous methodology for how to select the most suitable reactive distillation process design as well as its operational parameters, when a large number of process configuration alternatives is available.

Chapter 4 focuses on the control performance of reactive distillation processes. The limitations of the process, as well as the implications of the complexity on its control behaviour are considered. The need for a fundamental understanding on how reaction impacts on the controllability of the process, and how effective control strategies can be selected, is considered and is the main objective of this chapter.

Reactive distillation, as most chemical processes, includes an inherent uncertainty which amplifies the challenge related to the design and control of a rigorous process. As a consequence, having obtained an insight into the optimal design (Chapter 3) and control (Chapter 4) of reactive distillation processes, Chapter 5 focuses on developing a methodology for investigating the sensitivity of the designs towards various uncertainties and for identifying the corresponding design flexibility, for in turn to be able to identify the design required for the system to be able to deal with process failures.

Chapter 6 reflects on the initial project objectives related to the optimal design and control under uncertainty for reactive distillation systems. A number of recommendations for relevant future work, related to current software limitations, for instance, are made.

Finally, the thesis includes five appendices. Appendix A includes a gPROMS ProcessBuilder model validation, to increase the confidence in the software and model used for the work conducted in this project. Appendix B includes information on the solvers used for simulation and optimisation purposes in this work. Appendix C describes in detail the objective cost function used for the superstructure optimisation, as developed in collaboration with the industrial collaborator, Nouryon (formerly Akzo Nobel) and the academic collaborator, UTwente. Appendix D describes how VLE has
been considered in Multiflash and then imported in gPROMS, whilst the last appendix, Appendix E, presents an analysis of the generated results from Chapter 3, using dimensionless numbers, to help interpret the behaviour of reactive distillation systems further.
Chapter 2. Literature review

The aim of this chapter is to provide a review of the existing literature related to the design of reactive distillation processes and its associated controllability, as well as to the impact of uncertainty thereupon. First, the modelling approaches considered in the open literature are presented, in particular related to the equilibrium model used in this work. Advancements related to the design of the process, with a specific focus on optimisation strategies, are presented. Next, contributions which have considered the controllability of the process using conventional, as well as advanced, control strategies are discussed. Furthermore, the role of uncertainty on the design of the overall process is highlighted along with relevant contributions which deal with its implications on the design and operation of reactive distillation processes. Gaps in the open literature are identified in all three domains (design, control and uncertainty) and finally, the aims of, and motivation for, each main chapter in the thesis are described in more detail.
2.1 Introduction

The background presented in Chapter 1 suggests that fundamental understanding of the challenges related to the design and operation of reactive distillation processes, including parameter uncertainty, is required for a more widespread industrial implementation. Before proceeding to the framework developed in this work for the systematic investigation of the above, a critical review of what has previously been considered in the relevant literature will be presented. The review will provide an insight into the topics that have previously been considered, as well as discuss the challenges that researchers within the field have identified.

2.2 Approaches for modelling of reactive distillation processes

As reactive distillation systems are multicomponent, their mathematical description is complex, particularly as thermodynamic and diffusional coupling in the phases and at the interface are accompanied by complex chemical reactions (Noeres et al. 2003). As a result, the modelling of reactive distillation processes must take into consideration column hydrodynamics, mass transfer resistances as well as reaction kinetics, based upon which a classification of the reactive distillation modelling approaches is possible as can be seen in Figure 2.1.

Mass transfer

According to Figure 2.1, the mass transfer between the vapour and liquid phase can be described in different ways, most commonly either by a rigorous rate-based (non-equilibrium) approach or using a simple equilibrium stage model. The non-equilibrium model takes into account the mass and heat transfer rates between the two phases using either the film theory, the penetration theory or the surface renewal theory (Seader et al. 2010). These concepts have been used in relevant publications in order to calculate the mass transfer across the vapour-liquid interface by simplifying the complex hydrodynamic patterns. Of the three concepts, the film theory has often been applied to model non-equilibrium reactive distillation processes, mainly due to its simplicity (Kenig and Górak 2007). In the approach, the Maxwell-Stefan equations, which connect the diffusion fluxes of the components with their chemical potential gradients, are used to describe the multicomponent diffusion in the films (Keller 2014). Instead of the complex Maxwell-Stefan equations, effective diffusion coefficients can alternatively be used to achieve a reasonable simplification of the mass transfer equations. This method ignores
diffusional interaction and calculates mass transfer at the interface by neglecting the contribution due to the driving forces of the other components, thereby reducing the computational cost (Kenig and Górak 2007).

Instead of using the non-equilibrium model, mass transfer can be accounted for assuming thermodynamic equilibrium between the vapour and liquid phases (Taylor and Krishna 2000, Noeres et al. 2003). The equilibrium stage model assumes that each vapour stream leaving a tray or a packing segment is in thermodynamic equilibrium with the correspondent liquid stream leaving the same tray or segment (Taylor and Krishna 2000). For reactive distillation, the chemical reaction is additionally considered via reaction equilibrium equations or via rate expressions integrated into the mass and energy balances. It can be seen that although the non-equilibrium model is a more physically consistent way to describe a stage, it requires more data which is rarely available (Kiss 2013).

Figure 2.1: Modelling approaches of reactive distillation (adapted from Noeres et al. 2003).

Figure 2.2 illustrates the cost associated with each modelling approach as adapted from Górak et al. (2007) by Keller (2014). The accuracy of the simulation results heavily depends on the number and accuracy of the model parameters and usually, the higher
the complexity, the higher the number of model parameters required. However, the optimal modelling depth is not always the most rigorous possible, as it depends on the availability of model parameters and the associated costs for the estimation of the missing parameters (Keller 2014). The equilibrium stage model is therefore a sensible compromise between accuracy and modelling cost, commonly used in the open literature due to its simplicity, as well as its ability to describe the process sufficiently well.

Figure 2.2: Cost factors in the computer aided design of reactive distillation processes (Keller 2014).

**Chemical reaction**

With respect to chemical reaction, the reactive distillation process can be modelled either based on the assumption of chemical equilibrium (for fast reactions) or reaction rates (for slower reactions) in both the interface film and in the bulk of the liquid phase (given that reaction takes place only in the liquid phase), accounting for external and internal resistances (Taylor and Krishna 2000). The Hatta number (see Appendix E) is a very useful tool in the determination of how fast or slow the reaction is, and consequently, whether it takes place in the bulk or film (or both) (Kenig and Górak 2007). For fast reactions, the mass transfer model is solved simultaneously with the chemical equilibrium equation. For slower reactions, the kinetic expressions are integrated in the mass and energy balances. For moderate reactions, approaches have been proposed to consider the direct interaction of mass transfer and chemical reaction in the film region (Schneider et al. 2001). When catalyst is involved in the process, the phenomena in the
solid catalyst phase may sometimes also be considered. In many relevant publications a pseudo-homogeneous approach is used, assuming that the solid catalyst is homogeneously distributed in the liquid bulk phase and in this case, fast catalytic reactions can be described by using chemical equilibrium data (Keller 2014).

**Hydrodynamics**

With regards to hydrodynamic mixing, either ideal or non-ideal plug flow can be assumed. Most contributions in the literature assume ideal plug flow, thus simplifying the equations involved in the model. However, more complex models, such as axial dispersion models (Shah et al. 2012a) and cell models (Baur et al. 2000), have also been considered. The role of computational fluid dynamics (CFD) to predictive accurate hydrodynamic and mass transfer correlations for column internals is promising although computationally demanding (Klöker et al. 2003).

Modelling of reactive distillation processes has therefore been the subject of various publications and in some cases, the authors were able to validate their simulation results experimentally. For instance, Hanika et al. (1999) were able to validate the equilibrium stage model using experimental data from a reactive distillation pilot plant, for the production of butyl acetate. Similarly, Fernandez et al. (2013) performed a series of experiments for the esterification of acetic acid and ethanol in a heterogeneously catalyzed reactive distillation pilot column, to validate the equilibrium stage model used to describe the process. Shah et al. (2012b) validated the extended rate-based model for a polyester synthesis reactive distillation column, using the experimental data obtained from their pilot plant. These are some of the publications which confirm the suitability and accuracy of the models developed for the description of reactive distillation processes.

**2.3 Design of reactive distillation processes**

As mentioned in Chapter 1, over the past few decades, there has been an increasing focus on Process Intensification (PI) in an effort to reduce environmental impact, and to improve the economic performance of chemical processing plants (Boodhoo and Harvey 2013). Reactive distillation is one of the most well-known Process Intensification examples, and combines reaction and separation into one single unit, thus offering significant energy, capital and operational costs savings, obtained through
improvements in reaction selectivity and yield (Luyben and Yu 2008, Kiss 2013). However, the combination of the two different phenomena in the same unit, makes the design and operation of the process more demanding, mainly due to differences in the operational windows for reaction and separation, respectively, which do not always overlap (Harmsen 2007).

For conventional distillation, the specifications which have to be met are normally the concentration of heavy and/or light key at the top and bottom product streams, respectively. The liquid holdup has limited impact on the steady state design but has an impact on the dynamic behaviour of the column. The holdup is, however, very important in reactive distillation as reaction rates depend directly on the holdup and/or the amount of catalyst available on each tray, making the design of the column (residence time, liquid level on stages, column diameter etc.) a more demanding task (Kiss 2013). A very robust design is therefore required, which in some cases might involve the inclusion of additional equipment (to perform parts of the processing due to the operational window mismatch) in addition to the reactive distillation column.

Current literature suggests that three categories of methods have so far been successfully applied for the conceptual design of reactive distillation processes: a) graphical methods, b) evolutionary/heuristics-based methods and c) optimisation-based methods. Graphical methods, with the most well-known representatives being the fixed-point technique (Buzad and Doherty 1994, Buzad and Doherty 1995, Mahajani and Kolah 1996) and the residue curve mapping technique (Barbosa and Doherty 1988), include a range of methods. Most of those techniques are an extension of conventional, non-reactive, distillation column design methods, for instance, Lee et al. (2000) used short-cut visualisation methods such as Ponchon-Savarit method and McCabe-Thiele method to gain design insights for binary reactive mixtures whilst Lopez Arenas et al. (2019) combined the driving force method with Gibbs energy computation to design a binary reactive distillation column. Graphical methods can be a fast tool for feasibility assessment and preliminary design of a reactive distillation column. However, they are limited by: a) the number of degrees of freedom they can handle; b) their difficulty in visualisation for multi-component reaction systems due to the increased dimensionality; and c) limitations of the underlying assumptions in each case (e.g. VLE, binary mixtures etc.) (Buzad and Doherty 1994, Buzad and Doherty 1995, Mahajani and Kolah 1996, Lee et al. 2000, Lee and Westerberg 2000, Lee and Westerberg 2001). As a result, graphical
methods can only be used for initial screening or preliminary design, and not to obtain an optimal process design. Thus, additional optimisation strategies have often been employed on top of graphical methods in cases when the authors pursued an optimal design (Martínez et al. 2020).

The second category of methods applied for the design of reactive distillation processes includes evolutionary/heuristic approaches, as firstly developed by Subawalla and Fair (1999) and later extended by other authors (e.g. Tung and Yu 2007, Luyben and Yu 2008). Using these methods, it becomes possible to overcome some of the limitations of the graphical approaches such as the visualisation difficulty. Moreover, the possibility of also considering column internals (in terms of catalyst requirements) and economics is offered indirectly by considering reflux ratio and excess reactant requirements, respectively (Subawalla and Fair 1999). These methods are, however, mostly used as a post-design analysis tool as they require a pre-defined process structure to determine process parameters iteratively (Almeida-Rivera et al. 2004). In addition, these methods cannot guarantee optimal column design as no effective heuristics are available to ensure optimality (Huang et al. 2005).

The third category includes methodologies based on rigorous optimisation, and is the approach taken in this work. Only this category is capable of considering process design, operation and plant economics simultaneously, however, doing so leads to a significant increase in the complexity of this highly non-linear and highly non-convex mathematical problem, and consequently also to increased computational cost. Optimisation methods have been widely applied for the design of process equipment including, but not limited to heat exchanger networks (Zamora and Grossmann 1998, Papalexandri and Pistikopoulos 1994), reactors (Diagkelakis et al. 2017, Zhang and Smith 2004), distillation columns (Sargent and Gaminibandara 1976), pipelines with pumps (Grossmann and Sargent 1978) and even entire plants (Grossmann et al. 2016).

Optimisation methods considered in the literature for the optimisation of reactive distillation include Orthogonal Collocation on Finite Elements (OCFE) (Seferlis and Grievink 2001) to transform the discrete number of stages in the column into a continuous variable, solving the NLP formed. The OCFE technique, however, only approximates the tray-by-tray model and its application is challenging for dynamic systems. Another alternative includes the application of memetic algorithms. The latter was used by Urselmann et al. (2011) to find the optimal design for a single reactive
distillation column. However, the design of efficient memetic algorithms required the development and extensive testing of problem-specific representations, as well as recombination, mutation and selection mechanisms, as stressed by the authors. Zhang et al. (2020) performed multi-objective optimisation for a Fischer–Tropsch reactive distillation process where the optimal structure was determined from the Pareto optimal set. However, the authors discuss the need to include in future investigations the feed and product tray locations, which were not currently included in the problem. Other strategies found in literature, such as decomposition of the equation sets (Lima et al. 2006) or bypass efficiency method on pseudo-transient model (Ma et al. 2019), can either not guarantee global optimality or show poor numerical performance resulting in practically infeasible solutions as indeed pointed out by these authors.

Another approach for optimisation of reactive distillation is solving the Mixed-Integer Non-Linear (MINLP) optimisation problem, formed by considering all possible alternatives for the optimal design and operation of the process, as well as its dynamic equivalent, thus becoming a Mixed-Integer Dynamic Optimisation problem (MIDO). As an example, the dynamic problem was solved by Georgiadis et al. (2002) and later by Panjwani et al. (2005) for the optimal design and control of a dynamic reactive distillation column. Nevertheless, both contributions focused only on the structural and control decisions (e.g. total number of stages, controller tuning parameters) of a single reactive distillation column, and the methodology was not extended to more complex processes, i.e. including ancillary equipment.

2.4 Superstructure concept and MINLP optimisation

The most rigorous approach for the simultaneous determination of the optimal design and operation of a reactive distillation process, is thus solving a complex MINLP optimisation problem. The problem can be formulated in different ways, including using the concept of a superstructure as studied in this work. The first reference to the concept of a superstructure for optimisation was made by Sargent and Gaminibandara (1976), who described a methodology using MINLP optimisation for the optimal design of conventional distillation columns based on minimum cost. In their pioneering work, they solved the MINLP problem using a version of the variable-metric projection method. Their contribution laid the foundations for further research on solving this mathematically complex problem, as the authors themselves recognised that more complex systems needed to be considered and that development of techniques which
could deal with large-scale non-linear problems was needed. Since then, the complexity of the processes considered has been increased. For instance, Bertran et al. (2017) performed superstructure optimisation for processing route synthesis and design, demonstrating their multi-step methodology for an ethanol biorefinery and a CO$_2$ capture-utilisation case study.

The first application of MINLP to reactive distillation columns was made by Ciric and Gu (1994) for a non-equilibrium, kinetically controlled, reactive distillation process. The authors took into consideration multiple feed streams, however, by making a number of assumptions, such as ignoring the effect of liquid enthalpies, due to the increased mathematical complexity. The model was the first rigorous, tray-by-tray reactive distillation model and was solved using Generalized Benders Decomposition (GBD). The model was later applied to equilibrium reactions by Frey and Stichlmair (2000). The existence of binary variables (total number of stages, feed stage locations), however, complicated the solution which showed poor numerical performance, thus encouraged the development of alternative solution strategies for the MINLP problem.

For instance, Smith (1996) built blocks of reactive flash vessels combined to form a column, whilst Papalexandri and Pistikopoulos (1996) proposed that the problem could be solved as a set of mass and heat transfer modules that integrated to a given network, and both contributions thereby avoided the pre-postulation of a set of unit operations. These approaches were extended by Ismail et al. (2001) to form a block of process alternatives. All the above approaches are, however, nevertheless similar to the classical rigorous tray-by-tray model. Generalised disjunctive programming formulation (Jackson and Grossmann 2001), which uses logic-based outer approximations, is another strategy for the determination of the locally optimal design of kinetically controlled reactive distillation columns, based on the general representation and modelling framework suggested by Yeomans and Grossmann (1999) for distillation columns. A different strategy, using simulated annealing-based algorithms for the solution of the MINLP optimisation for a non-equilibrium reactive distillation equation system, was applied by Cardoso et al. (2000), however, their method could not guarantee global optimality as explained by the authors. Recently, Tian et al. (2020), worked towards a more systematic framework, considering the design of reactive distillation systems using a Generalised Modular Representation Framework (GMF), by solving the MINLP formed using GBD. The authors considered a number of factors for the optimal design of the reactive distillation
process, such as operability, cost, flexibility etc., however, the methodology included alternating (for the generation of results) between two different simulation tools (GAMS and gPROMS).

Overall, it is generally agreed that MINLP optimisation is required to simultaneously determine the optimal design and operation of a reactive distillation process given the complexity of the problem. Rigorous optimisation becomes even more attractive given the development of increasingly stronger mathematical tools, such as the enhanced Outer Approximation algorithm which is employed in this work (Process Systems Enterprise 2020), which does not have the numerical performance issues faced in the past, and which also enables locating the global optimum for convex problems with reduced computational cost.

2.5 Controllability of reactive distillation

Several authors have recognised that the control of reactive distillation processes is more challenging than the conventional distillation counterpart. In one of the early contributions, Sneesby et al. (Sneesby et al. 1997) mentioned that the combination of reaction and separation causes controllability problems and commented on when additional aims are imposed (e.g. catalyst ageing monitoring etc.) control becomes even more complex. Later, Kaymak and Luyben (2008) studied the controllability of a generic reactive distillation system as well as the conventional multi-unit process of reactor followed by two columns, highlighting that the integrated process is more difficult to operate and that the operability region is smaller due to the existence of fewer degrees of freedom. Kumar and Kaistha (2008b) also recognised that there is a need for deeper understanding of the interactions between the reaction and separation as input (e.g. reboiler duty, reflux rate etc.) multiplicities might cause state transition and incorrect control action, as also confirmed by Luyben (2006), who additionally found the control of the reactive distillation process more challenging due to the interaction between phase equilibrium and chemical reaction.

Regardless of the difficulties identified, there are a number of contributions in the open literature which deal with the controllability of reactive distillation processes, and current literature focuses on open- and closed-loop dynamics. Up to 2000, most of the publications studied the open-loop dynamics of the process (Al-Arfaj and Luyben 2000c), mainly focusing on the existence of multiple steady states and input/output multiplicities. However, during the last two decades, closed-loop dynamics have also
drawn attention since more information on the behaviour of reactive distillation has been brought into light and its industrial applicability and operability have been more widespread. Investigation of closed-loop dynamics mainly includes implementing either decentralised (i.e. conventional proportional (P), proportional-integral (PI) and proportional-integral-derivative (PID) controllers) or more advanced, centralised control strategies (e.g. model predictive control, state observers etc.), and evaluating the efficiency of each strategy towards set point or load changes using a number of different criteria (e.g. settling time, offset, oscillatory behaviour etc.).

**Decentralised control strategies**

Decentralised control is the strategy most commonly applied in the literature when considering reactive distillation, mainly due to the similarities to conventional distillation control. Whether the column operates in stoichiometric reactant balance or in reactant excess does not have a significant effect since both operations have been found to be controllable. Luyben (2000) was the first to make this statement, suggesting, however, that operation in excess is slower dynamically due to the recycle and the complexity of a two-column process as recycle of the excess reactant is then required. Literature includes a number of reactive distillation cases when conventional feedback (P, PI and PID) control loops have been found effective in controlling mainly product purity and reaction conversion, and the most comprehensive of these studies are included below to illustrate the application of this type of control schemes. For instance, Hung and his colleagues (Hung et al. 2006), studied a set of systems with acetic acid and different alcohols (C1 to C5) and showed that temperature control and feed ratio control was successful in all cases. Wang and his co-workers (Wang et al. 2003a), who investigated the control of a kinetically controlled n-butyl acetate reactive distillation process, applied feed ratio and temperature control (cascade) using stages insensitive to throughput or catalyst changes. Moraru and Bildea (2017) showed that direct composition control is sometimes required, using the n-butyl acrylate case study as an example. Lee and his group (Lee et al. 2007) studied the production of ethyl acetate using reactive distillation and suggested that for temperature inferential control to be applied, sensor locations should be based on closed-loop and not open-loop sensitivity analysis, in order to reduce steady state deviation and promote good control performance. Medina-Herrera et al. (Medina-Herrera et al. 2020) demonstrated that even dynamic transitions in a silicon multi-product reactive distillation column are feasible using switchability analysis, as
long as the location of the PI temperature control loop has been well investigated to avoid catalyst deactivation. Feedforward control has not often been considered, however, in a relevant contribution by Mahindrakar and Hahn (2016), feedforward control of a benzene hydrogenation system was found to be effective as long as time delay in composition measurement was small. In a different contribution, feedforward control schemes were applied for the successful control of a pressure-swing heat integrated reactive distillation process for methanol production, in case of feed flow rate and composition disturbances (Zhang et al. 2020).

In some cases, authors were able to draw some generic conclusions which could be used as heuristics for control system design for reactive distillation systems. For instance, Al-Arfaj and Luyben in a series of publications (2002a, 2002b) studied a number of generic and real systems using PI controllers concluding that: a) the use of dynamic elements (e.g. lag time) and knowledge of internal composition profiles is essential, b) PI control is efficient as long as there is appropriate management of feed streams, c) for single feed column, one-point temperature control is sufficient, however, for double feed column, internal composition control is also required, and d) for a two reactant-two product system, two-point temperature control is required. Similarly, Kaymak et al. (Kaymak and Luyben 2005, Kaymak and Luyben 2006, Kaymak et al. 2017, Oksal and Kaymak 2018) in a series of contributions found that when two feed streams are present, the feed chosen for the indirect manipulation of temperature is an important choice. In addition, he confirmed that for a two reactant-two product system no internal composition is required but that the location of the temperature controllers in order to have direct action is significant. Finally, he presented a reactive distillation column with double reactive sections (for heterogeneous catalytic reactions) as a sensible alternative to reactive distillation for separation of two-stage consecutive reversible reactions and showed that the novel configuration can be controlled using two temperature and two composition controllers.

In addition to simple reactive distillation columns, the controllability of more complex reactive distillation processes, still using conventional control schemes, has been studied. For instance, heat integrated reactive distillation processes have been studied in a number of contributions (Kiss 2011, Chen et al. 2016, Alcántara-Avila et al. 2017, Zhang et al. 2017) and were found to have good controllability characteristics. The authors agreed that heat integration can improve controllability compared to the
conventional reactive distillation process and that the application of conventional PI control loops (e.g. temperature inferential control by manipulating feed ratio) is successful. Internal heat integration by feed re-arrangement or catalyst re-distribution was studied by Kumar and Kaistha (2008a, 2008b) who found that internal heat integration may or may not be beneficial in terms of controllability, depending on the system considered. In a different study, a reactive distillation column with external recyle between the top and the bottom showed better controllability compared to the conventional reactive column (Chen et al. 2018), unlike a totally refluxed column studied by Liu (Liu et al. 2012) where slower dynamics and underdamped responses were observed and tight inventory control was proposed for effective control, which is not usually applied for single reactive columns.

**Advanced control strategies**

Although conventional distillation control schemes have been successfully applied to reactive distillation systems as presented by several authors, the combination of reaction and separation in a single unit was found to have, in some cases, negative impact on the controllability of the process. The non-linear nature of the process and process gain bi-directionality, for example, were often discussed in literature. For instance, Sneesby et al. (Sneesby et al. 2000) advised that process directionality must be carefully considered since inappropriate organisation of control loops could easily result in an unstable controller. Later, Kumar and Kaistha (2007) suggested that temperature difference should be controlled instead of using simpler temperature control loops when process gain “sign reversal” is observed due to non-linearities. Wang and his co-workers (Wang et al. 2003b) noticed multiplicities for the MTBE system between temperature and feed ratio loops but suggested that if the column is operated under constant reflux ratio then linear control is feasible and successful. In another contribution by Wang and Wong (2006), the problem of non-linearity was solved using variable transformation in order to successfully apply temperature and composition PI control.

Since conventional P, PI and PID control loops were not found to be sufficient for the effective control of the process in some cases due to the non-linear nature of the problem, several authors have discussed advanced, centralised model-based control. A number of contributions have compared the performance of model predictive control (MPC) strategies over the conventional PI/PID control loops. In the majority of cases, nonlinear MPC was found to be superior for set point tracking when experiencing feed
flow rate and composition disturbances (Agachi 2006, Athimathi and Radhakrishnan 2006, Chandra and Venkateswarlu 2007, Pham and Engell 2011, Sharma and Singh 2012, Purohit et al. 2013, Seban et al. 2015, Mahindrakar and Hahn 2016) although in some cases, the difference in control performance was not significant (Kawathekar and Riggs 2007). In those cases, model/plant mismatch was considered in order to indicate which strategy was superior, towards which MPC was found insensitive and therefore more effective.

As MPC will be further considered in Chapter 4, it is important to briefly present its fundamental theory. MPC (or alternatively known as receding horizon) uses the process model to make predictions of the plant’s future response. It is an optimal-control based method and depending on the model, it can either be linear or non-linear. At each sampling point, the MPC optimises the plant behaviour by calculating a series of future manipulated variable moves. The first input in the optimal series is fed to the plant, and the calculation sequence is repeated at the subsequent control intervals (Sharma and Singh 2012). Important components of MPC are the following parameters: a) sample time (how often the controller executes the control algorithm); b) prediction horizon (number of predicted future time steps indicating how far the controller is able to predict); c) control horizon (number of control moves at a given sampling interval to eliminate the predicted error) and d) variable weights within the objective function (e.g. manipulated variable tracking, output variable tracking, constraints violations etc.) (Agachi 2006).

In some contributions, other advanced control strategies such as pattern-based predictive control (Tian et al. 2003) were successfully applied and were found to be efficient when a good process model is difficult to obtain or implement in real-time control. Sharma and Singh (2012) showed that neural network predictive control and MPC give smoother and better control performance for the production of TAME comparing to its PID equivalent. Kumar and Daoutidis (1999) discussed that an ethylene glycol (EG) system requires an advanced nonlinear inverse based controller, although later Al-Arfaj and Luyben (2002a) suggested that for the same system such a strategy is not necessary and a simple PI structure is efficient. Dwivedi and Kaistha (2009) used both constrained dynamic matrix and decentralised control for an ideal and methyl acetate system to show that the advanced control strategy is recommended for both systems. Vora and Daoutidis (2001) detected input multiplicity and a designed nonlinear
state feedback controller for the model with slow dynamics was found superior and performed well under uncertainty. In another contribution, Bisowarno and his co-workers (Bisowarno et al. 2003) applied model gain scheduling to one-point control for the ethyl tert-butyl ether (ETBE) system showing that it could cope with nonlinear characteristics and overcome gain directionality issues, which cannot be handled by PI controllers. However, the authors recognised that such a strategy required pre-programming or online gain identification, and that large noise values could destabilise it and therefore suggested that in the case of feed composition changes a state estimator is needed.

State estimators, linear or nonlinear, have been used in a number of contributions. A linear state estimator was implemented by Olanrewaju and Al-Arfaj (2005, 2006) and was found to be effective under measurement errors, model uncertainties and erroneous initial conditions. However, the authors recognised that when model-plant mismatch is expected, limiting the state estimator to the inaccessible states only, and using additional composition analysers, is recommended. Furthermore, Grüner et al. (Grüner et al. 2003) developed a state observer for a real reactive column. The observer was based on temperature measurements and was found to be superior comparing to a well-tuned linear controller. Similarly, Jana and Banerjee (2018) found a neuro estimator-based inferential extended generic model control superior comparing to inferential PI control for the production of EG. Monroy-Loperena and his co-workers (Monroy-Loperena et al. 2000) used a first order output feedback compensator to cope with multiplicities which was found equivalent to PI control for the EG system.

Integrated design and control optimisation

Towards the development of more systematic procedures for reactive distillation control, a number of contributions have discussed optimisation strategies to efficiently design the control structure. Kookos (2011) developed a MINLP problem to find the optimal control structure for an ideal system aiming to minimise the cost associated with over-purification (reflux ratio), and found that a systematic and model-based control structure selection outperforms heuristics for reactive distillation systems. Later, Haßkerl et al. (Haßkerl et al. 2018a) investigated control based on cost optimisation of a multi-product reactive distillation process under model uncertainty. They were able to design robust controllers, however, the authors faced technical limitations (e.g. conflicting constraints between controllers which cannot be overcome unless relaxing or
removing the relevant constraints) which they aimed to resolve in order to validate their work experimentally. This was later achieved as the same authors (Haßkerl et al. 2018b) successfully applied nonlinear model-predictive control based on cost optimisation in their pilot plant facilities for the production of diethyl carbonate.

Current literature suggests that the design of the reactive distillation process impacts on its controllability, and this has been the subject of several contributions. Mansouri et al. (Mansouri et al. 2015) suggested that designing the reactive distillation process at the maximum driving force (i.e. difference in mole fraction of a component i between two coexisting phases) results in an optimal design in terms of controllability and operability, using as an example the production of MTBE. In addition, Contreras-Zarazú and his colleagues (Contreras-Zarazúa et al. 2017) performed multi-objective optimisation to determine the optimal design and control of the process and found that by altering the design (e.g. adding interlinking streams, larger column diameter etc.), controllability can be improved. This was also observed by Al-Arfaj and Luyben (2000c) who noticed the interaction between design and control by increasing holdup to improve dynamic controllability; by Cheng and Yu (2005) who suggested that feed rearrangement can enhance process controllability; and by Cho and Han (2018) who showed that the existence of a binary or ternary azeotrope may impact on the control structure design for azeotropic enhanced reactive distillation systems. Moreover, Georgiadis and his team (Georgiadis et al. 2002) suggested that simultaneous, and not sequential, optimisation of the design and control of a reactive distillation column is a more economically beneficial approach. Nevertheless, literature still lacks a systematic procedure to consider how the interaction of reaction and separation impacts on the controllability of the process, and how this interaction must be taken into consideration both for the steady state design of the process as well as for the design of an effective control strategy.

2.6 Consideration of impact of uncertainty

The role of uncertainty in reactive distillation processes

So far, literature has been presented related to the optimisation of the design and operation of reactive distillation processes, as well as methodologies for the evaluation of the associated controllability. However, as reactive distillation models depend heavily upon a broad range of accurate process parameters (such as kinetics, vapour-liquid equilibrium (VLE), hydrodynamics etc), uncertainty in these parameters may render the
design suboptimal, and/or the operation infeasible. As a result, the type and the effect of parameter uncertainties must be carefully considered during the design phase in order to ensure process robustness and flexibility, and considering key performance indicators (KPIs) such as product quality, operability, safety, environmental impact, economic performance etc.

For distillation processes, including for reactive distillation, design uncertainty is mainly introduced through the basic system data. For reactive distillation, these are the experimentally determined reaction rates and chemical equilibrium, as well as physical property data (components volatilities, heat of vapourisation, density etc.). For most industrial applications, there is nevertheless typically limited time available to collect all the necessary system data required to thoroughly develop a new and sustainable intensified process during feasibility screening and process design. In addition, operational deficiencies may occur during operation due to catalyst deactivation, fouling, feed flow rate and/or composition changes, disturbances in cooling water/heating medium flow rates etc. Finally, uncertainty in the commercial environment considered during the design phase may also occur due to deviation in the forecasted market demand and corresponding product price or even from stock availability.

As a result, given that uncertainty may be introduced in reactive distillation processes from various sources, and in some cases appear as combination of those, it is essential for the design engineer to be aware of its impact. If the uncertainty cannot be tolerated and may result in process failures, then mitigation steps have to be taken. Properly implemented mitigation strategies for reactive distillation systems can offer several benefits: a) time to obtain a preliminary design used for cost comparison or final process design can be reduced; b) pilot testing can be skipped (reducing the project time by approximately 1 year); c) decisions can be revised to improve system robustness; d) investment decisions can be supported; and e) risk to the environment can be reduced.

**Consideration of uncertainty in existing literature**

One of the first references to the importance of uncertainty within the PSE community was made by the seminal early work of Grossmann and Sargent (1978) who proposed a methodology for the rational overdesign of a chemical plant, when uncertain parameters, expressed as variables within a specific range, exist. In a later contribution, progress was made regarding the consideration of input uncertainty to ensure feasible
operation (Halemane and Grossmann 1983). The method included the optimisation of
the design of a process by solving a nonlinear infinite programming problem. In those
two contributions, a multiperiod design optimisation problem was formed to describe
the process (e.g. heat exchangers network) which had to be operated in a wide range of
conditions whilst satisfying process specifications.

The concept of flexibility was introduced by Swaney and Grossmann (1985) who first
introduced a quantitative feasibility index to measure the ability of a plant to operate
under a range of parameter uncertainty without violating the imposed constraints and
specifications, which was then used to redesign an existing process to enhance its
extended the concept of flexibility to systems under the influence of stochastic
disturbances by considering Gaussian distribution of parametric uncertainty, e.g. in inlet
temperatures of hot/cold streams in heat exchangers, whilst Ierapetritou and
Pistikopoulos (1994) incorporated process flexibility and economic loss in operational
planning by solving a mixed-integer programming formulation.

Flexibility and controllability of a process were later integrated in a unified framework in
the work presented by Mohideen and coworkers (Mohideen et al. 1996) and Bahri et al.
(Bahri et al. 1997), where the interaction between control and process design under
uncertainty was discussed. In a more recent approach, Sánchez-Sánchez and Ricardez-
Sandoval (2013) considered the optimisation of the design and control of a ternary
distillation column, in order to ensure dynamic feasibility and flexibility under
uncertainty in the feed composition. Their work was inspired by the work conducted by
Mohideen and coworkers (Mohideen et al. 1996), however, in their contribution they
perform the dynamic flexibility and feasibility analyses simultaneously, and not
sequentially as in Mohideen’s work, whilst the single MINLP formed was complemented
with simulations of the closed-loop dynamic model. In the majority of the contributions
mentioned so far, the methodology was illustrated using Heat Exchanger Networks
(HENs), Continuous Stirred Tank Reactors (CSTRs) or conventional distillation columns as
practical examples.

In a more theoretical approach, and from a process/product design point of view, Gani
and Constantinou (1996) discussed the need for estimation methods for properties
(mainly for pure components) which can give consistent values within a large application
range and with reliable extrapolation. At that time, reactive distillation also started
attracting attention and a similar observation to the observation made by Gani and Constantinou (1996) was made by Pilavachi et al. (Pilavachi et al. 1997), who mentioned the existence of a set of sensitive properties for reactive distillation systems as well. They also discussed that property prediction and model selection is essential, as incorrect choices may have a significant impact on the feasibility and performance of the system.

Several authors have considered uncertainty related to the design of reactive distillation systems. Seferlis and Grievink (2001) optimised the design of an ethyl acetate reactive distillation column considering perturbations in column pressure, reaction kinetics and feed composition using orthogonal collocation on finite elements to solve the optimisation problem formed. Kaymak et al. (Kaymak and Luyben 2004, Kaymak et al. 2004) later investigated the impact of uncertainty in relative volatilities and chemical equilibrium on the design and performance of reactive distillation systems. They highlighted that, when relative volatilities are not constant and decrease significantly for temperatures required for reasonable reaction rates, reactive distillation is no longer economically attractive over the conventional process. In terms of chemical equilibrium, it was shown that reducing chemical equilibrium from the steady state value leads to more expensive reactive distillation processes as the design becomes more demanding, e.g. more reactive trays may be needed.

Integration of uncertainty in the optimisation of the process

Most contributions considering reactive distillation systems deal with uncertainty by incorporating it into the optimisation algorithm used for the design of the control structure. Tian and his team (Tian et al. 2003) developed pattern-based predictive control for a pilot-scale reactive distillation process for the synthesis of ethyl tert-butyl ether (ETBE). The authors used feature pattern-based prediction incorporated with conventional proportional-integral (PI) control in order to reduce the requirement of good process models, thereby tolerating a larger degree of process uncertainties. Olanrewaju and Al-Arfaj (2006) considered uncertainty in relative volatilities in order to design and implement a state estimator in a feedback control system of a generic reactive distillation process, highlighting the need for an additional online analyser when an inaccurate process model is considered. Paramasivan and Kienle (2012) considered disturbances in vapour boil-up rate, reflux ratio and the purity of the two fresh feeds for an ideal reactive distillation column. They used the sigma point method for the
simultaneous optimisation of a decentralised (inferential) control structure and controller parameters under uncertainty. This approach was found superior towards heuristic or deterministic approaches of the given MIDO problem under uncertainty. Most recently, Haßkerl et al. (Haßkerl et al. 2018a) discussed control based on cost optimisation for a multi-product transesterification reaction. The authors increased the robustness of the controller using control optimisation under uncertainty in reaction equilibrium constants.

Few contributions have considered uncertainty in the simultaneous optimisation of design and control of a reactive distillation process. Georgiadis and his colleagues (Georgiadis et al. 2002) compared simultaneous optimisation and sequential optimisation of the design and control system for an ethyl acetate reactive distillation column considering uncertainty in the cooling water inlet temperature, and successfully solved the MIDO problem formed. The authors found that the simultaneous approach was economically more attractive and more efficient in terms of control. Very recently, Tian et al. (Tian et al. 2020) considered uncertainty in a unified framework for the design of flexible and operable reactive distillation processes, applying their methodology to the production of methyl tert-butyl ether (MTBE). The authors used a Generalised Modular Representation Framework (GMF) synthesis model to design a structure with guaranteed flexibility performance under feed flow rate uncertainty. No contributions to date have, however, focused on a systematic procedure for how to investigate the impact of uncertainty (kinetics, VLE etc.) in a reactive distillation column, and how this uncertainty can be considered in order to mitigate production failure issues and this will be considered in this work.

2.7 Concluding remarks

As reactive distillation systems are multicomponent, their mathematical description is complex, particularly as thermodynamics and diffusional coupling in the phases and at the interface between the phases are accompanied by complex chemical reactions. Considering column hydrodynamics, mass transfer resistances as well as reaction kinetics renders the modelling of the process a more demanding task compared to conventional distillation. With respect to mass transfer, two main approaches exist, the rate-based approach and the equilibrium model. The latter requires less data and can normally describe the process sufficiently well and has therefore been used in many relevant contributions, including this work.
Although reactive distillation has numerous benefits, the interaction between the two different phenomena, reaction and separation, within a single unit leads to, among other limitations, potential differences in the operating windows of reaction and separation. In addition, the impact of liquid holdup in the column on reaction residence time amplifies the challenge. The design of reactive distillation processes is therefore challenging, and three categories of design methods exist in the literature. The first two are graphical and evolutionary/heuristics-based methods. The third method, the optimisation-based approach, has been the subject of various publications. Despite its increased computational cost, it is the only method which is rigorous enough to handle the challenge associated with the mathematical complexity of the problem, which usually includes the design, control and economics of the process, simultaneously. Although a number of authors have successfully used this approach for the simultaneous optimisation of the design and operation of reactive distillation, most focus on a single reactive distillation column, neglecting the possibility of including auxiliary equipment which could improve the optimal solution as well as the overall process performance.

With regards to the controllability of reactive distillation, many authors have suggested that the existence of reaction in the separation zone hinders the controllability of the process, leading to control challenges such as multiple steady states or smaller operability region, making the dynamic operation of the process a demanding task. The control behaviour of reactive distillation systems has been investigated using conventional and advanced control strategies that have previously been applied to conventional distillation columns. A number of authors have incorporated the control parameters into an overall MINLP, thus integrating the design and control into a single optimisation problem. However, literature still lacks a systematic procedure to determine how the interaction of reaction and separation impacts on the controllability of the process, and how this can be taken into consideration both for the steady state design of the process as well as the design of an effective control strategy.

The impact of uncertainty on the design and performance of reactive distillation processes has also been considered, and approaches have been made to either incorporate uncertainty into the optimisation algorithm used for the design of the control structure, or by considering uncertainty in the simultaneous optimisation of the design and control of the process. A rigorous methodology for the consideration of
mitigation of production failure issues due to uncertainties related to design and/or operation is nevertheless missing.

2.8 Aims of thesis

Despite the growing interest related to many aspects of reactive distillation, the extension of conventional distillation design techniques to reactive distillation systems is still a challenge and a rigorous methodology for the optimal design and operation of complex reactive distillation processes has not yet been fully established. Authors who have discussed reactive distillation design and/or operation have generally only considered a single reactive distillation column, and to the best of the author’s knowledge, no contribution to date has considered the simultaneous determination of optimal design and operation of a complex reactive distillation process considering a large number of possible process alternatives (for instance pre/side-reactors, additional distillation column(s), side-stripper, side-reboiler etc.). The objective of Chapter 3 is therefore to provide a methodology for determining the optimal design (e.g. total number of stages, existence of additional equipment etc.) and operation (e.g. reflux ratio, flowrates to additional equipment etc.) of a complex reactive distillation process based on product-related constraints and a detailed objective cost function. The aim is also to demonstrate the applicability of this methodology to a number of industrially relevant case studies, developed to reflect various chemical systems with different combinations of reaction and separation parameters.

Having discussed how the design and operation of a complex reactive distillation superstructure can be simultaneously optimised in steady state to meet product quality constraints, the dynamic performance and controllability of optimal reactive distillation processes will be considered in Chapter 4. Authors who have discussed the controllability of reactive distillation systems have generally only considered the dynamic behaviour and control of reactive distillation systems, implementing various, conventional or advanced, control strategies to indicate which technique is the most effective in each case. Only few authors have addressed the interaction between the design and control of the process, and no contribution to date has considered how reaction and separation interact and what the impact of this interaction is on process controllability. The objective of this chapter is therefore to provide a systematic methodology for evaluating how reaction, separation, as well as their combination, impacts on the controllability of the reactive distillation process using time domain analysis. In addition, the aim is to
consider how this insight can impact on the design of the steady state process as well as its control strategy. The methodology will be demonstrated using a number of systems previously optimised in Chapter 3.

A range of methods has been considered in the literature for the design and/or dynamic operation under uncertainty for reactive distillation systems. However, no contribution has so far provided insight into how the uncertain parameters (their type, direction, range) impact on the optimal steady state design of the process as well as the corresponding dynamic performance. More specifically, no contribution has considered how, and to what extent, uncertainty impacts on the performance of the overall process and how this uncertainty must be considered in order to mitigate production failure issues. This will therefore be the objective of Chapter 5 which will provide a systematic methodology for the control, design and process mitigation of production failure issues as a result of design and/or operational deficiencies, including the evaluation of the impact of different types of design and operational uncertainties on optimal reactive distillation processes.

The simultaneous optimisation of the design and operation of reactive distillation process; the consideration of the controllability of the process; as well as the investigation of the impact of uncertainty; are all aspects which will be investigated individually in separate chapters. However, the overall aim of this thesis is a larger systematic methodology which aims to develop economically attractive and rigorous (from a control perspective), yet flexible, reactive distillation processes as illustrated in Figure 2.3. As shown in Figure 2.3, once the engineer has determined the optimal design and operational parameters of the process using the methodology developed based on superstructure optimisation, the controllability of the process is considered. If, under the control scheme and the process disturbances considered, the system is not able to meet specifications and tolerate the (short-term) disturbances introduced, then the design must be revised in order to improve its control performance. If, however, specifications are met and disturbances are tolerated, the design is provisionally acceptable. In this final step, the performance of the process is evaluated under uncertainty or long-term disturbances. If the system cannot tolerate these (i.e. failing to meet specifications) then the design must be revised. If the system is not sensitive to the uncertainties, then the engineer can be confident that the process designed is not only economically attractive,
but also capable of mitigating production failure issues due to design and/or operational deficiencies and model parameter uncertainties.

Figure 2.3: Overall methodology developed in this work.
Chapter 3. Optimal design and operation of reactive distillation systems based on a superstructure methodology

A novel methodology for the simultaneous optimisation of the design and operation of a complex reactive distillation process, considering a number of process alternatives (e.g. pre-/side-reactor, side-stripper etc.), is presented in this chapter. The methodology is based on a superstructure approach, and a detailed cost-based objective function, solved by MINLP optimisation. The methodology is illustrated using different case studies of industrial interest with varying separation and reaction characteristics. For easy separations, a single reactive distillation column is found to be optimal for both fast and slower kinetics. However, when the separation is more challenging, despite how fast or slow the kinetics are, the optimal design is more complex. In this case, additional processing units, such as a pre-reactor and/or additional distillation columns, are required to meet the product quality specifications. It is found that the design, i.e. the capital cost, mainly depends on the relative boiling point rankings. For operation, chemical reaction equilibrium is the dominant factor. It is demonstrated, however, that the combined effects of separation and reaction must be considered carefully when designing a reactive distillation process. The liquid holdup has an impact on the reaction performance, and proper choice of holdup can lead to a more flexible design, able to mitigate production failure issues even for slower
3.1 Introduction
As mentioned in the previous chapter, it is generally agreed that MINLP optimisation is required to simultaneously determine the optimal design and operation of a reactive distillation process given the complexity of the problem. Rigorous optimisation becomes even more attractive given the development of increasingly stronger mathematical tools, such as the enhanced Outer Approximation algorithm which is employed in this work (Process Systems Enterprise 2020), which does not have the numerical performance issues faced in the past, and which also enables locating the global optimum for convex problems with reduced computational cost.

In the following, a superstructure of a reactive distillation process including multiple ancillary units will be presented, and it will be shown how the MINLP can be formulated (units included, decision variables etc.) and solved using a systematic methodology. Next, a number of case studies with different key system characteristics (easy/difficult separation, fast/slow reaction, etc.) will be considered to illustrate the methodology, but also to show how the optimal design and operation of the overall reactive distillation process depend on these key system characteristics. The latter may provide useful insight when considering similar systems.

3.2 Methodology
The following section describes how the steady-state simulations and optimisation tasks were set up and performed using gPROMS ProcessBuilder v1.3.1 (Process Systems Enterprise 2020) with Multiflash v6.1 (Infochem 2020) on a 3.60 GHz and 32GB RAM Dell Precision 5820 Desktop. To be able to assess the impact of the parameters of the individual chemical systems on the derived optimal reactive distillation designs in general terms, it was decided to use ideal generalized user-defined components instead of a specific real chemical system. This way the parameters that describe a chemical system, such as boiling point rankings, relative volatilities and kinetic constants, can be altered individually in order to investigate different system characteristics, as well as their relative impact both individually and combined. All components therefore have the same basic thermodynamic properties, as shown in Section 3.4, except for the vapour pressures (and thus, the boiling points) which were manipulated using their Antoine vapour pressure coefficients to achieve the desired relative volatilities. The methodology used for the manipulation of vapour pressures is presented in Appendix D.
The superstructure of the overall reactive distillation process considered is shown in Figure 3.1 and all decision (manipulated) variables of the units involved, which form part of the optimisation problem, are shown in Table 3.1. Figure 3.1 applies in the cases when the desired product is either the heaviest or the lightest component. If the desired product is an intermediate-boiler then an additional column is needed, and the product will be removed either from DC1 (as bottom stream) or DC2 (as top stream), and the other stream of the additional column will be recycled back to the reactive column. Note that recycles were not included during optimisation for the case studies considered in this work due to current software limitations related to challenging initialisation procedures as will be explained in more detail later (Section 3.3). However, the recycles could be included in the investigation once the optimal design was found, to further improve the process through steady-state simulations, especially for those case studies where incomplete reactant conversion was observed. The methodology presented in this work can easily be modified to include these recycles when solvers which can tackle the challenging initialisation issues are used and/or become available.

All variables included in Table 3.1 are the decision variables considered in the optimisation. In the following, we shall refer to these as Set $\theta_1$ (continuous variables) and Set $\theta_2$ (integer and binary variables), respectively. All the decision variables are varied simultaneously such that the design and operation of the process are optimised simultaneously.

The superstructure shown in Figure 3.1 includes the following units: a pre-reactor (p-CSTR), a reactive distillation column (RDC), a side-reactor (s-CSTR), a side-reboiler (s-reboiler), a side-stripper (s-stripper), a vapour pump-around stream, as well as two distillation columns (DC1, DC2) for further purification of the distillate or the bottom streams of the reactive distillation column, respectively. The units may or may not exist in the optimal process, therefore the existence of all units depends on the result of the optimisation. The existence of a unit is determined either by the optimal capacity of the unit (e.g. a reactor with zero volume is considered non-existing), or by whether a stream flowing to the unit is selected (a unit with an input stream with an optimal binary variable of 0 is considered not selected).
Table 3.1: Superstructure decision variables considered.

<table>
<thead>
<tr>
<th>Unit Variable</th>
<th>Symbol</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Reactive distillation column (RDC)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total number of stages(^1)</td>
<td>N(_{TR})</td>
<td>Integer</td>
</tr>
<tr>
<td>Feed 1 location (from p-CSTR or feedstock)</td>
<td>N(_{FR1})</td>
<td>Integer</td>
</tr>
<tr>
<td>Feed 2 location (from p-CSTR or feedstock)</td>
<td>N(_{FR2})</td>
<td>Integer</td>
</tr>
<tr>
<td>Feed 3 location (from s-CSTR)</td>
<td>N(_{FR3})</td>
<td>Integer</td>
</tr>
<tr>
<td>Feed 4 location (from s-reboiler)</td>
<td>N(_{FR4})</td>
<td>Integer</td>
</tr>
<tr>
<td>Feed 5 location (from s-stripper)</td>
<td>N(_{FR5})</td>
<td>Integer</td>
</tr>
<tr>
<td>Feed 6 location (from vapour pump-around)</td>
<td>N(_{FR6})</td>
<td>Integer</td>
</tr>
<tr>
<td>Draw 1 location (from RDC to s-CSTR)</td>
<td>N(_{SR1})</td>
<td>Integer</td>
</tr>
<tr>
<td>Draw 2 location (from RDC to s-reboiler)</td>
<td>N(_{SR2})</td>
<td>Integer</td>
</tr>
<tr>
<td>Draw 3 location (from RDC to s-stripper)</td>
<td>N(_{SR3})</td>
<td>Integer</td>
</tr>
<tr>
<td>Draw 4 location (from RDC to vapour pump-around)</td>
<td>N(_{SR4})</td>
<td>Integer</td>
</tr>
<tr>
<td>Draw 1 flow rate</td>
<td>S(_{R1})</td>
<td>Continuous</td>
</tr>
<tr>
<td>Draw 2 flow rate</td>
<td>S(_{R2})</td>
<td>Continuous</td>
</tr>
<tr>
<td>Draw 3 flow rate</td>
<td>S(_{R3})</td>
<td>Continuous</td>
</tr>
<tr>
<td>Draw 4 flow rate</td>
<td>S(_{R4})</td>
<td>Continuous</td>
</tr>
<tr>
<td>Reflux ratio (-)</td>
<td>R(_{R})</td>
<td>Continuous</td>
</tr>
<tr>
<td>Bottom flow rate (kmol/hr)</td>
<td>B(_{R})</td>
<td>Continuous</td>
</tr>
<tr>
<td><strong>Pre-reactor (p-CSTR)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reactor diameter (m)</td>
<td>D(_{PR})</td>
<td>Continuous</td>
</tr>
<tr>
<td>Reactor length (m)</td>
<td>L(_{PR})</td>
<td>Continuous</td>
</tr>
<tr>
<td>Outlet stream split</td>
<td>S(_{PR})</td>
<td>Continuous</td>
</tr>
<tr>
<td><strong>Side-reactor (s-CSTR)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reactor diameter (m)</td>
<td>D(_{SR})</td>
<td>Continuous</td>
</tr>
<tr>
<td>Reactor length (m)</td>
<td>L(_{SR})</td>
<td>Continuous</td>
</tr>
<tr>
<td><strong>Top distillation column (DC1)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total number of stages</td>
<td>N(_{T1})</td>
<td>Integer</td>
</tr>
<tr>
<td>Feed stage location</td>
<td>N(_{F1})</td>
<td>Integer</td>
</tr>
<tr>
<td>Reflux ratio (-)</td>
<td>R(_{R1})</td>
<td>Continuous</td>
</tr>
<tr>
<td>Distillate flow rate (kmol/hr)</td>
<td>D(_{1})</td>
<td>Continuous</td>
</tr>
<tr>
<td><strong>Bottom distillation column (DC2)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total number of stages</td>
<td>N(_{T2})</td>
<td>Integer</td>
</tr>
<tr>
<td>Feed stage location</td>
<td>N(_{F2})</td>
<td>Integer</td>
</tr>
<tr>
<td>Reflux ratio (-)</td>
<td>R(_{R2})</td>
<td>Continuous</td>
</tr>
<tr>
<td>Distillate flow rate (kmol/hr)</td>
<td>D(_{2})</td>
<td>Continuous</td>
</tr>
<tr>
<td><strong>Side-stripper (s-stripper)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total number of stages</td>
<td>N(_{FS})</td>
<td>Integer</td>
</tr>
<tr>
<td>Bottom flow rate (kmol/hr)</td>
<td>B(_{S})</td>
<td>Continuous</td>
</tr>
<tr>
<td><strong>Side-reboiler (s-reboiler)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reboiler heat duty (kW)</td>
<td>Q(_{RB})</td>
<td>Continuous</td>
</tr>
<tr>
<td><strong>Stream selection</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feed 1 stream selection</td>
<td>S(_{F1})</td>
<td>Binary (0 or 1)</td>
</tr>
<tr>
<td>Feed 2 stream selection</td>
<td>S(_{F2})</td>
<td>Binary (0 or 1)</td>
</tr>
<tr>
<td>Top product stream selection</td>
<td>S(_{T})</td>
<td>Binary (0 or 1)</td>
</tr>
<tr>
<td>Bottom product stream selection</td>
<td>S(_{B})</td>
<td>Binary (0 or 1)</td>
</tr>
<tr>
<td>Reactive distillation column selection</td>
<td>S(_{R})</td>
<td>Binary (0 or 1)</td>
</tr>
<tr>
<td>Side-stripper existence selection</td>
<td>S(_{SR})</td>
<td>Binary (0 or 1)</td>
</tr>
<tr>
<td>Side-reboiler existence selection</td>
<td>S(_{RB})</td>
<td>Binary (0 or 1)</td>
</tr>
<tr>
<td>Side-reactor existence selection</td>
<td>S(_{SR})</td>
<td>Binary (0 or 1)</td>
</tr>
</tbody>
</table>
Figure 3.1: Reactive distillation superstructure (variables shown in Table 3.1). The black nodes with the red-colored $S$ show alternative stream directions, indicating units being included or excluded from the optimal process. The black node without the red colored $S$ shows a potential feed split which is a continuous variable.

A pre-reactor was added in the superstructure in order to consider the possibility of selecting the conventional process layout for an equilibrium limited reaction as the optimal solution, i.e. a reactor (p-CSTR) followed by one or more distillation columns (RDC and/or DC1 or DC2). A pre-reactor combined with a reactive distillation column may enhance the reaction conversion for slower reaction kinetics for which a single reactive distillation would be insufficient. A side-reactor (s-CSTR) is considered in order to provide

\footnote{Note that in the reactive distillation column, all stages (Stage 2 to $N_{TR}-1$) were considered reactive and thus, the manipulation of the total number of stages automatically affects the length of the reactive zone. Also, in gPROMS ProcessBuilder, Stage 1 is the condenser and Stage $N$ is the reboiler, and stage numbering takes place from the top to the bottom.}
additional liquid residence time to increase reaction conversion and potentially reduce the size of the reactive column (Bisowarno et al. 2004). A side-reboiler (s-reboiler) is considered in order to provide additional heat to improve separation. A vapour pump-around stream (Draw 4, Feed 6) was added to investigate potential benefits in process performance due to internal recycles. This pump-around design has, to the best of the authors’ knowledge, not previously been considered, and the exact benefits of this novel pump-around stream on the performance of reactive distillation columns should be further investigated. The addition of a side-stripper (s-stripper) offers the possibilities of:
a) elimination of the remixing effect (remixing of the heaviest/lightest component with a middle-boiler at the bottom/top of the column leading to reduced product composition and energy loss) that has been considered in literature case studies (Lee et al. 2012); b) removal of either an undesired product that could lead to catalyst deactivation in the reactive zone (Nguyen and Demirel 2011), or a middle-boiling product from a side-draw location; and c) thermal coupling, which may have energy and cost reduction benefits (Wang et al. 2008). Finally, the two distillation columns (DC1, DC2) can be used for further purification beyond that taking place in the reactive distillation column, if required, as well as part of the conventional (reactor plus distillation columns) process.

As shown in Table 3.1, the optimisation problem contains both integer and binary variables (e.g. total number of stages, stream selection etc.), as well as continuous (e.g. reflux ratio, flow rates etc.) variables, and therefore the problem is a Mixed Integer Non-Linear Programming (MINLP) optimisation problem. The general mathematical formulation of the MINLP optimisation is as follows (Biegler 2010):

\[
\begin{align*}
\min_{x, y} & \quad f(x, y) \\
\text{s.t.} & \quad h(x, y) = 0, \\
& \quad g(x, y) \leq 0, \\
& \quad x \in \mathbb{R}^{n}, \quad y \in \{0,1\}^{t}
\end{align*}
\]

where \(f(x, y)\) is the objective function (e.g. cost, energy consumption etc.), \(h(x, y) = 0\) are the equality constraints that characterise the performance of the system (e.g. mass balances, energy balances, phase distribution, inherent restricting relationships, kinetic expressions, summation equations etc.), and \(g(x, y) \leq 0\) expresses the inequality constraints often imposed by the user in order to include process specifications or constraints (e.g. product purity, safety constraints such as distillation column flooding
etc.). The real $n$-dimensional vector $x$ represents the continuous variables, such as unit dimensions and flow rates, whilst the $t$-dimensional vector $y$ represents the integer and binary variables which indicate whether a stream, a stage or a process unit, has been selected or not.

In this work, the objective function of the optimisation problem was a production-based Total Annualised Cost (annualised capital and operating cost divided by annual production rate) calculated as shown in Appendix C. The two constraints imposed on the system were the purity of the desired product, here component D, in the bottom product, $x_{B,D}$, as well as its recovery, $x_{rec,D}$, defined as the amount of component D recovered as product over the total amount of component D actually produced during the reaction. It should be noted that the methodology derived in this work is of course equally applicable to other objective functions or other product specifications. Equally, further ancillary units can also be added to the flowsheet (although further increasing the mathematical complexity of the problem), or removed, thus altering the superstructure considered but not the methodology.

Based on the description above, the mathematical expression of the MINLP formed in this work becomes:

$$\begin{align*}
\min_{\theta_1, \theta_2} & \text{ production-based TAC } (\theta_1, \theta_2) \\
\text{s.t.} & \quad h (\theta_1, \theta_2) = 0, \\
& \quad x_{B,D} \geq x_{B,D}^{spec}, \\
& \quad x_{rec,D} \geq x_{rec,D}^{spec}, \\
& \quad \theta_1 \in \mathbb{R}^n, \quad \theta_2 \in \{0,1\}^t
\end{align*}$$

As previously mentioned, $\theta_1$ refers to the set of continuous variables and $\theta_2$ refers to the set of binary and integer variables. Binary variables can by definition take a value of either 1 or 0 based on whether a stream is selected or not. Integer variables can also be considered of type 0/1, for instance a column stage can be selected as a feed stage (therefore taking the value 1) or not (value of 0).

In gPROMS ProcessBuilder, the condenser is Stage 1 and the reboiler is stage $N_T$, and the stage where the vapour boil-up from the reboiler returns to the column (stage $N_T-1$) is used as a variable to optimise the total number of stages ($N_T$) of the column. Figure 3.2
shows how the total number of stages is set and optimised whilst optimal feed stage locations are found similarly (Viswanathan and Grossmann 1990).

The solver used for the solution of the MINLP problem is OAERAP (Outer Approximation Equality Relaxation Augmented Penalty), which employs an outer approximation algorithm that guarantees global optimality for convex problems (Process Systems Enterprise 2020). The solver (see Appendix B for more details) first initialises the problem, then solves the fully relaxed NLP problem whilst treating all integer variables as continuous. Next, it solves the master MILP problem which involves linearisation of the objective function and of the constraints at the solutions of all problems considered in the previous steps, and finally solves the primal optimisation problem (NLP), having fixed the integer variables to suggested values from previous iterations. When there is no further improvement in the objective function for a feasible solution, the solver successfully indicates the optimum. For infeasible solutions, the solver terminates. Since the problem considered is highly non-convex, and this type of MINLP problems suffer from the existence of multiple local optima in the continuous sub-problems, the solver still cannot guarantee global optimality, hence different initial guesses were considered to enhance the possibility of locating the global optimum, as will be explained in the following.

Figure 3.2: Optimisation of total number of stages in gPROMS ProcessBuilder. Feed streams, side-draw streams and variables related to the reactive distillation column (e.g. reflux ratio) are not shown for clarity.
3.3 Optimisation strategy

The methodology developed in this work for the optimisation of the reactive distillation superstructure is illustrated in the tree diagram in Figure 3.3. The first three steps consider the initialisation of the superstructure flowsheet. I would like to stress the importance of a careful initialisation procedure for a flowsheet of such a high level of complexity due to the number of units included, and therefore large number of degrees of freedom. In addition to the complexity of the process, a large set of equations needs to be solved for the calculation of the cost-based objective function. The latter could either be based on the built-in gPROMS ProcessBuilder cost calculations or on user-defined cost calculations as considered in this work, although adding the same level of complexity in both cases. For optimisation based on a cost-based objective function using gPROMS, a Saved Variable Set (SVS) with initial guesses for all variables excluding costing is needed as the solver cannot otherwise initialise the cost calculation section as this requires a simulation to already have been performed. In this work, for the successful initialisation of the problem, including both the flowsheet and the cost calculation, a three-step strategy is employed (steps 1 to 3 in Figure 3.3), where the flowsheet is first gradually introduced and initialised without including the cost calculation, then repeated with the cost calculation based on the SVS. The next step is the actual optimisation of the steady-state process (step 4), which is repeated a number of times using different initial guesses (step 5) to increase the possibility of locating the global optimum. In the following, each step of the methodology will be considered in detail.

Step 1: Flowsheet set-up

First, all process units (distillation columns, reactors etc.) considered (including their feed streams) are added into the flowsheet, one by one starting with the reactive distillation column. Adding one unit at the time until the superstructure is complete was found to be the most efficient way to initialise the superstructure, as otherwise, adding all units simultaneously would in most cases create convergence issues. Setting up the reactive column first and then adding the two reactors (in any order) was found to be the most successful. Next, the side-reboiler, side-stripper and vapour pump-around stream were added in the flowsheet in this order. Finally, the top and bottom distillation columns were added one at a time to ensure that suitable column specifications were given. For the case studies shown later using gPROMS ProcessBuilder, the “Distillation column”
model was selected for the reactive and non-reactive distillation columns. For the pre/side-reactors, the “Reactor stirred tank” model was considered. For the side-reboiler, the “Evaporator kettle” model, whilst for the side-stripper, the “Distillation column reboiled” model was used. “Stream duplicators” and “Stream selectors” were also added in the flowsheet to represent the selection between many alternative streams feasible. Finally, “Source material” and “Sink material” models were added to model the feed inlets and product outlets, respectively.

**Step 2: Flowsheet initialisation, excluding economics**

Having set up the superstructure flowsheet, initial values for all units included are required, and this was done one unit at the time as explained in step 1. If the flowsheet could not converge after the addition of a unit, the initial values of the latter were manually adjusted to help the simulation initialise. This strategy was particularly helpful for the units which are connected to the reactive distillation column through a side stream, as the location of the side streams was often a reason for simulation failures. The side stream locations were then varied until the simulation could initialise without any issues. In other cases, when initialisation failures occurred with the addition of a unit, changing the specifications of the unit that the new unit was interacting with was more helpful instead of varying the specifications of the unit added last. It should be noted that the initial values provide a stable starting point for the optimisation and for convex problems only (thus not in our case) have no impact on the final optimal solution.

Closing recycling loops in the superstructure is numerically very demanding, and built-in initialisation procedures for recycle loops are often not adequate. Accurate initial guesses, in particular for temperature, pressure and exact composition of the recycle stream(s), may need to be provided for the flowsheet to converge. However, even using this strategy did not always lead to a successful flowsheet optimisation including recycle loops when using gPROMS ProcessBuilder. As a result, to ensure consistency across all the case studies considered, recycle streams were not considered during optimisation for the cases presented in this work. However, the recycles could be reintroduced in the investigation once the optimal design was found, to further improve the process through steady-state simulations, especially for those case studies where incomplete reactant conversion was observed. This procedure is clearly not optimal, but was the only option with the current software limitations.
It is of course possible for the optimisation to deselect one of the current existing units and to select other units not currently used. It is important to note that, although some units may not exist in the initial superstructure, they must nevertheless still be configured. If not all models are specified, then the overall flowsheet model will not be able to initialise. For instance, even though a stream that goes into a distillation column, e.g. DC1, was not initially selected, meaning that DC1 did not exist, the model of DC1 must still be configured. In other words, initial guesses for its total number of stages, feed stage location, reflux ratio and distillate flow rate must still be provided.

The steady-state model is first initialised without the cost calculation included. Following successful initialisation, a Saved Variable Set (SVS) that includes the steady-state values of all variables is created in the gPROMS ProcessBuilder results folder and copied to the working folder to provide the initial guesses required for the next step which includes the cost calculation.

**Step 3: Flowsheet full initialisation, including cost calculation**

After the initialisation of the superstructure excluding the cost calculation, the equations needed for the cost evaluation are added in the model. Although gPROMS ProcessBuilder has a built-in costing tool, in this work the cost calculation was added manually via the gPROMS language section. The gPROMS costing tool was not chosen in order to enable the use of a more detailed cost function, which can more easily be adjusted to meet user requirements. The Saved Variable Set (SVS) obtained from step 2 was used to initialise and solve the flowsheet, now including the calculation of cost.

**Step 4: Set-up and execution of MINLP optimisation**

To set up the MINLP optimisation, the objective function, decision variables and user-imposed constraints are selected, and in this work, this is done via a ProcessBuilder optimisation entity. For the decision variables, in addition to their corresponding initial values and variable range, the type of each variable is selected, which for this work is either continuous or discrete (the latter in gPROMS ProcessBuilder are named Special Ordered Set). The range of the continuous variables during optimisation should be considered carefully. For instance, the mass balances for the distillation column must be considered in order to ensure that the range provided for the optimisation of the distillate rate is in agreement with the amount expected from the top of the column (i.e. process capacity). If the range of the distillate rate exceeds or limits the amount that can
be removed from the top of the column then it is possible that optimisation will fail or will hit the upper or lower bound of the variable. When the entity is fully configured, the optimisation description is complete.

**Step 5: Investigation of sensitivity of optimal solution to initial guesses**

After the optimisation problem has been set up, a few steps are required in order to ensure that the solver can indicate a solution and increase the possibility that the solution found is the real global optimum. For instance, the length of the reactive zone in the reactive distillation column must be considered as the length cannot be directly manipulated in gPROMS ProcessBuilder for every optimisation iteration. For instance, when the initial guess for the total number of stages for the reactive distillation column was say 50, with stages 2-49 being in the column section and thus reactive, then during optimisation, those 48 reactive stages were not adjusted by ProcessBuilder to match the current total number of stages for that optimisation iteration. In other words, ProcessBuilder would continue to calculate the reaction conversion also for stages that were currently not present. To get around this issue, a manual adjustment of the reactive zone was necessary to ensure that the final total number of stages matched the reactive zone considered during initialisation. To deal with this, when the optimiser indicated a much lower number of stages compared to the number considered during initialisation, a new initialisation was configured with a lower number of stages, i.e. including fewer reactive stages to minimise the difference between the two variables during the iterations, and then re-optimised. This manual procedure is clearly inefficient but is currently the only way that this problem can be solved using ProcessBuilder.

In some cases, optimisation was difficult to complete. For instance, ProcessBuilder was able to solve the master MILP but when it came to the primal NLP problem, the optimiser could not converge and failed to find a solution. In such cases, the optimal NLP point (i.e. the latest successful iteration) could be located at the point just before the optimiser failed and this intermediate solution could be re-initialised and then re-optimised, to reach the final optimal solution. This strategy was found to be successful for those case studies in this work which included reactive columns with a large number of trays and/or designs with additional equipment.
Figure 3.3: Simultaneous MINLP optimisation strategy as performed in gPROMS ProcessBuilder.
Furthermore, the solver used in this work can only guarantee global optimality for convex problems. The MINLP problem developed in this work is highly non-convex, therefore global optimality is not guaranteed. To increase the confidence that the best solution has indeed been found, the optimisation is considered multiple times starting from different sets of initial guesses to ensure that the same optimum is found in all cases. In cases where the optimisation results only varied slightly in terms of the value of the objective function and the values of the optimal design and operational parameters, the optimal solutions were considered equivalent. In this work, this was considered valid when the difference in the objective function value was less than 0.01 €/kg, which is more than sufficient from an industrial point of view.

### 3.4 Case studies

The optimisation of the reactive distillation superstructure outlined in Section 3.2 and illustrated in Figure 3.1 was performed for a number of case studies for a quaternary system of components A and B which react towards components C and D, in order to demonstrate how the methodology described in Figure 3.3 can be applied, as well as to explore the optimal solutions for different conditions. Component C was considered to be aqueous (i.e. water) whilst components A, B and D were considered to be organic compounds, based on esterification systems often considered in the literature for reactive distillation studies (e.g. Luyben and Yu 2008). The case studies were selected based on their industrial relevance, in collaboration with the industrial partner. The impact of separation and reaction parameters on the optimal design and operation of different systems was also considered in order to evaluate the relative impact of separation vs kinetics on a reactive distillation process. In particular, the case studies consider systems of different separation difficulty, as well as different kinetic characteristics, to identify under which conditions the reactive column, and/or the associated ancillary units, would be needed.

The separation difficulty is defined in terms of the relative volatilities between the components. Five different systems of varying separation difficulty ($\alpha_{CA}, \alpha_{AB}, \alpha_{BD}$) were considered (Table 3.2), and for each, fast and/or slower kinetic expressions were investigated (Table 3.3). For all the case studies, the components were considered of equal density (900 kg/m$^3$) and of equal molecular weight (50 g/mol). In addition, the boiling point of the heavy reactant, component B, was also assumed to be fixed (413 K
at 1 atm) and all other volatilities were calculated using the heavy reactant as the reference (see Appendix D).

Table 3.2: Case studies with different separation difficulty considered.

<table>
<thead>
<tr>
<th>Relative volatility</th>
<th>Value</th>
<th>Calculated boiling points (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>System I</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha_{CA}$</td>
<td>2</td>
<td>$T_C=376.6$</td>
</tr>
<tr>
<td>$\alpha_{AB}$</td>
<td>1.5</td>
<td>$T_A=398.7$</td>
</tr>
<tr>
<td>$\alpha_{BD}$</td>
<td>2</td>
<td>$T_B=413.0$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$T_D=440.4$</td>
</tr>
</tbody>
</table>

| **System II**         |       |                              |
| $\alpha_{CA}$        | 1.2   | $T_C=362.1$                  |
| $\alpha_{AB}$        | 4.15  | $T_A=367.2$                  |
| $\alpha_{BD}$        | 1.2   | $T_B=413.0$                  |
|                      |       | $T_D=419.9$                  |

| **System III**        |       |                              |
| $\alpha_{CA}$        | 2     | $T_C=376.6$                  |
| $\alpha_{AB}$        | 1.5   | $T_A=398.7$                  |
| $\alpha_{BD}$        | 0.75  | $T_B=402.7$                  |
|                      |       | $T_D=413.0$                  |

| **System IV**         |       |                              |
| $\alpha_{CA}$        | 1.2   | $T_C=392.6$                  |
| $\alpha_{AB}$        | 1.5   | $T_A=398.7$                  |
| $\alpha_{BD}$        | 1.2   | $T_B=413.0$                  |
|                      |       | $T_D=419.9$                  |

| **System V**          |       |                              |
| $\alpha_{CA}$        | 1.2   | $T_C=376.6$                  |
| $\alpha_{AB}$        | 2.5   | $T_A=382.2$                  |
| $\alpha_{BD}$        | 2     | $T_B=413.0$                  |
|                      |       | $T_D=440.4$                  |

A quaternary system in which the following non-/auto-catalysed reversible reaction occurs in the liquid phase is considered, and applies to all units where reaction is present (e.g. RDC, p-CSTR etc.):

$$A + B \rightleftharpoons C + D$$

The kinetic expressions for the forward (f) and backward (b) reaction rates are the following:

$$r_f = k_f e^{-E_a f / RT} C_A C_B$$

$$r_b = k_b e^{-E_a b / RT} C_C C_D$$
where the reaction rates, \( r_f \) and \( r_b \), are expressed in kmol/(m\(^3\)·s); the pre-exponential kinetic factors, \( k_{f0} \) and \( k_{b0} \), are expressed in m\(^3\)/kmol·s; the activation energies, \( E_{\alpha f} \) and \( E_{\alpha b} \), are expressed in kJ/kmol (assumed to be 80 kJ/mol for both directions); and the concentration of component \( i \), \( C_i \), is expressed in kmol/m\(^3\). The heat of reaction was assumed to be negligible (which is typically the case for equilibrium limited reactions such as esterifications or etherifications), thus the activation energy is the same for both reaction directions and chemical equilibrium (\( K_{eq} \)) and equilibrium concentrations are independent of temperature.

For systems I, II, IV and V of Table 3.2, the following boiling point ranking applies: \( T_C < T_A < T_B < T_D \), which is the situation when the reactants are the middle-boilers and the two products are removed from the top and bottom of the column, respectively. For system III, the boiling point ranking is alternating: \( T_C < T_A < T_D < T_B \), and there is a different boiling point order between one reactant (high-boiler B) and one product (middle-boiler D). All five systems (in terms of boiling point ranking) apply to a range of industrial processes such as the production of ethyl/methyl acetate (Tang et al. 2005), and isopropyl ester (Reepmeyer et al. 2004).

Fast and slow kinetics, characterised by different chemical equilibrium (\( K_{eq} \) was used to calculate \( k_{b0} \) based on \( k_{f0} \), \( K_{eq}=k_{f0}/k_{b0} \)) were considered in combination with the relative volatility systems (Table 3.2), resulting in the case studies given in Table 3.3. Three different values for chemical equilibrium were considered: 0.184, 2.25 and 81 which correspond to a single pass reaction conversion of 0.3, 0.6 and 0.9, respectively. In addition, the values of \( k_{f0} \) were calculated based on the time needed to reach 90% conversion in a batch reactor, neglecting the backward reaction. Times considered were 15 min (\( k_{f0}=8.41 \cdot 10^6 \text{ m}^3/\text{kmol·s} \)), 60 min (\( k_{f0}=2.1 \cdot 10^6 \text{ m}^3/\text{kmol·s} \)) and 120 min (\( k_{f0}=1.05 \cdot 10^6 \text{ m}^3/\text{kmol·s} \)). The values of the reaction parameters, as well as relative volatilities, were selected based on industrial interest.
Table 3.3: Separation/reaction parameters for all case studies.

<table>
<thead>
<tr>
<th>Case study 1</th>
<th>System (Table 3.2)</th>
<th>Relative volatility (Table 3.2)</th>
<th>$k_0$ (m$^3$/kmol⋅s)</th>
<th>$K_{eq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>$\alpha_{CA}=2$</td>
<td></td>
<td>8.41⋅10$^6$</td>
<td>81</td>
</tr>
<tr>
<td></td>
<td>$\alpha_{AB}=1.5$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\alpha_{BD}=2$</td>
<td></td>
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<tr>
<td>Case study 2</td>
<td></td>
<td></td>
<td>2.10⋅10$^6$</td>
<td>2.25</td>
</tr>
<tr>
<td>Case study 3</td>
<td></td>
<td></td>
<td>1.05⋅10$^6$</td>
<td>2.25</td>
</tr>
<tr>
<td>Case study 4</td>
<td></td>
<td></td>
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<td>0.184</td>
</tr>
<tr>
<td>Case study 5</td>
<td></td>
<td></td>
<td>1.05⋅10$^6$</td>
<td>81</td>
</tr>
<tr>
<td>Case study 6</td>
<td>II</td>
<td>$\alpha_{CA}=1.2$</td>
<td>8.41⋅10$^6$</td>
<td>81</td>
</tr>
<tr>
<td></td>
<td>$\alpha_{AB}=4.15$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\alpha_{BD}=1.2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Case study 7</td>
<td></td>
<td></td>
<td>2.10⋅10$^6$</td>
<td>81</td>
</tr>
<tr>
<td>Case study 8</td>
<td>III</td>
<td>$\alpha_{CA}=2$</td>
<td>8.41⋅10$^6$</td>
<td>81</td>
</tr>
<tr>
<td></td>
<td>$\alpha_{AB}=1.5$</td>
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<td></td>
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<tr>
<td></td>
<td>$\alpha_{BD}=0.75$</td>
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<td></td>
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<td>Case study 9</td>
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<td>2.10⋅10$^6$</td>
<td>81</td>
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<tr>
<td>Case study 10</td>
<td></td>
<td></td>
<td>8.41⋅10$^6$</td>
<td>0.184</td>
</tr>
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<td>Case study 11</td>
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<td></td>
<td>1.05⋅10$^6$</td>
<td>0.184</td>
</tr>
<tr>
<td>Case study 12</td>
<td>IV</td>
<td>$\alpha_{CA}=1.2$</td>
<td>8.41⋅10$^6$</td>
<td>2.25</td>
</tr>
<tr>
<td></td>
<td>$\alpha_{AB}=1.5$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\alpha_{BD}=1.2$</td>
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<td>Case study 13</td>
<td></td>
<td></td>
<td>8.41⋅10$^6$</td>
<td>81</td>
</tr>
<tr>
<td>Case study 14</td>
<td>V</td>
<td>$\alpha_{CA}=1.2$</td>
<td>8.41⋅10$^6$</td>
<td>0.184</td>
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<td></td>
<td>$\alpha_{BD}=2$</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Case study 15</td>
<td></td>
<td></td>
<td>8.41⋅10$^6$</td>
<td>2.25</td>
</tr>
</tbody>
</table>

The following assumptions are made and hold for all steady state simulations throughout the thesis:

1) Thermodynamic vapour-liquid phase equilibrium is assumed on every stage of the distillation columns. For a trayed column, this is a reasonable description of the system physics and has been found to sufficiently describe the behaviour of most real columns (Halvorsen and Skogestad 2000).

2) Perfect mixing in the liquid and vapour phases was assumed (Halvorsen and Skogestad 2000). This assumption is considered valid at small or medium scales as for the case studies considered (Vora and Daoutidis 2001), however, at industrial scale, detailed mass transfer and reactant conversion analysis would be required to describe the process more accurately.

3) Constant relative volatilities were assumed throughout the columns (reactive and non-reactive). This is a commonly made assumption (Sargent and Gaminibandara 1976) which is reasonable for close to ideal systems when the temperature range in the column is not very wide and for when generic components, whose behaviour is not already known, are considered, as in this work.
4) Pressure drop was considered negligible for this work, but could easily have been included but would then increase the size of the optimisation problem further.

5) Reaction occurs only in the liquid phase, which holds for many reactions e.g. esterification systems for which reactive distillation has been successfully applied (Luyben and Yu 2008).

6) All column stages (stages 2 to N-1) were considered reactive in the reactive distillation column (RDC), with the same liquid holdup per tray.

7) There was no heat loss or gain from the environment in any of the equipment used, therefore all models were assumed to operate adiabatically.

For all case studies considered, the initial flowsheet included the reactive distillation column (RDC), as well as the side-stripper (s-stripper), the vapour pump-around stream and the top non-reactive distillation column (DC1). The pre- and side-reactors, as well as the side-reboiler and bottom non-reactive distillation column (DC2), were included in the flowsheet, however, were assumed to not participate in the superstructure process initially (Table 3.4). As mentioned previously, these units must also nevertheless be part of the initialisation, even if non-existing (i.e. to avoid zero flows etc.).

The pressure was fixed at 1 atm throughout the process. Manipulating column pressure significantly increased the complexity of the problem (as this involves manipulating pressure at the top and/or bottom of the column, and/or manipulation of the column pressure profile (linear etc.)). It was therefore decided to keep pressure fixed for all case studies to avoid this additional computational cost, being aware, however, of the impact that pressure has both on separation and reaction performance. Future work will include the consideration of pressure within the optimisation problem, as will be explained in Chapter 6. The feed streams to the overall system were one stream of reactant B (Feed 1) of flow rate 12.6 kmol/hr, and one stream of reactant A (Feed 2) of the same flow rate (1:1 feed molar ratio). This corresponds to 5 ktn/year of product D when full reactant conversion applies. The feeds were assumed to be at the corresponding boiling points. In addition, the liquid holdup of the reactive distillation column was fixed at 0.1 m³/reactive tray (holdup is specified for reactive columns only in gPROMS ProcessBuilder).
Table 3.4: Initial variable guesses for all case studies.

<table>
<thead>
<tr>
<th>Reactive distillation column (RDC)</th>
<th>Initial value</th>
<th>Min. bound</th>
<th>Max. bound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total number of stages</td>
<td>100</td>
<td>3</td>
<td>100</td>
</tr>
<tr>
<td>Feed 1 location (from p-CSTR or feed-stock)</td>
<td>5</td>
<td>2</td>
<td>99</td>
</tr>
<tr>
<td>Feed 2 location (from p-CSTR or feed-stock)</td>
<td>25</td>
<td>2</td>
<td>99</td>
</tr>
<tr>
<td>Feed 3 location (from s-CSTR)</td>
<td>28</td>
<td>2</td>
<td>99</td>
</tr>
<tr>
<td>Feed 4 location (from s-reboiler)</td>
<td>34</td>
<td>2</td>
<td>99</td>
</tr>
<tr>
<td>Feed 5 location (from s-stripper)</td>
<td>35</td>
<td>2</td>
<td>99</td>
</tr>
<tr>
<td>Feed 6 location (from vapour pump-around)</td>
<td>10</td>
<td>2</td>
<td>99</td>
</tr>
<tr>
<td>Draw 1 location (from RDC to s-CSTR)</td>
<td>10</td>
<td>2</td>
<td>99</td>
</tr>
<tr>
<td>Draw 2 location (from RDC to s-reboiler)</td>
<td>25</td>
<td>2</td>
<td>99</td>
</tr>
<tr>
<td>Draw 3 location (from RDC to s-stripper)</td>
<td>26</td>
<td>2</td>
<td>99</td>
</tr>
<tr>
<td>Draw 4 location (from RDC to vapour pump-around)</td>
<td>25</td>
<td>2</td>
<td>99</td>
</tr>
<tr>
<td>Draw 1 flow rate (kmol/hr)</td>
<td>0</td>
<td>0.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Draw 2 flow rate (kmol/hr)</td>
<td>4.2</td>
<td>0.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Draw 3 flow rate (kmol/hr)</td>
<td>4.2</td>
<td>0.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Draw 4 flow rate (kmol/hr)</td>
<td>0.5</td>
<td>0.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Reflux ratio (-)</td>
<td>2.0</td>
<td>0.1</td>
<td>40.0</td>
</tr>
<tr>
<td>Bottom flow rate (kmol/hr)</td>
<td>12.6</td>
<td>5.0</td>
<td>18.0</td>
</tr>
</tbody>
</table>

| Pre-reactor (p-CSTR)              |               |            |            |
| Reactor diameter (m)              | 1.0           | 0.0        | 5          |
| Reactor length (m)                | 1.0           | 0.0        | 5          |
| Outlet stream split               | 0.0           | 0.0        | 1.0        |

| Side-reactor (s-CSTR)             |               |            |            |
| Reactor diameter (m)              | 1.0           | 0.0        | 5          |
| Reactor length (m)                | 1.0           | 0.0        | 5          |

| Top distillation column (DC1)     |               |            |            |
| Total number of stages            | 50            | 3          | 50         |
| Feed stages location              | 24            | 2          | 49         |
| Reflux ratio (-)                  | 5.9           | 0.1        | 15.0       |
| Distillate flow rate (kmol/hr)    | 12.6          | 5.0        | 18.0       |

| Bottom distillation column (DC2)  |               |            |            |
| Total number of stages            | 50            | 3          | 50         |
| Feed stages location              | 24            | 2          | 49         |
| Reflux ratio (-)                  | 1.0           | 0.1        | 15.0       |
| Distillate flow rate (kmol/hr)    | 12.6          | 0.6        | 18.0       |

| Side-stripper (s-stripper)        |               |            |            |
| Total number of stages            | 10            | 2          | 10         |
| Bottom flow rate (kmol/hr)        | 1.8           | 0.0        | 5.0        |

| Side-reboiler (s-reboiler)        |               |            |            |
| Reboiler heat duty (kW)           | 0.0           | 0.0        | 500.0      |

| Stream selection                  |               |            |            |
| Feed 1 stream selection           | 1             | 0          | 1          |
| Feed 2 stream selection           | 1             | 0          | 1          |
| Top product stream selection      | 1             | 0          | 1          |
| Bottom product stream selection   | 0             | 0          | 1          |
| Reactive distillation column selection | 1          | 0          | 1          |
| Side-stripper existence selection | 1             | 0          | 1          |
| Side-reboiler existence selection | 0             | 0          | 1          |
| Side-reactor existence selection  | 0             | 0          | 1          |
A clarification is in order regarding the choice of liquid holdup value. Liquid holdup could not be used as an optimisation variable in ProcessBuilder, therefore it was kept at a fixed value, however, the impact of this choice was investigated separately (see Section 3.5.2). For case studies with more challenging separation and/or reaction characteristics, the choice of liquid holdup is expected to impact on the optimal design as a higher residence time may be needed, however, a fixed value was selected for all case studies for consistency and comparison. The value of 0.1 m$^3$/reactive tray was chosen in order to provide reasonable residence time for slow reactions and at the same time avoid very large tray weir heights and column pressure drop (for industrial scale scenarios where pressure drop is not ignored). Using a column with a diameter of 1 m (based on the flooding limit of 80% using Fair’s correlation (Perry and Green 1999)) as an example, which is reasonable given the process flow rates considered, the holdup will provide adequate residence time for reasonably slow kinetics using a tray weir height of approximately 12 cm, which is sensible from an internals’ point of view.

As previously mentioned, two inequality constraints were imposed on the optimisation problem, bottom product purity, $x_{B,D}$, required to be at least 99 mol%, and bottom product recovery of the main component (component D), $x_{rec,D}$, required to be at least 90%.

### 3.5 Results

In this section, the optimisation results for the case studies considered will be presented and discussed. More specifically, the optimal designs will first be discussed in terms of optimal cost, followed by a more detailed analysis for all case studies, categorised based on their relative volatility system. In parallel, the behaviour of the optimal systems will be explained, based on their temperature, composition and chemical driving force profiles. Then, a generic discussion with regards to the optimal designs based on their reaction and separation characteristics will take place, leading to the development of design guidelines and to a 3-D figure illustrating the optimal results, mainly in terms of the units involved. Investigations of the impact of liquid holdup on the optimal design and optimal cost, will follow.

#### 3.5.1 MINLP optimisation results

Using the methodology described in Section 3.2, the optimal results presented in Table 3.5 were obtained for the case studies given in Table 3.3 with initialisation values as
shown in Table 3.4. All steady-state simulations required for steps 1 to 3 of the methodology typically took about 2-120 s CPU time whilst the optimisation tasks took approximately 200-3000 s CPU time depending on the case study considered. Optimisations which indicated the existence of additional units were typically slower, requiring more time (up to 1 hr) due to the increased complexity of the problem.

As previously mentioned, the optimisation problem considered is highly non-convex, thus global optimality cannot be guaranteed. The optimisation tasks were therefore repeated with different initial guesses to ensure that the optimum found was indeed the overall optimum (step 5 of the methodology). In all cases considered, starting from different initial guesses still resulted in the same optimal results in terms of the units required, as well as very similar results in terms of total number of stages, feed stage locations and operational parameters, with only very small absolute differences in the objective function (order of $10^{-3}$ €/kg) which was below the tolerance used ($10^{-2}$ €/kg). As a result, it is concluded that, particularly from an industrial point of view, all the optimal solutions found for each case study are equivalent since their objective function is almost identical and their optimal parameters are very similar.

3.5.1.1 Evaluation of optimal costs

A comparison of the annualised capital and operating costs for the optimal designs is presented in Figure 3.4. Case studies 10 and 11 have significantly larger capital cost than any of the other case studies, mainly due to the large size of the reactive distillation column (85 and 78 stages, respectively), as well as the existence and size of the two additional distillation columns. The next most expensive in terms of capital cost is Case study 9, due to the presence of the pre-reactor, the reactive column and the two non-reactive columns. Case studies 7, 8, 12 and 14 also have reasonably high capital cost due to the existence of the pre-reactor (Case study 8) or the large reactive column (Case studies 7, 12 and 14) required, respectively. For the rest of the cases, capital cost is relatively similar since the designs are based on a single reactive column.

The operating cost is similar for most case studies, since the main contributor to the operating cost is feedstock which is fixed at $10.08 \times 10^6$ (€/yr). The operating cost for Case study 10 is the highest and Case study 11 the second highest, due to the high reboiler duty of the two additional distillation columns, the more expensive waste treatment due to unreacted A and B, as well as the higher maintenance cost which is a function of the capital cost. For larger scales, as capital cost scales with a factor of 0.6 whilst operating
cost scales linearly, it is expected that increasing capital cost will impact less significantly (comparing to operating cost) on the objective function, and most likely indicating the requirement of additional (side) equipment instead of additional operating cost.

An indicative breakdown of the capital (Figure 3.5a) and operating (Figure 3.5b) cost for Case study 8 (pre-reactor and reactive distillation) is presented in Figure 3.5 as an example. From Figure 3.5a it can be seen that the largest contributions to the capital cost stems from the reactive column shell, followed by the pre-reactor. Feed cost is the main contributor to the operational cost (Figure 3.5b), with reboiler duty and maintenance the next two significant operating cost factors. Waste cost is negligible for this system since there is negligible organic waste from the top stream, assuming that product C is water (see Appendix C for more information on this assumption).

In the following, a more detailed analysis of the optimal results, as presented in Table 3.5, is performed. Also, as the chemical reaction is a function of temperature, the temperature conditions in the reactive distillation column will have an impact on the progression of the reaction. Pressure can also impact on boiling points and reaction rates, however, its impact is not relevant in this work as pressure was considered constant throughout the column. To gain further insight into the optimal results obtained, it is therefore interesting to consider temperature profiles, and the associated composition and chemical driving force profiles, in some detail. Figure 3.6 presents the temperature profiles, and Figure 3.7 shows the corresponding liquid phase composition profiles, for the optimal reactive distillation column designs for all case studies. In addition, Figure 3.8 shows the chemical driving force (forward reaction rate divided by backward reaction rate) for all case studies. Feed stages are symbolised with a different marker symbol.
Figure 3.4: CAPEX and OPEX comparison for the optimal designs considered for all case studies (Table 3.5).

<table>
<thead>
<tr>
<th>Case study number</th>
<th>CAPEX (10^6 €/yr)</th>
<th>OPEX (10^6 €/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.5</td>
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</tr>
<tr>
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<td>15</td>
<td>9.5</td>
<td>8.5</td>
</tr>
</tbody>
</table>

Figure 3.5: Capital (a) and operating (b) cost breakdown of the optimal design of Case study 8 ($\alpha_{BD} = 0.75$, $k_0 = 8.41 \cdot 10^6$ m$^3$/kmol-s and $K_{eq} = 81$).

- **(a)** condenser | reboiler | column | internals | reflux drum | reactor
- **(b)** maintenance | waste | reboiler duty | feed

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Table 3.5: Optimal results for all case studies considered.

<table>
<thead>
<tr>
<th>Variable</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
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<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
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<tbody>
<tr>
<td>αCA - αAB - αBD</td>
<td>2.15-2</td>
<td>2.15-2</td>
<td>2.15-2</td>
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<td>System (Table 3.2)</td>
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<tr>
<td>K0 (m^3/(kmol-s))^2</td>
<td>8.41-10^6</td>
<td>2.1-10^6</td>
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<td>2.25</td>
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</table>

Optimal results

<table>
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<tr>
<th>CASE STUDIES</th>
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<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
</tr>
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<tbody>
<tr>
<td>RR_R (m)</td>
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<td>4.65</td>
<td>5.76</td>
<td>7.97</td>
<td>5.09</td>
</tr>
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<td>B_R (kmol/hr)</td>
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<td>12.6</td>
<td>12.6</td>
<td>12.6</td>
<td>12.6</td>
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</table>

2 The relative volatilities of all case studies are presented in Table 3.2.
3 The kinetic parameters of all case studies are presented in Table 3.3.
The objective function was calculated in €/ktn but is shown in €/kg to avoid a large number of decimals.

| $D_1$ (kmol/hr) | - | - | - | - | - | - | - | - | 11.1 | 9.7 | 6.8 | - | - | - | - |
| $N_1$ | - | - | - | - | - | - | - | - | 8 | 12 | 14 | - | - | - | - |
| $N_{11}$ | - | - | - | - | - | - | - | - | 14 | 17 | 17 | - | - | - | - |
| $RR_2$ | - | - | - | - | - | - | - | - | 6.79 | 8.95 | 13.76 | - | - | - | - |
| $D_2$ (kmol/hr) | - | - | - | - | - | - | - | - | 11.1 | 10.6 | 7.3 | - | - | - | - |
| $N_2$ | - | - | - | - | - | - | - | - | 19 | 27 | 29 | - | - | - | - |
| $N_{12}$ | - | - | - | - | - | - | - | - | 37 | 44 | 47 | - | - | - | - |
| $X_{REC}$ | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 0.90 | 0.98 | 0.96 | 1.00 | 1.00 | 1.00 | 1.00 |
| $X_{B,D}$ | 0.99 | 0.99 | 0.99 | 0.99 | 0.99 | 0.99 | 0.99 | 0.99 | 0.99 | 0.99 | 0.99 | 0.99 | 0.99 | 0.99 | 0.99 |
| $Q_c$ (kW) | -341.3 | -537.9 | -643.1 | -853.6 | -578.8 | -404.8 | -454.2 | -763.3 | -600.8 | -3539.1 | -1729.0 | -864.5 | -657.6 | -1145.1 | -448.6 |
| $Q_R$ (kW) | 227.9 | 424.7 | 530.0 | 740.5 | 466.2 | 284.6 | 344.1 | 637.9 | 479.6 | 3433.1 | 1717.8 | 757.4 | 549.2 | 1039.9 | 340.7 |
| $d_6$ (diameter, m) | 0.62 | 0.78 | 0.85 | 0.99 | 0.81 | 0.64 | 0.65 | 0.93 | 0.77 | 1.98 | 1.39 | 1.04 | 0.91 | 1.13 | 0.71 |
| $d_1$ (diameter, m) | - | - | - | - | - | - | - | - | 0.43 | 0.44 | 0.48 | - | - | - | - |
| $d_2$ (diameter, m) | - | - | - | - | - | - | - | - | 0.79 | 0.96 | 1.00 | - | - | - | - |
| OPEX (M€/yr) | 10.32 | 10.52 | 10.63 | 10.82 | 10.59 | 10.44 | 10.89 | 11.03 | 11.83 | 15.77 | 14.44 | 11.04 | 10.68 | 11.15 | 10.49 |
| CAPEX (M€/yr) | 0.15 | 0.27 | 0.35 | 0.43 | 0.35 | 0.29 | 0.71 | 1.00 | 1.28 | 4.80 | 4.44 | 0.76 | 0.40 | 0.55 | 0.31 |

$^4$ The objective function was calculated in €/ktn but is shown in €/kg to avoid a large number of decimals.
3.5.1.2 Process flowsheets and profiles

System I (Case studies 1-5)

It can be seen from Table 3.5 that the case studies considering System I (Case studies 1, 2, 3, 4 and 5, i.e. relative volatilities of 2-1.5-2 for $\alpha_{CA^{-}}\alpha_{AB^{-}}\alpha_{BD}$, respectively) needed only a single reactive column to meet the product specifications whilst minimising the objective function. Also, for these five case studies, the faster the kinetics, the lower the total number of stages and the reflux ratio, and therefore also the lower the production-based TAC ($k_{f0}=8.41\cdot10^6$ (m$^3/(kmol\cdot s)$) and $K_{eq}=81$ with corresponding TAC of 2.073 €/kg; $k_{f0}=2.1\cdot10^6$ (m$^3/(kmol\cdot s)$) and $K_{eq}=2.25$ with corresponding TAC of 2.140 €/kg; and $k_{f0}=1.05\cdot10^6$ (m$^3/(kmol\cdot s)$)) and $K_{eq}=0.184$, 2.25 and 81, respectively, with corresponding TAC of 2.231, 2.178 and 2.168 €/kg, respectively). The impact of $K_{eq}$ is limited, as Case studies 3 ($K_{eq}=2.25$) and 5 ($K_{eq}=81$), which have the same $k_{f0}$ (1.05$\cdot10^6$ (m$^3/(kmol\cdot s)$)), have very similar designs and therefore similar optimal TAC (2.178 and 2.168 €/kg, respectively). To demonstrate the benefits from process intensification, the optimal TAC for the conventional process (reactor followed by non-reactive distillation columns) for Case study 1 was found to be 2.424 €/kg, i.e. 16.9 % higher than the reactive distillation configuration (detailed results not shown).

For Case studies 1-5, the temperature profiles in Figure 3.6 indicate a gradual increase in temperature from the top to the bottom of the column, where feed stages only slightly disrupt the smooth increase. The gradually increasing temperature profile is due to the favourable relative volatilities which result in most of the reaction taking place in the top and middle section of the column (Figure 3.8) and, given the negligible heat of reaction, leave temperature change only to occur due to the liquid compositions as determined by the separation. Should heat of reaction not be neglected, more significant temperature changes through the reactive stages would be expected, subject to reflux ratio values. The case studies also show similar behaviour in the composition profiles in Figure 3.7 where the liquid mole fractions of products C and D increase gradually towards the top and bottom of the column, respectively.
Figure 3.6: Temperature profiles of the optimal column designs for all case studies (feed locations are marked with "o", data in Table 3.2 to Table 3.4).
Case study 1
$NF_1 = 12$
$NF_2 = 13$

Case study 2
$NF_1 = 11$
$NF_2 = 19$

Case study 3
$NF_1 = 9$
$NF_2 = 23$

Case study 4
$NF_1 = 8$
$NF_2 = 26$

Case study 5
$NF_1 = 9$
$NF_2 = 23$

Case study 6
$NF_1 = 6$
$NF_2 = 22$

Case study 7
$NF_1 = 5$
$NF_2 = 35$

Case study 8
$NF_1 = 10$
$NF_2 = 9$
Figure 3.7: Composition profiles of the optimal column designs for all case studies (data in Table 3.2 to Table 3.4).
Figure 3.8: Forward to backward reaction rate ratio of the optimal column designs for all case studies (feed locations are marked with “o”, data in Table 3.2 to Table 3.4).
System II (Case studies 6-7)

For System II (Case studies 6 and 7), the relative volatility between the products ($\alpha_{CD}$) remained the same as for System I ($\alpha_{CD}=6$), but $\alpha_{CA}$ and $\alpha_{BD}$ were reduced ($\alpha_{CA}=\alpha_{BD}=1.2$) and the relative volatility between the two reactants was increased ($\alpha_{AB}=4.15$). The relative volatility between components C and D, $\alpha_{CD}$, is calculated based on the rest of relative volatilities using the expression: $\alpha_{CD} = \alpha_{CA} \cdot \alpha_{AB} \cdot \alpha_{BD}$. For System II, the optimal results indicate the existence of a single, although larger, reactive column due to the large relative volatility between the reactants, as well as the more difficult separation at both column ends between the reactants and the products. It is also interesting to note that the increased TAC of Case study 7 ($k_{f0}=2.1 \cdot 10^6$ (m$^3$/(kmol∙s)) and $K_{eq}=81$ with corresponding TAC of 2.541 €/kg) comparing to Case study 6 ($k_{f0}=8.41 \cdot 10^6$ (m$^3$/(kmol∙s)) and $K_{eq}=81$ with corresponding TAC of 2.138 €/kg), mainly stems from the reduced production rate and not from the increased reflux ratio and total number of stages due to the slower kinetics. As reactant A is more volatile for System II, it moves quicker to the top of the column, thus reducing the residence time of the reaction (i.e. amount of component A in liquid phase). As a result, additional liquid holdup is needed and, as the liquid holdup per stage is fixed, more reactive and/or separation stages are therefore required in order to reach sufficient conversion and maintain the highest possible production rate. An alternative would be increasing reflux ratio, however, OPEX is a more significant contributor to the objective function comparing to CAPEX, therefore increasing the number of stages is preferred in terms of optimal TAC, justifying the choice of the optimiser. For both case studies, the optimal solutions additionally include a vapour stream that is removed from a lower point in the column (stage 25 and stage 33 for Case studies 6 and 7, respectively), and is recycled back to the reactive column, still as vapour, at a higher stage (stage 10 and stage 11, respectively). Simulations were performed for those two case studies, where all the optimal design and operational variables were kept the same, however, the vapour pump-around stream was removed from the column in order to investigate its benefits. The overall cost (TAC) for both case studies, which did not include the vapour pump-around stream, was approximately 0.01% higher showing that the difference, although existing, is limited and that the exact benefits of this novel pump-around stream on the performance of reactive distillation columns should be further investigated, as mentioned earlier.
For Case studies 6-7 most of the temperature change takes place at the top and the bottom of the reactive column whilst temperature remains almost stable in the middle of the column. Sharp temperature change breaks are also observed, which could potentially be used for inferential composition control. Also, due to the reduced $\alpha_{BD}$, the temperature level at the bottom of the columns decreased (as the boiling point of component B is fixed to 413 K), therefore the reaction rates were reduced comparing to System I (Figure 3.8). Due to the large difference in reactant volatilities ($\alpha_{AB} = 4.15$), most of the conversion takes place towards the upper end and middle of the column where both reactants are in liquid phase. For both case studies, the mole fractions of products C and D gradually increase towards the column ends (similarly to System I). However, the larger relative volatility between the reactants ($\alpha_{AB} = 4.15$) shifts the feed stages (and therefore the mole fraction peaks for the reactants) towards the column ends.

**System III (Case studies 8-11)**

For System III (Case studies 8, 9, 10 and 11), the relative volatility between the lightest components, $\alpha_{CA}$, and between the reactants, $\alpha_{AB}$, remains the same as for System I, however, the boiling point ranking is now alternating: $T_C<T_A<T_D<T_B$, i.e. there is a different boiling point order between one reactant (now high-boiler B) and one product (now middle-boiler D). The optimal results in Table 3.5 indicate that additional units are now required to meet product specifications for this more challenging system.

For Case study 8 ($k_{f0} = 8.41 \cdot 10^6$ (m$^3$/(kmol⋅s)) and $K_{eq} = 81$ with corresponding TAC of 2.389 €/kg), a pre-reactor is needed before the reactive distillation column to maximise the conversion (87.3% achieved within the pre-reactor, whilst the maximum expected for an infinitely large CSTR would be 90% given that $K_{eq}=81$, and close to 100% within the reactive column) in order to avoid the additional cost of two downstream distillation columns (for product purification) and recycle streams due to the low reaction conversion. For Case study 9 ($k_{f0} = 2.1 \cdot 10^6$ (m$^3$/(kmol⋅s)) and $K_{eq} = 81$ with corresponding TAC of 2.963 €/kg), this cost cannot be avoided since in addition to the pre-reactor and the reactive distillation column, two distillation columns are needed for further product purification due to the slower kinetics considered in the reactive units ($2.1 \cdot 10^6$ (m$^3$/(kmol⋅s))), which lead to a lower reaction conversion (85.1% conversion is achieved within the pre-reactor, which increases to 96.6% within the reactive column). For Case studies 10 ($k_{f0} = 8.41 \cdot 10^6$ (m$^3$/(kmol⋅s)) and $K_{eq} = 0.184$ with corresponding TAC of 4.861 €/kg) and 11 ($k_{f0} = 1.05 \cdot 10^6$ (m$^3$/(kmol⋅s)) and $K_{eq} = 0.184$ with corresponding TAC of 6.480 €/kg).
\( \text{€/kg} \), the chemical equilibrium considered is very low \((K_{eq}=0.184)\), therefore a pre-reactor does no longer improve the process performance as the conversion in the reactor is limited by chemical equilibrium which for these case studies favours the backward reaction, resulting in very low reactant conversion in a standard reactor. In these cases, in addition to a large reactive column (85 and 78 stages for Case study 10 and 11, respectively), two additional columns are needed to meet the product purity specification. It should be noted that for Case studies 9, 10 and 11, a recycle of the bottom product of DC1 and of the bottom product of DC2 back to the reactive column would be sensible to increase process performance and reduce waste. These two streams should mainly include the unreacted feed (A or B, respectively) as component C is removed as a top product of DC1 (using an additional purity specification \((x_{D,C} > 0.99)\) in the optimisation problem to increase its purity) and component D is removed as a top product of DC2. The absence of a recovery specification for product C in DC1 (as it was not the product of interest), however, led to the bottom stream of DC1 not always containing a large amount of A for Case studies 9, 10 and 11 (0.30, 1.77 and 4.98 kmol/hr, respectively, which correspond to 2.4%, 14% and 39.5% of the initial feed A flow rate) since product C was also present, therefore this additional constraint should be imposed, should this stream is to be considered for recycle. For DC2, the purity and recovery specifications for product D led to the bottom stream containing mainly reactant B for all three case studies (0.39, 1.91 and 5.01 kmol/hr, respectively, which correspond to 3.1%, 15.2% and 39.8% of the initial feed B flow rate). However, as already mentioned, the inclusion of recycles in the superstructure was not possible due to convergence issues, therefore the potential recycle streams were considered waste streams instead.

For Case studies 8-11, temperature changes mainly at the top of the column (unlike System I) where most of the reaction conversion takes place, after which temperature has smaller changes. This can also be seen in Figure 3.8 where the reaction rate ratio remains almost constant in the middle of the columns due to the almost constant temperature and compositions. This is due to the challenging volatility ranking (reactant B is less volatile than product D) which leads to the requirement of additional reactive trays to minimise the amount of unreacted reactant B as well as due to the high conversion achieved in the pre-reactor (for Case studies 8 and 9 only). For the challenging case studies of System III, alternative configurations could be considered, such as feeding part of A directly to the bottom of the column (and the rest to the pre-reactor) in order
to stimulate reaction at the lower part of the reactive column or operating with excess of reactant A. Such configurations are, however, not considered in the current superstructure but could be investigated further as individual designs.

**System IV (Case studies 12-13)**

For System IV (Case studies 12 and 13), the boiling point order is again \( T_C < T_A < T_B < T_D \). The relative volatility between the reactants is the same as for System I (\( \alpha_{AB} = 1.5 \)) but the separation at each end of the column is now more challenging (\( \alpha_{CA} = \alpha_{BD} = 1.2 \)). Case study 12 (\( k_{\text{f0}} = 8.41 \times 10^6 \), \( K_{\text{eq}} = 2.25 \)) with corresponding TAC of 2.390 €/kg has the same kinetic parameters (\( k_{\text{f0}} = 8.41 \times 10^6 \), \( K_{\text{eq}} = 2.25 \)) as Case studies 2 and 14 and it can be seen that they have the same design (single reactive distillation column), however, the more difficult the separation task, the more demanding the design and operational parameters (i.e. higher total number of stages, higher reflux ratio), as expected. Similarly, Case study 13 (\( k_{\text{f0}} = 8.41 \times 10^6 \), \( K_{\text{eq}} = 81 \)) with corresponding TAC of 2.210 €/kg) has the same kinetic parameters (\( k_{\text{f0}} = 8.41 \times 10^6 \), \( K_{\text{eq}} = 81 \)) as Case studies 1, 6 and 8, and it can be seen that the more difficult the separation task (including the boiling point order), the more demanding the design and operational parameters, as expected.

For System IV, similarly to System II and System III, temperature at the bottom of the column is lower compared to System I, due to the relative volatilities. Case studies 12 and 13 have a gradually increasing temperature profile similarly to System I, where feed stages only slightly disrupt the smooth increase. The gradually increasing temperature profile is due to the favourable relative volatilities which result in most of the reaction taking place in the middle of the column and, given the negligible heat of reaction, leave the temperature change only to happen due to separation. Also, better separation between reactants A and B can be observed. In addition, Case study 12 has lower \( \alpha_{BD} \) compare to Case studies 2 and 14 which leads to a lower concentration of the heavy reactant B in the middle of the reactive column (Figure 3.7).

**System V (Case studies 14-15)**

For System V, i.e. Case study 14 (\( k_{\text{f0}} = 8.41 \times 10^6 \), \( K_{\text{eq}} = 0.184 \)) with corresponding TAC of 2.390 €/kg) and Case study 15 (\( k_{\text{f0}} = 8.41 \times 10^6 \), \( K_{\text{eq}} = 2.25 \)) with corresponding TAC of 2.150 €/kg), the relative volatility between the reactants is higher than for System I and System IV (\( \alpha_{AB} = 2.5 \)), and the separation at the top of the column is more challenging (\( \alpha_{CA} = 1.2 \)) than at the bottom (\( \alpha_{BD} = 2 \)). Case study
12 and Case study 15 have the same reaction parameters, however, the difference in relative volatilities leads to higher temperatures towards the bottom of the column for Case study 15, and therefore to increased forward reaction rates compared to Case study 12 (shown in Figure 3.8), leading to a shorter column (27 stages compared to 42 stages). Case study 14 has the same kinetic parameters ($k_0 = 8.41 \times 10^6$, $K_{eq} = 2.25$) as Case studies 2 and 12 and it can be seen that they have the same design (single reactive distillation column), however, the more difficult the separation task, the more demanding the design and operational parameters (i.e. higher total number of stages, higher reflux ratio), as expected.

For Case study 14, temperature increases gradually similarly to System I and IV, however, between stages 9 to 25, the profile remains relatively flat, resulting in a steady chemical driving force through these stages (Figure 3.8). For the same case study, sharp changes are noticed for the mole fractions of products C and D, due to the very high reflux ratio required (10.66) and the large relative volatility between the two products ($\alpha_{CD} = 6$). This case study has a very low chemical equilibrium ($K_{eq} = 0.184$), and is the chemical equilibrium case that benefits the most from the intensified reactive distillation process since it is possible to overcome the unfavourable chemical equilibrium (Figure 3.8) and reach a high purity product with a single reactive column. For Case study 15, the profiles are similar to those of Case study 14 since the relative volatilities are the same, however, the change in the mole fractions of products C and D are not as sharp due to the lower reflux ratio. In addition, reactant B has a lower mole fraction in the middle of the column due to the faster consumption of the reactants in the reactive zone (Figure 3.8).

**Further notes**

Having discussed in a higher level the temperature and composition profiles in Figure 3.6 and Figure 3.7, respectively, and as kinetics are of particular interest due to the intensified nature of reactive distillation processes, a more detailed discussion follows with regards to the chemical driving force for the case studies considered. Overall, from Figure 3.8, it can be seen that for some case studies which belong to Systems I, II, IV and V (i.e. not case studies 8-11), the chemical driving force shows a peak near the feed stage locations as these are the stages where reactant concentrations are highest. Moreover, for these systems, the driving force is higher at the top of the column and decreases towards the bottom of the column. This is reasonable as concentration of component D at the top of the column is negligible. In addition, for the boiling point ranking
considered, the unreacted components A and B are both in the liquid phase mainly at the upper part of the column, due to heat transfer (between hot component A and cold component C) and bottom purity specification and boiling point (for component B). As a result, the unreacted A and B (with a mole fraction of less than 0.04) are removed from the top of the column (as at the bottom there is a purity specification), shifting the reaction equilibrium to the right. However, for case studies which belong to System III (Case studies 8, 9, 10 and 11) where the boiling point ranking is reverse, the unreacted component B is also in higher concentration (compared to the other case studies) through the middle and lower part of the column leading to a driving force increase below the feed stage locations. As a result, for those case studies, the behaviour of the driving force is reverse, i.e. increasing towards the bottom of the column. Also, the driving force remains almost constant for a large number of stages due to the almost constant temperature through the same stages as shown in Figure 3.6, and presents a peak at the bottom of the column. This peak is due to the increase in concentration of reactant B as shown in Figure 3.7, as it is the heaviest component and therefore tends to accumulate at the bottom of the column along with a small amount of component A (i.e. mole fraction lower than 0.004), given their low relative volatility ($\alpha_{AB}=1.5$).

3.5.1.3 Discussion

This section aims to evaluate the impact of the reaction/separation characteristics on the objective function as well as on the optimal design and operational parameters found for all the case studies considered. As an overall comment, it is worth mentioning that no case study indicated an optimal solution including a side-stripper and/or side-reboiler. However, if CAPEX contributes more significantly to the overall objective function, a side-reboiler could replace the requirement of a very large reactive column, given a fast reaction and a challenging separation task. In addition, the consideration of different systems, where the remixing effect is observed or thermal coupling is considered, could for instance indicate the requirement of a side-stripper in the optimal process.

Case studies 2 and 6 resulted in a similar optimal value of the objective function (TAC=2.140 and 2.138 €/kg, respectively) although their separation and reaction characteristics are different. This indicates that a system with slower kinetics in combination with an easy separation task (Case study 2) is economically similar to a system with faster kinetics in combination with a relatively more difficult separation task (Case study 6). It is interesting to note that Case studies 1 and 8 had the same kinetics
(\(k_{f0}=8.41\times10^6\ \text{m}^3/(\text{kmol}\cdot\text{s})\)) and \(K_{\text{eq}}=81\), however, the existence of different boiling point rankings had a significant impact on the optimal process design and operation. As mentioned earlier, reverse boiling point rankings (\(\alpha_{BD}=0.75\) for Case study 8) led to lower column temperatures (shown in Figure 3.6) and therefore reduced forward reaction rates (shown in Figure 3.8), as the boiling point of component B was fixed. As a result, Case study 8 required a pre-reactor in addition to the reactive column, as well as a higher reflux ratio (6.99 for Case study 8 versus 2.59 for Case study 1) with associated TAC of 2.073 €/kg for Case study 1 compared to 2.389 €/kg for Case study 8. The same applies for Case studies 4 and 11 where for the same kinetics (\(k_{f0}=1.05\times10^6\ \text{m}^3/(\text{kmol}\cdot\text{s})\)) and \(K_{\text{eq}}=0.184\), reverse boiling rankings (Case study 11) required two additional columns as well as a larger reactive column (78 stages for Case study 11 and 32 stages for Case study 4) and higher reflux ratio for the reactive column (18.24 versus 7.97). Similarly, for Case studies 14 and 10 where the same kinetics (\(k_{f0}=8.41\times10^6\ \text{m}^3/(\text{kmol}\cdot\text{s})\)) and \(K_{\text{eq}}=0.184\) were considered, different boiling point rankings again resulted in different process design and operational characteristics. Reverse boiling point rankings (Case study 10) required two additional distillation columns as well as a larger reactive column (85 stages for Case study 10 versus 36 stages for Case study 14) as well as a high reflux ratio (36.72 for Case study 10 versus 10.66 for Case study 14). Similarly, for Case studies 1 and 2, the same relative volatilities led to a similar process based on a single reactive column, indicating that different reaction kinetics had a limited impact. This is reasonable since for a small relative volatility between the reactants (\(\alpha_{AB}=1.5\)), the reactants tend to remain between the feed stage locations and therefore the system can tolerate lower reaction rates (i.e. even for Case study 2 with slower kinetics).

Case studies 1 and 6 also had the same reaction kinetics (\(k_{f0}=8.41\times10^6\ \text{m}^3/(\text{kmol}\cdot\text{s})\)) and \(K_{\text{eq}}=81\), resulting in a simple design for both processes. However, the difference in relative volatilities, with a high relative volatility between the reactants (\(\alpha_{AB}=4.15\) versus \(\alpha_{AB}=1.5\)) and a lower relative volatility between the top and bottom separations (\(\alpha_{CA}=\alpha_{BD}=1.2\) versus \(\alpha_{CA}=\alpha_{BD}=2\)) for Case study 6, led to the latter being benefited by the vapour pump-around stream for this case study. For Case studies 12 and 14, the TAC obtained is very similar as mentioned earlier, indicating that given fast kinetics, small chemical equilibrium and favourable relative volatilities (Case study 14) are economically equivalent to larger chemical equilibrium with less favourable relative volatilities (Case study 12). Furthermore, for Case studies 8 and 9, when the same relative volatilities were
considered ($\alpha_{CA}=2$, $\alpha_{AB}=1.5$, $\alpha_{BD}=0.75$) and chemical equilibrium was high enough to favour the forward reaction ($K_{eq}=81$), slower kinetics required two additional columns (Case study 9), in addition to the pre-reactor (Case study 8) to meet the specifications. However, when unfavourable chemical equilibrium ($K_{eq}=0.184$) was considered (Case studies 10 and 11), although the additional columns were still required, the pre-reactor was no longer required since the low chemical equilibrium ($K_{eq}=0.184$) would favour the backward reaction, therefore not leading to a high reaction conversion. For those two case studies, the slower kinetics (Case study 11) led to a higher cost (TAC=6.480 €/kg versus TAC=4.861 €/kg), which was mainly due to the lower production (bottoms) rate ($D_2=7.3$ kmol/hr versus $D_2=10.6$ kmol/hr). Case studies 1 and 13 had the same kinetics ($k_{f0}=8.41\cdot10^6$ (m$^3$/kmol∙s)) and $K_{eq}=81$), however, the more challenging separation at both column ends for Case study 13 ($\alpha_{CA}=\alpha_{BD}=1.2$ for Case study 13 instead of $\alpha_{CA}=\alpha_{BD}=2$ for Case study 1) led to a more demanding design in terms of total number of stages and reflux ratio. Finally, Case studies 14 and 15 had the same relative volatilities but different chemical equilibrium, with both requiring a single reactive distillation column. However, as expected, the case study with the lowest chemical equilibrium (Case study 14, $K_{eq} = 0.184$) led to a more expensive process (TAC=2.390 €/kg versus TAC=2.150 €/kg), both in terms of design (36 versus 27 stages) and operation (reflux ratio of 10.66 versus 3.70).

Overall, it appears that, for the relative volatility and reaction kinetics combinations considered in this work, favourable relative volatilities have more of an impact on the optimal TAC than does favourable kinetics. This can be seen in Table 3.6 and in more detail in Figure 3.9, where the optimal results (in terms of the units required in the optimal solution) are visualised as a function of the relative volatility between components B and D ($\alpha_{BD}$) (as this ratio had a significant impact on process design), the forward pre-exponential factor ($k_{f0}$) and the chemical equilibrium ($K_{eq}$). Instead of $K_{eq}$, for which values 0.184 and 2.25 would be very close and therefore could not be easily distinguished, to enhance clarity in the plot, the equivalent equilibrium conversion (see note 5) was plotted as the z-axis. This map can be used as a guideline for the optimal design of reactive distillation processes when other relative volatility and/or kinetics combinations than the ones presented here are considered. In Figure 3.9, green points indicate case studies where the optimal design includes a single reactive distillation column whilst orange points indicate case studies where in addition to the reactive distillation column, a vapour pump around stream is included in the optimal solution to
meet product specifications. Red points indicate that the optimal design for these case studies includes the reactive distillation column as well as additional equipment (i.e. pre-reactor and/or additional conventional distillation columns).
Table 3.6: Optimal results for all case studies as illustrated in Figure 3.9.

<table>
<thead>
<tr>
<th>Case study</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
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<th>12</th>
<th>13</th>
<th>14</th>
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<tr>
<td>$\alpha_{BD}$</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>1.2</td>
<td>1.2</td>
<td>0.75</td>
<td>0.75</td>
<td>0.75</td>
<td>1.2</td>
<td>1.2</td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>$k_0 \cdot 10^6$</td>
<td>8.41</td>
<td>2.1</td>
<td>1.05</td>
<td>1.05</td>
<td>8.41</td>
<td>2.1</td>
<td>8.41</td>
<td>2.1</td>
<td>8.41</td>
<td>1.05</td>
<td>8.41</td>
<td>8.41</td>
<td>8.41</td>
<td>8.41</td>
<td></td>
</tr>
<tr>
<td>$K_{eq}$</td>
<td>81</td>
<td>2.25</td>
<td>2.25</td>
<td>0.184</td>
<td>81</td>
<td>81</td>
<td>81</td>
<td>81</td>
<td>0.184</td>
<td>0.184</td>
<td>2.25</td>
<td>81</td>
<td>0.184</td>
<td>2.25</td>
<td></td>
</tr>
<tr>
<td>Conversion$^5$</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.6</td>
<td>0.9</td>
<td>0.3</td>
<td>0.6</td>
<td></td>
</tr>
</tbody>
</table>

Optimal design

- RDC
- $p$-CSTR
- DC1
- DC2
- Vapour pump-around stream

---

$^5$ $K_{eq}$ can be calculated based on the desired conversion $([D]/[A_0]=0.3, 0.6$ or $0.9)$ at reaction equilibrium. In addition, $k_0$ can be calculated using the following equation for a batch reactor: $k_0 \cdot t = \frac{\text{conversion}}{(1 - \text{conversion}) \cdot [A_0]}$ where $t$ is the time required for the reaction to reach 90% conversion, taken in this work as 15, 60 or 120 min for $k_0=8.41 \cdot 10^6, 2.1 \cdot 10^6, 1.05 \cdot 10^6$ m³/(kmol·s), respectively.
From Figure 3.9, and the results shown in Table 3.5 and Table 3.6, the following conclusions can be drawn which confirm the anticipated behaviour (from an engineering perspective) for the systems and specifications (e.g. quality constraints, objective function etc.) considered:
1. When reactants are middle-boilers ($\alpha_C < \alpha_A < \alpha_B < \alpha_D$), a single reactive distillation column (with simple or more demanding design in terms of number of stages and/or operation in terms of reflux ratio) is economically favourable.

2. Since the previous point applies to a range of different reaction kinetics (i.e. forward pre-exponential factor and chemical equilibrium values), it appears that relative volatilities (when favourable, in terms of boiling point rankings) have a more significant impact on the optimal design and the cost than does the reaction kinetics.

3. For favourable boiling point rankings, when relative volatility between the two reactants ($\alpha_{ab}$) is large, a vapour pump-around stream may be beneficial in terms of optimal cost and production rate.

4. When reverse boiling point rankings and large value of chemical equilibrium are considered, a pre-reactor is needed. Depending on how slow the kinetics are, additional distillation columns may also be required in order to retrieve the desired product. When chemical equilibrium is low enough to favour the backward reaction, the pre-reactor is no longer favourable, however, additional columns are required to meet the product purity specifications.

5. Reverse boiling point ranking in terms of relative volatility between B and D was found to be critical for the design of the process since the main desired product was D. Similarly, if the main desired product was component C, the relative volatility which would be critical would consequently be between C and A, and ancillary equipment is expected to be required when $\alpha_{CA} < 1$ (not shown).

6. The value of the reflux ratio when the optimal solution indicates the existence of a single reactive column, depends greatly on the chemical equilibrium of the reaction. Consider fast kinetics and large $\alpha_{BD}$ ($\alpha_{BD}=2$) for instance. For $K_{eq}=81$, a low reflux ratio is required (2.59 – Case study 1), however, for $K_{eq}=2.25$, a higher reflux ratio is needed (3.70 – Case study 15), and for $K_{eq}=0.184$, a very high reflux ratio (10.66 – Case study 14) is needed. A similar argument can be made for the need for increasing number of stages (18, then 27 and then 36, respectively). Similarly, consider slow kinetics and the same large $\alpha_{BD}$ ($\alpha_{BD}=2$) for instance. For $K_{eq}=2.25$, a lower reflux ratio is required (5.76 – Case study 3), however, for $K_{eq}=0.184$, a higher reflux ratio (7.97 – Case study 4) is needed.
These results, in terms of the units included in the optimal process flowsheet, were considered in relation to the reactive distillation feasibility framework presented by Kiss et al. (2011). Although his framework is based on a number of preliminary data (e.g. VLE, reaction kinetics etc.), and not on rigorous optimisation as performed in this work, the overall suggestions in terms of process feasibility and design show very good agreement between his shortcut method and our optimisations. These results, in order not to distract from the rest of the findings in this work, are presented at the end of this chapter, in Section 3.6.

3.5.2 Impact of liquid holdup

Liquid holdup is one of the most important parameters for reactive distillation systems, not only determining column pressure drop and hydraulics (e.g. tray weir height) as in conventional distillation, but for reactive distillation also providing the required residence time for the liquid-phase reaction to take place. Large liquid holdup leads to increased weir height and column pressure drop, whilst small liquid holdup may lead to incomplete reaction conversion. The value of the liquid holdup is therefore a very important process parameter in reactive distillation since it is directly linked to the chemical conversion.

In this section, the impact of liquid holdup (h) on the optimal design is investigated. Case study 1 and Case study 5 were selected for the investigation in order to consider the impact of both fast and slower kinetics, for the same separation and chemical equilibrium parameters. Optimisation was performed using the input given in Table 3.2 to Table 3.4 for a number of different liquid holdups ranging from 0.05 m$^3$/tray to 0.12 m$^3$/tray (note that so far, the liquid holdup has been assumed constant at 0.1 m$^3$/tray, and not considered a decision variable due to software limitations). The authors are aware that further increase of the value of liquid holdup beyond 0.12 m$^3$/tray would potentially be beneficial for the process, however, it is expected that there would be an upper limit on the value of liquid holdup due to increased weir heights and larger column pressure drop, however, this has not been considered in this work. All other parameters were kept the same for all optimisations, as the aim of this section is solely to investigate how the optimal design depends on the liquid holdup. The optimal designs are found for a number of different liquid holdup values (Table 3.7 and Figure 3.10).
From Table 3.7 it can be seen how the optimal results change based on the liquid holdup considered for both Case study 1 (Table 3.7a) and Case study 5 (Table 3.7b). As holdup increases, TAC decreases although only marginally for Case study 1 (approximately 0.1%). This is because as liquid holdup increases, the requirements for total number of stages and reflux ratio decrease. These differences are more visible for Case study 5 (TAC reduced by 0.7%) where kinetics are slower and therefore the system is more sensitive to changes in reaction volume (i.e. liquid holdup). This shows that dedicated reactive distillation internals, that can hold high liquid volumes, might be very promising for relatively slow equilibrium limited reactions as they can further reduce the overall cost.

For Case study 5 and for holdups lower than 0.07 m$^3$/tray, the optimal designs have lower reflux ratio than the expected and this is because from an economic point of view, it was more beneficial to reduce production rate (and thereby increase TAC) than to increase the reflux ratio by a large amount in order to maintain production at the same value (12.6 kmol/hr). Note that, if tray weir height had been considered in the objective function (currently it is not), then more significant differences would be observed as the holdup (and therefore weir height) increased. Feed stage location and bottom flow rate were found to be almost constant for all designs for Case study 1 due to the fast kinetics which could tolerate the reduction in liquid holdup. For Case study 5, however, feed stage location for the bottom feed varied proportionally with the liquid holdup, due to the slower kinetics present. It is therefore expected that differences in the optimal designs for different holdups will be more significant as kinetics become more challenging.

The most demanding design is the design for the lowest holdup of 0.05 m$^3$ per (reactive) tray considered for both case studies, which is expected as the residence time for the reaction is then the lowest. If the optimal design found for the lowest holdup of 0.05 m$^3$/tray (RR$_R$, B$_R$, N$_{FR1}$, N$_{FR2}$, N$_{TR}$) was considered for a process with an actual holdup of 0.1 m$^3$/tray, then the additional stages (20-18=2 stages for case study 1 and 37-29=8 stages for case study 5) beyond the initial requirement will tolerate slower (than the assumed) reaction rates and will enhance reaction and separation without increasing the TAC beyond that of the 0.05 m$^3$/tray optimal design, and the reflux ratio could decrease slightly without violating the product specifications. In other words, by using the most demanding holdup case (0.05 m$^3$/tray) as a design basis, a more flexible design is achieved which is suitable for slower kinetics without greatly affecting the TAC. Where
there is uncertainty in the reaction kinetics, this may therefore be a design strategy to ensure a flexible and robust design.

Table 3.7: Optimal design results as a function of liquid holdup based on: (a) Case study 1 and (b) Case study 5 as the base cases.

(a)

<table>
<thead>
<tr>
<th>Variable</th>
<th>Liquid holdup (h, m³/tray)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.05</td>
</tr>
<tr>
<td>RR</td>
<td>3.35</td>
</tr>
<tr>
<td>Bₙ (kmol/hr)</td>
<td>12.6</td>
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<tr>
<td>NFR₁</td>
<td>13</td>
</tr>
<tr>
<td>NFR₂</td>
<td>15</td>
</tr>
<tr>
<td>Nₜₜ</td>
<td>20</td>
</tr>
<tr>
<td>Production-based TAC (€/kg)</td>
<td>2.092</td>
</tr>
<tr>
<td>CAPEX (M€/yr)</td>
<td>0.18</td>
</tr>
<tr>
<td>OPEX (M€/yr)</td>
<td>10.38</td>
</tr>
</tbody>
</table>

*Base case

(b)

<table>
<thead>
<tr>
<th>Variable</th>
<th>Liquid holdup (h, m³/tray)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.05</td>
</tr>
<tr>
<td>RR</td>
<td>5.33</td>
</tr>
<tr>
<td>Bₙ (kmol/hr)</td>
<td>12.0</td>
</tr>
<tr>
<td>NFR₁</td>
<td>8</td>
</tr>
<tr>
<td>NFR₂</td>
<td>31</td>
</tr>
<tr>
<td>Nₜₜ</td>
<td>37</td>
</tr>
<tr>
<td>Production-based TAC (€/kg)</td>
<td>2.391</td>
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<tr>
<td>CAPEX (M€/yr)</td>
<td>0.60</td>
</tr>
<tr>
<td>OPEX (M€/yr)</td>
<td>10.86</td>
</tr>
</tbody>
</table>

*Base case
Figure 3.10a and Figure 3.10b show how TAC, CAPEX and OPEX, change for the different holdup cases, for Case study 1 and Case study 5, respectively. As presented in Table 3.7a and Table 3.7b, an increase in liquid holdup reduces TAC slightly, including OPEX and CAPEX individually, and more so for slower reactions. This is due to the fact that larger holdup leads to higher conversion, which in turn demands less reflux and fewer reactive stages for the same production rate, which is not generally the case for separation only. (Note that the CAPEX results are not smooth as the number of stages is an integer decision.)
Figure 3.10: Optimal TAC, OPEX and CAPEX as a function of liquid holdup (data in Table 3.7), based on: (a) Case study 1 ($\alpha_{BD}=2$, $k_{f0}=8.41\cdot10^6$ m³/(kmol·s) and $K_{eq}=81$); (b) Case study 5 ($\alpha_{BD}=2$, $k_{f0}=1.05\cdot10^6$ m³/(kmol·s) and $K_{eq}=81$).
3.6 Methodology check against feasibility framework proposed by Kiss et al. (2011)

In Section 1.4.3, a framework presented by Kiss et al. (2011) for the feasibility evaluation of reactive distillation was discussed. The framework is based on fundamental explanations and industrial applications from literature and offers an assessment of the feasibility of reactive distillation based on a set of basic data which characterize the process. All 15 case studies considered in this work were checked based on this framework and the overall suggestions in terms of process feasibility and design show very good agreement between the shortcut method presented by Kiss et al. (2011) and the optimisations performed in this work. In the following, results are shown for three indicative case studies (case studies 1, 6 and 8 in this work), with different optimal design and operational parameters.

Case study 1

The reaction considered has two reactants and two products, so now the temperature difference between separation and reaction needs to be checked. The temperature difference for this case study is less than 120 K (423-376.7=46.3 K) and temperatures (376.7 K to 439.6 K) and pressure (P=1 atm) in the column remain below the critical values (647.3 K and 218.3 atm, respectively). Equilibrium constant is acceptable (K_{eq}=81>0.01) and k_{f}≥0.2k_{b} for all reactive stages. There are no side-reactions present and relative volatility between the two products is larger than 1.1 (α_{CD}=6). Relative volatilities were not considered time-dependent and no inert gases were present. Heat of reaction was considered negligible and temperature difference between reaction and separation is lower than 50 K as mentioned above, therefore we move to the final step of the evaluation of production rate. Production rate was fixed at 5kt/yr therefore for the case study considered, reactive distillation is technically feasible and economically attractive. This agrees with the outcome from the optimisation performed therefore there is agreement between the two methodologies.

Case study 6

The reaction considered has two reactants and two products, so now the temperature difference between separation and reaction needs to be checked. The temperature difference for this case study is less than 120 K (423-362.3=60.7 K) and temperatures (362.3 K to 419.4 K) and pressure (P=1 atm) in the column remain below the critical values (647.3 K and 218.3 atm, respectively). Equilibrium constant is acceptable
(\(K_{eq} = 81 > 0.01\)) and \(k_i \geq 0.2k_b\) for all reactive stages. There are no side-reactions present and relative volatility between the two products is larger than 1.1 (\(\alpha_{CD} = 5.98\)). Relative volatilities were not considered time-dependent and no inert gases were present. Heat of reaction was considered negligible but this time, temperature difference between reaction and separation is larger than 50 K (\(=60.7\) K) as mentioned above, therefore for the case study considered, reactive distillation is technically feasible but not economically attractive. This agrees with the outcome from the optimisation performed which indicated that in addition to the reactive distillation column, a vapour pump-around stream is required for the economically optimal solution, therefore there is agreement between the two methodologies.

**Case study 8**

The reaction considered has two reactants and two products, so now the temperature difference between separation and reaction needs to be checked. The temperature difference for this case study is less than 120 K (\(423-376.7=46.3\) K) and temperatures (\(376.7\) K to \(402.7\) K) and pressure (\(P=1\) atm) in the column remain below the critical values (\(647.3\) K and \(218.3\) atm, respectively). Equilibrium constant is acceptable (\(K_{eq}=81 > 0.01\)) but the condition for reaction kinetics (\(k_i \geq 0.2k_b\)) is now not met for all reactive stages. According to the framework presented by Kiss et al. (2011), the conventional or a hybrid process is recommended, and this is in agreement with the optimisation result, which indicated that in addition to the reactive distillation column, a pre-reactor is required.

**3.7 Conclusions**

In this work, a novel methodology has been presented for the simultaneous optimisation of the design and operation of a complex reactive distillation process. Based on a superstructure approach involving a reactive distillation column, a pre- and side-reactor, a side-reboiler, a side-stripper, a vapour pump-around as well as two conventional distillation columns, various process alternatives were considered for different system characteristics based on separation performance, related to relative volatilities, and reaction kinetics as the key system characteristics.

gPROMS ProcessBuilder was used to solve the MINLP problem and to find the optimal design and operating parameters of the process for a number of different case studies varying in the key system characteristics. It was found that systems with larger relative volatilities met product purity and recovery specifications using a relatively simple
process design, i.e. a reactive distillation column with a reasonable number of stages and reflux ratio. For these systems, the requirement of a single reactive distillation column demonstrated that reactive distillation is an economically attractive Process Intensification (PI) example, compared to the conventional process of a reactor followed by regular distillation columns. For systems with more challenging relative volatilities, e.g. the product is a middle-boiler, then a pre-reactor, and even two additional columns for further purification, may be required depending on the reaction kinetics, demonstrating that the methodology can be applied also in such challenging cases.

It was shown that the system characteristics do impact on the optimal design and operation, and that the extent of the impact depends on the relative contributions from separation performance and from kinetics. Separation performance, in terms of relative volatilities, was found to have a larger effect on the process design (mainly in terms of the required units, the size of the reactive and non-reactive distillation columns etc.), whilst chemical equilibrium was found to have a larger effect on process operation (mainly in terms of required reflux ratio). This observation applies to all the cases considered in this work. It was demonstrated, however, that the combined effects must be considered carefully when designing a reactive distillation process as there are close interactions between the separation performance and the reaction performance. An optimal design map was presented that illustrates the relative contributions of key parameters to the optimal design, in particular, in relation to the number of units required.
Chapter 4. A methodology to evaluate the controllability of reactive distillation

In this chapter, a methodology for how to evaluate the controllability of reactive distillation processes is presented and applied to three different case studies with varying volatilities and kinetics to ascertain the influence of the reaction on the controllability. The control performance is compared to the conventional, non-reactive, equivalents. It is shown that the system with the slower kinetics demonstrates an increased difficulty in rejecting heavy feed flow rate and feed composition disturbances under both one point, V-only, and two point, LV, control configurations. In addition, it is demonstrated that revising the optimal design variables such as the total number of stages is beneficial in terms of controllability depending, however, on whether one- or two-point control is required. Different controller tuning parameters are considered, based on heuristics from literature and optimised, to show that the conclusions drawn are independent of controller parameter tuning methods. Linear MPC is also considered based on a state-space representation of the model, confirming that the system with the slower reaction kinetics is more difficult to control for both a set point change and a load disturbance.
4.1 Introduction

In the previous chapter, it was discussed how the design and operation of a complex reactive distillation superstructure can be simultaneously optimised at steady state to meet given product quality constraints. In this chapter, the dynamic performance and controllability of optimal reactive distillation processes will be considered. Authors who have discussed the controllability of reactive distillation systems have generally only considered the dynamic behaviour and control of specific chemical systems and reactive distillation designs by implementing various control strategies, conventional or advanced, to indicate which technique is the most effective in their specific case. Few authors (Mansouri et al. 2015, Contreras-Zarazúa et al. 2017, Al-Arfaj and Luyben 2000c, Cheng and Yu 2005, Cho and Han 2018 and Georgiadis et al. 2002) have addressed the interaction between the design of the system and the associated control of the process, as presented in Chapter 2.

Literature nevertheless still lacks a systematic procedure for how to consider the interaction of reaction and separation and how this impacts on the controllability of the process, as well as how this interaction can be taken into consideration, both for the steady state design of the process, as well as for the design and implementation of an effective control strategy. This, is therefore the aim of this chapter. The systematic procedure which will be presented and discussed next, will be applied to several case studies and it will be shown that the procedure is able to identify how reaction and separation characteristics, as well as their combination, impact on the controllability of the reactive distillation process, how reaction hinders the control behaviour of the distillation column and how process design can be taken into consideration to improve control performance.

4.2 Methodology

This section describes how controllability analysis was performed in the time domain using gPROMS ProcessBuilder v1.3.1 (Process Systems Enterprise 2020) and MATLAB R2018a (The MathWorks Inc. 2019) on a 3.60 GHz and 32GB RAM Dell Precision 5820 Desktop. The section also includes a description of how the dynamic models were set up in gPROMS ProcessBuilder along with the conventional control schemes configuration, as well as how state-space representation of a linearised model was used in order to consider advanced control strategies in MATLAB. A description of the criteria used for the evaluation of the control responses is also included.
Figure 4.1 presents the methodology with the left-half plane (Steps 1-L8) focusing on the configuration and evaluation of conventional control schemes within gPROMS ProcessBuilder, whilst the right-half plane (Steps 1-R10) focuses on the derivation of the state-space representation and the application of Model Predictive Control on the linear model using both gPROMS ProcessBuilder and MATLAB. The methodology should be repeated when new processes or conventional control schemes are considered and comparison of the performance of conventional and advanced control schemes is also possible when results are generated from both half-planes.

Overall, the methodology presented has the following objectives:

1. Evaluate the impact of separation and reaction on the controllability of the reactive distillation process for both conventional and advanced control strategies by considering case studies with different reaction/separation characteristics.

2. Provide insight into how reaction renders the control of a reactive distillation process more challenging by comparing the dynamic performance of a reactive distillation process to the performance of their non-reactive equivalent process.

3. Evaluate the impact of design parameters (e.g. number of stages, tray liquid holdup) on the controllability of reactive distillation columns.

4. Show that the conclusions drawn are generic, regardless of the method used for the tuning of the conventional PI controllers by either using literature or the optimised tuning parameters using the methodology in this work.
Figure 4.1: Methodology used in this work for the evaluation of controllability using conventional and more advanced control strategies. Left: evaluation of conventional control schemes within gPROMS ProcessBuilder, Right: evaluation of Model Predictive Control on the linear model using both gPROMS ProcessBuilder and MATLAB.
4.2.1 Dynamic model configuration

All the dynamic models used in this work are first configured at steady state in gPROMS ProcessBuilder. For the set-up of the steady state models, the same assumptions hold as presented in Chapter 3.

Once the model is set up in steady state, the model is transformed into dynamic mode. The steps the user has to take in order to complete the transition from steady state to dynamic mode in gPROMS ProcessBuilder are (Steps 1-3 in Figure 4.1):

- Specification of reactive distillation column diameter: In steady state, column diameter is calculated based on the flooding limit of the column (e.g. 80%), however, for the dynamic model to be configured, the user has to specify a column diameter (which can be taken from the steady state simulation) so that the latter is kept fixed during the dynamic simulations (and not varied based on the flooding factor which may vary as a function of time).
- Sizing of reflux drum and sump vessels: For the sizing of the reflux drum and sump of the column, heuristics are used and in this work assuming 5 min of liquid holdup when the vessel is half-full, based on the total liquid entering or leaving the vessel (Luyben 2006).
- Transition from flow-mode to pressure-driven mode: Steady state models are flow-driven simulations in gPROMS ProcessBuilder whilst dynamic models are pressure-driven simulations. In the latter, the pressure in the first and last unit of the process is fixed and flows are calculated based on flow-pressure correlations (i.e. flows are calculated based on the pressure drop between the inlet and outlet pressures).
- Column pressure drop calculation: A linear column pressure profile cannot sufficiently describe column performance, therefore pressure drop needs to be considered properly. In this work a heuristics value of 0.0069 bar/stage (Luyben 2006) is used for initialisation purposes, whilst the actual pressure drop inside the column is calculated by gPROMS ProcessBuilder based on column hydraulics using Bennett’s correlation for clear liquid height calculation and a simple Bernoulli correlation for pressure drop calculation (Process Systems Enterprise 2020).

When dynamic modelling is complete, reflux drum and sump liquid level control loops must be configured otherwise the dynamic model cannot initialise. For these two control
loops, P-only controllers are used as level control does not need to be perfect. When the two liquid level controllers are installed, with the rest of the loops (pressure and quality control) open, the dynamic simulation can run with the remaining system in open loop. The user can then add the remaining control loops (pressure and composition PI controllers) one at a time to ensure smooth operation and good convergence (Step L4).

For the consideration of disturbances required for the evaluation of the controllability of the process, these can be added to the dynamic model next (Step L5). In this work, disturbances were assumed to be sharp ramps instead of step responses, mainly for numerical reasons, but also because this is a more realistic and industrially relevant scenario. More details regarding the controllers (e.g. loop pairing, controller parameters etc.) and disturbances considered (type, direction etc.) are included in Section 4.3.

4.2.2 Closed-loop control performance evaluation

For the evaluation of the performance of control strategies following a disturbance in the system (Step L6 in Figure 4.1), there is a range of criteria used in literature (Stephanopoulos 1984, Luyben and Luyben 1997). In this work, the following metrics will be used as shown in Figure 4.2, which describe the response of the controlled variables following a disturbance in the system.

- **Overshoot** is the maximum amount by which the response differs from the steady state final value, often expressed as a percentage.
- **Settling time** is the time required by the response to reach the final steady state value given a calculation tolerance.
- **Offset** is the error between the final steady state value and the desired set point.

An alternative method to evaluate the control performance of a control configuration is by calculating the error i.e. the deviation from the set point. One error metric often used in controllability investigations is the Integral Absolute Error (IAE). The IAE calculates the sum of areas above and below the set point, and therefore penalises all errors equally regardless of the direction:

\[ IAE = \int_0^{time} |e(t)|dt \quad (Eq. 1) \]

Whilst the control evaluation could have been done based on the IAE rather than by considering overshoot, setting time and offset, we will instead use the IAE criterion for the tuning of the controllers, and the overshoot, settling time and offset to evaluate the control performance (Step L7 in Figure 4.1). More specifically, the tuning parameters of
the PI controllers (excluding the level controllers) will be optimised in order to minimise
the set point deviation, i.e. the product loss defined as the product mass flow that is
below and above the quality specification as shown in Figure 4.3. To evaluate the
benefits of this optimal controller tuning, the controllability evaluation will first take
place using tuning parameters based on literature suggestions or heuristic for all
conventional controllers (Luyben 2006). Then, the evaluation will be repeated using the
optimal parameters found as described above, and the performances will then be
compared and for both situations based on overshoot, settling time and offset (Step L8
in Figure 4.1).
Figure 4.2: Metrics used for control responses evaluation. (Note that the overshoot could also have been above the initial set point and new steady state.)

Figure 4.3: Optimisation of PI controllers tuning parameters based on minimisation of set point deviation (SP: set point).

4.2.3 State-space representation and Model Predictive Control

The following section describes how state-space representation of the reactive distillation model can be performed using a linearised form of the model. The aim of this strategy is to create the state-space model for use as a basis for application of linear Model Predictive Control within MATLAB R2018a (The MathWorks Inc. 2019), i.e. for advanced control.

Reactive distillation can be modelled and represented using mixed sets of non-linear differential and algebraic equations (Process Systems Enterprise 2020). These can be written in the general form (Skogestad and Postlethwaite 2005):

\[ f(x, \dot{x}, y, u) = 0 \quad (Eq. 2) \]
Here $x(t)$ and $y(t)$ are the sets of differential and algebraic variables respectively whilst $\dot{x}(t)$ are the derivatives of $x(t)$ with respect to time, $t$. In addition, $u(t)$ is the set of time-dependent input variables (e.g. reflux ratio). Now consider a desired operating point $(x^*(t), \dot{x}^*(t), y^*(t), u^*(t))$ that satisfies:

$$f(x^*, \dot{x}^*, y^*, u^*) = 0$$  \hspace{1cm} (Eq. 3)

By linearising the model $f$ and therefore the above equations around this operating point, one can obtain a linear expression of the non-linear model of the form:

$$\begin{bmatrix} \frac{\partial f}{\partial x} & \frac{\partial f}{\partial \dot{x}} & \frac{\partial f}{\partial y} & \frac{\partial f}{\partial u} \end{bmatrix} \delta x + \begin{bmatrix} \frac{\partial f}{\partial x} & \frac{\partial f}{\partial \dot{x}} & \frac{\partial f}{\partial y} & \frac{\partial f}{\partial u} \end{bmatrix} \delta \dot{x} + \begin{bmatrix} \frac{\partial f}{\partial x} & \frac{\partial f}{\partial \dot{x}} & \frac{\partial f}{\partial y} & \frac{\partial f}{\partial u} \end{bmatrix} \delta y + \begin{bmatrix} \frac{\partial f}{\partial x} & \frac{\partial f}{\partial \dot{x}} & \frac{\partial f}{\partial y} & \frac{\partial f}{\partial u} \end{bmatrix} \delta u = 0$$  \hspace{1cm} (Eq. 4)

For most differential-algebraic equation (DAE) systems of index 1, the matrix $\begin{bmatrix} \frac{\partial f}{\partial x} & \frac{\partial f}{\partial \dot{x}} \end{bmatrix}$ is non-singular, therefore the above expression can be re-written as follows:

$$\begin{bmatrix} \delta x \\ \delta y \end{bmatrix} = -\begin{bmatrix} \frac{\partial f}{\partial x} \\ \frac{\partial f}{\partial \dot{x}} \\ \frac{\partial f}{\partial y} \\ \frac{\partial f}{\partial u} \end{bmatrix}^{-1} \begin{bmatrix} \frac{\partial f}{\partial x} & \frac{\partial f}{\partial \dot{x}} & \frac{\partial f}{\partial y} & \frac{\partial f}{\partial u} \end{bmatrix} \begin{bmatrix} \delta x \\ \delta y \end{bmatrix}$$  \hspace{1cm} (Eq. 5)

which is a linearised expression of the original non-linear system (Eq. 2).

Using the linearised model $f$, a vector of input variables $U$ (subset of $u$) and a vector of output variables $Y$ (subset of $y$), the state-space representation of the systems is as follows:

$$\dot{X} = AX + BU$$  \hspace{1cm} (Eq. 6)

$$Y = CX + DU$$  \hspace{1cm} (Eq. 7)

where $\dot{X}$ is the vector of state variables that characterise the system and $A$, $B$, $C$, $D$ are real matrices based on the size of the problem. For a distillation column for instance, $\dot{X}$ would be a vector including system states such as component holdups per stage; $U$ would be a vector of the manipulated variables (e.g. condenser and reboiler duties) whilst $Y$ would be a vector of the controlled variables (e.g. pressure, product composition etc.). For a system with $n$ number of states, $i$ number of inputs and $j$ number of outputs then $A=[n \times n]$, $B=[n \times i]$, $C=[j \times n]$ and $D=[j \times i]$. At this point, it is worth stressing that this model should, as long as the system does not deviate too far from the linearised operating point, behave in exactly the same way as the non-linear model (Figure 4.4). As the purpose of control is to keep the system at the set point given by the operating point,
and the system will therefore not be deviating far from this point, the use of a linearised system is in most cases reasonably close to the operating point.

Figure 4.4: Non-linear model is linearised around the operating point. Non-linear and linear models should behave similarly in order for this approximation to be accurate.

Once the state-space representation is obtained (Eq. 6-7), the representation can be used for a number of different applications, including the application of linear Model Predictive Control (MPC). Below is a description of how this procedure can be performed using a combination of simulation tools, in this work, gPROMS ProcessBuilder and MATLAB.

Once the two level control loops are closed in gPROMS ProcessBuilder, and the dynamic simulation can initialise without any additional control loops or disturbances, the input/output variables are selected (Step R4 in Figure 4.1) and the \textit{LINEARISE} task is added in the Scheduling tasks of the gPROMS process. This task, which will be performed once the simulation has reached steady state, linearises the dynamic, non-linear, model at a specific operating point (i.e. steady state in our case) as explained above and in addition, generates the matrices A, B, C and D which characterise the process (Step R5 in Figure 4.1). After the dynamic simulation has completed, the user can access the abovementioned matrices in the results of gPROMS output file and transfer the matrices to MATLAB (Step R6 in Figure 4.1). It is important that within the \textit{LINEARISE} task, the input and output variables are introduced using exactly the same variable paths (names) used for the configuration of the conventional control loops, to ensure consistency between the two control strategies.

After transferring the matrices A, B, C and D to MATLAB, scaling of the input and output variables is sometimes required (Step R7 in Figure 4.1) if the order of magnitude of the variables varies considerably (Skogestad and Postlethwaite 2005). In this work, however,
the magnitude of all manipulated variables and the magnitude of all outputs were not significantly different therefore scaling was not applied. Once the scaling (if any) is complete, the user is ready to generate the state-space representation of the system using matrices A and D and the (updated if scaling is applied) matrices B and C (Step R8 in Figure 4.1).

After the state-space model is generated within MATLAB, the user can (optionally) perform model reduction (Skogestad and Postlethwaite 2005) in order to reduce the number of states (through the generation of fewer, new synthetic states via projection-based methods) which will speed up the subsequent calculations (Step R9 in Figure 4.1). Model reduction is useful when complex models with a large number of states are considered, given that input-output behaviour changes are small. In this work, model reduction was not performed as calculations were found to be very fast even for the full-scale model.

Finally, Model Predictive Control can be applied in the model (Step R10 in Figure 4.1), using the mpcDesigner platform within MATLAB (The MathWorks Inc. 2019). In this platform, the model (f) is imported into mpcDesigner and the plant inputs and outputs can be categorised as manipulated variables, controlled outputs etc. After that, the user can manipulate the type of disturbance introduced (set point change, load disturbance etc.), as well as the tuning parameters of the MPC controller (sample time, prediction horizon, control horizon and variable weights) and directly see the impact of the changes on the performance of the controller. Once the tuning has been completed and the controller shows satisfactory behaviour, the user can export the controller settings only (as a set of parameters), export the overall controlled process (i.e. model, MPC controller and disturbance introduced) as a script for further investigation or to export the controlled process as a Simulink model. In this work, once the controller was properly configured, the script was exported in order to run it in MATLAB and extract the values of the manipulated and controlled variables of each simulation scenario.

In the following, the methodology developed for both conventional and non-conventional control strategies will be applied to a series of case studies, and it will be demonstrated how the methodology can be used to evaluate the controllability, as well as the design, of the reactive distillation system. It might be worth noting that the methodology can easily be extended to also consider other systems, i.e. it is not limited to reactive distillation.
4.3 Case studies

In the previous chapter, a methodology was proposed for how to find the optimal design and operating parameters for a reactive distillation process and this methodology was illustrated using a number of case studies. For consistency purposes, three of those case studies are also used in this work (Case studies 1, 2 and 15 as mentioned in Table 4.1). The controllability of the optimal reactive distillation processes is investigated in order to explore how reaction and separation characteristics impact on the dynamic operation of the process. The case studies consider systems of different separation difficulty, as well as different kinetic characteristics, to identify how these two different phenomena contribute to the overall control performance of the system. For this reason, these three case studies were specifically selected as Case study 1 and Case study 2 have the same relative volatilities but different kinetics whilst Case study 1 and Case study 3 have the same kinetics but different relative volatilities, therefore conclusions can be drawn with regards to the relative impact of each parameter on process controllability.

These three case studies are based on a quaternary system in which the following autocatalysed reversible reaction occurs in the liquid phase:

\[ A + B \rightleftharpoons C + D \]

The kinetic expressions for the forward (f) and backward (b) reaction rates are the following:

\[ r_f = k_{f0} e^{-\frac{E_a f}{RT} C_A C_B} \]
\[ r_b = k_{b0} e^{-\frac{E_a b}{RT} C_C C_D} \]

where reaction rate, \( r \), is expressed in kmol/(m\(^3\)·s); pre-exponential kinetic factors, \( k_{f0} \) and \( k_{b0} \), are expressed in m\(^3\)/(kmol·s); activation energy, \( E_a \), is expressed in kJ/mol (assumed to be 80 kJ/mol for both directions); and component concentration \( C \) is expressed in kmol/m\(^3\). Heat of reaction was assumed to be negligible, thus the activation energy is the same for both reaction directions and \( K_{eq} \) is independent of temperature.

The separation difficulty is defined based on the relative volatilities between the components and for each alternative, fast and/or slower kinetic expressions were investigated. For all case studies, the components were considered of equal density (900 kg/m\(^3\)), equal molecular weight (50 g/mol) and equal boiling point of the heavy reactant, component B (413 K). This boiling point was assumed to be fixed and all other volatilities
were calculated using the heavy reactant as the reference (see Section 3.4 and Appendix D) in order to create the desired relative volatilities. Note that for Case study 3, although the VLE parameters are different compared to Case study 1 and Case study 2, the relative volatility between the products ($\alpha_{CD}$) is the same, equal to 6. Thus, it is the individual separation difficulties that change ($\alpha_{CA}$, $\alpha_{AB}$ etc.) in this case. Fast and slow kinetic characteristics were considered in combination with the relative volatility systems, resulting in the three case studies given in Table 4.1.

Table 4.1: Reaction and separation characteristics for the case studies considered and their optimal design and operational variables. Case study 1 and Case study 2 had the same numbering whilst Case study 3 in this chapter was Case study 15 in the previous chapter.

<table>
<thead>
<tr>
<th>System parameters</th>
<th>Case study 1</th>
<th>Case study 2</th>
<th>Case study 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_{CA}$</td>
<td>2</td>
<td>2</td>
<td>1.2</td>
</tr>
<tr>
<td>$\alpha_{AB}$</td>
<td>1.5</td>
<td>1.5</td>
<td>2.5</td>
</tr>
<tr>
<td>$\alpha_{BD}$</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>$k_f$ (m$^3$/kmol∙s)$</td>
<td>8.41∙10$^6$</td>
<td>2.1∙10$^6$</td>
<td>8.41∙10$^6$</td>
</tr>
<tr>
<td>$K_{eq}$</td>
<td>81</td>
<td>2.25</td>
<td>2.25</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Optimal design and operation variables</th>
<th>Case study 1</th>
<th>Case study 2</th>
<th>Case study 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of stages*</td>
<td>18</td>
<td>25</td>
<td>27</td>
</tr>
<tr>
<td>Light feed (A) stage**</td>
<td>13</td>
<td>19</td>
<td>23</td>
</tr>
<tr>
<td>Heavy feed (B) stage**</td>
<td>12</td>
<td>11</td>
<td>9</td>
</tr>
<tr>
<td>Reflux ratio</td>
<td>2.59</td>
<td>4.65</td>
<td>3.7</td>
</tr>
<tr>
<td>Bottoms flow rate (kmol/hr)</td>
<td>12.6</td>
<td>12.6</td>
<td>12.6</td>
</tr>
<tr>
<td>Reactive zone by stages</td>
<td>2.17</td>
<td>2.24</td>
<td>2.26</td>
</tr>
<tr>
<td>Bottom purity</td>
<td>0.99</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td>Top purity</td>
<td>0.99</td>
<td>0.99</td>
<td>0.99</td>
</tr>
</tbody>
</table>

* Stage 1 is the condenser and stage $N_T$ is the reboiler
** Counted from the top

For the three case studies considered, their conventional, non-reactive, equivalents were also considered in order to investigate the impact of the reaction on the controllability of the reactive distillation columns. This is not straightforward as the reactive case considers four different components, and it would obviously be wrong to only consider components A and B in the non-reactive case. For the non-reactive columns considered in this work therefore all design variables remained exactly the same as described in Table 4.1 (number of stages, feed stages, reflux ratio etc.). This means that the conventional columns may be perhaps overdesigned and, therefore the impact of the introduced disturbances might be smaller than in their optimised alternatives. Their feeds, however, did not consist of pure reactants A and B as in the reactive columns, but
instead of the products that came out of the top and bottom of their reactive equivalent column, i.e. mainly components C and D. For Case study 1, for instance, the reactive distillation column had as top product of 12.5 kmol/hr component C and 0.1 kmol/hr component A. This flow rate and composition is therefore considered to be the light feed for the non-reactive equivalent. Similarly, the bottom product of the reactive column was 12.5 kmol/hr component D and 0.1 kmol/hr component B, therefore this would be the heavy feed for the non-reactive column. Table 4.2 shows the feed flow rates and compositions for both reactive and non-reactive columns for all three case studies. As the comparison between the two systems, reactive and non-reactive, is difficult and may depend on the snapshot used for the non-reactive columns, reverse (in terms of component mole fractions) feed compositions were also considered to confirm the findings. In other words, for the example mentioned above, the reverse feed would consist of 12.5 kmol/hr component B and 0.1 kmol/hr component D and the same would apply to the light feed, as will be explained in Section 4.4. The comparison is not exact of course, but is as close as is possible when one of the systems has a reaction and the other does not.

Table 4.2: Feed input for the reactive distillation case studies as well as their non-reactive equivalents.

<table>
<thead>
<tr>
<th></th>
<th>Reactive Cases 1 and 2</th>
<th>Reactive Case 3</th>
<th>Non-reactive Case 1</th>
<th>Non-reactive Case 2</th>
<th>Non-reactive Case 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light feed</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composition (mol)</td>
<td>100% A</td>
<td>100% A</td>
<td>99.2% C / 0.8% A</td>
<td>99% C / 1% A</td>
<td>98.6% C / 1.4% A</td>
</tr>
<tr>
<td>Flow rate (kmol/hr)</td>
<td>12.6</td>
<td>12.6</td>
<td>12.6</td>
<td>12.6</td>
<td>12.6</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>389.5</td>
<td>381.2</td>
<td>375</td>
<td>375</td>
<td>375</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>1.01325</td>
<td>1.01325</td>
<td>1.01325</td>
<td>1.01325</td>
<td>1.01325</td>
</tr>
<tr>
<td>Heavy feed</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composition (mol)</td>
<td>100% B</td>
<td>100% B</td>
<td>99.2% D / 0.8% B</td>
<td>99% D / 1% B</td>
<td>98.6% D / 1.4% B</td>
</tr>
<tr>
<td>Flow rate (kmol/hr)</td>
<td>12.6</td>
<td>12.6</td>
<td>12.6</td>
<td>12.6</td>
<td>12.6</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>412</td>
<td>412</td>
<td>438</td>
<td>438</td>
<td>438</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>1.01325</td>
<td>1.01325</td>
<td>1.01325</td>
<td>1.01325</td>
<td>1.01325</td>
</tr>
</tbody>
</table>

The feed temperatures were assumed to be at the corresponding boiling points given their composition. In addition, liquid hold-up of all reactive distillation columns was assumed equal for all reactive stages and fixed at 0.1 m³/reactive tray (holdup is specified for reactive columns only in gPROMS ProcessBuilder and not for normal columns). More information on the selected value of liquid holdup can be found in Chapter 3.
**Conventional (decentralised) control schemes**

For the evaluation of the controllability of both the reactive and the non-reactive distillation columns, two conventional control schemes were considered: V-only and LV control (Figure 4.5). These two control schemes were selected as they are commonly used in literature and they are simple to implement in industry. In addition, as in LV control the loops remain the same as in V-only control, with only one additional loop included in the flowsheet, the application of these two control schemes will aid the understanding of process controllability. In both control schemes, the pressure ($P_T$) at the top of the column (stage 2) is controlled using condenser duty ($Q_C$) and the liquid levels of the reflux drum ($M_C$) and the sump ($M_R$) are controlled using distillate ($D$) and bottoms rate ($B$), respectively. In addition, in V-only control scheme, reboiler duty ($Q_R$) is manipulated in order to control bottom product purity (composition of component $D$, $x_{B,D}$). In the LV control scheme, bottom product purity is controlled in the same way as in the V-only scheme and additionally, the top product purity (composition of component $C$, $x_{D,C}$) is controlled by manipulating reflux ratio (RR), expending all degrees of freedom of the system in this case. Table 4.3 summarises the controlled and manipulated variables for each of the two control schemes. Note that the methodology presented is not limited to the control configurations considered in these case studies and could easily be applied also to other control schemes such as DB, (L/D V/B), ratio control etc. Should both product streams be controlled in terms of purity, then feed ratio control is a sensible choice, however, in this investigation it was assumed that only the bottom product (component $D$) is of interest and that any impurity in the top stream (component $C$) will be taken care of in waste-water after-treatment (downstream). For more information on the choice of product of interest and the aqueous nature of component $C$, the reader is directed to Chapter 3 and Appendix C.

Table 4.3: Manipulated-controlled variable pairings for V-only and LV control schemes (see Figure 4.5).

<table>
<thead>
<tr>
<th>Controller</th>
<th>Manipulated</th>
<th>Controlled</th>
<th>Manipulated</th>
<th>Controlled</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCT</td>
<td>$D$</td>
<td>$M_C$</td>
<td>$D$</td>
<td>$M_C$</td>
</tr>
<tr>
<td>LCB</td>
<td>$B$</td>
<td>$M_R$</td>
<td>$B$</td>
<td>$M_R$</td>
</tr>
<tr>
<td>PC</td>
<td>$Q_C$</td>
<td>$P_T$</td>
<td>$Q_C$</td>
<td>$P_T$</td>
</tr>
<tr>
<td>CCB</td>
<td>$Q_R$</td>
<td>$x_{B,D}$</td>
<td>$Q_R$</td>
<td>$x_{B,D}$</td>
</tr>
<tr>
<td>CCT</td>
<td>--</td>
<td>--</td>
<td>RR</td>
<td>$x_{D,C}$</td>
</tr>
</tbody>
</table>
For the two control configurations considered, two different disturbances were introduced to illustrate the methodology: a) a flow rate disturbance in the heavy feed (5% increase), and b) a feed composition disturbance (5% flow increase in heavy feed and in parallel, 5% flow decrease in light feed). Both disturbances were introduced as sharp ramps over 500s. Other disturbances that could have been introduced include, but are not limited to, disturbance in reboiler heating input, disturbance in feed temperature etc.

Overall, the two disturbances were introduced for each control configuration for each reactive distillation case study, as well as for their non-reactive equivalents, i.e. 24 simulations in total (2 disturbances for 2 control configurations for 3 case studies for 2 systems). For consistency, the same disturbances were used for all gPROMS ProcessBuilder simulations, including the revised designs (see later). For the linear MPC investigation, the same feed flow rate disturbance was considered in addition to a set point change (1% step increase in bottom product purity set point, i.e. product purity of 0.99 to product purity of 1), in order to also investigate the efficiency of MPC under set point change as well as load disturbance rejection.
4.4 Results

This section includes the results generated from the application of the methodology developed to the three case studies considered. First, a detailed description of how V-only and LV control works towards a feed flow rate disturbance in a reactive distillation column will be presented (Section 4.4.1), followed by an investigation of the impact of reaction and separation characteristics on control performance (Section 4.4.2). Next, an evaluation of the impact of reaction on the controllability of reactive distillation takes place, comparing the performance of a reactive column and its non-reactive equivalent (Section 4.4.3). This is followed by considering how design parameters, such as total number of stages and reactive tray liquid holdup can impact on control behaviour (Section 4.4.4). Section 4.4.5 investigates the impact of tuning parameters on the conclusions drawn whilst the last section (Section 4.4.6) evaluates the performance of the case studies considered, using advanced control scheme in order to confirm the findings from the previously presented conventional control schemes evaluation.

4.4.1 Impact of disturbances and controlled responses analysis

In this section, the impact of a load disturbance on the behaviour of Case study 2 under V-only and LV control, respectively, will be evaluated and explained. For each control scheme, the responses of the controlled and manipulated variables will be presented (Figure 4.6 and Figure 4.10, respectively), along with figures which will demonstrate how pressure, temperature, vapour and liquid flow rates change within the column through time, after the introduction of the disturbance and until the system reaches the new steady state (Figure 4.7 and Figure 4.11, respectively). Similar figures will be provided to illustrate the changes in reaction rates (in both reaction directions, Figure 4.8 and Figure 4.12, respectively) and composition profiles within the column through time (Figure 4.9 and Figure 4.13, respectively).

V-only control scheme

In order to understand the effect of the introduced disturbances, and the changes that the controlled reactive distillation column undertakes in order to reject them, a detailed analysis is initially performed for Case study 2 and the V-only control configuration, and considering a feed B (heavy reactant) flow rate disturbance (5% increase from steady state value) at \( t = 1.4 \) hrs. The tuning parameters of all controllers in this section were based on literature suggestions as presented in Table 4.4 (Luyben 2006).
Table 4.4: Initial control parameters based on literature tuning (Luyben 2006) (see Figure 4.5).

<table>
<thead>
<tr>
<th>Controller</th>
<th>Gain (Kc)</th>
<th>Integral time constant (τ, min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCT/LCB</td>
<td>2</td>
<td>167</td>
</tr>
<tr>
<td>PC</td>
<td>20</td>
<td>12</td>
</tr>
<tr>
<td>CCB/CCT</td>
<td>3</td>
<td>25</td>
</tr>
</tbody>
</table>

The graphs in Figure 4.6 show the responses of the manipulated (D, B, Q_C and Q_D) and controlled (M_C, M_R, P, x_B,D) variables for each of the four control loops. Top product composition is not shown as this loop is not controlled, however, it decreases as the excess amount of component B is removed as distillate. As can be seen, the impact on the reflux drum liquid level is minimal, but the distillate flow rate must increase (from 0.175 kg/s to 0.185 kg/s) in order to remove the additional component B over the top. The bottoms flow rate returns to the steady state value (0.175 kg/s) after the disturbance has settled in the column (as the amount of component D has not changed as the amount of reactant A has not changed). Pressure at the top of the column is controlled (condenser duty increases from -540.3 kW to -576.2 kW), but similarly to the levels, the impact is minimal and the control is efficient and relatively fast. The bottom product purity is retained at the set point (above 99 mol%), but the reboiler duty must now increase (from 426.9 kW to 463.0 kW) to push the extra component B over the top. This behaviour is expected based on the behaviour a regular distillation column would display, and therefore more information is needed in order to explore what the impact of the disturbance is in the column and how the reactive column manages to reject the disturbance.
Figure 4.6: Closed-loop responses for feed B flow rate disturbance (5% increase). Left axis is controlled variable-solid line and right axis is manipulated variable-dashed line. (Case study 2, V-only control scheme).

Figure 4.7 shows how the pressure, temperature, vapour and liquid mass flow rates, respectively, change in the column over time, and with the disturbance being introduced at $t=1.4$ hrs. As the disturbance hits the column, product purity decreases due to the accumulation of component B at the bottom of the column (Figure 4.6), therefore reboiler duty increases (Figure 4.6) to bring purity back to the set-point value. This leads to a small increase in vapour mass flow rate (Figure 4.7 bottom, left), which has the highest value at stage 2 (where due to condensation of the entering reflux mostly liquid can be found) after which it gradually decreases as vapour tends to concentrate at the top of the column (lighter components in the vapour phase) in contrast to the bottom of the column where the heavier components can be mainly found (in the liquid phase). As a result of the vapour flow rate increase (more intense evaporation), pressure at the top of the column increases (Figure 4.6). As a result, condenser duty increases in order to bring pressure back to the steady-state value, increasing liquid flows (Figure 4.7 bottom, right). In general, liquid flows decrease from the upper to the lower stages of the column as expected due to the vapourisation of the light components whilst Stage 25 has a very low value as this is the stage where the vapour generated in the reboiler goes back into
the column. Once the increased reboiler duty has brought purity back to the set-point (Figure 4.6) leading to a general pressure increase towards the bottom of the column as at the top it is controlled (Figure 4.7 top, left), and to a temperature increase at the top of the column (Figure 4.7 top, right), bottoms flow rate drops to the steady state value (Figure 4.6). In contrast, the distillate rate needs to stabilise at a higher value in order to accommodate the removal of the excess of reactant B (Figure 4.6).

Figure 4.7: Pressure (top, left), temperature (top, right), vapour mass flow rate (bottom, left) and liquid mass flow rate (bottom, right) change due to the introduction of feed B flow rate disturbance (5% increase). (Case study 2, V-only control scheme).
The reaction rates for the forward and backward reactions are given in Figure 4.8 for different times during the run whilst Figure 4.9 shows the concentration profiles in the column initially (dashed lines) and at the new steady state following the disturbance (solid lines). It can be seen that due to the changes in concentrations through the column (Figure 4.9), the reaction rates change as well. The higher concentration of reactant B at the top of the column leads to a shift of its composition profile at the top of the column and a wider composition peak (Figure 4.9) which directly leads to a slight shift in reaction rates (in both directions) towards the top of the column (Figure 4.8). The forward reaction rate is maximised just above feed A stage location (at stage 17), as at this stage the combination of the concentration of both reactants is at its maximum value (this is the first stage when feed B reacts with the large amount of feed A which has just entered the column), leading to a high reaction rate. For the rest of the stages, either feed A or feed B have lower compositions, leading to lower reaction rates and in general, the profile of component A remains almost the same as it is only slightly affected (its mole fraction is slightly reduced) due to the increase of component B flow rate. The final forward reaction rate after the introduction of the disturbance is slightly higher at the top of the column (stages 3 to 7) where the amount of B has increased and reacts with reactant A, as well as just around feed A stage location where again the amount of A is sufficiently high for fast reaction to take place. For the two products of the reaction, the profile of product C has become sharper towards the top of the column since its concentration drops due to the increase in the amount of component B, whilst the profile of component D is almost identical, reflected also in the limited change in temperatures at the bottom of the column (Figure 4.7 (top, right)). At this part of the column, forward reaction rate has slightly shifted to the right (at lower stages in the column) at the new steady state, due to the increased amount of reactant B which reacts with component A at the feed stage location of the latter. The backward reaction is twice as slow as the forward so there are only smaller changes in the column, although it generally follows the same trend as for the forward reaction, with the main rate changes noticed just above feed A stage location. In more detail, there is a drop at stage 18 due to the large amount of feed A which enters the column at stage 17, and since for the backward reaction component A is one of the two products, it shifts the reaction rate to the reverse direction, creating a local minimum.
Figure 4.8: Reaction rate (forward-top and backward-bottom) change due to the introduction of feed B flow rate disturbance (5% increase). Stages 1 (condenser) and 25 (reboiler) are not considered reactive, therefore reactive stages only are shown. (Case study 2, V-only control scheme).
Figure 4.9: Composition profiles change due to feed B flow rate disturbance (5% increase).
Initial: steady state value before the introduction of the disturbance, Final: new steady state value after the disturbance has settled in the column. (Case study 2, V-only control scheme).

**LV control scheme**

The same investigation was repeated for the LV control configuration for the same case study and considering the same disturbance in order to investigate the differences in the responses under the two different control schemes. The tuning parameters of all controllers in this section were again based on literature suggestions as presented in Table 4.4 (Luyben 2006).

The graphs in Figure 4.10 show the responses of the manipulated (D, B, Q_c, Q_D, and RR) and controlled (M_C, M_b, P, x_b,D and x_D,C) variables for each of the five control loops. As can be seen, the level responses are similar to for V-only control. Oscillations observed in the control responses are due to the tuning of the controllers, which at this stage was based on literature suggestions (Luyben 2006). Pressure at the top of the column is controlled (as condenser duty changes from -540.3 kW to -1114.9 kW), but similarly to the levels, the impact is minimal and the control is efficient and relatively fast. The bottom product purity is retained at the set point (above 99 mol%), but the reboiler duty must increase (from 426.9 kW to 1003.7 kW) to remove component B over the top. Top product purity cannot be maintained (as its final value is 0.945) and reflux ratio reaches its upper bound (RR=10). Simulations with relaxed upper bounds (i.e. reflux ratio up to 150) were performed (results not shown) and confirmed that the system cannot meet the top
product purity set-point regardless of the upper bound of reflux ratio, as it is impossible for the system to maintain both product purities due to the additional amount of component B which has to be removed from the top. The system is able to control bottom, and not top, product purity as the reboiler heat duty (vapour dynamics) exhibits quicker dynamics than the reflux ratio (liquid dynamics) (Stewart 1981). For this case study, the disturbance introduced in the LV control scheme is rejected with more difficulty than in the V-only control scheme, as shown by the changes that the manipulated variables have to undertake, which is expected since the LV control scheme is aiming to control both ends of the column and therefore introduces more interactions between the top and the bottom of the column, leading to higher overshoot and larger settling times. This difficulty of LV control is also attributed to the nature of the disturbance, for which maintaining both product purities is impossible. For a different type of disturbance (e.g. reboiler heat input failure), meeting both product purities could still be possible. The control behaviour discussed so far is again expected so further analysis is required.
Figure 4.10: Closed-loop responses for feed B flow rate disturbance (5% increase). Left axis is controlled variable-solid line and right axis is manipulated variable-dashed line. (Case study 2, LV control scheme).
Figure 4.11 shows how the pressure, temperature, vapour and liquid mass flow rates change in the column over time in order to aid the understanding of the impact of the disturbance, introduced at t=1.4 hrs. As the disturbance hits the column, the behaviour of the system is similar to the behaviour when V-only control is applied. In more detail, the change in feed B flow rate leads to a decrease in bottom product purity, which in turn leads to an increase in reboiler duty (Figure 4.10). The significantly increased vapour flows (Figure 4.11 bottom, left) due to the increased reboiler duty, lead to a pressure increase at the top (Figure 4.10) which triggers an increase in condenser duty (Figure 4.10), in order to bring pressure back to the steady-state value. At the same time, the decrease in top product purity leads to an increase in reflux ratio (Figure 4.10), which in turn leads to a significant increase in liquid flow rates (Figure 4.11 bottom, right). The increased reboiler duty, which brings bottom product purity back to the set-point (Figure 4.10) after a while, leads to a general pressure increase towards the bottom of the column as at the top pressure is controlled (Figure 4.11 top, left), and to a significant temperature increase at the top of the column (Figure 4.11 top, right). This shows that in general, the feed flow rate disturbance leads to a temperature increase in the entire column. This observation is different between the two control schemes. In V-only, temperature was maintained at the bottom of the column whilst under LV control, temperature increases in the entire column due to the dual-point control. As the bottom product purity has returned to the steady-state value, bottom flow rate returns to the set-point (Figure 4.10). In contrast, the distillate rate needs to stabilise at a higher value in order to accommodate the removal of the excess of reactant B (Figure 4.10) although this leads to violating top product purity specification (Figure 4.10).
Figure 4.11: Pressure (top, left), temperature (top, right), vapour mass flow rate (bottom, left) and liquid mass flow rate (bottom, right) change due to the introduction of feed B flow rate disturbance (5% increase). (Case study 2, LV control scheme).
The reaction rates for the forward and backward reactions are given in Figure 4.12 for different times during the run whilst Figure 4.13 shows the concentration profiles in the column initially and at the new steady state following the disturbance. It can be seen that due to the changes in concentrations through the column (Figure 4.13) caused by the increased reboiler duty and the excess of component B, reaction rates change as well. The forward reaction rate is maximised just above feed A stage location (at stage 18), as at this stage the combination of the concentration of both reactants is at its maximum value (this is the first stage when feed B reacts with the large amount of feed A which has just entered the column), leading to a high reaction rate. For the rest of the stages, either feed A or feed B have lower compositions, leading to lower reaction rates. The final forward reaction rate after the introduction of the disturbance is higher at the top of the column (stages 2 to 7 where the amount of B has increased and reacts with reactant A) as well as just around feed A stage location where again the amount of A is sufficiently high for fast reaction to take place, in combination with the higher reflux ratio. Due to the increase of the amount of component B, the mole fraction of component A decreases through the column and the profile of product C becomes sharper towards the top of the column since its concentration drops. As an overall comment, the peak in forward reaction rate has shifted to the right (at lower stages in the column) at the new steady state, more significantly compared to V-only control, due to the more significant temperature change (Figure 4.11 top, right). This is reflected to the shift of component D composition profile towards the bottom of the column due to the enhanced separation task (reboiler duty increase), however, its maximum value has also increased due to the increased reflux ratio which improves reaction rate. The backward reaction, slower than the forward, follows a different trend and the final backward reaction rate does not have a local minimum, and the maximum rate has shifted to the left due to concentration changes (shift in component B profile) and the higher reflux ratio.

Comparison

Overall, V-only control was found successful towards the disturbance introduced whilst the responses for dual-point control, caused by an increased reflux ratio which subsequently led to changes in the other manipulated variables, are more significant in the LV controlled system, in terms of manipulated variables changes, settling times and overshoot. Also, pressure, temperature, vapour and liquid flow rates have higher values after the introduction of the feed flow rate disturbance under LV control. The impact of
the disturbance on reaction rates was also more visible (profile shift, maximum values), and the column temperature and composition profiles changed more significantly, under LV control. This is of course expected as both ends of the column are now controlled, although it is noted that the distillate composition specification cannot be reached at the top of the column. As already mentioned, the nature of the disturbance (imbalance of feed flow rates which results in incomplete conversion of reactant B) is expected to have had an impact on the performance of LV control. It is therefore expected that for other types of disturbances, LV control would be sufficient.

Figure 4.12: Reaction rate (forward-top and backward-bottom) change due to the introduction of feed B flow rate disturbance (5% increase).
Stages 1 (condenser) and 25 (reboiler) are not considered reactive, therefore reactive stages only are shown. (Case study 2, LV control scheme).
4.4.2 Impact of reaction and separation on controllability

In this section, the impact of reaction and separation characteristics on the controllability of reactive distillation will be evaluated, based on the control performance (with regards to pressure and product purities) of the three case studies considered, under LV control and towards feed flow rate and feed composition disturbances (Figure 4.14). The responses presented in the previous section indicate that the behaviour of the process is more complex when LV control is considered, therefore further investigation of it is required and this is why the latter was selected for the analysis of this section as well, instead of V-only control.

Figure 4.14 shows a number of control variables responses towards the disturbances introduced for the three reactive columns under LV control. All responses are shown as % difference from their steady state value to allow for easier comparison between the case studies. Figure 4.14 (top) shows the pressure response for the LV control scheme following a feed flow rate (5% Feed B increase) and feed composition disturbance (5% Feed B increase and simultaneously, 5% Feed A decrease) at t=1.4 hrs, for all three case studies. For the feed flow rate disturbance, it can be seen that all case studies have similar responses in terms of settling time (approximately 5.92 hrs), and that this settling time is quite long. Case study 1 (easy separation, fast kinetics) and Case study 3 (difficult
separation, fast kinetics) have an overshoot of approximately 0.07% in pressure whilst Case study 2 (easy separation, slower kinetics) has a slightly higher overshoot of about 0.1%. For the feed composition disturbance (right), it can be seen that the three systems have similar response in terms of settling time (3.26 hrs). Case study 2 (easy separation, slower kinetics) has a slightly higher overshoot (0.23%), whilst Case study 1 (easy separation, fast kinetics) and Case study 3 (difficult separation, fast kinetics) show more similar behaviour in terms of overshoot (0.20% and 0.18%, respectively). Pressure is maintained for all case studies, and as a PI controller is used, there is no offset observed.

Figure 4.14: Response to feed flow rate disturbance (5% Feed B increase) (left) and feed composition disturbance (5% Feed B increase and 5% Feed A decrease) (right) for all case studies. Top: pressure; Middle: Bottom product purity; Bottom: Top product purity. (LV control scheme).
Figure 4.14 (middle) shows the bottom product purity response. For the feed flow rate disturbance and for the LV control scheme, Case study 1 (easy separation, fast kinetics) and Case study 3 (difficult separation, fast kinetics) have similar responses in terms of settling time (6.61 hrs) and very small overshoot (-0.5%). Case study 2 (easy separation, slower kinetics) has a shorter settling time (5.06 hrs) but a slightly higher overshoot (-0.7%). For the feed composition disturbance, the response is similar in terms of settling times (3.86 hrs) for all case studies. Case study 2 (easy separation, slower kinetics) has a slightly increased overshoot (loss of off-spec product) with a value of -1.44%. Again, no offset is observed as a PI controller was used.

Figure 4.14 (bottom) shows the top product purity response for the LV control scheme. It can be seen that none of the systems considered are able to maintain the top product purity using two-point control for either of the two disturbances. This is because the dynamics of the reboiler are faster than the dynamics of the top product purity control loop, therefore the increase of the reboiler duty cannot be compensated by the required increase in reflux ratio to meet top product purity specification, leading to the additional reactant B being removed from the top of the column. Also, given that bottom purity is controlled and mass balances must be respected, top purity cannot be maintained as the excess of (unreacted) component B needs to be removed from the top of the column. In this case, an additional column would be needed to mitigate this disturbance, such that product C can be separated in the additional column and the remaining feed can be recycled back to the reactive column. Again, Case study 2 (easy separation, slower kinetics) shows a slightly worst control performance in terms of offset, although all case studies are unable to maintain the distillate composition.

From Figure 4.14 it is found that Case study 2 (easy separation, slow kinetics) has slightly worst responses (in terms of settling time and/or overshoot/offset) compared to Case study 1 (easy separation, fast kinetics) and Case study 3 (difficult separation, fast kinetics) which indicates that for dynamic operation and process control, kinetics may have a more dominant impact compared to relative volatilities, although the impact is quite modest. Also, the similar behaviour of Case study 1 and Case study 3 shows that although the two processes have different designs, the fact that they have the same kinetics mainly determines their similar behaviour. This contrasts with steady state operation where it was shown that relative volatilities have a stronger impact on design and operation (see Chapter 3). However, for all case studies, the responses do not show any
major difference which indicates that the impact of reaction kinetics and separation characteristics on control performance, although existing, is limited.

4.4.3 Impact of reaction on the controllability of the process

This section investigates how the existence of reaction impacts on the controllability of reactive distillation by comparing the performance of the reactive column of Case study 1 with its conventional, non-reactive, equivalent. The responses of the controlled variables (pressure and product purities) for each column will be presented in Figure 4.15. Recall that the feed streams considered are not exactly the same, i.e. for the reactive system the feed is the reactants, i.e. components A and B, whilst for the non-reactive system the light and heavy feeds (which at t=1.4 hrs change according to the expected heavy feed flow rate and feed composition disturbance) are considered to be the respective distillate and bottoms streams from the reactive system. The comparison is therefore not entirely accurate, but is as close as it is possible for two such different systems. Also, by comparing these two column alternatives, it is recognised that the difference between the two columns is investigated more from the separation, rather than the reaction perspective. It would be possible to investigate the impact of reaction by considering the reactive column more as a reactor (e.g. by letting each stage to reach chemical equilibrium), however, this was not considered in this work.

Figure 4.15 (top) shows the pressure response for the two systems of Case study 1 for both disturbances and under LV control scheme. Pressure change of the conventional system of Case study 1 is negligible whilst for the reactive system (easy separation, fast kinetics), reaction introduces a large settling time (approximately 5.3 hrs for feed flow rate and 3.6 hrs for feed composition disturbance) but only a minor overshoot of 0.07% and 0.19%, respectively. It can also be seen that for the feed flow rate disturbance, pressure remains steady at the overshoot value until t=6.4 hrs when it sharply drops to the set point. This behaviour is because the manipulated variables (reboiler and condenser duties) interact and their rate of change counteract until they stabilise to their new steady state values thus, affecting the control responses. Oscillations are also observed for the reactive system at the start of the feed flow rate disturbance due to the tuning of the pressure controller. It is also shown that for the feed composition disturbance, the two processes have a reverse control action which is reasonable due to the difference in feeds for the two columns. More specifically, in the conventional non-reactive column, feed composition change (increase of heavy feed-component D and
simultaneous decrease of light feed-component C) leads to an initial decrease of pressure, due to the decrease of the amount of product C. However, for the reactive column, the heavy feed consists of component B, therefore feed composition change increases pressure due to the increased evaporated amount of component B. This behaviour should be taken into consideration when catalyst ageing/deactivation is expected, therefore reaction kinetics become slower potentially leading to difference in the expected control action or even reverse action if catalyst completely deactivates.

Figure 4.15 (middle) shows the bottom product purity response of both systems of Case study 1 towards both disturbances for the LV control scheme. The conventional system has a short settling time (1.86 hrs) as well as a very low overshoot (0.2%) for the feed composition disturbance. The reactive system, however, has a larger settling time (3.36 hrs) and a slightly larger overshoot (-1.34%) showing that again, reaction hinders the controllability of the process. The same behaviour is observed for the feed flow rate disturbance as well (i.e. reactive system has larger overshoot and settling time). It is also shown that the two processes in this case have a reverse control action which is reasonable due to the difference in feeds for the two columns. More specifically, in the conventional non-reactive column, feed composition change (increase of heavy feed-component D and simultaneous decrease of light feed-component C) leads to an initial increase of bottom product purity, due to the increase of the amount of product D. However, for the reactive column, the heavy feed consists of component B, therefore feed composition change has a negative impact on bottom product purity.

Figure 4.15 (bottom) shows the top product purity response of both systems of Case study 1 towards both disturbances for the LV control scheme. With regards to the top product purity response, the conventional column shows a very short settling time, a very low overshoot and no offset, i.e. the column maintains both top and bottom product purities for both disturbances. However, the reactive column is not able to maintain product purity after a feed flow rate disturbance as it shows an offset of approximately -4%, a settling time of 6.6 hrs and an overshoot of -1% whilst for a feed composition disturbance it shows an offset of approximately -8%, a settling time of 4.36 hrs and an overshoot of -2%.
Figure 4.15: Response to feed flow rate disturbance (5% increase) (left) and feed composition disturbance (5% Feed B increase and 5% Feed A decrease) (right) for the reactive distillation column and its conventional equivalent. Top: pressure; Middle: Bottom product purity; Bottom: Top product purity. (Case study 1, LV control scheme).
To confirm these findings, the same simulations were repeated but this time, the feed composition of the conventional column was altered such that the main component of each feed stream was a reactant (light feed consists of 99.2% A and 0.08% C rather than 99.2% C and 0.08% A, and heavy feed consists of 99.2% B and 0.08% D rather than 99.2% D and 0.08% B). The investigation confirms that even with the alternative feed composition, the existence of reaction hinders controllability as explained above (detailed results not shown). This is due to the complex interactions between vapour-liquid equilibria and reaction kinetics as in case reaction is present, in addition to the VLE (i.e. distribution of components in liquid/vapour phase), components are generated which need to be evaporated (increasing heating demand) or remain in the liquid phase (increasing cooling/reflux demand), based on their boiling points. Also, in a regular distillation column, temperature interacts with composition only, however, this is not the case for reactive distillation where temperature additionally impacts on reaction rates.

It has therefore been shown that the impact of reaction on the controllability of a reactive distillation column is significant. The conventional non-reactive column is able to reject a feed flow and feed composition disturbance and maintain both product purities. The reactive column, on the other hand, is able to maintain only one of the two purities. It should be noted that this finding is based on our comparison of a binary distillation system with a two-reactant/two-product reactive system and to the control configurations considered, and may not be general, however, nevertheless significant.

4.4.4 Impact of design considerations

As mentioned in Section 2.5, the number of stages and the reactive tray liquid holdup have been found to impact on the controllability of the column (Al-Arfaj and Luyben 2000c). The impact of increasing the total number of stages, as well as of changing the reactive tray liquid holdup on the control performance of the reactive distillation column, will therefore be investigated in this section as follows: a) the base case total number of stages as found during optimisation (i.e. the minimum required to achieve the specified level of reaction/separation); and b) the tray liquid holdup (which was fixed during optimisation). As mentioned already, the focus of this section is on bottom product purity only as this is often the main product industrially (see Chapter 3 and Appendix C for more details) and it has already been shown that liquid levels and pressure are sufficiently controlled using the control schemes considered. As a result, in the following,
the impact of design variables on product purity control performance will be considered for both disturbances and under both control schemes (Figure 4.16 for total number of stages and Figure 4.17 for liquid holdup).

**Impact of total number of stages**

For Case study 1, the impact of increasing the number of stages on the controllability of the process was investigated. This parameter was investigated since by increasing the optimal number of stages (found during optimisation) the overall cost is not significantly affected (see Chapter 3) and tolerance to failures due to inadequate separation and/or reaction is expected to improve. Adding a number of additional trays is a common strategy in conventional distillation to mitigate failures and it is therefore interesting to investigate whether adding a number of stages improves dynamic performance as well.

Figure 4.16 shows the bottom product purity response under V-only (Figure 4.16a) and LV (Figure 4.16b) control scheme, for the reactive distillation column. The responses are shown towards both disturbances for the base case total number of stages as well as for an additional two and four stages (added evenly in the stripping and rectifying section), respectively, for Case study 1. From Figure 4.16a it is shown that under V-only control, increasing the total number of stages deteriorates the performance in terms of settling time for the reactive column. This is sensible as increasing the number of stages and, therefore the overall liquid holdup, leads to longer response times, delaying control action (given that control takes place only at the bottom of the column and, therefore there is no parallel action at the top to reduce settling time) and therefore increasing overshoot as well. Oscillations observed in all responses are due to controllers tuning parameters which were initially literature-based as explained earlier. For the LV control scheme (Figure 4.16b) and for both disturbances, the responses of the reactive column are very similar, unlike V-only control where responses are different, and the base case design is only slightly better in terms of settling time. This is reasonable since increasing the number of stages, although leading to control loop decoupling, introduces some delays in responses which are, however, minimal as there is parallel control action at both column ends. Overall, it is shown that the impact of total number of stages is more significant under V-only control for the reactive column.
Figure 4.16: Bottom product purity response to feed flow rate (left) and feed composition (right) disturbance for revised number of stages of reactive column (Case study 1, a) V-only control scheme; b) LV control scheme).
Impact of liquid holdup

Similarly, the impact of increasing liquid holdup (practically this would mean an increase in tray weir height and/or column diameter) on the controllability of the process is investigated. A 20% and 50% increase of the base case value (0.1 m$^3$/reactive tray) was considered. Case study 2 was considered this time, as it included slower kinetics, which are more dependent on tray liquid holdup in terms of reaction residence time. It is expected that increased holdup will increase pressure drop across the column, however, the focus of this section is the impact of the holdup on the controllability of the process so the impact on column hydraulics is not considered in further detail.

Figure 4.17a shows the response of bottom product under V-only control scheme whilst Figure 4.17b shows the same response, under LV control scheme. For the V-only control scheme (Figure 4.17a), it was found that an increase of liquid holdup may deteriorate control performance. This is sensible as increasing liquid holdup, leads to longer response times, delaying control action (i.e. reboiler duty increase to evaporate the excess of component B, given that control takes place only at the bottom of the column and, therefore there is no parallel action at the top to reduce settling time) and therefore increasing overshoot as well. This observation is in agreement with the previous investigation, where the overall liquid holdup was increased through the addition of reactive stages in the column. From Figure 17b, it can be seen that increasing the liquid holdup (especially for feed flow rate disturbance) improves overshoot slightly, given that control action takes place at both ends, therefore the manipulation of reflux ratio and reboiler duty reduce overshoot for bottom product purity control as they both increase separation performance. Increasing tray liquid holdup, however, increases settling times in all responses, due to the larger liquid flows and, therefore larger response times. However, the responses are fairly similar, given that control action takes place at both ends, therefore the manipulation of reflux ratio and reboiler duty reduce settling times for bottom product purity control as they both increase separation performance. In order to investigate whether lower holdup is, in general, easier to control, the same simulations were performed for Case study 2, using lower values of liquid holdup (up to 0.07 m$^3$/reactive tray), however, the results (not shown) were fairly similar to the base case results, indicating that the behaviour does not stem from the value of holdup, but from the system characteristics.
Comparison
Overall, when V-only control scheme is considered, the initial optimal design responds better to feed flow rate and feed composition disturbances as increasing the overall holdup (i.e. reaction residence time, through adding more stages or increasing the holdup per stage) leads to slower responses and larger overshoot. When both product purities need to be controlled, however (e.g. LV control scheme is applied), adding a number of additional stages and/or increasing tray liquid holdup may be beneficial for the controllability of the column, mainly in terms of overshoot.

Figure 4.17: Bottom product purity response to feed flow rate (left) and feed composition (right) disturbance for revised reactive tray liquid holdup (Case study 2, V-only (a) and LV (b) control scheme).

4.4.5 Impact of tuning parameters of controllers
This section will provide insight into whether the conclusions drawn so far depend on the choice of tuning parameters for the controllers. The improvement in bottom product purity control due to the optimisation of controllers’ tuning parameters will be indicatively shown for Case study 1 (Figure 4.18). In addition, the findings of the previous sections with regards to the impact of reaction kinetics and reaction in general (Figure
(4.19) on control performance using literature parameters, will be cross-checked using the optimised parameters and illustrated for pressure and bottom product purity control, respectively.

As the tuning parameters considered so far were based on literature suggestions, a number of simulations was performed using optimised tuning parameters for all PI controllers (not level controllers as levels are not tightly controlled), using as a criterion the minimisation of the off-spec amount as described earlier. The optimised tuning parameters, as found for the case studies and disturbances considered in this section, are presented in Table 4.5. Figure 4.18 shows how the control responses can be improved, using as an example bottom product purity response to a feed flow rate disturbance for Case study 1 under LV control configuration. The settling time was reduced from 6.26 hrs to 2.86 hrs and the overshoot decreased from -0.52% to -0.48%. However, the improved controller was also more aggressive and introduced some oscillations in the control behaviour. Next, a couple of results are repeated to show that the conclusions drawn so far are independent of the controller tuning parameters.

Table 4.5: Optimised control parameters based on off-spec product loss minimisation tuning (see Figure 4.5).

<table>
<thead>
<tr>
<th>System</th>
<th>Case study 1</th>
<th>Case study 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reactive</td>
<td>Conventional</td>
</tr>
<tr>
<td>Parameter</td>
<td>Kc</td>
<td>τ (min)</td>
</tr>
<tr>
<td>PC</td>
<td>33.27</td>
<td>6.72</td>
</tr>
<tr>
<td>CCB</td>
<td>4.13</td>
<td>9.08</td>
</tr>
<tr>
<td>CCT</td>
<td>3.88</td>
<td>9.11</td>
</tr>
</tbody>
</table>
In an effort to confirm that slower kinetics impact on control performance, regardless of tuning parameters, Figure 4.19 (top) shows the pressure responses for Case study 1 and Case study 2 towards a feed composition disturbance under LV control scheme. It is shown that the settling time of Case study 1 (easy separation, fast kinetics) is 1.86 hrs and the overshoot is almost 0.12% whilst for Case study 2 (easy separation, slower kinetics) settling time is 2.36 hrs and overshoot is almost 0.4%. As a result, by using the optimised tuning parameters, the conclusion that slower kinetics hinder reactive distillation process controllability still holds.

In addition, in order to validate the fact that reaction impacts negatively on the control performance of the column, regardless of the tuning parameters, Figure 4.19 (bottom) shows the bottom product purity responses of both the reactive and its conventional non-reactive column for a feed composition disturbance for Case study 1, under LV control scheme using the optimised controllers tuning parameters. The figure shows that the response of the reactive column is worse in terms of settling time and overshoot, comparing to the response of the conventional system. This agrees with the behaviour observed using the literature tuning parameters. Overall, from this investigation it was shown that the behaviours observed and the conclusions drawn so far are independent of the method used for the tuning of the controllers.
Figure 4.19: Control responses to feed composition disturbance using optimised tuning parameters as shown in Table 4.5 (LV control scheme). Pressure response is shown for Case study 1 and Case study 2 whilst bottom product purity response is shown for the reactive distillation column of Case study 1 and its conventional equivalent.
4.4.6 Linear MPC results

In this section, the performance of linear MPC will be evaluated and compared to the conventional control schemes applied so far, indicatively for Case study 1 (Figure 4.20). In addition, the control behaviour for the three case studies will be evaluated using MPC and considering a bottom product purity set-point change (Figure 4.21) and load disturbance (Figure 4.22) in order to investigate whether the abovementioned findings with regards to the impact of reaction kinetics on the controllability of the reactive distillation column are valid, even when advanced control is considered.

For all case studies, the non-linear dynamic models were linearised in gPROMS ProcessBuilder and following the procedure described previously, the state-space representation was generated and an MPC controller was designed in MATLAB using the mpcDesigner tool. The condenser and reboiler duties were considered manipulated variables and the remaining three inputs (both feed flow rates and reflux ratio) were considered measured disturbances. In addition, pressure and bottom product purity were considered measured outputs whilst top product purity was considered an unmeasured output. This decision was made since it was previously (from the conventional scheme simulations) shown that the reactive column cannot maintain both product purities, at least not for the cases considered in this work. It was therefore decided that the MPC would have two control goals, maintain pressure at the top of the column and bottom product purity, instead of three. Testing this decision and adding a third control goal in the MPC scheme led indeed to unsuccessful control for both product purities.

For all case studies, the same tuning parameters were used: a sample time of 30 s, a prediction horizon of 120 s and a control horizon of 30 s and these parameters were found to work well for all the systems. The sample time was chosen based on the desired closed-loop response. In addition, usually, the prediction horizon is selected to be longer than the control horizon as then the control system is less sensitive to model error. Also, the weights of the variables (i.e. factors which penalise deviations from the relevant target values) were kept at their default values and instead, a beta parameter which is related to how aggressive or closed-loop stable the controller is was manipulated. This beta parameter adjusts all weights in order to make the controller more or less aggressive. In more detail, as the beta parameter increases, the weights of manipulated and controlled variables (i.e. set-point tracking) increase whilst the manipulated
variables increment suppression decreases. In this work, a beta parameter of approximately 2.23 was chosen, which would mean that in the controller’s objective function, the manipulated variables increment suppression would be halved whilst the output variable tracking would be twice as important, in order to penalise any significant deviation from the product quality specification. In the mpcDesigner platform, the user can manipulate the value of the beta parameter through the relevant tuning sliding bar thus in this work the bar was fixed just above 2, which was the desired point.

First, for Case study 1, the performance of the conventional control scheme versus the performance of the MPC for a feed B flow rate disturbance (5% increase) was evaluated and shown in Figure 4.20. It is shown that the MPC not only reduces the settling time and eliminates the oscillations observed for the conventional control scheme but it also reduces the overshoot of the bottom product purity, therefore improves the response significantly.

![Figure 4.20](image)

Figure 4.20: Difference in bottom product purity response to feed flow rate disturbance using conventional V-only control scheme (solid line) and linear MPC (dashed line).

Next, the performance of all case studies using MPC was evaluated, towards two different disturbances: a) a set point change in bottom product purity (1% increase) and b) a feed B flow rate disturbance (5% as considered so far).

Figure 4.21 shows the control performance of MPC for all case studies towards the bottom product purity set point change. From Figure 4.21 (top) it is shown that all systems are able to follow the set point change. Case study 1 (easy separation, fast kinetics) and Case study 3 (difficult separation, fast kinetics) meet the new bottom product purity set point faster (approximately 3 hrs) whilst Case study 2 has a larger settling time (5.6 hrs). This is also expected by looking at the behaviour of reboiler duty...
(Figure 4.21, bottom). For Case study 1 and Case study 3, reboiler duty quickly reaches a new steady state value (after about 3 hrs), however, this is not the case for Case study 2, where reboiler duty shows oscillations and instability, in fact requiring approximately 55 hrs before it finally stabilises, therefore leading to larger settling times for the control variables (condenser duty has similar behaviour, not shown). Increasing the beta parameter for Case study 2, keeping the rest of tuning parameters (i.e. sample time, prediction and control horizons as they did not significantly improve the performance) the same, to a value of approximately 4.57 (i.e. making the controller more aggressive), reduces the settling time to approximately 39 hrs. This indicates that even with improved controller settings (variable weights), Case study 2 requires more time to reach the new steady state, due to the slower kinetics, as observed and discussed in Section 4.4.2 for the conventional control schemes as well. The unstable behaviour of Case study 2 may indicate a potential state transition (i.e. multiple steady states), which should be investigated further in a separate investigation.

Figure 4.21: Control performance of MPC for all case studies towards bottom product purity set point change. Bottom product purity response and reboiler duty are presented from top to bottom, respectively. Left figures show full time scale whilst figures on the right focus on the period when Case study 1 and Case study 3 manage to reach steady state, unlike Case study 2.
Figure 4.22 shows the control performance of MPC for all case studies towards the feed B flow rate disturbance. From Figure 4.22 it can be seen that Case study 2 (easy separation, slow kinetics) shows difficulty in rejecting the load disturbance introduced. Case study 1 (easy separation, fast kinetics) and Case study 3 (difficult separation, fast kinetics) show successful rejection of feed B flow rate increase and the manipulated variables settle to the new set points within 1.7 hr. However, this is not the case for Case study 2 where slow responses are observed for bottom product purity (35 hrs approximately) and pressure (33 hrs approximately), and instability is observed for condenser duty as it needs almost 55 hrs before it finally stabilises (reboiler duty has similar behaviour, not shown). A comment needs to be made regarding pressure response. Case studies 1 and 3 show an increase in pressure before dropping it back to its set point. However, for Case study 2, a decrease in pressure is observed (reverse behaviour), from which the system shows difficulty to recover. This is due to the unstable behaviour of the controller, as both condenser and reboiler duties show an aggressive increase (absolute increase for condenser duty) which cannot be easily stabilised, suggesting that, again, the tuning of the MPC for Case study 2 would need revision (e.g. change of variable weights) in order to be more stable and successfully reject faster the changes introduced. As a result, it is shown that the same tuning which leads to a successful control strategy (MPC) for Case study 1 and Case study 3 (fast kinetics), is not sufficient for the control of Case study 2 (slower kinetics) which requires more careful tuning, and further investigation with regards to the possibility of state transition.
Figure 4.22: Control performance of MPC for all case studies towards feed B flow rate disturbance. Bottom product purity, pressure and condenser duty are presented from top to bottom, respectively. Left figures show full time scale whilst figures on the right focus on the period when Case study 1 and Case study 3 manage to reach steady state, unlike Case study 2.
4.5 Conclusions

In this chapter, a methodology for how to evaluate the controllability of reactive distillation processes has been presented and applied to three different case studies with varying difficulty of separation in terms of volatilities, and reaction characteristics in terms of kinetics. The conclusions are, therefore drawn based on the analysis of the three case studies considered and for them to be generalised, further work would be required. It was overall demonstrated that for conventional control schemes, kinetics is a more determinant factor compared to relative volatilities in terms of deciding the controlled performance. This is in contrast to findings for steady state design and operation, as slower kinetics had a negative, although limited, impact on dynamic control responses.

The impact of reaction on the controllability of reactive distillation columns was also investigated by comparing the behaviour of the reactive columns to that of their non-reactive counterparts. Under the same disturbances and the same control configurations, the existence of reaction introduced larger settling times and larger overshoot. The most important difference was that for the reactive distillation column, maintaining both product purities was infeasible unlike the conventional column. The importance of design variables on the controllability of reactive distillation was also investigated by considering increasing the total number of stages and the tray liquid holdup. The benefits of the increases in terms of controlled variables settling time, overshoot and offset depended, however, on the type of conventional control strategy.

Different tuning methods were also considered, one based on heuristics from literature and the other by optimising the control parameters based on the minimization of the loss of off-spec bottom product, and although the controller performance was improved, the impact of the reaction was the same. Finally, linear MPC was considered and it was demonstrated how linear MPC improves the control performance comparing to the conventional control schemes, as well as confirmed the findings regarding the impact of reaction and separation on reactive distillation controllability.
Chapter 5. A methodology to evaluate the impact of uncertainty on reactive distillation systems

This chapter presents a general methodology to systematically investigate the impact of uncertainty on the design and operation of reactive distillation processes. Performing uncertainty simulations allows to evaluate whether an economically optimal process found using the superstructure methodology presented in Chapter 3 is adequately flexible to tolerate the design and/or operational uncertainties introduced. Re-designing the controlled system as well as revising the entire process, including the possibility to add ancillary equipment, are included as mitigation options in the methodology presented. Three case studies are considered, showing that uncertainty in pre-exponential factors impacts more significantly on the performance of the system, comparing to the same range of uncertainty in chemical equilibrium. It is also shown that in some cases, the initial optimal design is rigorous enough to tolerate even combined design uncertainty. However, in other cases and under design uncertainty, an economically optimal controlled system may nevertheless face performance issues and in these cases, revising the control scheme or adding ancillary equipment is therefore required, in order to mitigate production failure issues due to design deficiencies. The methodology also considers the impact of operational uncertainties on the process, showing that a system which can tolerate design uncertainty may nevertheless be sensitive to operational uncertainties, in which case, the mitigation strategies presented in this work should be applied to enhance system robustness.
5.1 Introduction

Uncertainty exists in every aspect of chemical engineering, including the design, optimisation and operation of chemical processes. Every chemical process, which aims to convert raw materials to the desired products through physical and chemical operations (e.g. reaction, separation etc.) may suffer from uncertainty which can lead to products not meeting quality specifications as well as sub-optimal or even infeasible operation. Reactive distillation is an intensified process where reaction and separation take place simultaneously, in a single unit. Due to the integration of the two different phenomena, the effect of uncertainty is amplified, and it should therefore be carefully investigated to evaluate its potential impact on the process and develop mitigation strategies in order to tackle consequent production failure issues.

In Chapter 2 it was discussed that a range of methods has been used for the design and/or dynamic operation under uncertainty for reactive distillation systems. However, no contribution to date provides insight into how the uncertain parameters (their type, direction, range) impact on the optimal steady state design of the process as well as on the corresponding dynamic performance. More specifically, to the best of the authors’ knowledge, no contribution considers how, and to what extent, uncertainty impacts on the performance of the overall process and how this uncertainty can be considered in order to mitigate production failure issues. These issues could be the result of design uncertainty (uncertainty in kinetic parameters, tray efficiency uncertainty etc.) and/or operational uncertainties (e.g. market demand change, feed composition disturbance, catalyst fouling etc.). This will therefore be the objective of this chapter, to provide a systematic methodology for the control, design and process mitigation of production failure issues due to design and/or operational deficiencies, which includes the evaluation of the impact of different types of design and operational uncertainties on optimal reactive distillation processes.

5.2 Monte Carlo method and Global System Analysis in gPROMS

In Chapter 2, the importance of evaluating the impact of uncertainties during the design of a reactive distillation process was highlighted and available methodologies in the existing literature were reviewed. This section will describe how uncertainty is implemented in the reactive distillation models considered in this work, using the Global System Analysis tool of gPROMS ProcessBuilder (Process Systems Enterprise 2020) for
the performance of Monte Carlo (uncertainty) simulations, when this was possible. It will be described how, for instance, the impact of slower kinetics or more challenging relative volatilities on process performance can be evaluated when the type of uncertainty (and its distribution) as well as the KPIs (e.g. product purity) are known. First, an introduction to the Monte Carlo method will be provided, followed by a presentation of the Global System Analysis tool in gPROMS ProcessBuilder.

Monte Carlo method

Monte Carlo methods is a well-known category of statistical methods for the calculation of the impact of uncertainty and is used in various disciplines, including Process Systems Engineering. The method is applied to predict the possible outcomes of an uncertain event. Different definitions exist but in general the Monte Carlo method may be defined as a method that involves deliberate use of random numbers in a calculation that has the structure of a stochastic process (i.e. a sequence of states whose evolution is determined by random events). In a computer, these states are generated by deterministic algorithms producing a sequence of pseudo-random numbers which mimic the properties of truly random numbers (Kalos and Whitlock 2008).

Although individual references for the use of random numbers date back to 1777 (Kalos and Whitlock 2008), the first application of the Monte Carlo method was based on the work of a team of scientists, von Neumann, Fermi, Ulam and Metropolis, who were working on the development of nuclear weapons in Los Alamos Laboratory in the 1940’s (Hammersley and Handscomb 1964). In their work, they refined the direct simulations with certain variance-reducing techniques and identified the possibility of applying the method also to deterministic problems (Hammersley and Handscomb 1964). Metropolis and Ulam, in a later publication, described the method as a statistical approach to the study of differential equations, or more generally, of integro-differential equations. These equations were studied as they appeared in various disciplines, including statistical physics. Based on Fermi’s suggestion in 1948 for instance, the authors obtained Monte Carlo estimates for the eigenvalues of the Schrödinger equation (Metropolis and Ulam 1949). Their work set the foundations for further advancements in the Monte Carlo method and as a result, Monte Carlo methods are today widely applied for sampling, estimation and optimisation in various disciplines and application areas such as (Kroese et al. 2014):
• Process modelling including simulation of inventory processes, optimal process design, job scheduling, vehicle routing etc.
• Physical processes and structures including a number of applications such as simulation of neutron transport, photon transport through biological tissue etc.
• Random graphs and combinatorial structures made possible by using statistical physics probability theory and computer science for instance.
• Economics and finance for risk analysis and pricing of financial instruments.
• Computational statistics used in climate science and computational biology.

In this work, by performing Monte Carlo simulations, the following possibilities are provided:

• Prediction of the effect of parameter uncertainty on plant performance and profitability.
• Prediction of the effect of variability in raw material on product quality.
• Quantification of the risk of plant performance problems due to operational deficiencies.

Monte Carlo simulations can be performed in gPROMS ProcessBuilder (Process Systems Enterprise 2020) for probabilistic input using the Global System Analysis tool (GSA), the configuration and capabilities of which are described below. As the input considered in this work is deterministic only (more details included in Section 5.4.3), the model is therefore not evaluated directly using Monte Carlo simulations but its input is sampled along a grid. The uncertainty simulations are still performed within the GSA tool in gPROMS, which is presented below.

Global System Analysis in gPROMS ProcessBuilder

The investigation of the impact of uncertainty based on the methodology developed in this work and performed in gPROMS ProcessBuilder is possible by performing uncertainty simulations on the model considered, using the GSA tool. The GSA tool in gPROMS, performs multiple model evaluations (simulations) with deterministically and/or probabilistically selected model input (i.e. uncertain input). The results of these evaluations are then used to determine the uncertainty in the model output and thereby to evaluate model robustness.

The procedure followed to perform a GSA analysis is presented in Figure 5.1. The procedure is exactly the same regardless of whether the mathematical model is
considered in steady state or dynamic mode and is explained below. The reader is
directed to the previous chapters for a detailed description on the steady-state (Chapter
3) and dynamic configuration (Chapter 4) of reactive distillation models considered.

Using the base-case values of the uncertain parameters, the user has to ensure that the
simulation initialises successfully. When this is ensured, a GSA file is created in gPROMS
where the user specifies a number of parameters for the process (i.e. model) considered.

These parameters determine the type of input considered (deterministic/probabilistic)
and the sample generation method; the uncertainty factors (along with their probability
distribution); as well as the output considered (Process Systems Enterprise 2020):

- **Sample generation method**: This selection determines how the generated
  random data set will fill the uncertainty space. For deterministic input a sample
generation method is not of interest as the input is sampled along a grid,
however, the default selection of gPROMS in that case is pseudo-random
sampling. When pseudo-random sampling is selected, the user also has to select
a seed for the random data set. The selected seed determines the starting point
of this data set, for which all generated data sets are always identical. The seed
values must be positive integer values in the range from 0 to $2^{32}-1$ and selecting
the same seed allows reproduction of the results in the future in case additional
factors and/or responses are added. For the deterministic input used in this work
(pre-exponential factors), sampling seed equal to 0 was always selected.

- **Uncertainty factors and model responses**: For the analysis to be performed,
  input variables under uncertainty consideration (named as factors) and output
  variables on which the impact of uncertainty will be investigated (named as
  responses) must be defined. The selection of ranges (lower/upper bound),
distributions and constraints for the factors must be performed carefully
because they can have a large impact on the estimated ranges and distributions
for the responses.

- **Probability distribution**: The user has to select the type of distribution to be
  applied to the uncertainty factors. For individual factors,
  normal/uniform/discrete distribution, gridded set etc., are some of the possible
  variability/probability selections. For grouped factors (i.e. factors which vary
  similarly), multivariate normal or discrete distribution, as well as multivariate
  enumerated set, are the possible choices.
When factors (along with their ranges, constraints etc.), responses and the sample generation method are defined, the user can perform the analysis. The number of total realisations (i.e. simulations) of the model to be performed depends on the type and method of analysis and for uncertainty analysis is equal to $N_d \cdot N$, where $N_d$ is the number of deterministic cases and $N$ is the number of user-defined uncertainty scenarios. When the analysis is complete, it is possible to generate a number of result elements such as: distribution statistics table, histograms, scatter plots etc. and/or export the results and analyse them using a different software. Monte Carlo simulations are usually fast to perform, although time increases significantly for higher sample numbers and/or complex flowsheets with slow initialisation procedures. More details on the specific selections made in this work regarding the above-mentioned input, on the parameters considered as well as typical calculation times are included in Section 5.4.3.

![Diagram](image)

**Figure 5.1:** Procedure for investigating uncertainty using GSA in gPROMS. $x$ corresponds to uncertain input whilst $y$ corresponds to the output (KPI). $P$ corresponds to probability.
5.3 Methodology

A general methodology, illustrated in Figure 5.2, has been developed to systematically investigate the impact of uncertainty on the design and operation of reactive distillation processes and to apply suitable mitigation strategies to tackle production failure issues. The methodology is demonstrated for reactive distillation in this work, however, can also be extended to different distillation processes such as conventional distillation, dividing-wall columns etc. The methodology can be applied to different case studies, different key performance indicators (KPIs) (e.g. product purity, recovery, production rate or total annualised costs), different uncertainties (e.g. in reaction kinetics or VLE) and different control schemes (for instance, single- or dual-point control), based on the requirements and the desired outcome of the investigation. The methodology considers uncertainty in design parameters, however, parallel consideration of operational disturbances can also be considered as shown in Section 5.5.4.

Below, the methodology as shown in Figure 5.2 will be outlined in detail. This methodology is applied to three case studies as will be described in Section 5.4.1 and the results will be presented in Section 5.5. The methodology can be applied for one uncertain parameter at a time or for combinations of uncertain parameters, as will be later demonstrated in Section 5.5. The methodology presented in Figure 5.2 starts with the optimisation of the process in steady state, without considering uncertainty (Step 1) and proceeds to Step 2 to evaluate the performance of the optimal, dynamic system under uncertainty. If the design can tolerate the uncertainty considered (Step 3), the methodology terminates (Step 9). Otherwise, it proceeds to Step 4 where revision of the control scheme is considered. Step 5 investigates the possibility of reducing the uncertainty range and if this is not possible, in Step 6 the design is optimised using the lower bound of the uncertainty considered to ensure that the optimal design can tolerate even the worst-case uncertainty. If a feasible solution is not found (Step 7), adding ancillary equipment is considered. Otherwise, the operation of the optimal design found in Step 6 is adjusted, using the base-case input (i.e. no uncertainty) to meet specifications (Step 8). The methodology continues until the flexible design tolerates the uncertainty considered (Step 9).

Following Figure 5.2:

1. Optimise the base case system at steady state without considering uncertainty. Optimisation can be performed using the superstructure methodology
developed and presented in Chapter 3. In this step, an optimal design (for
distillation total number of stages, feed stage locations, reflux ratio etc.) is found
which meets the problem constraints, such as product quality constraints, and
minimises or maximises the given objective function, e.g. the minimum
production-based total annualised cost.

2. For this optimal design, now consider the system as a dynamic, controlled
system. Based on the chosen control strategy (see Chapter 4), define the
uncertainty range for the chosen variable(s) and the key performance indicators
(KPIs), add this uncertainty to the problem description and run uncertainty
simulations (see Section 5.2) to evaluate the impact of the uncertainty on the
KPIs. This step will illustrate how robust the controlled optimal system is to the
uncertainties considered, and will determine if the optimal design can still meet
the specifications given this uncertainty (control mitigation), and if not, how far
away from the specifications the system may be. This step could also be
performed using the steady-state model, however, this would not provide any
additional insight into how tolerant the model is towards operational
uncertainty as in the steady-state model all operational parameters (which in a
dynamic model are considered degrees of freedom) are fixed.

3. If the whole uncertainty range considered is tolerated, and all specifications (e.g.
purity, recovery, production rate) are still met, then the optimal design is robust
(for the points considered within the uncertainty range) and the control strategy
is able to mitigate the uncertainty, hence no further action is required and go to
Step 9. Increasing the number of sample points can further increase the
confidence on process robustness, although will also increase the associated
computational cost. If some or all of the uncertainty range is not tolerated, then
proceed to Step 4.

4. In Step 4, it should be considered if the control scheme must, or can be, changed,
either by including more control loops or by changing control parameters. If the
control scheme can/should be revised, then revise it and repeat from Step 2. If
not, then proceed to Step 5. For distillation, if for instance one-point control has
already been considered and has been found insufficient, then dual-point or
advanced process control (e.g. Model Predictive Control etc.) can be considered.

5. In Step 5, the opportunity of reducing the uncertainty range considered is given.
It may be that the initial uncertainty range considered is in fact larger than the
actual uncertainty. Uncertainty in experimental data can be reduced by increasing the amount of data collected (i.e. performing more experimental work) which may delay the project and/or increase research cost. However, it is expected that the smaller (i.e. more accurate) range will result in a less expensive design (compared to the design based on a wider uncertainty range), therefore counteracting any extra cost or delay that may have occurred. If the uncertainty range should be reduced, either because the current range is wider than it would be in reality, or because the current range could not be successfully accommodated by a new optimal design (found in Step 6), then reduce the uncertainty range and return to Step 2. If the range should not be reduced, then proceed to Step 6.

If the optimised design from Step 1 is not able to meet the specifications for the uncertainty range considered, and the control scheme should not be revised and the uncertainty range should not be (further) reduced, then the actual design must be reconsidered. The starting point for this is the initial base-case system but now including the worst-case uncertainty that led to the specifications being violated, in other words, the worst-case input (upper or lower bound of the uncertain parameters). In the case when a combination of uncertain parameters is considered, the worst-case uncertainty is introduced for the parameter that has more impact on the system, based on previous separate investigations (as will be shown in Section 5.5). At this point, a question is raised into why uncertainty simulations are used given that the system is now optimised using the worst-case input, which is a single point. By initially performing uncertainty simulations (Steps 2-5), the entire range of scenarios between the worst-case scenario and the best-case scenario can be investigated in order to confirm expected behaviour, observe new trends and potentially allow the prediction of system behaviour beyond the current uncertainty bounds considered. If simulations were performed just for the two end-points (base case and worst case), then the observed behaviour could not be evaluated and potential simulation failures at the uncertainty bounds (due to the extreme nature of the simulated end-points) could not be justified. However, as will be explained later in Section 5.4.3, for uncertainty factors which cannot currently be used in the GSA tool in gPROMS ProcessBuilder (i.e. VLE which is externally configured in Multiflash (Infochem 2020)), simulations will be performed just for the two end-points (i.e. lower and upper bound of uncertainty range).
6. In Step 6, re-optimise the design now based on the worst-case input (i.e. the lower or upper bound of the uncertainty range considered, which has the worst impact on process performance) of the parameters that led to specification violations for the original base-case optimal design. This step indicates a way of mitigating the uncertainty or risk by changing the design (design mitigation). The new design is expected to have more demanding design/operational characteristics such as increased total number of stages, increased reflux ratio etc. for reactive distillation, but will now be able to tolerate even the worst uncertainty. It should be noted that if this optimisation had instead been performed for moderate uncertainty values (i.e. between the base- and worst-case input) in order to potentially reduce the cost of the new flexible design, then the new design could still not meet specifications using control mitigation under the entire uncertainty range. Therefore, the worst-case input is a sensible choice for the re-optimisation to ensure consistency (i.e. always optimising using worst-case input) between case studies and that the new design can tolerate all uncertainty, although most likely leading to a more expensive design.

7. If the optimisation is feasible and an acceptable solution that meets all the specifications has been found, then move to Step 8. If a feasible and/or acceptable solution is not achievable, then this is likely to mean that ancillary equipment must be added to the process to mitigate the uncertainty, such as pre-/side-reactors or additional distillation columns for reactive distillation. Ancillary equipment should then be added to the design and the methodology restarted from Step 1 (process mitigation). If no ancillary equipment should be added (e.g. because all suitable ancillary units have already been considered but do not improve the performance), then the methodology terminates and the uncertainty considered cannot be tolerated by the process using the mitigation strategies considered.

8. With the new optimal design found in Step 6, which was obtained considering the worst-case uncertainty, return to the base-case values for the uncertain parameters and, considering the worst-case optimal design with the base-case parameter values, adjust the operational parameters (reflux ratio and bottoms rate) such that the product purity and recovery are meeting the same
specifications as in Step 1. Return to Step 2 with this revised optimal design and operation to investigate the uncertainty for the revised process.

9. At Step 9, a flexible design (including control, design and/or process mitigation) that can meet the specifications for the uncertain scenarios considered has been found and no further action is needed.

10. Further investigation is required, for instance to include a safety evaluation, but this is not considered in this work.

The applicability of the proposed methodology was evaluated using three reactive distillation case studies, the outcomes of which are presented in the following. The three case studies are characterised by different combinations of reaction and separation parameters, and their input is presented next.
Figure 5.2: Methodology for mitigation of uncertainty in reactive distillation systems.
5.4 Case studies

5.4.1 Systems considered

In Chapter 3, a methodology was presented for how to determine the optimal design (total number of stages, feed stage locations, reflux ratio etc.) of a reactive distillation process and illustrated this methodology for a quaternary system of components A and B which react towards components C and D based on 15 case studies. For consistency purposes, three of those case studies are also used in this work (Case studies 1, 2 and 13 as mentioned in Table 5.1). The same (superstructure) methodology is used as Step 1 in the uncertainty mitigation methodology developed in this work using three of the case studies. The impact of uncertainty is investigated in order to explore how rigorous the earlier identified designs presented in Chapter 3 are under both design and operational uncertainties. The case studies consider systems of different separation difficulty as well as different kinetic characteristics to identify how these parameters impact on the design of an economically attractive and flexible process and to identify if the process is able to mitigate production failure issues due to design and/or operational deficiencies. Rather than considering a specific chemical system, generic components were used instead such that the impact of specific parameter types could be investigated.

The separation difficulty is defined based on the relative volatilities between the components and fast and/or slower kinetic expressions were investigated (Table 5.1). For all case studies, the components were considered of equal density (900 kg/m$^3$), equal molecular weight (50 g/mol) and equal boiling point of the heavy reactant, component B (413 K). This boiling point was assumed to be fixed and all other volatilities were calculated using the heavy reactant as the reference in order to create the desired relative volatilities (see Appendix D).

A quaternary system in which the following auto-catalysed reversible reaction occurs in the liquid phase is considered, with component D as the desired product:

$$A + B \rightleftharpoons C + D$$

The kinetic expressions for the forward (f) and backward (b) reaction rates are the following:

$$r_f = k_{f0}e^{-E_a_f/RT}C_AC_B$$

$$r_b = k_{b0}e^{-E_a_b/RT}C_CC_D$$
where reaction rate, $r$, is expressed in kmol/(m$^3$·s), pre-exponential kinetic factors, $k_{f0}$ and $k_{b0}$, are expressed in m$^3$/(kmol·s), activation energy, $E_a$, is expressed in kJ/mol (assumed to be 80 kJ/mol for both directions), and component concentration $C_i$ is expressed in kmol/m$^3$. Heat of reaction was assumed to be negligible, thus the activation energy is the same for both reaction directions and $K_{eq}$ is independent of temperature, based on the previous assumptions.

Fast and slow kinetic characteristics were considered in combination with the relative volatility systems, resulting in the three case studies given in Table 5.1. The values of the reaction parameters as well as relative volatilities were selected based on industrial interest. A clarification is needed at this point with regards to Table 5.1. The three case studies were previously presented in Chapter 3, however, $k_{f0}$ was then expressed in m$^3$/(kmol·s) as these units occur from the reaction rate expression. In this chapter, $k_{f0}$ is expressed in m$^3$/(kmol·hr) as these are the units gPROMS (and thus GSA) uses for this variable and would, therefore aid the systematic analysis of the results. As a result, the values of $30.276 \times 10^9$ m$^3$/(kmol·hr) and $7.56 \times 10^9$ m$^3$/(kmol·hr) in Table 5.1 are equal to $8.41 \times 10^6$ m$^3$/(kmol·s) and $2.1 \times 10^6$ m$^3$/(kmol·s), presented in Table 3.3.

For the steady state and dynamic systems considered, the same assumptions as presented in Chapter 3 and Chapter 4 still hold.
Table 5.1: Case studies considered. Reaction and separation characteristics, feed conditions and optimal results according to superstructure base case optimisation (Chapter 3). Case study 1 and Case study 2 had the same numbering whilst Case study 3 in this work was Case study 13 in Chapter 3.

<table>
<thead>
<tr>
<th>Case study 1</th>
<th>Case study 2</th>
<th>Case study 3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Input</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha_{CA}$</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>$\alpha_{AB}$</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>$\alpha_{BD}$</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>$k_0$ (m$^3$/(kmol-hr))</td>
<td>30.276$\times10^9$</td>
<td>7.56$\times10^9$</td>
</tr>
<tr>
<td>$K_{eq}$</td>
<td>81</td>
<td>2.25</td>
</tr>
<tr>
<td><strong>Feed 1</strong> (component B)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$F$ (kmol/hr)</td>
<td>12.6</td>
<td></td>
</tr>
<tr>
<td>$T$ (K)</td>
<td>413</td>
<td></td>
</tr>
<tr>
<td>$P$ (atm)</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td><strong>Feed 2</strong> (component A)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$F$ (kmol/hr)</td>
<td>12.6</td>
<td></td>
</tr>
<tr>
<td>$T$ (K)</td>
<td>398.5</td>
<td></td>
</tr>
<tr>
<td>$P$ (atm)</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

**Optimal results**

<table>
<thead>
<tr>
<th></th>
<th>Case study 1</th>
<th>Case study 2</th>
<th>Case study 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heavy feed (B) stage ($N_{T_1}$)</td>
<td>12</td>
<td>11</td>
<td>15</td>
</tr>
<tr>
<td>Light feed (A) stage ($N_{T_2}$)</td>
<td>13</td>
<td>19</td>
<td>20</td>
</tr>
<tr>
<td>Number of stages ($N_T$)</td>
<td>18</td>
<td>25</td>
<td>31</td>
</tr>
<tr>
<td>Reflux ratio ($RR_{T}$)</td>
<td>2.59</td>
<td>4.65</td>
<td>6.2</td>
</tr>
<tr>
<td>Bottoms flow rate (B, kmol/hr)</td>
<td>12.6</td>
<td>12.6</td>
<td>12.5</td>
</tr>
<tr>
<td>Reactive stages</td>
<td>2-17</td>
<td>2-24</td>
<td>2-30</td>
</tr>
<tr>
<td>Column diameter ($D_C$, m)</td>
<td>0.62</td>
<td>0.78</td>
<td>0.91</td>
</tr>
<tr>
<td>Bottom purity ($x_{B,D}$, mol/mol)</td>
<td>0.99</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td>Product recovery ($x_{REC}$, mol/mol)</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Top purity ($x_{D,C}$, mol/mol)</td>
<td>0.99</td>
<td>0.99</td>
<td>0.98</td>
</tr>
<tr>
<td>Production - TAC (€/kg)</td>
<td>2.073</td>
<td>2.140</td>
<td>2.210</td>
</tr>
<tr>
<td>OPEX (M€/yr)</td>
<td>10.32</td>
<td>10.52</td>
<td>10.68</td>
</tr>
<tr>
<td>CAPEX (M€/yr)</td>
<td>0.15</td>
<td>0.27</td>
<td>0.40</td>
</tr>
</tbody>
</table>

The feed streams to the overall system (Table 5.1) were one stream of reactant B (Heavy feed in Figure 5.3) of flow rate 12.6 kmol/hr, and one stream of reactant A (Light feed in Figure 5.3) of the same flow rate (1:1 feed molar ratio). This corresponds to 5 ktn/year of product D for full reactant conversion. The feeds were assumed to be at the corresponding boiling points at 1 atm. In addition, liquid hold-up of the reactive distillation column was assumed equal for all reactive stages, fixed at 0.1 m$^3$/reactive tray.

The following KPIs are considered: bottom product purity ($x_{B,D}$), product recovery (i.e. amount of component D in the bottom product divided by the total amount of component D generated from the reaction, $x_{REC}$) and bottoms flow rate (B). In addition
to these KPIs, the values of the following variables were monitored in order to investigate the behaviour of the systems: top product purity ($x_{D,C}$), distillate flow rate ($D$), pressure at the top of the column ($P_t$), condenser and reboiler duties ($Q_C$ and $Q_R$, respectively), reflux drum and sump liquid level ($M_C$ and $M_R$, respectively) and molar reflux ratio (RR). Regarding the top product purity ($x_{D,C}$) in particular, although it is a controlled variable indicating top product purity, it is not used as a KPI as the steady-state optimisation is performed using product quality constraints only on the main product, component D. As a result, component C is not a product of interest and the reason that its composition is controlled in LV control is such that the system is under tighter control, taking advantage of all degrees of freedom. As a result, the aim will not be for $x_{D,C}$ to always meet a specific and high purity target value, but to remain at the set-point of the control loop. In addition, with regards to B for which the base-case value is 12.6 kmol/hr, values down to 12.55 kmol/hr were considered acceptable, as a production rate of 12.55 kmol/hr still meets the desired production target of 5 ktn/yr of component D.

Figure 5.3: V-only (left) and LV (right) control configurations.
5.4.2 Control schemes configuration

This section describes the configuration of the dynamic controlled systems as implemented in this work (Step 2 of the methodology), which is based on the work of Chapter 4. For any ancillary units considered (e.g. pre-reactor) perfect liquid level and temperature control is assumed as the main focus of the investigation is on the performance of the reactive distillation columns and additional control loops could introduce inconsistencies (i.e. additional assumptions) between the models.

For the reactive distillation systems, Figure 5.3 shows the configuration of the two control schemes which will be used in this work for the reactive distillation columns. Two conventional control schemes are considered: V-only (single-point) and LV (dual-point) control. In both control schemes, pressure at the top (stage 2) is controlled using condenser duty (PI control, PC loop, $K_c = 20$ and $\tau = 12$ min) and the liquid levels of the reflux drum (P-only, LCT loop, $K_c = 2$) and the sump (P-only, LCB loop, $K_c = 2$) are controlled using distillate and bottoms rate, respectively. For V-only control, reboiler duty is manipulated in order to control bottom product purity (PI control, CCB loop, $K_c = 3$ and $\tau = 25$ min) (composition of component D, the main product). For LV control, bottom product purity is controlled in the same way as for V-only and additionally the top product purity (composition of component C, side product) is controlled (PI control, CCT loop, $K_c = 3$ and $\tau = 25$ min) by manipulating the reflux ratio, expending all degrees of freedom of the system in this case. A reasonable alternative to direct composition control would be temperature inferential control, i.e. indirectly controlling composition by manipulating the temperature of a column tray where a sharp change in temperature profile is observed. However, as this tray would differ for every reactive distillation column considered, direct composition control was preferred to ensure that all composition control loops are configured in a consistent way. The tuning parameters remained the same for all case studies and are based on literature (Luyben 2006). The methodology presented is not limited to the control configurations considered and could be applied to other conventional control schemes such as DB, (L/D V/B) as well as advanced control strategies (e.g. model predictive control, adaptive control etc.).

5.4.3 Types of uncertainties considered

As mentioned earlier, uncertainty can be introduced in the process design by model uncertainty (model parameters), dynamic operation through disturbances (process disturbances) and/or by the commercial environment (market changes etc.). All types
are considered in this work in order to evaluate the tolerance of the system towards both
design (lower frequency) uncertainty and towards operational (higher frequency)
uncertainties/disturbances. The design uncertainties considered are in the reaction
kinetics (forward pre-exponential kinetic factor, $k_{f0}$ and chemical equilibrium, $K_{eq}$ through
varying the backward pre-exponential kinetic factor, $k_{b0}$), separation performance
(relative volatility $\alpha_{BD}$), as well as their combination ($k_{f0}$ and $\alpha_{BD}$, and $K_{eq}$ and $\alpha_{BD}$). The
operational uncertainties considered are a feed flow rate disturbance as well as a change
in the target bottom product purity due to changing market demand.

5.4.3.1 Design uncertainty

Before presenting in detail the design uncertainties considered in this work, it is
important to explain how the latter are usually introduced in the design of a reactive
distillation process. In the initial design stage (screening phase) basic data is typically
limited and usually obtained through screening experiments or industrial experience of
the considered process. In this early design phase, the number of possible process
alternatives is reduced to a small number of options (e.g. 2 or 3). Knowing which
parameters are critical to the overall cost of the project, and properly understanding
their impact, can contribute to making a good final decision. In the second phase, when
the selected alternatives are investigated in more detail, more information (data) is
collected and becomes available which, however, usually contains a certain level of
uncertainty originating from the way the data is obtained (i.e. experimental work,
parameter estimation etc.). The goal in this phase is typically to get sufficient data to
improve the initial choice, as the time required for implementation (market opportunity)
is very important and usually short, and therefore limited time is available to minimise
the uncertainties. Errors or uncertainties in basic data in this phase can be caused due to:

- Experimental work and/or equipment errors: Such errors include impurities or
  inaccurate concentration of reactants, errors in sensor readings, insufficient
  mixing of liquid phase, wrong recording of sampling time, continuation of
  reaction between sampling time and analysis time, analytical errors etc. In VLE
  measurements for reactive distillation there is also the issue of reaction between
  components which can lead to measurement errors.

- Models used to describe the experimental trends: Models used are usually a
  simplification of real behaviour. For reactions, errors can originate from the
selected reaction mechanism and the units used (kg/l, mol/l, activity, mol/mol etc.) for the reaction rate expression basis (i.e. concentration, activity, mole fraction etc.). In addition, decisions need to be made regarding the importance of small side-reactions and how VLE will be modelled (typically via binary interaction).

- Fitting errors: For an equilibrium reaction (as considered in this work), the forward pre-exponential factor is typically fitted based on the initial reaction rate (low conversion) whilst chemical equilibrium is based on the composition at the end of the reaction. Note that in a batch reactor (which is typically used to determine conversion time), different conversions are expressed as functions of time whilst in a reactive distillation column each stage operates at a specific conversion. It may happen that a significant part of the reactive column operates at conditions (e.g. close to equilibrium) that are rather difficult to fit accurately from batch experiments, thus leading to errors.

As a result, having a good understanding of the impact of design uncertainty in the early design phase using the methodology developed in this work can help to direct the experiments required in obtaining the model parameters. The latter may be performed in later stages of the design in order to reduce uncertainty in the factors which are most impactful on the performance of the process considered.

a) Reaction kinetics

In this work, for the reaction kinetics, uncertainty in $k_0$ and $K_{eq}$ is investigated. These two parameters are considered as they characterise the reaction rate equations of the system, and uncertainty in their values may lead to lower than expected reaction conversion, rendering the design of the process inefficient. In order to consider faster/slower kinetics, where uncertainty may or may not be introduced in $K_{eq}$, two situations are investigated:

- a) $k_0$ is varied along with $k_{b0}$ to keep $K_{eq}$ constant (Table 5.1).
- b) $k_0$ remained at the nominal value (Table 5.1), varying $K_{eq}$ and therefore $k_{b0}$.

In this work, the pre-exponential factors are deterministic input, therefore the range generated for this input is not a result of probabilistic distribution but of sampling along a grid with specified values. Although the simulations are performed using the GSA tool in gPROMS, they do not make use of the Monte Carlo method as in order to use the term
Monte Carlo, probabilistic input would be required (not used in this work). The methodology so far presented can, however, take probabilistic factors into consideration in which case, they can be investigated using Monte Carlo simulations within the GSA tool.

The forward and backward pre-exponential factors are grouped and varied as a multivariate enumerated set within the GSA tool. Defining $k_{f0}$ and $k_{b0}$ as a multivariate enumerated set allows their varied values (i.e. grid) to be specified (so that their ratio always yields the desired $K_{eq}$) and associated with a scenario to facilitate the analysis of the responses. This is necessary as the ratio of $k_{f0}$ and $k_{b0}$ needs to be kept to the desired $K_{eq}$ value and this cannot be guaranteed if uniform or normal distribution is applied to $k_{f0}$ and $k_{b0}$ individually. The number of combinations of $k_{f0}$ and $k_{b0}$ considered is 100 in a single scenario therefore the number of model realisations (i.e. simulations) performed once the GSA is completed is 100.

b) Separation performance

For uncertainty in separation performance (VLE), uncertainty in relative volatilities was considered. The relative volatility between heavy reactant, component B, and desired product, component D ($\alpha_{BD}$) was selected as source of uncertainty, as this parameter impacts directly on the product purity and recovery which are the specifications for the steady-state optimisation.

For this type of uncertainty, Monte Carlo simulations cannot be performed due to the way VLE is imported into gPROMS ProcessBuilder, which is the software tool used in this work. As an alternative, the bounds of the uncertainty range are therefore instead investigated for two scenarios, worst-case and best-case, with the worst-case input being the lower bound of $\alpha_{BD}$ and the best-case input being the upper bound. If relative volatilities between the other components were to be considered ($\alpha_{CD}$, $\alpha_{CA}$ etc.), the worst-case input would again be the lower bound, but would be the upper bound of $\alpha_{AB}$ as in that case it is harder to keep the reactants in the reactive zone.

5.4.3.2 Operational uncertainty

In addition to the design uncertainties mentioned above, operational uncertainties are considered in: a) molar flow rate of the heavy feed (Feed B) as a disturbance and b) bottom product purity specification ($x_{B,D}$) due to market demand. These two disturbances were considered as they are both considered industrially relevant scenarios.
for a reactive distillation process. In this work, the disturbances were introduced as sharp ramps over 500s as this is both numerically less challenging and industrially more relevant compared to a direct step change which is not the way a disturbance is usually introduced in a real system. The disturbances were introduced at time t=0.5 hr, whilst each simulation lasted t=15 hrs to ensure that the system had definitely reached the new steady state. It has to be noted that operational uncertainty was considered in parallel with design uncertainty, therefore for every pair of the uncertain parameters $k_{f0}$ and $k_{b0}$, the disturbance was introduced and the output of the uncertainty simulation was taken at the final time i.e. after the end of the 15 hrs.

5.5 Results

The methodology developed in this work is illustrated by considering three case studies (Table 5.1). The case studies were selected so that they explore all three types of mitigation strategies included in the methodology (control, design and process revision) and are characterised by different combinations of reaction and separation parameters. Case study 1 was selected as it is characterised by both favourable kinetics and relative volatilities. Case study 2 was selected as it is characterised by the same relative volatilities as Case study 1 although the kinetics are less favourable. As a result, the impact of slower kinetics on the performance of the system under uncertainty could be investigated. Finally, Case study 3 is characterised by favourable kinetics (as in Case study 1) but challenging relative volatilities so that the impact of less favourable volatilities on the performance of the system under uncertainty could be investigated. The optimal designs (Table 5.1) for the three case studies are found using the superstructure methodology described in Chapter 3.

In terms of the computational time required for the simulations to be completed, uncertainty simulations are usually fast to perform, although time increases significantly for higher sample numbers and/or for complex flowsheets with slow initialisation procedures. In this work, the uncertainty simulations using GSA in gPROMS ProcessBuilder v1.3.1 (Process Systems Enterprise 2020) needed approximately 0.2-5 min CPU time on a 3.60 GHz and 32GB RAM Dell Precision 5820 Desktop. The short times are due to the fact that the number of samples (100) and the number of factors ($k_{f0}$ and $k_{b0}$) and responses (controlled and manipulated variables, objective function value) was moderate as was the complexity of the flowsheet. The number of samples was chosen in collaboration with the industrial supervisors based on the physical meaning of the
parameters considered (i.e. reaction kinetics) as for the range considered, a much larger number of samples would indicate a very small step which would not be evident to the reaction/separation system itself.

In the following, the impact of the uncertainties (design uncertainties in Sections 5.5.1 to 5.5.3 and operational uncertainties in Section 5.5.4) on the KPIs (presented in Section 5.4.1) is considered and appropriate mitigation strategies are applied. The production-based TAC of the final flexible process obtained using the methodology in this work is compared to the production-based TAC of the initial optimal process to evaluate the cost penalty required to design the process such that it can implicitly mitigate uncertainty.

5.5.1 Case study 1

In this section, the methodology presented in Section 5.3 will be applied to Case study 1, considering uncertainty in reaction kinetics as well as combined uncertainty in kinetics and separation performance. Case study 1 is characterised by fast kinetics, large chemical equilibrium and favourable relative volatilities, i.e. all main process parameters are favourable.

5.5.1.1 Uncertainty in reaction kinetics

As mentioned in Section 5.4.3, two cases (case a: uncertainty in \( k_{f0} \), case b: uncertainty in \( K_{eq} \)) are considered for uncertainty in kinetics. For both cases, the uncertainty range considered was ±50% based on industrial experience and the two pre-exponential factors were grouped and varied as a multivariate enumerated set (i.e. 100 pairs of the predefined values of the two pre-exponential factors to uniformly cover the uncertainty range). Such a high uncertainty will also allow the illustration of the methodology properly. Based on the base-case values presented in Table 5.1, the value ranges considered for uncertainty cases a and b are therefore:

a) \( 15.138 < k_{f0} = 30.276 < 45.414 \) \( (10^9 \text{ m}^3/(\text{kmol} \cdot \text{hr})) \) and \( 0.187 < k_{b0} = 0.374 < 0.561 \) \( (10^9 \text{ m}^3/(\text{kmol} \cdot \text{hr})) \) to keep \( K_{eq} \) constant (here at 81).

b) \( 40.5 < K_{eq} = 81 < 121.5 \), i.e. \( 0.249 < k_{b0} = 0.374 < 0.748 \) \( (10^9 \text{ m}^3/(\text{kmol} \cdot \text{hr})) \) and \( k_{f0} = 30.276 \times 10^9 \text{ m}^3/(\text{kmol} \cdot \text{hr}) \)

In the following, the methodology in Figure 5.2 will be applied with these uncertainties. The results will present KPIs as a function of the uncertain reaction kinetic parameters.

**Step 1:** Case study 1 is optimised using base-case input and the optimal parameters are obtained (Table 5.1).
**Step 2:** In Step 2, uncertainty in kinetics is introduced in the dynamic, controlled, system initially using V-only control. The values of product purity ($x_{B,D}$), product recovery ($x_{REC}$), and bottoms production rate (B) are monitored as KPIs in order to investigate whether the uncertainty is tolerated and if not, how far away from the specifications the system is. In addition, the values of condenser and reboiler duties ($Q_R$ and $Q_C$) are presented in order to show the corresponding control actions along with the values of the top product purity ($x_{D,C}$) to also show the impact on top purity (although not controlled under V-only control).

Figure 5.4 (left: case a, right: case b) shows that the product purity ($x_{B,D}$) is maintained (top of Figure 5.4) by the V-only controlled system (consider the V-only lines), but this is only possible by reducing the bottom production rate (i.e. $B < 12.55 \text{ kmol/hr}$, see Section 5.4.1) when:

a) $k_{10} < 18.2 \cdot 10^9 \text{ m}^3/(\text{kmol-hr})$ (top left of Figure 5.4)

This means that with the current optimal design and control configuration, slower kinetics (case a) down to $18.2 \cdot 10^9 \text{ m}^3/(\text{kmol-hr})$ can be mitigated by control action alone for the V-only control scheme. Note that the red line ($x_{B,D}$-V only) overlaps with the blue ($x_{B,D}$-LV) and green line ($x_{B,D}$-combined). Uncertainty in $K_{eq}$ does not impact on the performance of the system as for all the $K_{eq}$ considered, the system met specifications (right in Figure 5.4). This therefore shows that for the uncertainties considered, slower kinetics ($k_{10}$) have a more significant impact on the performance than lower $K_{eq}$. It should be noted that the 50% uncertainty range considered for $K_{eq}$ corresponds to a range of 86.4 % to 91% conversion (the base case conversion, i.e. for $K_{eq}=81$, is 90%) which is not a broad range. Changes in the condenser and reboiler duties, as well as in $x_{D,C}$ due to uncertainty in pre-exponential factors ($k_{10}$ and $k_{20}$) (case a) are more significant compared to changes due to uncertainty in $K_{eq}$ (case b), as expected. $x_{REC}$ is well above (1) its specification (0.90) for both uncertainty cases and for all the ranges considered (not shown).
Figure 5.4: Case study 1 uncertainty simulations. Product purity ($x_{B,D}$) together with bottom production rate ($B$), condenser ($Q_C$) and reboiler ($Q_R$) duties and top product purity ($x_{D,C}$) together with molar reflux ratio (RR) for initial optimal dynamic controlled V-only (lines indicated as V-only) and LV (lines indicated as LV) design. Uncertainty in kinetics (case a-left, case b-right) as well as combined kinetics-VLE uncertainty (lined indicated as combined).
Step 3: This step decides whether the current design can tolerate the uncertainty range. For both slower kinetics (case a) and lower equilibrium (case b), the purity is maintained, however, this is only possible with an undesired reduction in production rate (B) for slower kinetics (case a), which cannot be tolerated. Hence, we proceed to Step 4.

Step 4: Single-point (V-only) control is initially considered for the dynamic system, however, dual-point control can alternatively be investigated to evaluate the tolerance of the system towards the introduced uncertainty. As a result, we return to Step 2 where we repeat the uncertainty simulations for the same range of uncertainty, now considering LV control for the dynamic system. In the LV control scheme, the pairings are exactly the same as in the V-only control scheme and in addition, top product purity \( x_{D,C} \) is controlled using molar reflux ratio (RR). Repeating steps will be indicated for all case studies using the symbol R (for round) next to the associated methodology step, to demonstrate the fact that this is the \( i^{th} \) time the methodology starts from Step 2.

Step 2 (R2): The uncertainty range considered is introduced in the dynamic controlled system now using LV control scheme, as shown in Figure 5.4 (consider the LV lines in Figure 5.4). As can be seen, the system is now able to tolerate the entire range of uncertainty in kinetics considered, not only in terms of product purity and recovery (not shown) but also maintaining production rate at the desired level also for slower kinetics (case a). Changes in chemical equilibrium (case b) as expected do not have an impact on performance, similarly to the behaviour observed using V-only control. Changes in condenser and reboiler duties are more significant for slower kinetics (case a) than for lower chemical equilibrium (case b), as observed previously for V-only control. The bottom plots of Figure 5.4 show the top product purity \( x_{D,C} \) and the corresponding changes of molar reflux ratio to maintain this, when LV control is applied in the initial, optimal design and shows that the top purity is maintained at the set point.

Step 3 (R2): Since the uncertainty considered is now tolerated when LV control is implemented, no further control/design/process changes are required and we go directly to Step 9, and at this step, the procedure terminates. As no revision of the design was required, the production-TAC remained at its initial optimal value of 2.073 €/kg.

5.5.1.2 Combined uncertainty in kinetics and separation performance

This section considers the effect of combined uncertainty in both reaction kinetics and in the separation performance and considers the optimal controlled system under LV control. In addition to the uncertainty in kinetics considered in the previous section,
uncertainty in the relative volatility between the heaviest reactant B and the product D ($\alpha_{BD}$) was considered in a reasonable range (±40%). A wider range would lead to reverse boiling point rankings, for which the current design would be clearly inefficient, as shown in Chapter 3. Therefore, the lower bound for the uncertainty (i.e. worst-case input) was $\alpha_{BD}=1.2$ and the upper bound (i.e. best-case input) was $\alpha_{BD}=2.8$ as the base case value was $\alpha_{BD}=2$. All the other relative volatilities remained the same, except for the volatility between components C and D $\alpha_{CD}$ which was changed accordingly. This was due to the fact that the boiling points of components A, B (the reference component for vapour pressure calculation), and C remained unchanged therefore the relative volatilities between those components ($\alpha_{CA}$, $\alpha_{AB}$) remained the same as well. However, the boiling point of component D changed in order to agree with the new value for $\alpha_{BD}$, therefore $\alpha_{CD}$ had to be changed accordingly. As mentioned in Section 5.4.3, uncertainty simulations as those presented above when considering uncertainty in kinetics cannot be performed for uncertainty in VLE using gPROMS ProcessBuilder, therefore worst- and best-case input must be introduced as input in the system separately in order to study the impact of those two bounds, in addition to the uncertainty in kinetics.

In the following, the methodology described previously and presented in Figure 5.2 will be applied for the worst-case VLE uncertainty as this is a more challenging situation in terms of system performance compared to the best-case VLE input for which the system will easily meet the specifications (results not shown).

**Step 1:** Case study 1 is optimised using base-case input and the optimal parameters are obtained (Table 5.1) as before.

**Step 2:** In Step 2, uncertainty in kinetics is introduced in the dynamic, controlled system (LV) using the worst-case relative volatilities ($\alpha_{BD}=1.2$). The results are again presented in Figure 5.4 (lines indicated as combined), and it can be seen that even the combined VLE and kinetics uncertainty can be mitigated by LV control action alone. The bottom product purity ($x_{B,D}$) and recovery ($x_{REC}$, not shown), as well the bottoms product rate (B), meet the specifications for the entire range of uncertainty. However, it is shown that the changes that the system has to undertake, in terms of condenser and reboiler duties as well as reflux ratio, in order to meet the specifications under the combined uncertainty considered are much more significant compared to uncertainty in kinetics only, showing the significant impact of the combined uncertainty on the system. The set-point of the top product purity ($x_{D,C}$) is different between the initial and combined design as only $x_{B,D}$
needs to meet specification of 0.99 and the value of \( x_{D,c} \) is an output of the model based on its design and operational parameters, without any (optimisation) specification.

**Step 3:** As the system is able to mitigate the combined uncertainty introduced, no further steps need to be considered (**Step 9**). At this point, the engineer can have confidence that with \( \pm 50\% \) uncertainty in reaction kinetics and 40\% reduction in relative volatility, the initial, controlled system will still be able to meet product specifications under LV control. As no revision of the design was required, the production-TAC at the design phase remained in its initial value of 2.073 €/kg. However, when worst-case VLE and uncertain kinetics are encountered, operational parameters (i.e. heating and cooling duties, reflux ratio, bottom flow rate etc.) adjust to meet specifications, leading to increased production-based TACs ranging from 2.240 €/kg (worst VLE and best-case kinetics) up to 2.480 €/kg (worst VLE and worst-case kinetics).

5.5.2 Case study 2

In this section, the methodology presented in **Section 5.3** is applied to Case study 2, considering uncertainty in reaction kinetics. Case study 2 is characterised by slower kinetics and lower chemical equilibrium compared to Case study 1, whilst the relative volatilities are the same as in Case study 1. The range of uncertainty in kinetics is again \( \pm 50\% \). The value ranges considered are therefore:

\[
\begin{align*}
\text{a)} & \quad 3.78 < k_f^0 = 7.56 < 11.34 \ (10^9 \text{ m}^3/(\text{kmol} \cdot \text{hr})) \text{ and } 1.68 < k_b^0 = 3.36 < 5.04 \ (10^9 \text{ m}^3/(\text{kmol} \cdot \text{hr})) \text{ to keep } K_{eq} \text{ constant (here at 2.25)} \\
\text{b)} & \quad 1.125 < K_{eq} = 2.25 < 3.375, \text{ i.e. } 2.24 < k_b^0 = 3.36 < 6.72 \ (10^9 \text{ m}^3/(\text{kmol} \cdot \text{hr})) \text{ and } k_f^0 = 7.56 \times 10^9 \text{ m}^3/(\text{kmol} \cdot \text{hr})
\end{align*}
\]

**Step 1:** The optimal parameters for Case study 2 are presented in Table 5.1. The optimal design for Case study 2 is more demanding compared to the design of Case study 1, showing that slower kinetics do impact on the optimal design and operation as additional reactive/separation stages as well as higher reflux ratio are required in the reactive distillation column to meet the specifications.

**Step 2:** In Step 2, uncertainty in kinetics is introduced in the dynamic, controlled system (LV control). LV control was selected as it was previously shown for Case study 1 that a single point scheme cannot successfully control the process. The results from the uncertainty simulations are shown in Figure 5.5 (left: case a, right: case b).
Figure 5.5 shows that bottom product purity and recovery (not shown) are maintained (top of Figure 5.5) by the controlled system. However, it can be seen that for faster kinetics (i.e. higher $k_0$), simulations are infeasible and no results can be generated. This is because for faster kinetics, the system can easily meet the top and bottom specifications and unless the condenser and reboiler duties as well as reflux ratio are lowered compared to the base case, the system will exceed the specifications. For instance, for the fastest kinetics considered the system is able to reach top product purities up to 0.997 with the base-case reflux ratio (4.65), while maintaining the bottom specification of $x_{B,D} = 0.990$. As a result, to maintain the top product purity set-point of 0.990, the reflux ratio needs to be lower significantly, leading to unacceptably reduced column liquid flowrates given the specified column diameter and as a result, infeasible operation. This case study demonstrates one of the limitations of the computational tools and reminds the importance of the trained engineer to be critical. Although in practice a higher purity product is not an issue, the software solves the model in order to meet the given specification of 0.990 for the entire uncertainty range. As a result, it is not able to accept the solutions resulting in higher purity for some of the uncertainty values and therefore fails those simulations which in reality would be less challenging as the kinetics are faster. Consequently, although in reality the initial design would be able to tolerate the entire uncertainty range considered, this cannot be confirmed by the simulations and the next step of the methodology needs to be taken.

With the current optimal design and control configuration, and the given control set points, kinetics up to $9.51\times10^9$ $m^3/\text{(kmol-hr)}$ can be mitigated by control action alone. Uncertainty in $K_{eq}$ did not impact on the performance of the system as for all the $K_{eq}$ considered, operation was feasible leading to successful model evaluations (simulations) and the system met the specifications (Figure 5.5, right). It has to be noted that, for Case study 2 and for a $K_{eq} = 2.25$ (60% conversion) the 50% range corresponds to 51.5 % to 64.8% conversion which is a larger range compared to Case study 1. However, for both cases the same observation is made, that $k_0$ and $k_{30}$ have a more significant impact than $K_{eq}$ on the performance of the system under the uncertainty considered. This validates one of the most important benefits of reactive distillation as a process. The fact that the top and bottom products are continuously removed shifts the chemical equilibrium towards the products, therefore any potential reduction in chemical equilibrium is less evident in the system. Product recovery (not shown) under both forms of kinetic uncertainty (cases a and b) was well above specification (1.0 vs 0.90). Changes in
condenser and reboiler duties as well as reflux ratio due to slower kinetics (case a) are more significant compared to changes in chemical equilibrium (case b), as expected.

At this point, it is useful to compare the behaviour of Case study 1 and Case study 2. As Case study 2 had the same favourable relative volatilities but slower kinetics, and Case study 1 could tolerate the same uncertainty in kinetics considered, it can be seen that when one of the two phenomena of the process is more challenging, mitigation strategies are likely to be required to tackle the impact of design uncertainty, as here for Case study 2.

**Step 3:** For Case study 2 and for both slower kinetics (case a) and lower equilibrium (case b), the purity is maintained, however, for faster kinetics (i.e. higher $k_0$) the performance of the system cannot be evaluated as simulations/operations are infeasible, hence we proceed to Step 4. Note that even though Case study 1 had faster kinetics than Case study 2, and increasing the speed of the reaction for Case study 2 towards that of Case study 1, the optimal design is different in the two cases and the performance can therefore not be directly compared.

**Step 4:** Dual-point control is already considered in this system and in order to illustrate the methodology, the control scheme in this case study is considered suitable and will therefore not be revised. Thus, we proceed to Step 5.

**Step 5:** This step considers whether the uncertainty range can be reduced. In this case study, the uncertainty range is assumed to be the narrowest possible and should therefore not be reduced. As a result, we proceed to Step 6.

**Step 6:** This step re-optimises the design but now based on the worst-case uncertainty. Here, the worst-case input for reaction kinetics is the lowest kinetics values considered. Although faster kinetics lead to infeasible operation in this case, re-designing the system to be flexible based on the most challenging kinetics is expected to be more beneficial from a design and operation perspective (i.e. potential increase in stages will lead to smaller column diameter which will allow lower liquid flowrates for faster kinetics), compared to optimising the system using the best-case values which may result in a design unable to tolerate slower kinetics. Given that uncertainty in kinetics (case a) has a more significant impact than uncertainty in $K_{eq}$, the optimisation is performed for the uncertainty in kinetics (case a), i.e. $k_0=3.78\times10^9 \text{ (m}^3/(\text{kmol-hr})\text{)}$ (minimum value) and $K_{eq}=2.25$ (base case value), and the results are given in the middle column of Table 5.2.
The results show that nine additional reactive/separation stages are required to meet the specifications using the worst-case input and the new column also has smaller diameter, as expected. The reflux ratio has also increased.

Table 5.2: Optimal results for Case study 2, considering uncertainty in kinetics.

<table>
<thead>
<tr>
<th></th>
<th>Initial optimal design (Step 1)</th>
<th>Optimal design (Step 6)</th>
<th>Flexible design (Step 8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_0$ (m$^3$/kmol·hr)</td>
<td>7.56·10$^9$</td>
<td>3.78·10$^9$</td>
<td>7.56·10$^9$</td>
</tr>
<tr>
<td>$K_{eq}$</td>
<td>2.25</td>
<td>2.25</td>
<td>2.25</td>
</tr>
<tr>
<td>$\alpha_{BD}$</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

Values in optimal design

- Heavy feed (B) stage ($N_{T1}$): 11
- Light feed (A) stage ($N_{T2}$): 19
- Number of stages ($N_T$): 25
- Reflux ratio ($R_{R,-}$): 4.65
- Bottoms flow rate (B, kmol/hr): 12.6
- Reactive stages: 2-24
- Column diameter ($D_C$, m): 0.78
- Bottom purity ($x_{B,D}$, mol/mol): 0.99
- Product recovery ($x_{REC}$, mol/mol): 1.00
- Top purity ($x_{D,C}$, mol/mol): 0.99
- Production TAC (€/kg): 2.140
- OPEX (M€/yr): 10.52
- CAPEX (M€/yr): 0.27

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Step 7: Since a feasible and acceptable solution was achievable, i.e. the specifications are met and the new design parameters are acceptable, we proceed to Step 8.

Step 8: The re-optimisation in Step 6 was performed assuming the worst-case situation in terms of uncertainty. The current design therefore represents the most stringent situation. In this step, we return to the base-case kinetics whilst maintaining these new design parameters for design, i.e. the number of stages and feed stage locations found in Step 6, but not necessarily the new operating parameters to explore if the new design can now tolerate the entire uncertainty range based on only control mitigation. The operating parameters, here the reflux ratio, is now likely to be too high for normal conditions without disturbances, as the base case kinetics are faster than those considered for the re-optimisation. The product purity is therefore higher than the specification, hence the reflux ratio can be reduced until the purity is returned to the specification which will reduce the operating costs. The new reflux ratio required for the base-case kinetics is shown in the final column in Table 5.2 and has been reduced from 5.75 to 3.48.

Next, we return to Step 2, where uncertainty simulations are performed for the same range of uncertainty on the new flexible design found in Step 8.
Figure 5.5: Case study 2 uncertainty simulations. Product purity ($x_{B,D}$) together with bottom production rate ($B$), condenser ($Q_C$) and reboiler ($Q_R$) duties and top product purity ($x_{D,C}$) together with molar reflux ratio (RR) for initial optimal (lines indicated as initial) and flexible (lines indicated as flexible) dynamic controlled LV design. Uncertainty in kinetics (case a-left, case b-right).
Step 2 (R2): The uncertainty range considered is introduced in the new flexible, dynamic controlled system (LV control) and the results are shown in Figure 5.5 (lines indicated as flexible). The system is now able to tolerate the entire range of uncertainty in kinetics, not only in terms of product purity and product recovery (not shown) but also maintaining production rate at the desired level for slower kinetics (case a). Model evaluations (simulations) are now feasible for the entire range of uncertainty considered. Changes in condenser and reboiler duties as well as in reflux ratio, in other words the control actions for the system to maintain the controlled variables at the set-points are more significant for slower kinetics (case a) than for lower chemical equilibrium (case b).

Step 3 (R2): As shown above, since the entire range of uncertainty is now tolerated and operation in the entire range is feasible, we go directly to Step 9. In this step, the procedure terminates. The user can now have confidence that the new flexible LV controlled design can mitigate the uncertainty considered, here up to ±50% uncertainty in kinetics.

Compared to the initial design, the new flexible design (including nine additional reactive-separation stages) can tolerate the uncertainty in kinetics considered, with an approximately 3% increase in the objective function as shown in Table 5.2 (TAC=2.140 €/kg vs 2.195 €/kg) indicating an effective, and cost-attractive, mitigation option.

5.5.3 Case study 3
In this section, the methodology presented in Section 5.3 is applied to Case study 3, considering uncertainty in separation performance. Case study 3 is characterised by the same fast kinetics and large chemical equilibrium as for Case study 1 but with more challenging relative volatilities. This will allow the investigation of the impact of uncertainty in a system where VLE is more challenging whilst kinetics are favourable.

Uncertainty in relative volatility between the heaviest reactant B and the product D, $\alpha_{BD}$, was considered in the same range as before (±40%). This range is considered as it allows the investigation of the case where the impact of uncertainty leads to a change in boiling point ranking, which will clearly impact on the performance of the system. Therefore, the worst-case scenario was $\alpha_{BD}=0.72$ (reverse boiling points as $\alpha_{BD} < 1$) and the best-case scenario was $\alpha_{BD}=1.68$ (base case $\alpha_{BD}=1.2$). All the other relative volatilities remained the same, except for $\alpha_{CD}$ which changed accordingly, as explained in Case study 1.
Step 1: The optimal parameters for Case study 3 are presented in Table 5.1. It can be seen that Case study 3 has a more demanding design and operation compared to Case study 1 showing that challenging relative volatilities lead to a requirement of additional reactive/separation stages as well as a higher reflux ratio in the reactive distillation column.

Step 2: In Step 2, uncertainty in VLE is introduced in the dynamic, controlled system based on LV control. Table 5.3 shows that the best-case relative volatility is successfully accommodated by the system. This means that with the current optimal design and control configuration, larger $\alpha_{BD}$ up to 1.68 can be mitigated by control action alone, which is obvious as the separation is now easier than expected. Table 5.3 shows that for $\alpha_{BD}=1.68$, it is easier for the system to meet the specifications, leading to lower condenser and reboiler duties as well as lower reflux ratio compared to the values obtained for $\alpha_{BD}=1.20$. However, it can also be seen that the worst-case scenario ($\alpha_{BD}=0.72$) cannot be successfully simulated. This is clearly because with the current design, the system cannot meet the product specifications given the worst-case VLE as for $\alpha_{BD}=0.72$, the heaviest component is reactant B, therefore given the incomplete conversion, the target top and bottom product purities cannot be achieved.

At this point, it is useful to compare the behaviour of Case study 1 and Case study 3. As Case study 3 had the same favourable reaction kinetics but more challenging separation characteristics compared to Case study 1, and Case study 1 could tolerate the same uncertainty in separation performance considered, it can be seen that when one of the two phenomena of the process is more challenging, mitigation strategies are likely to be required to tackle the impact of design uncertainty. This observation was also made in Case study 2 showing that, when uncertainty is considered, there is no single factor (between reaction kinetics and separation performance) which is more dominant, and as long as one of the two is more challenging, it is possible that the system cannot tolerate potential design uncertainty, requiring the application of mitigation strategies.

Step 3: For the worst-case VLE, uncertainty cannot be tolerated and the simulation is infeasible, hence we proceed to Step 4.
Table 5.3: Results for Case study 3, considering ±40% VLE uncertainty range in initial optimal design (Step 2).

<table>
<thead>
<tr>
<th></th>
<th>$\alpha_{BD}=0.72$</th>
<th>$\alpha_{BD}=1.20$</th>
<th>$\alpha_{BD}=1.68$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Manipulated variables</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Q_c$ (kW)</td>
<td>-660.850</td>
<td>-477.011</td>
<td></td>
</tr>
<tr>
<td>$Q_R$ (kW)</td>
<td>551.544</td>
<td>371.558</td>
<td></td>
</tr>
<tr>
<td>RR</td>
<td>6.20</td>
<td>4.20</td>
<td></td>
</tr>
<tr>
<td>D (kmol/hr)</td>
<td>12.7</td>
<td>12.7</td>
<td></td>
</tr>
<tr>
<td>B (kmol/hr)</td>
<td>12.5</td>
<td>12.5</td>
<td></td>
</tr>
<tr>
<td><strong>Controlled variables</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$P_T$ (bar)</td>
<td>0.966</td>
<td>0.966</td>
<td>0.966</td>
</tr>
<tr>
<td>$x_{BD,D}$ (-)</td>
<td>0.99</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td>$x_{D,C}$ (-)</td>
<td>0.98</td>
<td>0.98</td>
<td>0.98</td>
</tr>
<tr>
<td>$M_C$ (-)</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>$M_R$ (-)</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
</tr>
</tbody>
</table>

**Step 4**: Dual-point control is already considered in this system and in order to illustrate the methodology, the control scheme in this case study is considered suitable and will therefore not be revised. Thus, we proceed to Step 5.

**Step 5**: To illustrate the use of the methodology, it will be assumed that the uncertainty range can be reduced. This is not unusual for the later stages of a design as more information may have become available (e.g. more experimental work). In the following, the uncertainty range is thus reduced to ±20%. Thus, the worst-case scenario now is $\alpha_{BD}=0.96$ and the best-case scenario is $\alpha_{BD}=1.44$. Using the new uncertainty range, we return to Step 2.

**Step 2 (R2)**: Table 5.4 shows that the best-case relative volatility ($\alpha_{BD}=1.44$) is successfully accommodated by the system. This means that with the current optimal design and control configuration, larger $\alpha_{BD}$ up to 1.44 can easily be mitigated by control action alone as expected from previous results for $\alpha_{BD}=1.68$ and because the separation is easier than for the base case. It is now easier for the system to meet the specifications, leading to lower condenser and reboiler duty as well as lower reflux ratio compared to the values obtained for the base case ($\alpha_{BD}=1.2$). However, it can also be seen that the worst-case scenario ($\alpha_{BD}=0.96$) cannot be, again, successfully simulated as for $\alpha_{BD}=0.96$ the boiling point range is still reversed.
Table 5.4: Results for Case study 3, considering ±20% VLE uncertainty range in initial optimal design (Step 2-R2).

<table>
<thead>
<tr>
<th></th>
<th>$\alpha_{BD}=0.96$</th>
<th>$\alpha_{BD}=1.20$</th>
<th>$\alpha_{BD}=1.44$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Manipulated variables</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Q_c$ (kW)</td>
<td>Infeasible</td>
<td>-660.850</td>
<td>-507.091</td>
</tr>
<tr>
<td>$Q_R$ (kW)</td>
<td></td>
<td>551.544</td>
<td>399.738</td>
</tr>
<tr>
<td>RR</td>
<td>6.20</td>
<td></td>
<td>4.56</td>
</tr>
<tr>
<td>D (kmol/hr)</td>
<td>12.7</td>
<td></td>
<td>12.7</td>
</tr>
<tr>
<td>B (kmol/hr)</td>
<td>12.5</td>
<td></td>
<td>12.5</td>
</tr>
<tr>
<td><strong>Controlled variables</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$P_T$ (bar)</td>
<td>0.966</td>
<td>0.966</td>
<td>0.966</td>
</tr>
<tr>
<td>$x_{0,D}$ (-)</td>
<td>0.99</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td>$x_{0,C}$ (-)</td>
<td>0.98</td>
<td>0.98</td>
<td>0.98</td>
</tr>
<tr>
<td>$M_{C}$ (-)</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>$M_{R}$ (-)</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
</tr>
</tbody>
</table>

**Step 3 (R2):** For the worst-case VLE, uncertainty cannot be tolerated, hence we proceed to Step 4.

**Step 4 (R2):** Dual-point control is already considered in this system and in order to illustrate the methodology, the control scheme in this case study is considered suitable and will therefore not be revised. Thus, we proceed to Step 5.

**Step 5 (R2):** It is now assumed that the uncertainty range considered cannot be further reduced, therefore we proceed to Step 6.

**Step 6 (R2):** Here, the worst-case input for VLE is $\alpha_{BD}=0.96$ hence re-optimisation of the system is performed.

**Step 7 (R2):** The optimisation of a single reactive distillation column was infeasible given the worst case volatility as even for a very large number of stages ($N_T=100$) the system could still not meet the specifications and provide an optimal solution for the worst-case VLE. The existence of ancillary equipment must therefore be considered as this may increase the reaction and/or separation efficiency of the overall process and as a result may lead to a feasible solution. Thus, we add ancillary equipment and return to Step 1. As a first attempt, we add a pre-reactor (CSTR) as in Chapter 3 it was found that a pre-reactor is included in the optimal solution for systems with this type of reverse boiling point rankings.
**Step 1 (R3):** Case study 3, now including the pre-reactor, was re-optimised using the base-case input (Table 5.1) and the optimal parameters are presented in the final column of Table 5.5 showing that the cost of the optimal process is 2.441 €/kg.

Table 5.5: Optimal results for Case study 3, considering base-case values of VLE (Step 1) with and without additional ancillary equipment.

<table>
<thead>
<tr>
<th></th>
<th>Initial optimal design (Step 1)</th>
<th>Optimal design incl. ancillary equipment (Step 1-R3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_b$ (m²/(kmol·hr))</td>
<td>$30.276 \times 10^9$</td>
<td>$30.276 \times 10^9$</td>
</tr>
<tr>
<td>$K_{eq}$</td>
<td>81</td>
<td>81</td>
</tr>
<tr>
<td>$\alpha_{BD}$</td>
<td>1.2</td>
<td>1.2</td>
</tr>
</tbody>
</table>

**Values in optimal design**

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Heavy feed (B) stage (N_{T1})</td>
<td>15</td>
<td>20</td>
</tr>
<tr>
<td>Light feed (A) stage (N_{T2})</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Number of stages (N_{T})</td>
<td>31</td>
<td>41</td>
</tr>
<tr>
<td>Reflux ratio (RR)</td>
<td>6.2</td>
<td>14.05</td>
</tr>
<tr>
<td>Bottoms flow rate (B, kmol/hr)</td>
<td>12.5</td>
<td>12.5</td>
</tr>
<tr>
<td>Reactive stages</td>
<td>2-30</td>
<td>2-40</td>
</tr>
<tr>
<td>Column diameter (D_{C}, m)</td>
<td>0.91</td>
<td>1.33</td>
</tr>
<tr>
<td>Reactor diameter (D_{R}, m)</td>
<td>-</td>
<td>1.3</td>
</tr>
<tr>
<td>Reactor length (L_{R}, m)</td>
<td>-</td>
<td>1.3</td>
</tr>
<tr>
<td>Bottom purity (x_{B,D})</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td>Product recovery (x_{REC})</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Top purity (x_{D,C})</td>
<td>0.98</td>
<td>0.98</td>
</tr>
<tr>
<td>Production TAC (€/kg)</td>
<td>2.210</td>
<td>2.441</td>
</tr>
<tr>
<td>OPEX (M€/yr)</td>
<td>10.68</td>
<td>11.39</td>
</tr>
<tr>
<td>CAPEX (M€/yr)</td>
<td>0.40</td>
<td>0.80</td>
</tr>
</tbody>
</table>

Next, we proceed to Step 2, where simulations are performed for the same VLE uncertainty on the new optimal design found in Step 1 using the base-case VLE and the ancillary equipment.

**Step 2 (R3):** The two VLE scenarios considered (worst case and best case) are introduced in the new flexible, LV controlled system. Table 5.6 shows that the best-case relative volatility is successfully accommodated by the system. This means that with the current optimal design (reactive distillation column and pre-reactor) and control configuration (LV control scheme), larger $\alpha_{BD}$ up to at least 1.44 can be mitigated by control action alone (as expected).

Table 5.6 shows that for $\alpha_{BD}=1.44$, it is easier for the system to meet the specifications, leading to lower condenser and reboiler duty as well as lower reflux ratio compared to...
the values obtained for $\alpha_{BD}=1.2$. However, it can also be seen that the worst-case scenario ($\alpha_{BD}=0.96$) again cannot be successfully simulated. This is because with the current design, the economically optimal system (optimised with the base-case input) cannot meet the product specifications given the worst-case VLE, even with the existence of the pre-reactor. This indicates that re-designing the existing process including the pre-reactor is required so that the system can tolerate the uncertainty in VLE considered.

Table 5.6: Results for Case study 3, considering ±20% VLE uncertainty range in initial optimal design including pre-reactor (Step 2-R3).

<table>
<thead>
<tr>
<th>$\alpha_{BD}$</th>
<th>$\alpha_{BD}$=0.96</th>
<th>$\alpha_{BD}$=1.20</th>
<th>$\alpha_{BD}$=1.44</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Manipulated variables</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Q_c$ (kW)</td>
<td>Infeasible</td>
<td>-1385.05</td>
<td>-491.604</td>
</tr>
<tr>
<td>$Q_R$ (kW)</td>
<td></td>
<td>1261.04</td>
<td>369.209</td>
</tr>
<tr>
<td>RR</td>
<td></td>
<td>14.05</td>
<td>4.36</td>
</tr>
<tr>
<td>D (kmol/hr)</td>
<td></td>
<td>12.7</td>
<td>12.7</td>
</tr>
<tr>
<td>B (kmol/hr)</td>
<td></td>
<td>12.5</td>
<td>12.5</td>
</tr>
<tr>
<td><strong>Controlled variables</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$P_T$ (bar)</td>
<td>0.972</td>
<td>0.972</td>
<td>0.972</td>
</tr>
<tr>
<td>$x_{B,D}$ (-)</td>
<td>0.99</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td>$x_{D,C}$ (-)</td>
<td>0.98</td>
<td>0.98</td>
<td>0.98</td>
</tr>
<tr>
<td>$M_C$ (-)</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>$M_R$ (-)</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
</tr>
</tbody>
</table>

**Step 3 (R3):** For worst-case VLE, operation is not feasible and simulation fails, hence we proceed to Step 4.

**Step 4 (R3):** Dual-point control is already considered thus we proceed to Step 5.

**Step 5 (R3):** The uncertainty range is assumed to be the narrowest possible and should therefore not be reduced and we proceed to Step 6.

**Step 6 (R3):** The worst-case input for VLE is $\alpha_{BD}=0.96$ and the results of the re-optimisation are presented in Table 5.7. The results show that a larger CSTR and 13 additional reactive/separation stages are needed to meet the specifications when considering the worst-case input.
Table 5.7: Optimal results for Case study 3, considering ±20% uncertainty in VLE (Steps 6 and 8).

<table>
<thead>
<tr>
<th></th>
<th>Initial optimal design (Step 1)</th>
<th>Optimal design (Step 6-R3)</th>
<th>Flexible design (Step 8-R3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_0$ (m$^3$/(kmol ∙ hr))</td>
<td>30.276$\cdot10^9$</td>
<td>30.276$\cdot10^9$</td>
<td>30.276$\cdot10^9$</td>
</tr>
<tr>
<td>$K_{eq}$</td>
<td>81</td>
<td>81</td>
<td>81</td>
</tr>
<tr>
<td>$\alpha_{BD}$</td>
<td>1.2</td>
<td>0.96</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Values in optimal design

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Heavy feed (B) stage ($N_{T1}$)</td>
<td>15</td>
<td>23</td>
</tr>
<tr>
<td>Light feed (A) stage ($N_{T2}$)</td>
<td>20</td>
<td>23</td>
</tr>
<tr>
<td>Number of stages ($N_T$)</td>
<td>31</td>
<td>54</td>
</tr>
<tr>
<td>Reflux ratio ($RR_r$)</td>
<td>6.2</td>
<td>16.6</td>
</tr>
<tr>
<td>Bottoms flow rate (B, kmol/hr)</td>
<td>12.5</td>
<td>12.6</td>
</tr>
<tr>
<td>Reactive stages</td>
<td>2-30</td>
<td>2-53</td>
</tr>
<tr>
<td>Column diameter ($D_C$, m)</td>
<td>0.91</td>
<td>1.18</td>
</tr>
<tr>
<td>Reactor diameter ($D_R$, m)</td>
<td>-</td>
<td>1.30</td>
</tr>
<tr>
<td>Reactor length ($L_R$, m)</td>
<td>-</td>
<td>2.17</td>
</tr>
<tr>
<td>Bottom purity ($x_{B,0}$)</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td>Product recovery ($x_{REC}$)</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Top purity ($x_{C,0}$)</td>
<td>0.98</td>
<td>0.98</td>
</tr>
<tr>
<td>Production TAC (€/kg)</td>
<td>2.210</td>
<td>2.632</td>
</tr>
<tr>
<td>OPEX (M€/yr)</td>
<td>10.68</td>
<td>11.84</td>
</tr>
<tr>
<td>CAPEX (M€/yr)</td>
<td>0.40</td>
<td>1.45</td>
</tr>
</tbody>
</table>

Step 7 (R3): Since a feasible and acceptable solution was achievable, i.e. the specifications are met and the new design parameters are acceptable (middle column in Table 5.7), we proceed to Step 8.

Step 8 (R3): The re-optimisation in Step 6 was performed assuming the worst-case situation in terms of uncertainty. In this step we fix the design and consider the operation of the process. The new reflux ratio is shown in the final column in Table 5.7 and has been reduced from 16.6 to 10.96.

Next, we return to Step 2.

Step 2 (R4): The uncertain VLE scenarios considered are introduced in the new flexible, dynamic LV controlled system and the results are shown in Table 5.8. The system is now finally able to tolerate both worst- and best-case uncertainty in relative volatility, and product purity, product recovery (not shown) and bottoms rate are maintained at their target values. Changes in condenser and reboiler duties as well as in reflux ratio, are more significant for worst- rather than best-case uncertainty, as expected.
Step 3 (R4): Since the entire range of uncertainty is now tolerated and operation in the entire range is feasible, we go directly to Step 9. In this step, the procedure terminates. The user can now have confidence that the new flexible LV controlled design can mitigate the uncertainty considered, here up to ±20% uncertainty in α_{BD}.

Comparing the very initial design (see Table 5.7, first column), the new flexible design (see Table 5.7, final column) including an additional pre-reactor and 23 additional reactive-separation stages can tolerate the ±20% uncertainty in VLE considered, with a 16% increase in the objective function as shown in Table 5.7 (TAC=2.210 €/kg vs 2.572 €/kg) indicating an effective, and cost-attractive, mitigation option.

Table 5.8: Results for Case study 3, considering ±20% VLE uncertainty range in new, flexible design (Step 2-R4).

<table>
<thead>
<tr>
<th></th>
<th>α_{BD}=0.96</th>
<th>α_{BD}=1.20</th>
<th>α_{BD}=1.44</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Manipulated variables</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Q_c (kW)</td>
<td>-1604.09</td>
<td>-1129.51</td>
<td>-1059.86</td>
</tr>
<tr>
<td>Q_b (kW)</td>
<td>1477.00</td>
<td>1004.37</td>
<td>936.87</td>
</tr>
<tr>
<td>RR</td>
<td>16.6</td>
<td>11.38</td>
<td>10.64</td>
</tr>
<tr>
<td>D (kmol/hr)</td>
<td>12.6</td>
<td>12.6</td>
<td>12.6</td>
</tr>
<tr>
<td>B (kmol/hr)</td>
<td>12.6</td>
<td>12.6</td>
<td>12.6</td>
</tr>
<tr>
<td><strong>Controlled variables</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P_t (bar)</td>
<td>0.947</td>
<td>0.947</td>
<td>0.947</td>
</tr>
<tr>
<td>x_{B,D} (-)</td>
<td>0.99</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td>x_{D,C} (-)</td>
<td>0.98</td>
<td>0.98</td>
<td>0.98</td>
</tr>
<tr>
<td>M_C (-)</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>M_R (-)</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
</tr>
</tbody>
</table>

5.5.4 Impact of operational disturbances

Having considered design uncertainties in the previous sections, this section considers the impact of operational disturbances on process performance, in addition to the design uncertainties investigated so far. The goal is to evaluate the tolerance of the system towards the combined effect of design and operational uncertainty, and to investigate how far the system is from the specifications, in case it is incapable of meeting those. Two different disturbances were considered and applied to Case study 1: a) a molar flow rate disturbance in the heavy feed (2% increase) in Section 5.5.4.1 and b) a change in target purity (x_{B,D}) from 0.990 to 0.995 required due to market demand in Section 5.5.4.2.
5.5.4.1 Operational disturbance 1: Feed flow disturbance

In this section, the performance of the system under a load disturbance in addition to design uncertainties is investigated. A 2% increase in Feed B (heavy feed) flow rate is considered in addition to both kinetics uncertainty and VLE uncertainty. Case study 1 is considered and suitable mitigation strategies are proposed.

**Step 1:** As before and given in Table 5.1.

**Step 2:** In Step 2, a 2% increase in Feed B (heavy feed) flow rate was introduced in the LV controlled system. The worst-case VLE design uncertainty ($\alpha_{BD}=1.2$) was also considered as this scenario was expected to have the worst impact on the performance of the system, as was the design uncertainty in kinetics (the design uncertainties as presented in Section 5.5.1), combining both types of uncertainty, design and operation. Uncertainty simulations were performed to evaluate how the system responds to the feed flow rate disturbance, in addition to uncertain kinetics and the worst-case VLE, and the results are shown in Figure 5.6. It can be seen that for the worst-case VLE uncertainty and uncertain kinetics (both in cases a and b) in addition to the feed flow rate disturbance, the system cannot meet the desired production rate (12.6 kmol/hr), reducing to production rates down to 10.7 kmol/hr due to the reduced production of component D. For all cases, bottom product purity and recovery (not shown) remain at their target values, however, not the top product purity, as expected, due to the additional amount of component B needed to now be removed from the top. Figure 5.6 also shows the changes in condenser and reboiler duties as well as in reflux ratio. For the latter, reflux ratio reaches the upper bound without being able to meet the target top product purity. The maximum reflux ratio was set to 150, although practically any number above 10 will result in a very low distillate flow rate. From Figure 5.6 it appears that the effect of low chemical equilibrium (case b) seems more significant than slow kinetics (case a), which is not what was observed so far. This is because in both cases, the reflux ratio reaches a very high value in which almost all of the overhead stream (which mainly consists of C) returns to the column, shifting the chemical equilibrium to the left, therefore making it harder for the system to reach the specifications. As the reflux ratio is at the upper bound, however, this result is not conclusive and results presented later will confirm that when no variable hits their bounds, the slower kinetics (case a) are indeed more impactful than lower chemical equilibrium (case b), showing that this reverse trend was only due to the variable hitting the bound.
Step 3: For both slower kinetics (case a) and lower equilibrium (case b), the purity is maintained, however, this is only possible with reduced production rate hence we proceed to Step 4.

Figure 5.6: Case study 1 uncertainty simulations. Product purity ($x_{D,C}$) together with bottom production rate ($B$), condenser ($Q_C$) and reboiler ($Q_R$) duties and top product purity ($x_{B,D}$) together with molar reflux ratio (RR) for initial optimal (lines indicated as initial) and flexible (lines indicated as flexible) dynamic controlled LV design. Uncertainty in kinetics (case a-left, case b-right) and VLE, as well as operational (feed flow rate increase) uncertainty.
Step 4: Dual-point control is already considered and we proceed to Step 5.

Step 5: The uncertainty range of kinetics and VLE remains constant to be consistent with Section 5.5.1 and for the feed flow disturbance the value is considered reasonable (both from an academic and industrial perspective) and should therefore not be reduced. As a result, we proceed to Step 6.

Step 6: Here, the worst-case input for reaction kinetics is the lowest kinetics values considered and the worst-case VLE. Feed flow rate disturbance is not considered for the re-optimisation as in Chapter 4 we have shown that this type of operational disturbances (when only these are present) are easily rejected by the system. As a result, for Step 6, only worst-case kinetics and worst-case VLE are considered. The re-optimisation is therefore performed for uncertainty in kinetics (as this is usually more impactful as shown so far), i.e. $k_{f0}=15.138\times10^9$ (m$^3$/kmol·hr) and $K_{eq}=81$, as well as for $\alpha_{bo}=1.2$, and the results are given in Table 5.9. The results show that seven additional reactive/separation stages are needed to meet the specifications using the worst-case combined input.

Step 7: Since a feasible and acceptable solution was achievable, i.e. the specifications are met and the new design parameters are acceptable, we proceed to Step 8.

Step 8: The re-optimisation in Step 6 was performed assuming the worst-case situation in terms of uncertainty. The new reflux ratio required for the base-case kinetics is shown in Table 5.9 and has been reduced from 4.54 to 2.72.

Next, we return to Step 2, where uncertainty simulations are performed for the same range of uncertainty on the new optimal design found in Step 8 with the base-case kinetics.

Step 2 (R2): The uncertainty range considered is introduced in the new flexible LV controlled system and the results are shown in Figure 5.6 (lines indicated as flexible). The system is now able to tolerate the entire range of uncertainty in kinetics, VLE and the feed flow rate increase considered, not only in terms of product purity and product recovery (not shown) but also maintaining production rate at the desired level for case a. Changes in condenser and reboiler duties as well as in reflux ratio, are more significant for slow kinetics than for lower chemical equilibrium, which is the observed behaviour so far given that the reflux ratio now has lower and more reasonable values. In this way, the choice of re-optimisation using the worst-case input of slow kinetics (case a) rather
than low chemical equilibrium (case b) is validated. In addition, changes in the manipulated variables are less significant for the flexible design compared to the initial design, as expected, which is also desired from a safety perspective.

**Step 3 (R2):** Since the entire range of combined uncertainty is now tolerated, we go directly to Step 9, and in this step, the procedure terminates. The user can now have confidence that the new flexible controlled design can mitigate the uncertainty considered, here up to ±50% uncertainty in kinetics, -40% in relative volatility and a 2% feed flow rate increase, under LV control.

Comparing the initial design to the new flexible design (including seven additional reactive-separation stages), the new design can tolerate the uncertainty in kinetics and VLE, as well as the operational uncertainty considered, with a 2% increase in the objective function as shown in Table 5.9 (TAC=2.114 €/kg vs 2.073 €/kg) indicating an effective, and cost-attractive, mitigation option.

Table 5.9: Optimal results for Case study 1, considering uncertainty in VLE, kinetics and operational disturbances (2% feed flow rate increase).

<table>
<thead>
<tr>
<th></th>
<th>Initial optimal design (Step 1)</th>
<th>Optimal design (Step 6)</th>
<th>Flexible design (Step 8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_0 (m^3/(kmol\cdot hr))$</td>
<td>30.276-$10^9$</td>
<td>30.276-$10^9$</td>
<td>30.276-$10^9$</td>
</tr>
<tr>
<td>$K_{eq}$</td>
<td>81</td>
<td>81</td>
<td>81</td>
</tr>
<tr>
<td>$\alpha_{BD}$</td>
<td>2.0</td>
<td>1.2</td>
<td>2.0</td>
</tr>
</tbody>
</table>

**Values in optimal design**

<table>
<thead>
<tr>
<th></th>
<th>Heavy feed (B) stage ($N_{T1}$)</th>
<th>Light feed (A) stage ($N_{T2}$)</th>
<th>Number of stages ($N_T$)</th>
<th>Reflux ratio ($R_{R,T}$)</th>
<th>Bottoms flow rate (B, kmol/hr)</th>
<th>Reactive stages</th>
<th>Column diameter ($D_C, m$)</th>
<th>Bottom purity ($x_{B,D}$)</th>
<th>Product recovery ($x_{REC}$)</th>
<th>Top purity ($x_{D,C}$)</th>
<th>Production TAC (€/kg)</th>
<th>OPEX (M€/yr)</th>
<th>CAPEX (M€/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>12</td>
<td>13</td>
<td>18</td>
<td>2.59</td>
<td>12.6</td>
<td>2-17</td>
<td>0.62</td>
<td>0.99</td>
<td>1.00</td>
<td>0.99</td>
<td>2.073</td>
<td>10.32</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

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5.5.4.2 Operational disturbance 2: Set-point product purity increase

So far, the impact of design uncertainty (Sections 5.5.1-5.5.3), as well as the impact of undesired operational disturbance (Section 5.5.4.1) on the performance of a reactive distillation process have been investigated. It is also important to investigate how the system responds to a desired change in process performance. Therefore, the second operational disturbance investigated is the increase of the target bottom product purity, \( x_{b,D} \), from 0.990 to 0.995 due to market demand. This investigation aims to evaluate the flexibility of the system to adjust to a product purity specification increase under combined design uncertainty, considering both kinetics uncertainty and VLE uncertainty. Case study 1 is considered.

**Step 1:** Case study 1 was presented in Table 5.1.

**Step 2:** VLE uncertainty and kinetics uncertainty was considered as presented in Section 5.5.1 and uncertainty simulations were performed as shown in Figure 5.7. The system is able to tolerate the entire range of uncertainty in kinetics considered for all three VLE scenarios (worst, base, best) as well as maintain the increased product purity specification whilst also maintaining the production rate at the desired level. It is therefore shown that in this case, the impact of a load disturbance (feed flow rate disturbance shown in Section 5.5.4.1) is more significant than the impact of a tighter product purity specifications. For condenser and reboiler duties and reflux ratio, slower kinetics are more significant than lower chemical equilibrium, showing that similarly to design uncertainties, for operational disturbances, uncertain equilibrium has less impact than uncertain pre-exponential factors. The most significant changes are observed for the worst-case VLE as expected, however, unlike the feed flow disturbance, the initial design is able to meet specifications. Also, it is noticed that the base- and best-case VLE systems undertake similar and smaller changes to meet specifications comparing to the worst-case VLE system.

**Step 3:** For all cases, the purity is maintained along with the desired production rate for the product purity set-point change. As a result, we directly go to **Step 9**. In this step, the procedure terminates. The user can now have confidence that the initial controlled design can mitigate the uncertainty considered, here up to ±50% uncertainty in kinetics, ±40% in relative volatility and a 0.5% product purity specification increase, under LV control. As no revision of the design was required, the initial production-TAC remained
at its initial value of 2.073 €/kg. However, for the worst uncertainties the production-based TACs ranged from 2.609 €/kg up to 3.080 €/kg, nearly a 50% increase in costs which is a considerable difference compared to the initial estimated cost.

Figure 5.7: Case study 1 uncertainty simulations. Product purity ($x_{B,D}$) together with bottom production rate (B), condenser ($Q_C$) and reboiler ($Q_R$) duties and top product purity ($x_{D,C}$) together with molar reflux ratio (RR) for initial optimal dynamic controlled LV design. Uncertainty in kinetics (case a-left, case b-right), VLE (lines indicated as worst-base-best for each VLE scenario) and operational (target product purity change) uncertainty.
5.6 Conclusions

In this chapter, a systematic methodology for how to consider the impact of uncertainty on reactive distillation systems was presented. Both design and operational uncertainties were considered and the framework was demonstrated using three case studies with different reaction and separation characteristics. The methodology presents mitigation strategies for reactive distillation systems, however, can be extended to different processes and for different control schemes and can also be used for different uncertainties and KPIs to reflect different process requirements.

The methodology demonstrated, based on the case studies considered, that an economically optimal process may nevertheless be inefficient when design uncertainty (in reaction kinetics and separation performance) and/or operational uncertainty (in feed flow rate and target product purity changes) is considered, and that different mitigation strategies may be required to make the process more robust depending on the reaction and separation characteristics of the system. The mitigation strategies considered in this work include applications of tighter process control, enhancement of process flexibility by revising its design and operational parameters, as well as addition of ancillary equipment.

When design uncertainty was considered, it was shown that when both reaction and separation characteristics were favourable (fast reaction and easy separation), then the controlled system could tolerate the uncertainty in reaction kinetics and separation performance without requiring any changes to the design. However, when either reaction or separation performance was more challenging, the system could not tolerate the entire range of the design uncertainty considered. In this case, the process was redesigned by for instance adding more stages and/or increasing the reflux ratio. Alternatively, ancillary equipment (e.g. a pre-reactor) may need to be added for the system to meet specifications under the uncertainty considered. Furthermore, it was found that uncertainty in pre-exponential factors (slower/faster kinetics) affected the performance to a larger extent than uncertainty in reaction equilibrium (equilibrium conversion). It was also shown how a system which can tolerate design uncertainties, may nevertheless be sensitive in the presence of operational uncertainties, in which case revising the design and operational parameters is necessary.

The findings indicate that when uncertainty is expected in a reactive distillation process, a careful consideration of its impact prior to the design of the system is essential as an
economically optimal solution may be very sensitive to uncertainties. This consideration can be performed using the systematic methodology presented in this work, which considers a range of different mitigation strategies with which production failure issues due to design and/or operational deficiencies can be prevented, thus ensuring the desired process performance.
Chapter 6. Conclusions and Future Work

The aim of this chapter is to provide an overview of the project objectives and discuss how these were successfully met. The methodologies developed in this work allow first the simultaneous determination of the optimal design and operation of a complex reactive distillation superstructure, considering a large number of steady state alternatives. Using a large number of case studies, guidelines are developed related to how reaction and separation characteristics impact on the optimal parameters. The associated controllability is evaluated using both conventional and more advanced control schemes to investigate how reaction impacts on the control performance of the reactive distillation column as well as how the combination of reaction and separation parameters determine the latter. The role of design parameters on the control behaviour of the system is also discussed. The overall methodology is completed with a procedure for how to consider the impact of uncertainty on the optimal designs. Mitigation strategies are discussed so that the system can deal with design and/or operational deficiencies. This chapter also discusses various aspects related to future work. These considerations include, but are not limited to, current limitations of the software used, characteristics of the systems considered etc.
6.1 Review of project objectives

The motivation for this work is based on the challenges associated with reactive distillation, mainly related to the optimal design and control of the process, and considering the impact of uncertainty. These aspects currently hinder its industrial implementation, therefore the development of rigorous methodologies which can reduce the associated risks is essential to encourage a greater acceptance of the technology and this was therefore the overall aim of the thesis.

6.1.1 Optimal design

Chapter 3 focused on superstructure optimisation, where a novel methodology for the simultaneous optimisation of the design and operation of a complex reactive distillation process, considering a large number of process alternatives, was successfully developed. Using a superstructure approach, involving a reactive distillation column, a pre- and side-reactor, a side-reboiler, a side-stripper, a vapour pump-around as well as two conventional distillation columns, various process alternatives were considered. MINLP optimisation was performed to find the optimal solution to the resulting complex mathematical problem. The methodology was demonstrated using a large number of different case studies with varying separation and reaction characteristics, all based on industrial relevance.

It was shown that the system characteristics do impact on the optimal design and operation, and that the extent of the impact depends on the relative contributions from separation performance and from kinetics. Separation performance, in this work represented in terms of relative volatilities, was found to have a larger effect on the process design (mainly in terms of the required units, the size of the reactive and non-reactive distillation columns etc.), whilst chemical equilibrium was found to have a larger effect on process operation (mainly in terms of required reflux ratio). This observation applies to all the cases considered in this work. It was demonstrated, however, that the combined effects must still be considered when designing a reactive distillation process as there are close interactions between the separation performance and the reaction performance. An optimal design map was presented that illustrates the relative contributions of the key parameters on the optimal design, in particular, in relation to the number and type of units required.
General rules related to how reaction and separation parameters impact on the design and operation of the process, as well as to when additional equipment is required to meet process specifications, were proposed. It was found that systems with larger relative volatilities met product purity and recovery specifications using a relatively simple process design, i.e. a reactive distillation column with a reasonable number of stages and reflux ratio. For these systems, the requirement of a single reactive distillation column demonstrated that reactive distillation is an economically attractive Process Intensification (PI) example compared to the conventional process of a reactor followed by regular distillation columns. For systems with more challenging relative volatilities, e.g. the product is a middle-boiler, then a pre-reactor, and even two additional columns for further purification, may be required depending on the reaction kinetics, demonstrating that the proposed optimal design methodology can be applied even in such challenging cases. The impact of liquid holdup on the design of the process was investigated in detail given its impact on the reaction performance, and it was shown how an appropriate choice of tray liquid holdup can lead to a more rigorous yet cost-effective design, able to mitigate production failure issues even for slower reaction kinetics.

6.1.2 Control

In Chapter 4, a methodology for how to evaluate the controllability of reactive distillation processes using time domain simulations was presented. Three reactive distillation systems were considered with different combinations of reaction parameters and relative volatilities under conventional (V-only and LV) and advanced (linear Model Predictive Control (MPC)) control configurations. It was investigated how reaction and separation characteristics impact on the control performance of the system as well as how the existence of reaction affects the controllability of a reactive column, compared to a conventional column.

It was shown that for case studies with the same separation characteristics (i.e relative volatilities), the existence of faster or slower kinetics had an impact on the controllability of the process, mainly in terms of settling time, offset and/or overshoot, both for the conventional control schemes as well as the MPC scheme. It was demonstrated that, in dynamic operation, kinetics is a more dominant factor compared to relative volatilities, unlike during steady state design and operation. However, the controllability characteristics were found similar for all case studies considered when considering the
responses towards feed flow rate and feed composition disturbances under either V-only or LV control configuration, showing that the impact of kinetics, although existing, was limited.

The impact of reaction on the controllability of reactive distillation processes was also investigated. A reactive distillation process and its conventional, non-reactive, equivalent were considered. Under the same disturbances and the same control configurations, the existence of reaction introduced larger settling times and larger overshoot. The most important difference was that for the reactive distillation column, maintaining both product purities was impossible unlike for the conventional column. This applies only to the comparison of a binary distillation column with a two-reactant/two-product reactive column and to the control schemes investigated in this work. A different control strategy e.g. including feed ratio control, could potentially be successful in maintaining both purities.

In addition, it was demonstrated how design parameters such as the total number of stages can be considered to improve process controllability. When one-point control is required (called V-only in this work), revising the optimal design (e.g. by increasing total number of stages or increasing tray liquid holdup) hinders the controllability of the process as it introduces additional response time. However, when two-point control is required (LV in this work), revising the optimal design may be beneficial in terms of controlled variables settling time, overshoot and offset. This is due to the fact that increasing the total number of stages and/or tray liquid holdup leads to control loop decoupling, therefore reduced control loop interactions, given that control actions at both ends of the column improve process performance.

Different controller tuning parameters were used for the conventional control configurations in order to show that the conclusions drawn are independent of controller parameter tuning methods. This was demonstrated using literature values for PI controllers gain and integral time as well as optimised parameters in order to minimise the loss of off-spec bottom product.

6.1.3 Uncertainty

Chapter 5 presented a general methodology to systematically investigate the impact of uncertainty on the design and operation of reactive distillation processes. The methodology can, however, be extended to different processes and under different control schemes and can be used for different uncertainties and KPIs to reflect process
requirements. Performing uncertainty simulations allows the evaluation of whether an economically optimal process found using the superstructure methodology presented in Chapter 3 is adequately flexible to tolerate the design and/or operational uncertainties it may encounter.

Three case studies were considered with different combinations of reaction and separation characteristics, showing how uncertainty in kinetic parameters and/or separation performance impacts on the performance of the system. The methodology demonstrated that an economically optimal process may nevertheless be inefficient when design uncertainty (reaction kinetics and separation performance), and/or operational (feed flow rate and target product purity changes) uncertainty, is considered and that different mitigation strategies may be required to make the process more robust, depending on the reaction and separation characteristics of the system. The mitigation strategies considered in this work include applications of different or more advanced process control, enhancement of process flexibility by revising its design and operational parameters, as well as the addition of ancillary equipment.

When design uncertainty was considered, it was shown that when both reaction and separation characteristics were favorable, the controlled system could tolerate the uncertainty considered in reaction kinetics and separation performance. However, when either reaction or separation performance was more challenging, the system could not tolerate the entire range of the introduced design uncertainty. In this case, re-designing the process or adding ancillary equipment was necessary for the system to meet specifications under the uncertainty considered. Furthermore, it was found that uncertainty in pre-exponential factors (slower/faster kinetics) affected the performance of the system to a larger extent compared to uncertainty in reaction equilibrium (equilibrium conversion). It was also shown how a system which can tolerate design uncertainties, may nevertheless be sensitive in the presence of operational uncertainties, in which case revising the design and operational parameters is necessary.

The abovementioned findings indicate that when uncertainty is expected in a reactive distillation process, a careful consideration of its impact prior to the design of the system is essential as an economically optimal solution may be very sensitive to uncertainties. This consideration can be performed using the systematic methodology presented in this work, which considers a range of different mitigation strategies with which production
failure issues due to design and/or operational deficiencies can be prevented, thus reducing the risk and ensuring the desired process performance.

6.2 Recommendations for future work

It is hopefully clear from the work in this thesis that there are significant advantages to be gained by the use of the proposed framework for the design of economically attractive, rigorous, yet flexible, reactive distillation systems. However, several limitations have been identified therefore potential directions for future work are discussed in the following section.

6.2.1 Software limitations related to the superstructure

Inclusion of recycle streams in the superstructure

As mentioned in Chapter 3, the reactive distillation superstructure developed in gPROMS ProcessBuilder cannot currently accommodate the existence of recycle streams due to the mathematical complexity of the flowsheet which results in convergence failures. Recycle streams are not only necessary for the minimisation of waste or potential heat integration, but they can increase reactant conversion when returning back to a reactor or a reactive distillation column, thereby improving the overall process performance and should therefore ideally be included. Consequently, the current exclusion of the recycle streams possibly limits the further improvement of the objective function and of the optimal solution as the engineer must perform manual simulations to further investigate solution improvements including recycle streams once an initial optimal solution is found. The development of alternative initialisation procedures, or of different optimisation solvers with stronger mathematical capabilities, could potentially allow the inclusion of recycles in the flowsheet in the future. This would permit the investigation of an even larger number of process alternatives within the developed superstructure.

Reactive zone and other parameters as optimisation variables

Another current limitation of the software used is the way the reactive zone is coupled in the distillation model. Although the user has the freedom to specify the length of the reactive zone (the starting and ending reactive stages), this specification does not exist as an optimisation variable, therefore the reactive zone cannot be manipulated during optimisation. For this reason, a manual procedure described in Chapter 3 is employed which obviously is not practical. Improving the model so as to include the reactive zone
parameters as optimisation variables would certainly improve the optimisation strategy currently used. Also, it is not clear how multiple reactive zones could be considered in the current software. Although auto-catalysed reactions were considered in this work, and therefore multiple reactive zones were not of interest, for heterogeneous or homogeneous reactions to be considered a clearer indication of how to include multiple reactive zones in the reactive column interface would be necessary.

In addition, this work was conducted based on a number of assumptions such as constant liquid holdup, negligible column pressure drop for steady state design etc. Investigating the impact of these assumptions and potentially adding those parameters in the optimisation problem could further improve the methodology.

6.2.2 Conventional process inclusion in the superstructure

The current reactive distillation superstructure presented in Chapter 3 includes the possibility of excluding the reactive distillation column from the process. In other words, the outlet of the pre-reactor (in case it exists) can either enter the reactive column or directly enter a conventional distillation column. This would allow the desired product to be removed from the bottom of the conventional column and the rest of the components to be removed from the top of the column (DC1 or DC2). Given that no recycle streams are considered and that the product specification is set at the bottom stream only, this possibility covers the conventional process. However, for unfavourable volatilities (i.e. either difficult separations or reverse boiling point rankings) or incomplete reactant conversion, this configuration will not ensure the desired product quality, if the reactive column is not included in the flowsheet. In this case, an additional column, not currently included in the superstructure as it would further increase the mathematical complexity of the problem, would be necessary for both products to be separated and the remaining reactants to be recycled back to the reactor. Therefore, for the conventional process to be properly included in the flowsheet, a second conventional distillation column would potentially be required, following DC1 or DC2.

6.2.3 Uncertainty investigation

Starting with the factors which were considered in the uncertainty investigation in Chapter 5, relative volatilities could not be considered within the GSA tool in gPROMS ProcessBuilder. This was because the thermophysical properties of the components of the system were modelled in an external tool (Multiflash) and therefore relative volatilities were not parameters of the reactive distillation model in gPROMS. This led to
the uncertainty in separation performance being investigated through simulations manually and not automatically using GSA. However, it is expected that gPROMS ProcessBuilder will introduce a thermophysical property method tool within the platform in the future and that update will allow the evaluation of the impact of uncertainty of relative volatilities, among other properties, through GSA.

In addition, the procedure for how to evaluate the impact of uncertainty on optimal reactive distillation processes was demonstrated in Chapter 5 using reaction kinetics and separation performance as uncertain design parameters. However, the methodology is not limited to the parameters considered and can be applied to any design variable which could be expected to include uncertainty, such as tray efficiencies. In addition, in case the factors considered were probabilistic, then the Monte Carlo method within the GSA tool in gPROMS would be applied.

Furthermore, in Chapter 5, a limitation of the software is discussed. For one of the case studies considered, the system was found to be sensitive to the uncertainty introduced although in reality the system would be capable of dealing with the uncertainty. However, this is not identified by the simulation tool which, due to simulation failures (convergence/mathematical issues), indicates that revision of the design is required. This case reminds us that although simulation tools are capable of successfully dealing with problems of very high mathematical complexity, the role of a trained engineer and their critical thought remains significant.

6.2.4 Systems considered

To demonstrate the superstructure optimisation methodology, a large number of case studies was set up based on which the optimal results were generated. Some of those case studies were also used for the controllability and uncertainty investigations. All case studies were based on a generic quaternary reaction system with certain properties such as density, molecular weight etc. However, it would be very interesting in future investigations to consider real, industrially relevant systems and evaluate whether the generated conclusions based on the generic ideal systems in this work also apply to specific real, non-ideal, systems.

6.2.5 Reaction and separation parameters selection

Similarly to the previous point, the case studies considered in order to demonstrate how the framework presented in the three chapters work are characterised by specific
reaction and separation parameters. Reaction parameters were selected so that they consider both fast and slower reactions, as well as high and low chemical equilibrium cases (for a complete justification related to the kinetic parameters selections the reader is advised to return to Chapter 3). In addition, separation parameters were selected so that they reflect common industrial separation tasks in terms of relative volatilities and boiling point rankings. Although a large number of different combinations of reaction and separation parameters was considered, applying the methodology to case studies with different parameters may provide additional insight in future investigations.

6.2.6 Control schemes and disturbances

In Chapter 4, the controllability of the optimal designs was evaluated using conventional and advanced control schemes. The conventional schemes considered were single-point (V-only) and dual-point (LV) whilst the advanced control scheme considered was linear Model Predictive Control. Although the main conclusions drawn are not expected to vary depending on the control scheme, the methodology could nevertheless be applied using alternative control configurations. For instance, cascade, inferential or ratio control schemes could have been considered as conventional configurations whilst non-linear MPC or adaptive control could have been alternative advanced control configurations.

Furthermore, the operational disturbances considered both in Chapter 4 and Chapter 5 were a feed flow rate (load change) and feed composition change, as well as a target product purity change (set-point change). Those disturbances were selected as they are commonly used in similar investigations in relevant literature and they are also commonly introduced in real-plant operation. Although the methodology is not limited to those disturbances and evaluation of other operational deficiencies is possible, gPROMS ProcessBuilder does not currently allow the manipulation of all model variables, consequently limiting the simulation of various potential operational failures. For instance, a failure in the condenser cooling medium valve could cause a decrease in the flow of cooling medium in the condenser leading to insufficient condensation, decrease in top product purity as well as potential temperature increase at the top of the column. However, this scenario cannot be considered using the current software and was therefore not investigated in this work as the cooling medium valve is not included in the list of variables and cannot therefore be manipulated. Investigation of various operational failures could potentially provide a better understanding related to which disturbances are more impactful in a reactive distillation process; this was not one of the primary objectives of this work though.
6.2.7 Objective function

The development of the objective function was a joint effort between UCL, Nouryon and University of Twente. The aim was to develop an objective cost function which includes all the main cost sources in a reactive distillation process superstructure, with up-to-date correlations as well as a reasonable simplicity in order to avoid additional computational cost given the existing complexity of the superstructure. However, as presented in the relevant appendix, the cost of the feed is the main contributor to the operational cost and is also leading to operational cost being approximately 2 orders of magnitude larger than the capital cost. As a result, optimisation mainly aimed to minimise operational cost, indicating in some cases columns with a very large number of trays. Future work could investigate whether balancing OPEX and CAPEX in the objective function indicates alternative optimal solutions, e.g. shorter reactive column with side-reactor with potential benefits from a control and/or safety perspective.

6.2.8 Summary

From this section it is clear that future work can focus on a number of aspects. The most significant aspect would be the development of stronger initialisation and simulation solvers in order to render the inclusion of recycles in the superstructure feasible. In addition, including the reactive zone, liquid holdup, pressure drop etc. as optimisation variables could further improve the methodology developed. Once those issues are overcome, future work could focus on the inclusion of additional columns in the process in order to take into consideration the full potential of the conventional process as well. Furthermore, the type of uncertain parameters and the way these are implemented in gPROMS ProcessBuilder could also be a subject for future research. Moreover, extending the framework developed to real systems and/or systems with different characteristics could provide additional insight into the capabilities of the work presented, similarly to considering alternative control schemes and/or operational disturbances for the controllability evaluation. Finally, future work could be directed towards the investigation of the impact of the developed objective function on the optimal solutions and its potential adjustment to further improve the latter.
This chapter includes all references used in this thesis. References from Chapter 1 to Chapter 6, as well as from the appendices that follow are included.


optimization." Chemical Engineering and Processing - Process Intensification, 155: 108059.


from biomass pyrolysis/gasification of biomass in a two-stage fixed bed reaction system."


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Appendix A. gPROMS ProcessBuilder reactive distillation model validation

The aim of this appendix is to validate the reactive distillation model used in gPROMS ProcessBuilder. For this reason, two validation case studies are presented. The first uses as a comparison basis a literature case study whilst the second validates the results generated from gPROMS ProcessBuilder with the results generated from Aspen Plus for a generic, ideal system, to increase the confidence in the model used.
a) Model validation - literature methyl acetate case study

In order to validate the reactive distillation model used in gPROMS ProcessBuilder v.1.3.1 (Process Systems Enterprise 2020), a literature case study (Al-Arfaj and Luyben 2002d) for the production of methyl acetate was replicated. This case study was selected as methyl acetate is a component of industrial interest, investigated in various reactive distillation case studies in the existing literature. The case study was simulated using the reactive distillation model in gPROMS ProcessBuilder and the generated results show very good agreement with the literature results.

Methyl acetate (MA) is an organic molecule used as a solvent in numerous industrial and cosmetic applications such as glues, paints and nail polish remover. The major use of methyl acetate is as a solvent in dyes and fast drying paints such as lacquers and in the manufacturing of cellulose adhesives and perfumes. It is also used in the production of motor vehicle coatings, cleaning products, cosmetics, furniture and industrial coatings as its boiling point is very low, making it a useful solvent for many resins and oils (Solventis 2020).

The global demand for methyl acetate (for paints and coatings, inks, personal care industry, and others) is driven by various geographic regions (Asia Pacific, North America, Europe, Middle East, and South America). Among the leading methyl acetate manufacturers are Eastman Chemical Co., Celanese Corp., China Petrochemical Corp., EuroChem Group AG and Wacker Chemie AG (MarketWatch 2020). The global market worth of methyl acetate is currently valued at 132.9 million USD in 2020 and is expected to increase by 16.04 million USD (approximately 7%) from 2019 to 2023 (Businesswire 2020). Price data for methyl acetate are difficult to find in the open literature, however, as a point of reference, the price of methyl acetate was 135 USD/kmol in 2010 (Diemer and Luyben 2010). In addition, it was recently announced that the Eastman Company would raise the price of methyl acetate by 0.110 USD/kg, indicating that methyl acetate remains a chemical of great industrial interest (Eastman Chemical Company 2019).

Methyl acetate, for the case study considered (Al-Arfaj and Luyben 2002d), is produced in an esterification reaction between acetic acid and methanol:

\[
\text{Acetic acid} + \text{Methanol} \rightleftharpoons \text{Methyl acetate} + \text{Water}
\]
Two facts suggest that reactive distillation may be a suitable alternative for the production and purification of methyl acetate, and have motivated several studies on the use of reactive distillation for this process (with the most well-known representative the process designed by the Eastman Company): the boiling point ranking of the components and the formation of azeotropes. In this system, the boiling points ranking is not favourable, i.e. acetic acid (heavy reactant) is heavier than water (heavy product), rendering the separation of these two components a challenge. In addition, the formation of azeotropes increases the complexity of the separation in conventional distillation columns. Two minimum-boiling azeotropes can be found in the system, one between methyl acetate and water and one between methyl acetate and methanol. In the following, the specific case study used for model validation, along with the generated results, will be discussed.

In this work, the WILSON thermophysical property method is used as this was also used by the literature source (Al-Arfaj and Luyben 2002d). The thermophysical property method is configured in Multiflash (Infochem 2020) and then imported into gPROMS as explained in Appendix D. The WILSON model in Multiflash can describe VLE of strongly non-ideal mixtures (although it cannot handle two liquid phases, VLLE), using binary parameters from both literature and from regression of experimental data in the INFOBIPS Bank. The WILSON thermophysical property method uses the Wilson activity coefficient model for the liquid phase, the ideal gas equation of state for the vapour phase and the DIPPR model for the calculation of liquid molar density, saturated liquid thermal conductivity etc.

It should be noted that Al-Arfaj and Luyben (2002d) used Marek’s method in addition to Wilson coefficients for the description of the liquid phase VLE (to correlate the VLE in mixtures containing a vapour-phase associating (i.e. monomer and dimer molecules exist in both phases) substance, such as acetic acid) and Peng-Robinson for the equation of state for the vapour phase (which was not possible in Multiflash and the ideal gas equation of state was used instead). Small differences in the results are therefore expected due to this difference in VLE.

The physical properties obtained in this work are given in Table A1 and Figure A1. Figure A1 shows the ternary diagram for methyl acetate, methanol and water at a pressure $P=125$ kPa. Aspen Plus (AspenTech 2017) was used to obtain the thermophysical properties as Multiflash cannot be used to generate phase equilibrium diagrams, ternary
diagrams etc. The two azeotropes can be seen with the red circles on the diagram, limiting the separation of methyl acetate in a conventional distillation column.

Table A1: Components boiling points and azeotropes formed in the methyl acetate system considered at 125 kPa (AspenTech 2017).

<table>
<thead>
<tr>
<th>Components</th>
<th>Boiling point °C (125 kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl acetate</td>
<td>63.20</td>
</tr>
<tr>
<td>Methanol</td>
<td>69.97</td>
</tr>
<tr>
<td>Water</td>
<td>106.01</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>124.98</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Azeotropes (components, temperature)</th>
<th>Components mole fractions in azeotrope</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl acetate/Water (60.81 °C)</td>
<td>0.8642/0.1358</td>
</tr>
<tr>
<td>Methyl acetate/Methanol (59.33 °C)</td>
<td>0.6555/0.3445</td>
</tr>
</tbody>
</table>

Figure A1: Ternary diagram for methyl acetate-methanol-water system (P= 125 kPa). Azeotropes are shown with red circle (AspenTech 2017).
Al-Arfaj and Luyben (2002d) considered two feeds containing acetic acid and methanol, respectively, for the production of methyl acetate (Figure A2) at constant pressure (125 kPa) as shown below:

\[
CH_3COOH + CH_3OH \rightleftharpoons CH_3COOCH_3 + H_2O
\]

(124.98 °C) (69.97 °C) (63.20 °C) (106.01 °C)

The reaction rate is given by the following expression (Al-Arfaj and Luyben 2002d):

\[
\tau_{MA} = \frac{M_{cat} \cdot k_1 \cdot (a_{acid} \cdot a_{methanol} - \frac{a_{MA} \cdot a_{water}}{K_{eq}})}{(1 + K_{acid} \cdot a_{acid} + K_{methanol} \cdot a_{methanol} + K_{MA} \cdot a_{MA} + K_{water} \cdot a_{water})^2}
\]

where

\[
k_1 = 6.942 \cdot 10^9 \exp \left(\frac{-6287.7}{T}\right)
\]

\[
K_{eq} = 2.32 \exp \left(\frac{782.98}{T}\right)
\]

\[
K_{acid} = 3.18
\]

\[
K_{methanol} = 4.95
\]

\[
K_{MA} = 0.82
\]

\[
K_{water} = 10.5
\]

\[
a_i = \gamma_i x_i
\]

where \(a_i\) is the activity for each component \(i\), \(\gamma_i\) is the liquid activity coefficient for component \(i\), \(x_i\) is the liquid mole fraction for component \(i\), \(k_1\) is the reaction rate constant (mol/(g_cat∙h)), \(M_{cat}\) is the mass of the catalyst (g), and \(T\) is the temperature (K). One of the side reactions in the methyl acetate system is the dehydration of methanol to dimethyl ether and water:

\[
2 \text{ Methanol (CH}_3\text{OH)} \rightarrow \text{Dimethyl ether (C}_2\text{H}_6\text{O)} + \text{Water (H}_2\text{O)}
\]

(69.97 °C) (-19.86 °C) (106.01 °C)
The literature source (Al-Arfaj and Luyben 2002d) ignores this side reaction therefore it was also ignored in the model validation study. Figure A2 shows the process flowsheet whilst Table A2 includes all input used for the replication of the case study considered.

From Table A2 it can be seen that stages 8-25 were considered reactive with 1000 kg/tray of catalyst which corresponds to approximately 0.8 m$^3$/tray of catalyst (column diameter was 2.4 m). The two specifications required by gPROMS were the molar reflux ratio and the distillate rate. The system was simulated using the distillation column model within gPROMS ProcessBuilder 1.3.1, which describes a (reactive or non-reactive) two-phase (vapour-liquid) column. More details on how the model is solved, as this depends on specifications provided by the user, are provided in Appendix B. The system was simulated using the input and specifications from literature presented in Table A2 and the results from this work in comparison with the literature results are given in Table A3.

![Flowsheet of methyl acetate process considered (Al-Arfaj and Luyben 2002d).](image)

Good agreement with the literature values is achieved using gPROMS ProcessBuilder as seen in Table A3. The product composition (methyl acetate, top stream) is almost identical to the literature values and only small differences in the mole fractions of acetic acid and water in the product streams are observed, which is mainly due to the way VLE was calculated as explained earlier. In the (top) product stream it can be seen that the
methyl acetate mole fraction achieved (0.9499) overcomes the methyl acetate/water azeotropic composition (0.8642/0.1358, respectively), as the existence of the liquid phase reaction permits the azeotrope to be “reacted away”. Water and methanol exist only in small quantities in the top, or main, product stream. The bottom stream consists mainly of water, with acetic acid and methanol having very low and similar mole fractions. Methyl acetate is not found in the bottom stream, due to its low boiling point. Column profiles could not be considered as these were not presented in the literature source.
Table A2: Case study for the production of methyl acetate specifications (Al-Arfaj and Luyben 2002d).

<table>
<thead>
<tr>
<th></th>
<th>Pressure (kPa)</th>
<th>Temperature (K)</th>
<th>Stage number (from top)</th>
<th>Molar composition</th>
<th>Total Feed (kmol/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Acetic acid feed</strong></td>
<td></td>
<td>125</td>
<td>374.3 (liquid phase)</td>
<td>8</td>
<td>300</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Methanol feed</strong></td>
<td></td>
<td>125</td>
<td>349.2 (vapour phase)</td>
<td>25</td>
<td>300</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Column internals</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>35 (incl. reboiler/condenser)</td>
<td>8-25</td>
<td>Amberlyst 15</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Specification</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Forward reaction conversion</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>95%</td>
</tr>
</tbody>
</table>

- Pressure (kPa): 125
- Temperature (K): 374.3 (liquid phase)
- Stage number (from top): 8
- Molar composition: Acetic acid only
- Total Feed (kmol/hr): 300
- Pressure (kPa): 125
- Temperature (K): 349.2 (vapour phase)
- Stage number (from top): 25
- Molar composition: Methanol only
- Total Feed (kmol/hr): 300
- Number of stages: 35 (incl. reboiler/condenser)
- Reactive stages: 8-25
- Catalyst Information: Amberlyst 15
- Catalyst hold-up (kg/reactive stage): 1000
- Reflux ratio (molar): 1.816
- Distillate rate (kmol/hr): 300
- Type of condenser: Total
- Type of reboiler: Kettle
- Pressure drop/stage (kPa): Negligible
- Forward reaction conversion: 95%
Table A3: Results from gPROMS simulation for the production of methyl acetate and comparison with literature results (input in Table A2).

<table>
<thead>
<tr>
<th></th>
<th>Top stream mole fraction</th>
<th>Bottom stream mole fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>This work</td>
<td>(Al-Arfaj and Luyben, 2002d)</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>trace</td>
<td>0.0136</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.0021</td>
<td>0.0024</td>
</tr>
<tr>
<td>Methyl acetate</td>
<td>0.9499</td>
<td>0.9500</td>
</tr>
<tr>
<td>Water</td>
<td>0.0480</td>
<td>0.0340</td>
</tr>
</tbody>
</table>

b) Model validation - generic case study (comparison of gPROMS with Aspen Plus)

In the previous section, a literature case study was validated showing that the results of gPROMS were well aligned with the results of the literature source. In order to increase the confidence of the accuracy of gPROMS ProcessBuilder 1.3.1, a different, generic case study was also considered, in order to consider a different type of reaction rate expression. The results of this case study from gPROMS were compared with the results of the same case study simulated in Aspen Plus V8.8 (AspenTech 2017). Aspen Plus was selected for this validation as it is also a well-established and accurate process simulator used widely over the last decades in industry and academia. Again, the results showed a very good agreement as will be shown below, with some minor differences observed due to the different way VLE is calculated in the two tools.

The case study considered is validated with the reactive distillation model in gPROMS ProcessBuilder as used in the previous section and with the RadFrac column model in Aspen Plus. RadFrac is an inside-out rigorous method/model for simulating all types of multistage vapour-liquid fractionation operations. It is suitable for three phase systems (VLLE), narrow-boiling and wide-boiling systems and for systems exhibiting strong liquid phase non-ideality. In addition, RadFrac can detect and handle a free water phase or a second liquid phase anywhere in the column and it can decant free water from the condenser. It can handle solids on every stage, and model columns where chemical reactions are occurring. The latter can have fixed conversions, or be equilibrium, rate controlled or electrolytic (Aspentech 2017).
A reversible reaction is considered for this case study, where components A and B react towards components C and D as shown below:

\[ A + B \rightleftharpoons C + D \]

The ideal components A, B, C and D are the same components considered in this work, with the same properties (molecular weight, density etc.) as presented in Chapter 3. The thermophysical property method used by both simulators for the four components was the ideal method for the VLE model, for consistency. The IDEAL property method in Aspen Plus accommodates both Raoult’s law and Henry’s law. This method uses the ideal activity coefficient model for the liquid phase \((\gamma = 1)\), the ideal gas equation of state for the vapour phase and the Rackett model for the liquid molar volume. In gPROMS (i.e. in the Multiflash file which is then imported into gPROMS), the IDEAL method also uses the ideal activity coefficient model for the liquid phase as well as the ideal gas equation of state for the vapour phase as by Aspen, and for the rest of the required properties such as liquid molar density, thermal conductivity etc., DIPPR is used. However, for one of the most important properties for the systems considered, the vapour pressure, there are some differences observed. Although vapour pressure is calculated in both tools using Antoine’s equation, slightly different values are used for parameters A, B, etc. and there are some differences in the equations used:

Antoine’s equation in Aspen Plus: 
\[ \ln P = A + \frac{B}{T+C} + D \cdot T + E \cdot \ln T + FT^G \]

\[ \text{for } T_L < T < T_U \]

Antoine’s equation in Multiflash: 
\[ \ln P = A + \frac{B}{T+C} + D \cdot T^F + E \cdot \ln T + \frac{G}{T^2} \]

\[ \text{for } T_L < T < T_U \]

These differences in the third and fifth terms are expected to be important mainly at the top section of the column, where lighter components are found and therefore the impact of vapour pressure is more significant. However, the differences are expected to be minor and this is confirmed later in Figure A4 where the vapour pressure for all components is presented, as calculated by the two simulation tools.

The generic components were configured in such a way that the relative volatilities are fixed at the values presented in Table A4 for both tools. As the system is considered ideal,
no azeotrope is formed and the boiling point ranking is favourable (i.e. the products are low- and high-boiling components, respectively).

Table A4: Relative volatilities and boiling points for the generic case study considered.

<table>
<thead>
<tr>
<th>Relative volatility</th>
<th>Value</th>
<th>Boiling point (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_{CA}$</td>
<td>2</td>
<td>$T_C = 376.6$</td>
</tr>
<tr>
<td>$\alpha_{AB}$</td>
<td>1.5</td>
<td>$T_A = 398.7$</td>
</tr>
<tr>
<td>$\alpha_{BD}$</td>
<td>2</td>
<td>$T_B = 413.0$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$T_D = 440.4$</td>
</tr>
</tbody>
</table>

The reaction rate expression for the non-/auto-catalysed system considered is given by the following equations:

$$
\begin{align*}
    r_f &= k_f \cdot C_A \cdot C_B \\
    r_b &= k_b \cdot C_C \cdot C_D 
\end{align*}
$$

with

$$
\begin{align*}
    k_f &= 8.410 \cdot 10^6 \cdot e^{-\frac{80000}{R \cdot T}} \\
    k_b &= 0.104 \cdot 10^6 \cdot e^{-\frac{80000}{R \cdot T}} 
\end{align*}
$$

where $R$ is the gas constant (in J/(mol K)), $k_f$ and $k_b$ are the forward and backward reaction rate constants in m$^3$/(kmol·s), the activation energy $E_a$ is expressed in J/mol ($E_a = 80,000$ J/mol) and $T$ is the temperature (in K).

The process flowsheet considered is shown in Figure A3. After the implementation of the same input and specifications in both simulation tools (Table A5), the results from the two simulations are presented below (Table A6), including top and bottom stream compositions and column results. In addition, temperature and composition profiles across the column generated by the two tools are presented in Figure A5 and Figure A6, respectively.
It can be seen in Table A6 that the top and bottom stream results are very close for both tools. Some differences can be observed in the mole fractions of components A and C in the top stream and these differences are due to the differences in the vapour pressure calculation for the two lighter components between the two tools (Figure A4). As explained earlier, the impact of vapour pressure is more significant at the top of the column, affecting mainly the lighter components, in this case components A and C. The bottom stream compositions show an excellent agreement as, at the bottom of the column, the impact of vapour pressure is less significant. The values of the calculated condenser and reboiler heat duties, as well as the boilup ratio show a very good agreement as well (Table A6). In addition, the temperature profiles generated by the two tools (Figure A5) show very good agreement, with some small differences at the top of the column, caused by the differences in the vapour pressure calculation as explained earlier. The composition profiles (Figure A6) show a good agreement, indicating that the reactive distillation model in gPROMS ProcessBuilder is an accurate and rigorous model for the execution of the simulation and optimisation work considered in this work.
Table A5: Specifications for the generic case study.

<table>
<thead>
<tr>
<th>Light feed (component A)</th>
<th>Pressure (atm)</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature (K)</td>
<td>398.5 (saturated liquid)</td>
</tr>
<tr>
<td></td>
<td>Stage number (from top)</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>Molar composition</td>
<td>A only</td>
</tr>
<tr>
<td></td>
<td>Total Feed (kmol/hr)</td>
<td>12.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Heavy feed (component B)</th>
<th>Pressure (atm)</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature (K)</td>
<td>412.8 (saturated liquid)</td>
</tr>
<tr>
<td></td>
<td>Stage number (from top)</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>Molar composition</td>
<td>B only</td>
</tr>
<tr>
<td></td>
<td>Total Feed (kmol/hr)</td>
<td>12.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Column internals</th>
<th>Number of stages</th>
<th>18 (incl. reboiler/condenser)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reactive stages</td>
<td>2-17</td>
</tr>
<tr>
<td></td>
<td>Catalyst Information</td>
<td>No catalyst</td>
</tr>
<tr>
<td></td>
<td>Liquid tray hold-up (m$^3$/tray)</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>Reflux ratio (molar)</td>
<td>2.59</td>
</tr>
<tr>
<td></td>
<td>Bottoms rate (kmol/hr)</td>
<td>12.6</td>
</tr>
<tr>
<td></td>
<td>Type of condenser</td>
<td>Total</td>
</tr>
<tr>
<td></td>
<td>Type of reboiler</td>
<td>Kettle</td>
</tr>
<tr>
<td></td>
<td>Pressure drop/stage (atm)</td>
<td>Negligible</td>
</tr>
</tbody>
</table>
Figure A4: Vapour pressure calculation in Aspen Plus and gPROMS, for the case study considered.

Table A6: Stream and column results comparison (input in Table A5).

<table>
<thead>
<tr>
<th>Components</th>
<th>Liquid mole fractions</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Top stream</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>0.0059</td>
<td>0.0040</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>0.0029</td>
<td>0.0027</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.9912</td>
<td>0.9933</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>trace</td>
<td>trace</td>
<td></td>
</tr>
<tr>
<td>Bottom stream</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>0.0036</td>
<td>0.0039</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>0.0055</td>
<td>0.0052</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.0009</td>
<td>0.0009</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>0.9900</td>
<td>0.9900</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Column results</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Condenser heat duty (kW)</td>
<td>-344.88</td>
<td>-341.32</td>
</tr>
<tr>
<td>Reboiler heat duty (kW)</td>
<td>231.89</td>
<td>227.90</td>
</tr>
<tr>
<td>Boilup ratio (-)</td>
<td>1.79</td>
<td>1.76</td>
</tr>
</tbody>
</table>
Figure A5: Temperature profile for both tools (Stage 1 is condenser whilst stage 18 is the reboiler. Solid line corresponds to gPROMS results whilst dashed lines to Aspen Plus.).

Figure A6: Composition profiles for both tools (Stage 1 is condenser whilst stage 18 is the reboiler. Solid lines correspond to gPROMS results whilst dashed lines to Aspen Plus.).
Summary

Overall, for the validation of the reactive distillation model in gPROMS ProcessBuilder, two case studies were considered. The first used as a comparison basis a literature case study whilst the second validated the results generated from gPROMS ProcessBuilder with the results generated from Aspen Plus for a generic, ideal system. Both case studies have shown that the model used is accurate and can therefore be used for this work.
Appendix B. Solvers information

This appendix provides brief information about the mathematical solvers used for the steady-state and dynamic simulations within gPROMS ProcessBuilder. Information is also provided regarding the solvers used for the MINLP optimisation tasks, along with an outline of the relevant optimisation algorithm.
**Introduction**

gPROMS supports a number of model-based activities: simulation, optimisation, parameter estimation and experiment design. In this work, the model-based activities of interest are simulation and optimisation. Most mathematical solvers for simulation and optimisation need to make use of sub-solvers for the solution of sets of algebraic or differential equations for (re-)initialisation, linear algebra calculations or solution of the optimisation problem and for each solver, a number of parameters, named algorithmic parameters and found in the solution parameters section of the process entity, needs to be set (either take their default values or be specified by the user, based on the choices available). In the following, information related to the simulation and optimisation solvers used in this work, along with their sub-solvers and their algorithmic parameters, are provided.

**a) Simulation activities**

**Differential and algebraic equations (DAE) solver**

Three standard mathematical solvers are available within gPROMS for the solution of mixed sets of differential and algebraic equations: DAEBDF, DASOLV and SRADAU, of which DAEBDF is the default.

The DAEBDF and DASOLV solvers are based on a variable time step, variable order Backward Differentiation Formulae (BDF). Although these solvers have been found to be efficient for a wide range of problems, BDF solvers suffer from loss of stability for certain types of problems (for example, highly oscillatory ones) and are not very efficient for problems with frequent discontinuities. The SRADAU solver implements a variable time step, fully-implicit Runge-Kutta method. The solver has been found (e.g. Olaleye et al. 2014) to be efficient for the solution of problems arising from the discretisation of partial differential algebraic equations with highly oscillatory ordinary differential equations, and models with frequent discontinuities.

The DAEBDF solver (used in this work) constitutes a complete rewrite of the DASOLV solver, aimed to improve performance and robustness. One of the most significant algorithmic changes is the exclusion of algebraic variables from error tests. While this is appropriate for dynamic systems, purely algebraic systems that are solved over time may suffer from reduced performance. The re-introduction of algebraic variables in error tests is therefore possible using solution parameters. Other algorithmic changes with
significant performance benefits for many models concern step size calculations and the handling of reductions. Both solver types described above are designed to deal with large, sparse systems of equations in which variable values are restricted to specified lower and upper bounds. Moreover, the solvers can handle situations in which some of the partial derivatives of the equations with respect to the variables are available analytically while the rest must be approximated. Efficient finite difference approximations are used for this purpose.

The configuration of the DAEBDF solver includes the definition of various parameters (which can either keep their defaults values or be set by the user in the solution parameters section of the process entity), including but not limited to:

- The absolute integration and relative tolerances to determine whether or not a time step taken by the solver is sufficiently accurate.
- The event tolerance which is the maximum time interval within which discontinuities during integration are located.
- The lower/higher order bias factor to determine whether to reduce/increase the order of integration within the DAEBDF solver to influence the integrator towards reducing/increasing the step.
- The maximum number of corrector iterations allowed during a single attempt to solve the system, that is, before reducing the step. On rare occasions, the DAEBDF solver will fail and report a "Corrector step failure" in the output. Similarly, it can reject an integration step and report "Rejecting integration step due to error test failure". These indicate that it is not possible to establish a set of variable values that satisfy the system equations with a given accuracy at a particular point. The messages are often caused by errors or bad scaling in modelling equations which result in either excessively large steps taken in corrector iterations in some of the variables or in step sizes that are too large to satisfy the required accuracy.
- The maximum number of successive corrector failures allowed before declaring an integration failure.
- The output level, i.e. an integer in the range of [-1, 7] which controls the amount of information generated by the solver, and where -1 corresponds to the minimum amount of information generated.
i. Initialisation and re-initialisation sub-solver

The BDNLSOL solver is used as the default initialisation and re-initialisation non-linear solver when the DAEBDF solver is used for simulation activities. BDNLSOL stands for “Block Decomposition NonLinear SOLver”. It is a new implementation of a general solver for solving sets of nonlinear algebraic equations rearranged to block triangular form and employs a novel algorithm for the handling of equations with reversible symmetric discontinuities (IF equations). As a modular solver component, BDNLSOL can in principle make use of any other nonlinear solver component to solve its individual blocks.

The BDNLSOL solver is designed to deal with large, sparse systems of equations in which the variable values are restricted to lie within specified lower and upper bounds. Moreover, the solver can handle situations in which some of the partial derivatives of the equations with respect to the variables are available analytically while the rest have to approximated. In gPROMS models, almost all partial derivatives are computed analytically from expressions derived using symbolic manipulations. The main exception is partial derivatives of equations involving any Foreign Object methods that are not capable of returning partial derivatives. An efficient combination of finite difference approximations and least-change secant updates is used for the latter purpose.

ii. Linear algebra sub-solver

This selection determines the sub-solver to be used for the solution of linear algebraic equations at each step of the integration within the differential and algebraic equation solver. Three mathematical solvers are available in gPROMS for the solution of linear algebraic equations: MA28, MA48 (default) and LASLU. All of them employ direct LU-factorisation algorithms, designed for large, sparse and asymmetric systems of linear equations and MA48 in particular as used in this work, makes use of block triangularisation as a means of accelerating the factorisation and solution of linear systems and of Basic Linear Algebra System (BLAS) for vector and matrix operations.
b) Optimisation activities

Dynamic optimisation solver

The mathematical solver used for optimisation in gPROMS (Process Systems Enterprise 2020) is called CVP_SS. CVP_SS can solve optimisation problems with both discrete and continuous decision variables (i.e. mixed integer optimisation), and both steady-state and dynamic problems are supported.

For dynamic optimisation problems, CVP_SS is based on a control vector parameterisation (CVP) approach which assumes that the time-varying control variables are piecewise-constant (or piecewise-linear) functions of time over a specified number of control intervals. The precise values of the control variables over each interval, as well as the duration of the latter, are generally determined by the optimisation "single-shooting" algorithm as explained below. As the number of control variables is usually a small fraction of the total number of variables in the problem, the optimisation algorithm has to deal only with a relatively small number of decisions, which makes the CVP approach applicable to large problems.

The CVP_SS solver implements a "single-shooting" dynamic optimisation algorithm (Binder et al. 2001). The term "single-shooting" arises from the second step in the algorithm which involves a single integration of the dynamic model over the entire horizon, involving the following steps:

1. The optimiser chooses the duration of each control interval, and the values of the control variables over it.
2. Starting from the initial point at time t=0, the dynamic system model is solved over the entire time horizon to determine the time-variation of all variables x(t) in the system.

The above information is used to determine the values of the objective function to be optimised and any constraints that have to be satisfied by the optimisation. Based on this, the optimiser revises the choices made at the first step, and the procedure is repeated until convergence to the optimum is achieved. As a default, CVP_SS employs the DASOLV code (Jarvis and Pantelides 1992) for the solution of the underlying DAE problem and the computation of its sensitivities (see above for more information on DASOLV). In principle, this can be replaced by a third-party solver with similar capabilities. This is possible by linking external software (i.e. solver in this case) to
gPROMS via the Foreign Object Interface. When implementing the Foreign Object, no
modifications need to be made in the model considered.

i. Initialisation, re-initialisation and linear algebra sub-solvers
Within the dynamic optimisation solver, selections for the initialisation, re-initialisation
and linear algebra sub-solvers and their parameters need to be made. In this work, the
same sub-solvers and their settings were used for each activity as described in the
simulation section (i.e. DAE solver) above.

ii. Mixed-integer non-linear optimisation sub-solver
The OAERAP solver within the CVP_SS solver, employs an outer approximation (OA)
algorithm (Duran and Grossmann 1986) for the solution of the mixed-integer non-linear
optimisation problem (MINLP) and also includes an equality relaxation (ER) scheme
(Kocis and Grossmann 1987) for handling equality constraints. It should be emphasised
that, in the case of optimisation problems defined in gPROMS, this relaxation is applied
only to endpoint equality constraints that may appear in the optimisation entity. The
algorithm described below is guaranteed to obtain the globally optimal solution to
convex optimisation problems posed. This is unlikely to be the case in many problems of
engineering interest including the problem considered in this work which is highly non-
linear and highly non-convex. As a result, an augmented penalty (AP) strategy
(Viswanathan and Grossmann 1990) is employed in order to increase the probability of
a global solution being obtained. Solving the MINLP from different starting points also
increases the probability of locating the global optimum as described in detail in the
optimisation strategy section (Chapter 3).

In more detail, the OAERAP algorithm uses a relaxation of the linearisations of the master
problem, thus expanding the feasible regions in order to reduce the probability of cutting
part of the feasible region due to one of the linearisations. However, this does not
guarantee the possible elimination of part of the feasible region and therefore the
determination of the global optimum cannot be ensured. The linearisations in the master
problem are relaxed by including slack variables in the constraints and the violations of
the linearisations are penalised by including weighted sums of the slack variables in the
objective function (Du and Pardalos 1998).

The OAERAP algorithm applied by gPROMS involves solving a sequence of simpler
optimisation problems, including nonlinear programming (NLPs) problems at steps 1 and
3, and mixed integer linear programs (MILPs) at step 2. An outline of the OAERAP algorithm is given below, demonstrated for the solution of a MINLP minimisation problem. The starting point of the algorithm is providing initial guesses for all optimisation (discrete \(y\) and continuous \(x\)) variables followed by the solution of the sub-problems formed.

**Step 0: Initialisation**

The value of the objective function at the best solution that is currently available, \(\varphi_{\text{best}} := +\infty\) and the value of the objective function at the best solution that may be obtained, \(\varphi_{\text{LB}} := -\infty\) are set.

**Step 1: Solve fully relaxed problem**

A continuous non-linear optimisation problem (NLP), treating all discrete variables as continuous (within their pre-defined lower and upper bounds) to determine the optimal values \(x^{FR}\) and \(y^{FR}\) of the optimisation decision variables \(y\) and \(x\) and of the objective function, \(\varphi^{FR}\), is solved. When such a solution is found and if \(y^{FR}\) is not discrete, then the algorithm proceeds to the next step. Otherwise, at this point, the algorithm can terminate in case of two scenarios:

1. If the above problem is infeasible as initially posed.
2. If all discrete optimisation variables have discrete values at the solution of the above problem, as the optimal solution of the original problem is \(x^{FR}, y^{FR}\) with an objective function value of \(\varphi^{FR}\).

**Step 2: Solve master problem**

If the optimal solution is \(\varphi^{FR}\) with the optimal parameters \(x^{FR}, y^{FR}\) with \(y^{FR}\) not discrete, then a mixed integer linear programming (MILP) problem is constructed which:

a) involves appropriate linearisations of the objective function and the constraints carried out at the solutions of all continuous optimisation problems solved so far,

b) excludes all combinations of discrete variable values that have been considered at step 2 so far.
Next, the above MILP problem formed is solved to determine optimal values of both the continuous and discrete variables, $x^{MP}$ and $y^{MP}$, and to calculate the corresponding value of the objective function $\varphi^{MP}$.

If the above problem is infeasible, or if $\varphi^{\text{best}} - \varphi^{MP} \leq \varepsilon \max(1, |\varphi^{\text{best}}|)$, then the algorithm terminates as there are no more combinations of discrete variables that can be usefully considered. If $\varphi^{\text{best}} = +\infty$, then the original problem was infeasible. Otherwise, the optimal solution is $x^{\text{best}}, y^{\text{best}}$ with a corresponding objective function value of $\varphi^{\text{best}}$. In this case, the MILP provides an improved bound on the best solution that may be obtained and therefore the algorithm updates $\varphi^{LB} := \varphi^{MP}$ and proceeds to the next step.

**Step 3: Solve primal optimisation problem**

At this step, all discrete optimisation decision variables are fixed at their current values, $y^{MP}$. The formed continuous optimisation problem (NLP) is therefore solved to determine the optimal value of the objective function, $\varphi^{PR}$ and the optimal values of the continuous optimisation decision variables, $x^{PR}$.

If the above NLP is feasible and $\varphi^{PR} < \varphi^{\text{best}}$, then an improved solution to the original problem has been found and $\varphi^{\text{best}} := \varphi^{PR}$, $x^{\text{best}} := x^{PR}$, $y^{\text{best}} := y^{MP} := y^{PR}$. Then, the algorithm proceeds to the next step.

**Step 4: Iterate**

In this final step, the next set of values of the discrete optimisation decision variables is set, $y^{MP}$, and the algorithm returns to step 2 to repeat the procedure until the final optimal solution is found within the desired tolerance.

For the configuration of the OAERAP solver, a number of parameters needs to be defined. Although all parameters have a default setting, the user can change these settings based on the nature of their problem, in the solution parameters section of the process entity, as mentioned earlier:

- **Convexity-based termination criterion:** This parameter is defined to select the termination criterion. If set to TRUE (default selection), termination takes place based on the lower bound of the objective function of the MINLP problem, as
produced by the MILP master problem. This criterion is used for those cases when it is known a-priori that the convexity conditions are satisfied and therefore valid lower bounds of the objective function are provided by the MILP. If set to FALSE (mainly for non-convex problems), the optimisation will be terminated when either of the following conditions is satisfied, and the optimal solution will be the point corresponding to the best objective function value of the primary NLP:

a) The number of iterations reaches the pre-defined value or
b) The number of successive iterations without improvement in the objective function of the NLP sub-problem reaches the pre-defined value.

• MILP solver: This option specifies a CAPE-OPEN (CO-LaN 2020) compliant mixed-integer linear solver to be used for the solution of the mixed integer linear programming (MILP) problems at step 2 of the algorithm described above. The default selection is LPSOLVE (Berkelaar 2004), which is a linear (integer) programming solver based on the revised simplex method and the Branch-and-Bound method for the integers.

• Maximum iterations: An integer in the range [1, 100000] which involves the maximum number of iterations performed in steps 2-4 of the algorithm described above (default value is 10000). This is essentially the maximum number of distinct alternatives to be considered by the algorithm.

• Maximum iteration number without improvement in the NLP sub-problem: An integer number in the range [0, 100000] (default 1) which describes the maximum number of successive iterations without improvement in the objective function of the NLP sub-problem.

• NLP solver: This option specifies a CAPE-OPEN compliant non-linear solver to be used for the solution of the nonlinear programming (NLP) problems at steps 1 and 3 of the algorithm described above. The default selection is SSOptTR, which takes advantage of the nature of the steady-state optimisation problem to increase the performance of the optimisation relative to a full dynamic
optimisation. One of the largest computation overheads associated with
dynamic optimisation is the integration of the sensitivity equations, which
provide the optimiser with the gradients of the constraints and objective
function with respect to the decision variables. For steady-state optimisations,
SSOptTR does not need to perform these expensive sensitivity integrations until
the steady-state solution has been found, thus significantly reducing the
computational effort. In a dynamic optimisation problem, the system must be
reinitialised for every minor optimisation iteration (where the decision variables
are optimised along a fixed search direction) and this means reinitialising using
the initial conditions and performing a full sensitivity integration each time. The
SSOptTR solver can simply use the steady-state solution from the last minor
iteration to reinitialise the problem and then perform the sensitivity evaluation,
thus avoiding the more complex initialisation and sensitivity integration.

- Initial guesses for the NLP sub-problem: This selection determines the source of
  initial guesses for the NLP primal optimisation. The OAERAP algorithm employs
two methods of obtaining initial guesses for the NLP Primal Problems (step 3
from the outline above). The first is to use the solution of the fully-relaxed
problem (step 1) as initial guesses for the solution of the primal problem (step 3)
 at each iteration. To use this method, "FullyRelaxedNLP" should be selected. An
alternative approach is to use the solution of the MILP master problem, at the
current iteration, to provide the initial guesses for the NLP primal problem. This
is the default method, specified by setting "MILPMasterProblem" as initial guess
for the NLP sub-problem.

The effectiveness of the method selected depends on the nature of the problem
being solved. One advantage of obtaining initial guesses from the MILP master
problem (MILPMasterProblem, used in this work) is that because the discrete
variables in the NLP problem will be set to the values in the solution of the MILP,
the values of the continuous variables will be consistent with the discrete
variables and so should provide a good initial guess for the NLP problem. A
common example of this behaviour is process synthesis problems, where binary
variables can be used to represent the existence of a process in a flowsheet. If
the solution of an MILP implies that a unit does not exist, then the MILP of step
2 will force some related continuous variables (e.g. the flows through these
units) to be zero and these are, of course, excellent initial guesses for the NLP problem (by contrast, these might not be zero in the solution of the fully-relaxed NLP). However, if the problem is highly non-linear, then the solution of the linearised equations in the MILP may not be such a good initial guess for the NLP. In these cases, it may be better to use the solution of the relaxed NLP as the initial guess for each NLP primal problem.

- Optimisation tolerance: This is a real number in the range [0.0, 1.0] used in the termination criterion (ε) at step 2 of the algorithm described above. Default selection is $10^{-4}$.

- Output level: An integer in the range [-1, 0] reflecting the amount of information generated by the solver as set by the user. When the level is set to -1, then no information is provided regarding the solution. When the level is set to 0 then the solution of fully relaxed point, solution of master problem, solution of primal optimisation problem and final solution are provided.
Appendix C. Objective function

This appendix presents the mathematic formulation of the economic function used for the optimisation of reactive distillation processes described in Chapter 3, based on the collaborative discussion between UCL, Nouryon and UTwente. Detailed explanations on how capital and operating costs were calculated and how the overall objective function was formulated are included.
Introduction

Although ProcessBuilder, which is the tool used for simulation and optimisation in this work, provides functionalities for economic evaluation, it was decided to nevertheless use open source costing functions such that a more comprehensive analysis of different costing elements could be conducted. The objective function considered is taken to be the production-based total annualised cost of the process (in €/ktn), which is the sum of annualised capital and operating costs (in €/yr) divided by the annual production rate (in ktn/yr):

\[ \text{Production-based TAC (€/ktn)} = \frac{\text{TAC (€/yr)}}{\text{Production rate (ktn/yr)}} \]

The currency is chosen to be in € as this is most convenient for the industry sponsor. The main reference considered for the costing functions is Coulson and Richardson’s textbook (Sinnott and Towler 2020) although other textbooks (e.g. Seider et al. 2009) could of course also be used.

Total Annualised Cost, \( \text{TAC} \), is the sum of the annualised capital cost, \( \text{annual. CAPEX} \), and the annualised operating cost, \( \text{annual. OPEX} \):

\[ \text{TAC (€/yr)} = \text{annual. CAPEX} + \text{annual. OPEX} \]

Capital cost includes the bare equipment cost of all the units considered and is multiplied by a Lang factor to also include the installation cost. Note that the correlations used to calculate the CAPEX do not include cost of land, control room or feedstock/product storage. Cost indices are used to bring the costs up to present costs (January 2019). Furthermore, interest rate and depreciation of the capital cost are also considered.

Operating cost includes feedstock, utilities and waste treatment costs, as well as maintenance costs, and are based on 2019 costs, hence cost indices are not needed.

Both capital and operating costs need to be annualised (i.e. expressed as cost per year of plant operation) so that the total annualised cost, \( \text{TAC} \), can be used as a profitability measure for the comparison of various process alternatives.

In Table C1 and Table C2, mathematical expressions for capital (Table C1) and operating (Table C2) costs are presented, followed by a description of how these are annualised.
A) Capital Cost Estimation

In Table C1, the equations used to calculate the individual equipment costs are listed, which are based on the cost correlations suggested by Coulson and Richardson (Sinnott and Towler 2020). All the cost variables (also called driver-cost variables, e.g. W_{shell} in the C_{DC} calculation) were taken from gPROMS ProcessBuilder to ensure consistency. For instance, the distillation column shell weight in gPROMS ProcessBuilder is calculated based on column diameter, shell thickness, material density and column length as explained by Seider et al. (Seider et al. 2009). In addition, valves are not included in Table C1 as valve cost is typically included in installation cost (see Lang factor below). With regards to distillation column cost, Carpenter 20CB-3 was assumed as column shell and internals material to increase corrosion resistance. Therefore, as the correlations of C_{DC} and C_{ST} were based on 304 stainless steel, both were then multiplied by 1.9, to take into consideration the specific material cost (Seider et al. 2009).

The value of the heat transfer coefficient (750 W/m²·K) for the calculation of the condenser and reboiler duty (see Note 6) was chosen using an average value for a tubular reboiler with evaporation with natural circulation and for a tubular condenser (Engineering ToolBox 2003). For both units, a temperature difference of 10 K was assumed as this is a reasonable value for the heating and cooling medium temperature difference in condensers and reboilers of distillation columns (Engineering ToolBox 2004). For the reflux drum capacity calculation, a residence time of 5 min was assumed (Seider et al. 2009). The dollar exchange rate was taken as 0.9 based on the average value for the rates published between January 2019 and January 2020 (Reuters 2020). Finally, interest rate (15%), plant life (10 years) and annual operating hours (8000 hrs/yr) were considered reasonable values from an industrial point of view, which were in agreement with the ranges provided by Coulson and Richardson (Sinnott and Towler 2020).

The bare equipment cost is then given by:

\[
C_{T1}(\$) = N_{DC} \cdot C_{DC} + N_{ST} \cdot C_{ST} + N_{R} \cdot C_{R} + N_{C} \cdot C_{C} + N_{S} \cdot C_{S} + N_{RC} \cdot C_{RC} + N_{RD} \cdot C_{RD}
\]

(C.1)

where \(N_i\) is the total number of units \(i\) of each type of equipment used, i.e. \(i = [DC, ST, R, C, S, RC, RD]\).
Table C1. Cost calculation correlations (in $) for standard distillation related capital costs taken from Coulson and Richardson (Sinnott and Towler 2020) based on 2007 costs.

<table>
<thead>
<tr>
<th>Cost ($)</th>
<th>Type of equipment</th>
<th>Additional information</th>
<th>Cost calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{DC}$</td>
<td>Distillation column (shell) exl. heads, ports, internals etc.</td>
<td>Vertical pressure vessel, Carpenter 20CB-3</td>
<td>$C_{DC} = 1.9 \times (15000 + 68 \times (W_{\text{shell}}, \text{kg})^{0.85})$ where from gPROMS ProcessBuilder: $W_{\text{shell}}(\text{lb}) = \pi \times (D_t + t_s) \times (L + 0.8D_i) \times t_s \times d$ (L is calculated using total number of stages and tray spacing (default value of 0.6 m)) $t_s = \frac{(t_p + t_w)}{2}$ $t_p = P_d \times D_i / (2 \times S \times E - 1.2 \times P_d)$ $t_w = \frac{(0.22 \times (D_o + 18) \times L^2)}{(S \times D_o^2)}$ (for symbols please see Notation list)</td>
</tr>
<tr>
<td>$C_{ST}$</td>
<td>Column internals</td>
<td>Sieve trays, Carpenter 20CB-3 (for each tray)</td>
<td>$C_{ST} = 1.9 \times (110 + 380 \times (D_{\text{tray}}, \text{m})^{1.8})$</td>
</tr>
<tr>
<td>$C_R$</td>
<td>Reboiler</td>
<td>U-tube kettle reboiler$^6$</td>
<td>$C_R = 25000 + 340 \times (Q_{\text{reboiler}} / (7500 - 10, \text{m}^2))^{0.9}$</td>
</tr>
<tr>
<td>$C_C$</td>
<td>Condenser</td>
<td>U-tube shell and tube$^6$</td>
<td>$C_C = 24000 + 46 \times (Q_{\text{condenser}} / (7500 - 10, \text{m}^2))^{1.2}$</td>
</tr>
<tr>
<td>$C_S$</td>
<td>Stripper</td>
<td>Vertical pressure vessel, stainless steel</td>
<td>$C_S = 15000 + 68 \times (W, \text{kg})^{0.85}$</td>
</tr>
<tr>
<td>$C_{RC}$</td>
<td>Reactor</td>
<td>Jacketed, agitated, stainless steel</td>
<td>$C_{RC} = 53000 + 28000 \times (V,R, \text{m}^3)^{0.8}$</td>
</tr>
<tr>
<td>$C_{RD}$</td>
<td>Reflux Drum</td>
<td>Cone roof tank</td>
<td>$C_{RD} = 5000 + 1400 \times (V, \text{m}^3)^{0.7}$ Volume based on 5 min residence time</td>
</tr>
</tbody>
</table>

In equation C.1 and as shown in the notation list, DC stands for distillation column, ST for sieve trays, R for reboiler, C for condenser, S for stripper, RC for reactor and RD for reflux drum. To account for installation cost, bare equipment cost is usually multiplied by a Lang factor ($a_{\text{lang}}$) in order to provide an estimate of the fixed capital cost. For a processing plant predominantly handling fluids, the Lang factor, $a_{\text{lang}}$, is usually assumed to be 4 (Sinnott and Towler 2020). Taking into consideration conversion from dollars to

$^6$The variable used in Table C1 for the calculation of reboiler and condenser cost, Q (W), is the heat duty required for the operation of each of these units. Q is divided (as $Q = U \times A \times \Delta T$) by the product of the heat transfer coefficient (750 W/m$^2$·K) and temperature difference (10 K), i.e. 7500 W/m$^2$, to replace the surface area A (m$^2$) of the condenser/reboiler which is originally included in the cost calculation.

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euros ($rate_{exch}$, assumed to be equal to 0.9 (€/$)), the fixed capital cost is finally expressed as:

\[
\text{CAPEX}_1(\text{€}) = 4 \cdot C_{T1} \cdot 0.9(\text{€}/\text{$}) = 3.6 \cdot C_{T1} \tag{C.2}
\]

**B) Operating Costs Estimation**

Table C2 presents the equations used for the calculation of each type of operational cost, based on utility costs provided by Nouryon. The cost of cooling water for the condenser is ignored. Although feed cost is much larger than the other operating costs, leading to OPEX being much larger than CAPEX, it was nevertheless included in the objective function due to its significance as a cost factor. The cost of the feed was taken to be 1 €/kg, an average value for typical organic liquids purchase cost, as provided by Nouryon.

In more detail, the objective function was defined as the overall cost (capital and operating) divided by the production rate in order to minimise the overall cost to the lowest possible per amount of the desired component produced (i.e. minimise costs whilst maximising production rate). Therefore, feed cost was included so that the objective function would take into account design and energy costs, considering the cost related to incomplete reactant conversion (i.e. product losses) and/or product recovery for the given fixed feed flow rate since production rate was not fixed.

With regards to the operational cost related to waste treatment, further treatment is needed for streams that contain aqueous products with organic impurities. In the case studies presented in this work, component C was considered to be aqueous whilst components A, B and D were considered to be organic compounds, based on esterification systems often considered for reactive distillation in literature (e.g. Luyben and Yu 2008). As a result, waste treatment for all case studies was calculated for the streams that contained mainly product C (e.g. distillate stream from reactive distillation column for Case study 1 etc.) as well as organic impurities i.e. component A, B and/or D. If this stream did not contain any organic impurities (e.g. in case of a single reactive column and full reactant conversion) then the waste treatment cost would be zero.

The total (not annualised) operation cost is the sum of all the individual operating costs:

\[
\text{OPEX (€/s)} = C_{OS} + C_{OF} + C_{OW} + C_{\text{main}} \tag{C.3}
\]
Table C2. Cost calculation correlations (in €/s) for standard distillation operating costs provided by Nouryon.

<table>
<thead>
<tr>
<th>Cost (€/s)</th>
<th>Type of operational cost</th>
<th>Cost calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{OS}</td>
<td>Steam</td>
<td>( C\textsubscript{OS} = Q\text{reboiler}(\text{J/s}) \cdot 24\cdot10^{-9}(\text{€/J}) )</td>
</tr>
</tbody>
</table>
| C\textsubscript{OF} | Feedstock | \( C\text{OF}=F\text{T}(\text{kg/s}) \cdot 1(\text{€/kg}) \)  
\( FT=F_1+F_2+···+F_N \),  
where \( N \) is the number of feed streams |
| C\textsubscript{OW} | Waste treatment | \( C\text{OW}=F\text{OW}(\text{kg/s}) \cdot 0.22(\text{€/kg\text{organic}}) \) |
| C\text{main} | Plant maintenance | \( C\text{main}=(0.1 \cdot \text{CAPEX}\text{2019}) \cdot (\text{€}) / (8000 \cdot 3600) \cdot (\text{s}) \) |

C) Annualisation of the costs

As explained earlier, annualisation is necessary so that the total annualised cost, TAC, can be used for direct comparison of profitability of various process alternatives. However, before annualisation, the equipment cost, which was based on 2007 prices (Sinnott and Towler 2020), needs to be brought up to present cost and this is done by the use of cost indices.

Two different cost indices, CEPCI (Chemical Engineering Plant Cost Index) and NF (Nelson-Farrar Refinery Construction Cost), were considered by Coulson and Richardson (Sinnott and Towler 2020) to account for price inflation of equipment. CEPCI will be used in this work as it applies to an average of all chemical processing industries whilst NF is restricted to the petroleum industry (Seider et al. 2009).

When updating the cost, equipment cost based on a reference year (2007) is multiplied by the ratio of the current year’s index (e.g. 2019, CEPCI = 619.2) to the reference’s year index (2007, CEPCI = 509.7). Thus, costs for 2019 are updated as follows:

\[
\text{CAPEX}\text{2019} (\text{€}) = \text{CAPEX}_1 \cdot \left(\frac{\text{CEPCI}_{2019}}{\text{CEPCI}_{2007}}\right) = \text{CAPEX}_1 \cdot \left(\frac{619.2}{509.7}\right) = 1.21 \cdot \text{CAPEX}_1 \quad \text{(C.4)}
\]
The 2019 index has been used here based on the preliminary 2019 CEPCI index (Jenkins 2019), as this was the only value available when this work started, but can be updated when more recent index values become publicly available.

For the capital costs, one also needs to take into account investment rate and depreciation. These two cost elements can be taken into account as follows (Sinnott and Towler 2020), assuming that the interest rate is 15% and that the plant life is 10 years as previously stated:

\[
CRF (yr^{-1}) = \frac{\text{interest}}{(1-(1+\text{interest})^{-\text{life}})} = \frac{0.15}{(1-(1+0.15)^{-10})} = 0.20
\]  
(C.5)

There are other methods for the consideration of interest rate and depreciation based on literature (Seider et al. 2009), however, these methods require more data such as plant salvage value at the end of the plant life. The equation above was therefore chosen based on its simplicity.

The final annualised capital cost, including investment rate and depreciation (i.e. Capital Recovery Factor, CRF), can then be expressed as follows:

\[
\text{annual. CAPEX (€/yr)} = \text{CAPEX}_{2019}(€) \cdot \text{CRF (1/yr)}
\]
\[
= \text{CAPEX}_{2019}(€) \cdot 0.20 (1/yr) = 0.20 \cdot \text{CAPEX}_{2019}
\]  
(C.6)

To annualise the operating cost, assuming 8000 hr/yr operation (to take into consideration yearly shut-down for maintenance during which there is no plant operation), the calculation is as follows:

\[
\text{annual. OPEX (€/yr)} = \text{OPEX (€/s)} \cdot 8000 (hr/yr) \cdot 3600 (s/hr)
\]
\[
= 288 \cdot 10^5 \cdot \text{OPEX (€/yr)}
\]  
(C.7)

Total Annualised Cost (TAC) is then the sum of the annualised CAPEX and OPEX, thus calculated as:

\[
\text{TAC (€/yr)} = \text{annual. CAPEX} + \text{annual. OPEX}
\]  
(C.8)

As a result, the final form of the objective function is as follows:

\[
\text{Production-based TAC (€/ktn)} = \frac{\text{TAC (€/yr)}}{\text{Production rate (ktn/yr)}}
\]  
(C.9)
Appendix D. Vapour Liquid Equilibrium in Multiflash

This appendix outlines how the properties of the chemical components considered in this work were modelled in Multiflash v6.1 in order to obtain the desired boiling point (volatility) rankings. The Antoine equations used are presented along with an example on how the vapour pressure of the components was configured.
Multiflash (Infochem 2020) is an advanced thermodynamics software and fluid property engine underpinning other simulation tools such as gPROMS ProcessBuilder (Process Systems Enterprise 2020). It is a comprehensive PVT (pressure, volume, temperature) and physical properties package which allows for complete modelling of the phase behaviour of complex mixtures and pure substances. As explained in Chapter 3, once the components and their properties are configured in Multiflash, the file created is imported by ProcessBuilder in order to use these components and their properties in the process flowsheet.

Vapour pressure (in Pa) in Multiflash is calculated using the following version of the Antoine equation:

\[
\ln P_i = A_i + \frac{B_i}{T+C_i} + D_i T^{F_i} + E_i \ln T + \frac{G_i}{T^2} \quad \text{for } T_{\text{min}} \leq T \leq T_{\text{max}}
\]  

(D.1)

In this work, differences in the dependence of vapour pressure on temperature between components are ignored, therefore all Antoine coefficients except \( A_i \) were considered equal for all components \( i \). As a result, for two components \( i=a, b \), their vapour pressures are related as follows:

\[
\ln P_a - \ln P_b = A_a - A_b
\]

(D.2)

The relative volatility \( \alpha_{ab} \) can be expressed based on relative vapour pressures using the following relationship:

\[
\ln \left( \frac{P_a}{P_b} \right) = \ln \left( \alpha_{ab} \right) = A_a - A_b
\]

(D.3)

For instance, let’s consider a desired relative volatility of \( \alpha_{ab} = 2 \):

\[
\ln (2) = 0.693 = A_a - A_b \quad \text{so if for instance } A_a = 10 \text{ then } A_b = 9.307.
\]

As mentioned above, Antoine coefficients \( B_i, C_i, D_i, E_i, F_i \) and \( G_i \) are considered equal for all components \( i \), using the values of the reference component, which in this work is for the heavy reactant, component B, for all case studies as shown in Table D1.
Table D1: Antoine coefficients for component B as used in Multiflash for all case studies presented in this work.

<table>
<thead>
<tr>
<th>Antoine coefficient</th>
<th>Value as used in Multiflash</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_B )</td>
<td>52.6</td>
</tr>
<tr>
<td>( B_A - B_B - B_C - B_D )</td>
<td>-6304.5</td>
</tr>
<tr>
<td>( C_A - C_B - C_C - C_D )</td>
<td>0</td>
</tr>
<tr>
<td>( D_A - D_B - D_C - D_D )</td>
<td>8.9 \times 10^{18}</td>
</tr>
<tr>
<td>( E_A - E_B - E_C - E_D )</td>
<td>-4.3</td>
</tr>
<tr>
<td>( F_A - F_B - F_C - F_D )</td>
<td>6</td>
</tr>
<tr>
<td>( G_A - G_B - G_C - G_D )</td>
<td>0</td>
</tr>
<tr>
<td>( T_{\text{min}} (K) )</td>
<td>273</td>
</tr>
<tr>
<td>( T_{\text{max}} (K) )</td>
<td>800</td>
</tr>
</tbody>
</table>
Appendix E. Dimensionless numbers

This appendix describes the importance of dimensionless numbers in the interpretation of the behaviour of reactive distillation systems. Dimensionless numbers currently used in literature are presented followed by the description of the dimensionless numbers which were developed in this work. The calculation of the numbers for the case studies considered in Chapter 3 is presented, and the conclusions drawn from the generated results are discussed.

It will be shown that the numbers considered in this work, the NEQ number and the DLS number, are unfortunately not sufficiently meaningful to be of help in the design of reactive distillation columns.
Dimensionless numbers are a useful tool for the understanding of the behaviour of reactive distillation systems as well as the evaluation of its suitability compared to the conventional process (i.e. reactor followed by distillation columns). Two dimensionless numbers are widely used in the existing literature for the investigation of reactive distillation processes, the Hatta and the Damköhler number (e.g. Shah et al. 2012c, Chen et al. 2000). The two numbers are used in order to understand where reaction takes place in the liquid phase (bulk, film or both) and to compare residence time with reaction time, respectively.

The use of the Hatta number along with other parameters (forward rate constant, mass transfer coefficient and interfacial area) can help in the identification of the working regime of the reactive distillation process. In other words, the number provides insight into whether the process is mass transfer- or kinetically-controlled (or neither) by indicating whether the reaction takes place only in the bulk phase or also in the film (Kiss 2013). The Hatta number is defined as the ratio of the maximum possible conversion in the liquid film to the maximum diffusion transport through the liquid film therefore indicating where chemical reaction occurs. For higher order reactions of two components the Hatta number is defined as follows (Roizard and Wild 2002):

$$ H_a = \sqrt{\frac{2}{n + 1} \cdot k_f \cdot C_i^{n-1} \cdot C_B \cdot D_A \cdot k_i^2} $$

where $n$ is the order of reaction (-), $k_i$ is the forward reaction rate constant (s$^{-1}$), $C_i$ is the concentration of component $i$ (mol/m$^3$), $D_A$ is the diffusivity (m$^2$/s), and $k_L$ is the mass transfer coefficient (m/s). A low value of the Hatta number ($H_a < 1$) represents a slow process where reaction takes place in the bulk phase, while a high value ($H_a > 1$) represents a fast process with the reaction taking place both in the bulk phase and in the liquid film.

The second dimensionless number used in the existing literature when considering reactive distillation is the Damköhler number, and its mathematical description is as follows:

$$ Da = \frac{H_o k_f}{V_t} $$
where, $H_0$ is the tray liquid holdup (mol), $k_f$ is a forward reaction rate constant (s$^{-1}$), and $V_t$ is the vapour rate (mol/s) on the tray. The Damköhler number is the ratio of characteristic residence time ($H_0/V_t$) to characteristic reaction time ($1/k_f$). For low values of $Da$ ($Da \leq 0.1$) the reaction rate on each reactive tray is relatively slow compared to the residence time available on each stage, and the system is dominated by phase equilibrium. For larger values of $Da$ ($Da > 10$), the reaction rate is fast and chemical equilibrium is approached on the reactive stages. If the Damköhler number lies between these values ($0.1 < Da < 10$), then neither the phase equilibrium nor the chemical equilibrium is controlling, therefore the process is kinetically-controlled (Venimadhavan et al. 1994).

Considering the calculated Damköhler number and the value of $K_{eq}$ together can give useful insight into whether a reactive distillation process is suitable for a given reaction/separation task leading to the following heuristics:

- For low $Da$ ($Da \leq 0.1$) and high $K_{eq}$ ($K_{eq} > 1$), or high $Da$ ($Da > 0.1$) and low $K_{eq}$ ($K_{eq} \leq 1$), as proposed by Venimadhavan et al. (1994), reactive distillation is significantly beneficial:
  - Although a low $Da$ and high $K_{eq}$ represent a slow forward reaction, they also represent a slower reverse reaction, therefore high product formation and reactive distillation is beneficial.
  - A high $Da$ and low $K_{eq}$ represent a fast product formation but at the same time a fast reverse reaction which leads to little product formation. Reactive distillation is in this case beneficial as the continuous product removal shifts equilibrium to product side. However, in this case, the process must not be mass transfer-controlled as the product removal rate solely depends on the rate of mass transfer between phases.

- The combination of high $Da$ and high $K_{eq}$ represents a fast forward reaction and a slower reverse reaction, leading to the situation of an instantaneous irreversible reaction; therefore a simple reactor is generally sufficient to carry out the process and a reactive column is not needed.

- Reactive distillation is not beneficial when the process demonstrates a combination of low $Da$ and low $K_{eq}$. Such a combination represents a slow forward reaction and a fast reverse reaction, which essentially leads to limited product formation. This class of processes requires an optimally designed reactor with a large holdup or distillation with side-reactor (Shah et al. 2012c).
As illustrated above, dimensionless numbers can be very useful in understanding reactive distillation processes. Nevertheless, the latter was not the main focus in this work, therefore Ha and Da were not used. However, two novel dimensionless numbers were developed in discussion with the industrial partner, which are expected to aid the interpretation of the optimal results found in Chapter 3 and could be used as an additional tool in future projects within the company. Using those two dimensionless numbers, to be defined below, a supporting method was therefore developed in order to explain the behavior of the 15 optimal designs found using superstructure optimisation. The two dimensionless numbers aim to provide insight into how close to chemical equilibrium each reactive tray is, and whether chemical reaction or separation is dominating on each reactive tray.

The first novel dimensionless number, **NEQ** (Non-EQuilibrium), explores how far from reaction equilibrium (indicating non-equilibrium) every reactive tray is, and is expressed as follows:

\[
NEQ = 1 - \left(\frac{\prod_{products} x_i}{\prod_{reactants} x_i}\right) \frac{1}{K_{eq}}
\]

where \(x_i\) corresponds to the liquid mole fraction of component \(i\) and \(K_{eq}\) corresponds to the reaction chemical equilibrium (assumed to be constant for all reactive trays). The NEQ number expresses the ratio between the backward and forward reaction rate and is therefore a measure to identify how close/far away from chemical equilibrium the system is and potentially provide insight into the column reaction rates. A NEQ number close to 1 shows that forward reaction is very fast and therefore the effect of the backward reaction can be neglected indicating a kinetically-limited tray or even design. On the other hand, a number close to 0 indicates that the system is close to \(K_{eq}\) which is usually the aim. Negative values of the number show that there is actually consumption of the product, which is a negative and undesired effect. Also, by converting mole fractions to molar concentrations and using the reaction rate equations \(r_f = k_f \cdot C_A \cdot C_B\) and \(r_b = k_b \cdot C_C \cdot C_D\) then the NEQ becomes:

\[
NEQ = 1 - \frac{r_b}{r_f}
\]

The second novel dimensionless number, **DLS** (Design Limiting Step), expresses whether reaction (production of desired components) or separation (i.e. transition from liquid to vapour phase and therefore VLE) is more effective (thereby identifying the limiting task)
on each reactive tray. Component C was selected as a basis for the mathematical
development of the number as this is the lightest component in all case studies,
therefore its transition to the vapour phase occurs easily. This number therefore
expresses the limiting step of the design for component C and the mathematical
expression is formed as follows:

$$DLS = \frac{V_{total} \times R_C}{\varphi_i \times \gamma_{C,i} - \varphi_{i+1} \times \gamma_{C,i+1}}$$

where $V_{total}$ corresponds to the total tray liquid volume (m$^3$), $R_C$ (kmol/m$^3$∙hr) corresponds
to the overall (considering both $r_{f,C}$ and $r_{b,C}$) reaction rate of component C, $\varphi$ (kmol/hr)
corresponds to the total vapour flow at stage $i$ and $\gamma_i$ is the vapour mole fraction of
component C at each stage $i$. A DLS number close to 1 shows that reaction and separation
are equally effective on the reactive stage considered. A DLS number larger than 1
indicates that reaction is more effective than separation whilst a DLS number lower than
1 indicates that separation is more effective on the reactive stage considered.

**Sample calculation**

An indicative calculation of the two novel dimensionless numbers for Case study 1 (tray
1 is not considered reactive, see Chapter 3) is presented below:

1) NEQ number calculation for tray 2 of the reactive column. For:

- $K_{eq} = 81$ (specified for the case study)
- $x_A = 0.007897$ (from gPROMS simulation)
- $x_B = 0.008106$ (from gPROMS simulation)
- $x_C = 0.983900$ (from gPROMS simulation)
- $x_D = 0.000096$ (from gPROMS simulation)

$$NEQ = 1 - \frac{(0.000096 \times 0.98390)/(0.007897 \times 0.008106)}{81} = 0.982$$
indicating a kinetically-limited tray.

2) DLS number calculation for tray 2 of the reactive column. For:

- $V_{total} = 0.1$ m$^3$ (specified for the case study)
- $R_C = 0.001904$ kmol/(hr∙m$^3$) (from gPROMS simulation)
\[ \phi_2 = 45.1443 \text{ kmol/hr} \quad \text{(from gPROMS simulation)} \]

\[ y_{C,2} = 0.993263 \quad \text{(from gPROMS simulation)} \]

\[ \phi_3 = 45.11372 \text{ (kmol/hr)} \quad \text{(from gPROMS simulation)} \]

\[ y_{C,3} = 0.986506 \quad \text{(from gPROMS simulation)} \]

\[ DLS = \frac{0.1 \times 0.001904}{45.1443 \times 0.993263 - 45.11372 \times 0.986506} = 5.68 \times 10^{-4} \]

Indicating that chemical reaction is limiting (i.e. is less effective) tray performance.

**Analysis of the numbers as a function of the column length**

Following the same procedure, the two dimensionless numbers were calculated for all trays and for the 15 optimal designs, resulting in Figure E1 for NEQ and Figure E2 for DLS. Both numbers were plotted as a function of the % length of the column as the actual number of stages was different for the different case studies. 0% corresponds to tray 0 and given that all columns start from tray 1, 0% has no corresponding dimensionless numbers value for any of the designs. 100% column length corresponds to the last tray i.e. the reboiler. For instance, for a column with 18 trays in total (as in Case study 1), tray 1 (condenser) corresponds to \((1/18) \times 100\% = 5.56\%\), tray 2 corresponds to \((2/18) \times 100\% = 11.11\%\) etc. For all columns considered, tray 2 was the first reactive tray (as condenser is not considered reactive) whilst the last reactive tray is the tray just before the reboiler (i.e. total number of stages minus 1).
Figure E1: NEQ number for the 15 optimal designs considered as a function of the reactive column length. 0% corresponds to stage number 0 whilst 100% corresponds to the reboiler stage.

Figure E1 shows that there is no particular trend observed for the 15 designs. Most of the designs have a NEQ number between 0 and 1, however, there are 4 designs which, for the upper section of the column, have negative NEQ values. These designs correspond to the case studies with reverse boiling point rankings showing that for those 4 designs, we actually have consumption of the product in the upper section of the column, which is an undesired effect. For the 11 designs with the preferred boiling point rankings, it appears that there is no correlation between the reaction and separation characteristics and their corresponding NEQ as a function of column length. Values close to 0 are observed for some of the case studies towards the bottom of the column where the heavy component D has a high liquid mole fraction, however, values close to 1 as well as intermediate values are observed for various case studies, making the drawing of specific conclusions difficult.
The second dimensionless number, DLS, was also plotted as a function of column length (Figure E2). Most of the case studies have values between 0 and 1 showing that for those, reaction is slower than transition from liquid to vapour phase indicating that kinetics, and not VLE, are limiting the design. Case study 1 and Case study 10 have values larger than 1, however, the only common characteristic between those two case studies is the fast forward pre-exponential factor \( k_{f0} = 8.41 \times 10^6 \) m\(^3\)/kmol∙s. A number of other case studies have the same pre-exponential factor and their values of DLS do not exceed 1, therefore no connection can be made between reaction and separation characteristics and the DLS number. In addition, only two case studies have a negative DLS value, Case study 14 and Case study 15 which have the same relative volatilities \( \alpha_{CA} = 1.5, \alpha_{AB} = 2.5, \alpha_{BD} = 2 \) and same forward pre-exponential factor \( k_{f0} = 8.41 \times 10^6 \) m\(^3\)/kmol∙s, so this particular relative volatility set could be further investigated. Overall, similarly to the NEQ number, no specific connections can be found between reaction and separation characteristics and DLS as a function of column length as most of the case studies follow a similar trend with no other major differences except for those already mentioned.

### Analysis of reaction rates as a function of NEQ

In an attempt to correlate the NEQ number to the column reaction rates, Figure E3 and Figure E4 are generated, indicatively for Case study 1 and Case study 12. For both cases it can be seen that high reaction rates can still be achieved for low values of NEQ,
therefore NEQ cannot be an indication of reaction rates in the reactive column. As a result, since a NEQ number close to 1 does not ensure high reaction rates, it cannot be used as an indicator of the latter but more as an indicator for component concentrations (i.e. $C_A \cdot C_B >> C_C \cdot C_D$).

Figure E3: Production rate of component C as a function of NEQ for Case study 1.

Figure E4: Production rate of component C as a function of NEQ for Case study 12.
Figure E5: Production rate of component C as a function of NEQ for Case study 8.

As mentioned earlier, for the cases where reverse boiling point ranking is observed (cases 8, 9, 10 and 11), NEQ takes negative values as well. Focusing on Case study 8 as an example, an additional observation made is that negative values (i.e. negative $R_C$ which indicates consumption of component C) can take values as low as -306, however, all positive values remain between 0 and 1. Also, from Figure E5 it can be seen that, similarly to Figure E3 and Figure E4 high reaction rates can be achieved for low NEQ values and in addition, for negative NEQ numbers, reaction rates are low as well, which is expected as in these sections, we have consumption of the product.

**Correlation between DLS and reaction rates**

In an effort to investigate the correlation between the DLS number and reaction rate (production rate of component C) for the reactive stages, Figure E6 and Figure E7 were generated for Case study 1 and Case study 2, respectively. Case study 1 has higher reaction rates due to the faster kinetics, however, for both case studies it can be seen that only highly reactive stages can achieve higher values of DLS, indicating insufficient (or at least less effective) separation.
Figure E6: Production rate of component C and DLS number as a function of tray number for Case study 1.

Figure E7: Production rate of component C and DLS number as a function of tray number for Case study 2.
Analysis of dimensionless numbers based on relative volatilities

Another effort was made to use the dimensionless numbers generated in order to explain the behavior of the optimal designs, this time by grouping the optimal designs based on their relative volatilities. For System I volatility cases ($\alpha_{CA}=2$, $\alpha_{AB}=1.5$, $\alpha_{BD}=2$) the comparisons are shown in Figure E8.

![Graphs showing NEQ, DLS, and production rate of component C as a function of column stages for different case studies.](image)

Figure E8: NEQ, DLS and production rate of component C as a function of column stages for System I volatility cases ($\alpha_{CA}=2$, $\alpha_{AB}=1.5$, $\alpha_{BD}=2$) (Case studies 1, 2, 3, 4 and 5).
For all cases of this relative volatility set, it can be seen that the system is closer to chemical equilibrium (i.e. NEQ is closer to 0) at the bottom section of the column (Figure E8). In addition, DLS is higher than 1 only in Case study 1, indicating that some trays produce more component C than the amount which is removed through separation. Furthermore, cases 3, 4 and 5 show similar reaction rates on their trays, although their $K_{eq}$ and the calculated NEQ number vary significantly. It can also be observed that Case 4 has trays which are closer to chemical equilibrium although this does not result in lower reaction rates. The impact of this behaviour can be mainly seen in the higher reflux ratio of Case study 4 compared to the rest of the case studies in the group. Also, it appears that the maximum reaction rate does not scale with the forward pre-exponential factor, and the NEQ value at this maximum reaction rate is close to 1 for most cases (except Case study 4) which is an observation that needs further study.

The same analysis was performed for volatility System II ($\alpha_{CA}=1.2$, $\alpha_{AB}=4.15$, $\alpha_{BD}=1.2$) as shown in Figure E9.

**Figure E9:** NEQ, DLS and production rate of component C as a function of column stages for System II volatility cases ($\alpha_{CA}=1.2$, $\alpha_{AB}=4.15$, $\alpha_{BD}=1.2$) (Case studies 6 and 7).
For this volatility system (Case study 6 and Case study 7), neither designs are limited by chemical equilibrium as NEQ is approximately 1 for the entire column (Figure E9). In addition, reaction rate seems to be limited by dilution of the reactants as the peak of reaction rates is observed around the feed stage location (stage 22 for Case study 6 and stage 35 for Case study 7) of the light reactant.

The next relative volatility system, System III, \((\alpha_{CA}=2, \alpha_{AB}=1.5, \alpha_{BD}=0.75)\) is characterised by reverse boiling point rankings and includes Case studies 8, 9, 10 and 11 (Figure E10).

![Figure E10: NEQ, DLS and production rate of component C as a function of column stages for System III volatility cases \((\alpha_{CA}=2, \alpha_{AB}=1.5, \alpha_{BD}=0.75)\) (Case studies 8, 9, 10 and 11).](image)

For this system, all cases have negative overall reaction rate at the top stages (consumption of product) and most of the conversion occurs at the top section. Cases 10 and 11 are limited at the bottom section of the column by chemical equilibrium, and high concentration of D inside the column indicate low concentrations of components A and B, and therefore slow reaction rates. Maximum reaction rates do not scale with \(k_0\) and that can be understood by comparing Case 8 with Case 10 or Case 8 with Case 11. For
these cases, considering DLS with a different component as a basis (and not C) might be beneficial as the problems seem to occur due to the challenging relative volatility between reactant B and product D, $\alpha_{BD}$.

The next set of relative volatilities, System IV, includes Case study 12 and Case study 13 ($\alpha_{CA}=1.2$, $\alpha_{AB}=1.5$, $\alpha_{BD}=1.2$). It can be seen that highest conversion is achieved for lower or higher NEQ numbers, respectively, so concentration seems to be more important for overall production rate compared to the driving force based on chemical equilibrium, which therefore cannot act as a basis for conclusions (Figure E11).

Figure E11: NEQ, DLS and production rate of component C as a function of column stages for System IV volatility cases ($\alpha_{CA}=1.2$, $\alpha_{AB}=1.5$, $\alpha_{BD}=1.2$) Case studies 12 and 13.

The last relative volatility set, V, ($\alpha_{CA}=1.2$, $\alpha_{AB}=2.5$, $\alpha_{BD}=2$) includes Case studies 14 and 15 (Figure E12).

Figure E12: NEQ, DLS and production rate of component C as a function of column stages for System V volatility cases ($\alpha_{CA}=1.2$, $\alpha_{AB}=2.5$, $\alpha_{BD}=2$) (Case studies 14 and 15).
Both cases have a negative reaction rate in the bottom section and both cases are limited by chemical equilibrium at the bottom part (even Case study 14 which has $K_{eq}=81$). High reaction rates can be achieved at low NEQ numbers as already mentioned for other cases.

An alternative route for comparing case studies with the same characteristics is by comparing designs with the same kinetics but different relative volatilities. For instance, by comparing Case studies 1 and 6 or Case studies 2, 12 and 15, although it can be seen that no particular connection can be made. NEQ numbers vary and in general, higher reaction rates are likely to result in DLS closer to 1, however, these observations are general and not specific for any reaction/separation characteristics.

**Conclusion**

Overall, reaction/separation characteristics as indicated by the two dimensionless numbers defined in this work, the NEQ number and the DLS number, do not seem to provide sufficient insight into separation limitations for any meaningful conclusions to be drawn. The DLS number does not seem to depend on kinetics or VLE parameters. On the other hand, the NEQ number is a good indicator for $K_{eq}$ limitations, but not for reaction rates. As a result, the use of the suggested dimensionless numbers may provide some insight into the limitations of the optimal designs, however, further work is required in order to be able to use those dimensionless numbers as a supporting method for the interpretation of the reactive distillation designs.