

Synthesis and design of integrated reaction- separation systems with complex configurations and rigorous models

**A dissertation submitted to the University of Manchester for the degree of
Master of Science in Advanced Chemical Engineering
in the Faculty of Science & Engineering**

Melissa Bariani Bremermann

**School of Chemical Engineering and Analytical Science
The University of Manchester**

-2019-

Table of Contents

List of Figures	4
List of Tables	6
Abstract	7
Declaration	8
Intellectual Property Statement	9
Acknowledgments	10
Chapter 1: Introduction	11
1.1. Objectives	14
1.2. Overview of the dissertation	14
Chapter 2: Background	16
2.1. Process synthesis and design	16
2.1.1. Reactor network synthesis and design	19
2.1.2. Separation network synthesis and design	20
2.1.3. Simultaneous reaction-separation network synthesis and design	23
2.2. Construction of superstructures	24
2.2.1. Construction of reactor network superstructure	24
2.2.2. Construction of separation network superstructure	28
2.2.3. Construction of reaction-separation network superstructure	29
2.3. Formulation of optimisation problem	30
2.3.1. Mathematical modelling and programming concepts	30
2.3.2. Formulation strategies for reactor networks	34
2.3.3. Formulation strategies for separation networks	35
2.3.4. Formulation strategies for reaction-separation networks	38
2.4. Solving strategies for superstructure optimisation	39
2.4.1. Solving strategies for reactor networks	40

2.4.2.	Solving strategies for separation networks.....	41
2.4.3.	Solving strategies for reaction-separation networks.....	42
2.5.	Conclusions.....	44
Chapter 3: Methodology		45
3.1.	Construction of superstructures	45
3.2.	GDP model of superstructure.....	47
3.2.1.	Reactor network modelling.....	47
3.2.2.	Separation network modelling	49
3.3.	Model reformulation	58
3.3.1.	Reformulation of reactor network disjunction using convex hull.....	58
3.3.2.	Reformulation of reactor network disjunction using bypass efficiency	60
3.4.	Economic model and other equations.....	60
3.4.1.	Economic equations for reactor network	60
3.4.2.	Economic equations for separation network.....	61
3.4.3.	Total costs and objective function.....	63
3.5.	Solution strategy	63
3.6.	Case study: benzene chlorination process	65
3.6.1.	Description.....	65
3.6.2.	Superstructures specifications.....	66
3.6.3.	Modelling specifications.....	66
3.6.4.	Solution strategy.....	68
Chapter 4: Results and discussion		69
4.1.	Results.....	69
4.1.1.	Flowsheet.....	69
4.1.2.	Separation system	69
4.1.3.	Economic results.....	76
4.2.	Comparison of results with previous studies.....	77

4.3. Limitations	78
Chapter 5: Conclusions.....	80
5.1. Future work	81
Appendix A: Data of case study	82
Appendix B – Nomenclature for reaction network model	84
Appendix C – Nomenclature for separation network model	86
References	90

List of Figures

Figure 1: The Onion model of process design. (Smith 2016)	16
Figure 2: Complex configuration distillation columns. A) Prefractionation without thermal coupling; B) Petlyuk column; C) Dividing wall column; D) Side stripper; E) Side rectifier. (Jobson 2019)	22
Figure 3: Temperature-enthalpy effects of thermal coupling. A) Conventional sequence (direct); B) Prefractionator arrangement; C) Thermally coupled prefractionation. (Jobson 2019)	23
Figure 4: Reactor types of CSTR, PFR and differential side-stream reactors (SFR, MMR and DSR). (C. A. Schweiger and Floudas 1999)	24
Figure 5: Representation of a DSR with PFR in series. (C. A. Schweiger and Floudas 1999)	25
Figure 6: Reactor network superstructure used by Ma et al. (Ma et al. 2018).....	27
Figure 7: Representation of STN formulation and equivalent	29
Figure 8: Representation of feasible regions for A) the original problem; B) the big-M reformulation; C) the convex hull reformulation. (Vecchietti et al. 2003).....	34
Figure 9: Tray structures for the modelling of complex columns (Yeomans and Grossmann 2000b).....	37
Figure 10: Bypass efficiency model (Ma et al. 2018).....	38
Figure 11: Solution strategy proposed by Ma et al. (Ma et al. 2018).....	42
Figure 12: Solution strategy proposed by Ma et al. (Ma et al. 2019)	43
Figure 13: Connection of reactor and separation network superstructures.	45
Figure 14: Arrangement of permanent and conditional trays in the separation network superstructure.	46
Figure 15: Proposed model for permanent trays.	49
Figure 16: Solution approach for the present study.	65
Figure 17: Benzene chlorination. (Zhang et al. 2018)	65
Figure 18: Optimal process configuration.....	70
Figure 19: Optimal distillation system.....	71
Figure 20: Temperature profile - section 1.	72
Figure 21: Temperature profile - section 2.	73
Figure 22: Liquid composition - section 1.	73
Figure 23: Liquid composition - section 2.	74

Figure 24: Vapour composition - section 1 74

Figure 25: Vapour composition - section 2 75

List of Tables

Table 1: Diameters calculated for different sections.	75
Table 2: Economic results.	76
Table 3: Results from the present and previous works.	77

Abstract

Chemical engineering, and specially process design, synthesis and intensification, are well positioned to support both society and industry in overcoming present global challenges of environment degradation, energy supply, water scarcity and food supply. These challenges have been translated into industrial problems that involve the design of chemical processes with decreased water and energy consumption, and improved efficiencies. In this context the present study focuses on the simultaneous synthesis and design of reaction-separation systems including complex configuration distillation columns and using rigorous models. The study is considered a further step in this research area, as previous works have usually focused on the synthesis of sub-networks and have used shortcut models. Additionally, among complex configuration, thermally coupled distillation columns are reported to present significant savings in terms of the total annualised cost of the system. Among the available approaches to synthesis and design, a superstructure optimisation approach is used. The procedure involves the construction of a superstructure that includes a reaction superstructure, taken from Ma et al. (Ma et al. 2019) and a separation superstructure, proposed by Sargent and Gaminibandara (Sargent and K. Gaminibandara 1976). The modelling is performed using generalised disjunctive programming (GDP) to produce a logic-based model. This model is then reformulated into a mixed-integer nonlinear programming (MINLP) optimisation problem, where the objective is to minimise the total annualised cost of the process. For the reformulation convex hull and bypass efficiency methods are used. A modified version of the solving strategy presented by Ma et al. (Ma et al. 2019) is used, which involves using the solver SBB in General Algebraic Modelling System (GAMS).

The proposed framework is applied to a case study previously addressed by Zhang et al. (Zhang et al. 2018) and Ma et al. (Ma et al. 2019). Economic models and assumptions made in those studies are maintained in order to evaluate the benefits of including complex configuration columns in the design possibilities. Results present a flowsheet with one PFR reactor and complex configuration distillation columns that are partially thermally coupled. The total annualised cost of the process is 5.85×10^5 \$/yr, which is 6.3% and 4.7% less than the value achieved by Zhang et al. (Zhang et al. 2018) and Ma et al., respectively. Results show that it is both possible and beneficial to consider complex configuration distillation columns, including thermally coupled ones, in the simultaneous synthesis and design of reaction-separation systems using rigorous models.

Declaration

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

Melissa Bariani Bremermann

Intellectual Property Statement

- i) The author of this dissertation (including any appendices and/or schedules to this dissertation) owns certain copyright or related rights in it (the 'Copyright') and s/he has given The University of Manchester certain rights to use such Copyright, including for administrative purposes.
- ii) Copies of this dissertation, either in full or in extracts and whether in hard or electronic copy, may be made only in accordance with the Copyright, Designs and Patents Act 1988 (as amended) and regulations issued under it or, where appropriate, in accordance with licensing agreements which the University has entered into. This page must form part of any such copies made.
- iii) The ownership of certain Copyright, patents, designs, trademarks and other intellectual property (the 'Intellectual Property') and any reproductions of copyright works in the dissertation, for example graphs and tables ('Reproductions'), which may be described in this dissertation, may not be owned by the author and may be owned by third parties. Such Intellectual Property and Reproductions cannot and must not be made available for use without the prior written permission of the owner(s) of the relevant Intellectual Property and/or Reproductions.
- iv) Further information on the conditions under which disclosure, publication and commercialisation of this dissertation, the Copyright and any Intellectual Property and/or Reproductions described in it may take place is available in the University IP Policy (see <http://documents.manchester.ac.uk/display.aspx?DocID=487>), in any relevant Dissertation restriction declarations deposited in the University Library, The University Library's regulations (see <http://www.manchester.ac.uk/library/aboutus/regulations>) and in The University's Guidance for the Presentation of Dissertations. (www.researchsupport.eps.manchester.ac.uk/learning_bytes/academic_writing).

Acknowledgments

Firstly, I would like to acknowledge my supervisor, Dr. Jie Li, for his support, supervision, feedback and time throughout the development of the dissertation. Many thanks as well to PhD student Yingjie Ma, for his support and patience. Also, thank you to professors from all the modules of the masters course: the knowledge they shared this last year, and the passion they did it with, helped shape this dissertation.

I would like to thank Chevening Awards for the scholarship I received from them, that allowed me to pursue masters studies in the University of Manchester. To the Forest Process Engineering Group, at the Faculty of Engineering, Universidad de la República, Uruguay, thank you for your support and encouraging me to grow.

To my all my family, and especially to my mum, dad and brother, thank you for your support, always, and for encouraging me to follow my dreams. To Facundo, thank you for your constant support, kindness and patience this year. To “la banda” at home, thank you for being part of this experience in the distance.

To all the friends I have made this year, I am infinitely grateful for having the opportunity to know you and share with you. To Ceci, “the soup table”, “la banda latina”, Uruguayan cheveners, Mancunian cheveners, and many more... this would have not been the same without you. Thank you all.

Meli.-

Chapter 1: Introduction

Economic, social and environmental systems around the world display evident signs of stress, (Azapagic and Perdan 2011) and will be further affected if worldwide population grows as expected to 8 billion by 2025 and 9 billion by 2050 (Azapagic and Perdan 2011; Cremaschi 2015). Due to population growth, growing consumption rates and excessive poverty, it is expected that energy and natural resource demands will increase substantially, together with waste and emissions released into the environment. This will intensify current global challenges of environment degradation, energy supply, water scarcity and food supply faced by modern society (Cremaschi 2015; Bertran et al. 2017).

Chemical engineering, and specially process design, synthesis and intensification, are well positioned to support both society and industry in overcoming these challenges (Cremaschi 2015; Chen and Grossmann 2017). These disciplines play a critical role in the decrease of water and energy consumption, the improvement of process efficiencies and the reduction of waste and emissions to the environment. Together, they can attain remarkable accomplishments that alleviate mentioned global challenges, such as: (1) the creation of chemical routes to increasingly substitute traditional raw materials, specifically oil and gas, for biomass; (2) the design of chemical processes that use renewable energy sources; (3) the management of greenhouse gas emissions with carbon capture technologies (Barnicki and Sirola 2004; Bertran et al. 2017).

Approaches and tools in process design and synthesis have significantly evolved, associated to industrial developments and its large expansions throughout the decades, as shown by the work of Barnicki and Sirola (Barnicki and Sirola 2004). The development of studies in these areas increased until the decade of 1990s, when significant works were developed; this was followed by an interest decline, because it was believed that no new chemical plants would be built in the United States (Chen and Grossmann 2017). Until 2013 the study of subsystems was favoured over the study of whole processes, with their focus on optimisation-based synthesis and design of separation networks and heat exchanger networks. However, since then there has been a renewed interest in process synthesis and design, mainly because of three factors: (1) the expansion of shale gas in the United States; (2) the implementation of continuous processes and Quality by Design in the pharmaceutical industry; (3) the increasing tendency to consider environmental

concerns in early stages of process design, to obtain more efficient processes and adapt them to the use of bio-based raw materials (Chen and Grossmann 2017).

At the same time, process intensification has displayed significant growth and achievements, including the reduction of equipment sizes and the increase of reaction rates by orders of magnitude (Chen and Grossmann 2017). The use of thermally coupled distillation columns can be included amongst these developments, presenting important energy and capital savings, between 10% and 50% of the total annualised cost, compared with conventional distillation sequences (Calzon-McConville et al. 2006; Caballero and Grossmann 2004; Dünnebier and Pantelides 1999; Fidkowski and Agrawal 2001).

Optimisation-based approaches have been widely used in process design, synthesis and intensification. Consequently, the development of these disciplines has been closely associated with developments in computational sciences, such as improvements in processors, memory capacities and theoretical and practical aspects of mathematical modelling and solving (Bixby and Rothberg 2007). Emphasis is made particularly in the development of Generalised Disjunctive Programming (GDP) and Object-Oriented Modelling (OOM), which have facilitated structured model creation. These tools are used nowadays to work towards a standardise model-building process, facilitating error-checking and validation (Chen and Grossmann 2017).

Although chemical processes present complex interactions between their different elements, the focus of studies has been mainly in subsystems. In these studies, heat-exchanger networks, separation networks and reaction networks are designed and optimised independently, and the interactions between them are not completely accounted for. In these cases, the result is a suboptimal process. (Bariani Bremermann 2019) Regarding complete processes, efforts have been made to synthesise specific processes, such as phosphoric acid production (Papadopoulos and Seferlis 2009), styrene polymerisation (Diaconescu et al. 2002), vinyl chloride production (Lakshmanan et al. 1999), natural gas to liquid fuels process (Baliban, Elia and Floudas 2013) and biomass to liquid fuels processes (Baliban, Elia, Floudas, et al. 2013). However, only few studies have focused on the creation of general frameworks that can be suitable for the synthesis and design of a wide range of processes; as stated in a study by Recker (Recker et al. 2015), no general framework for the automatic generation of flowsheets is known from literature.

In addition to the subsystems included in studies, the complexity and accuracy of models can be significantly influenced by the selection of either shortcut or rigorous models for the representation of unit operations. For example, in the case of reactor networks the reaction advance can be represented by kinetic expressions of varying complexities or conversion efficiencies for the reactants and products involved. In the case of separation networks, distillation processes can be represented with tray-by-tray models that use material balances, energy balances, summation and equilibrium equations (MESH equations) or by less complex equations such as the Underwood–Fenske–Gilliland approximate equations (Smith 2016).

Consequently, even though studies have addressed separately the development of general frameworks for the synthesis and design of processes, flowsheets including two or more subsystems and the use of rigorous models for the unit operations, there are scarce studies that propose to develop general frameworks of more than one subsystem using rigorous models simultaneously. Some of the most recent studies that propose this, are those by Zhang et al. (Zhang et al. 2018) and Ma et al. (Ma et al. 2019). While both works use conventional distillation columns in their separation superstructures, they use different reaction networks. By using the same assumptions and solving the same example, Ma et al. (Ma et al. 2019) compares the results found by both studies and assesses the effect of their proposed reactor network.

In this context, the present work contributes to the continuity of these studies; it develops an optimisation framework for the simultaneous synthesis of reaction and separation networks, using rigorous models, selecting the reactors superstructure used by Ma et al. (Ma et al. 2019) and including thermally coupled distillation columns in the separation superstructure. Consequently, by solving the same case study it is possible to evaluate the influence of the proposed change in the separation network, in terms of the total annualised cost. In addition, the present study is considered a further step in the in the area of simultaneous synthesis of reaction and separation systems, as no previous studies that addressed this subject has included thermally coupled distillation columns into the design.

1.1. Objectives

The specific objectives of the present study are:

1. Creation of a superstructure that includes the reactor and separation networks, including the following complex column configurations: side stripper, side rectifier, Petlyuk column and prefractionator arrangement. It is desired to obtain a rich superstructure that is not redundant at the same time.
2. Modelling of the obtained superstructure with Generalised Disjunctive Programming (GDP) and transformation of the GDP model into a mixed-integer nonlinear programming (MINLP) model. The transformation is performed using the convex hull and bypass efficiency techniques, according to which one is considered more suitable for the different parts of the superstructure. The selection of convex hull and bypass efficiency techniques is explained in Chapter 3.
3. Adaptation of the solution method proposed by Ma et al. (Ma et al. 2019) and application to solve the model obtained in the point above, for a case study of benzene chlorination process, which has been solved also by Zhang et al. (Zhang et al. 2018) and Ma et al. (Ma et al. 2019).
4. Comparison of the results obtained with those from the works of Zhang et al. (Zhang et al. 2018) and Ma et al. (Ma et al. 2019) in terms of the total annualised cost.

1.2. Overview of the dissertation

The present study is structured in five Chapters. Chapter 1 presents the motivation for the study, as well as an introduction to the subject it addresses and to the state of the art. In addition, it establishes the specific objectives of the study.

Chapter 2 presents the subject of process synthesis and design, how it has evolved and the array of approaches that can be used to address the synthesis and design problem. It focuses specially in the approach of superstructure optimisation, as it is the one used by the present study. Sections 2.3., 2.4. and 2.5. present the three steps included in this approach: the construction of the superstructures, their reformulation and solving strategies, respectively. For each one of the steps previous works developed in the synthesis of reaction, separation and simultaneous reaction-separation systems is presented. In addition, mathematical programming concepts that are widely used in these areas are explained prior to the presentation of the reformulation stage, in Section 2.3. Similarly, tools used to solve the different types of optimisation problems are

explained at the beginning of Section 2.4., before describing which tools previous works have used.

Chapter 3 describes the methodology of the present study, which includes the selection of the superstructure, the formulation of the model as an optimisation problem and its application to a case study. Results are presented and discussed in Chapter 4, where the resulting flowsheet is shown. In addition, the results are compared with those presented by Zhang et al. (Zhang et al. 2018) and Ma et al. (Ma et al. 2019) for the same case study. Finally, conclusions on the synthesis and design of simultaneous reaction-separation systems that include complex configuration columns are stated in Chapter 5, together with suggestions to continue the study of the subject.

Chapter 2: Background

2.1. Process synthesis and design

Chemical processes present a hierarchy that is frequently represented by the onion diagram, as shown in Figure 1. This model shows that processes requiring the transformation of some components into others will have to specify the reaction stage prior to the separation and recycle stages, and so on with the heat recovery system, the heating and cooling utilities requirements and the water, emissions and effluent treatment (Bariani Bremermann 2019).

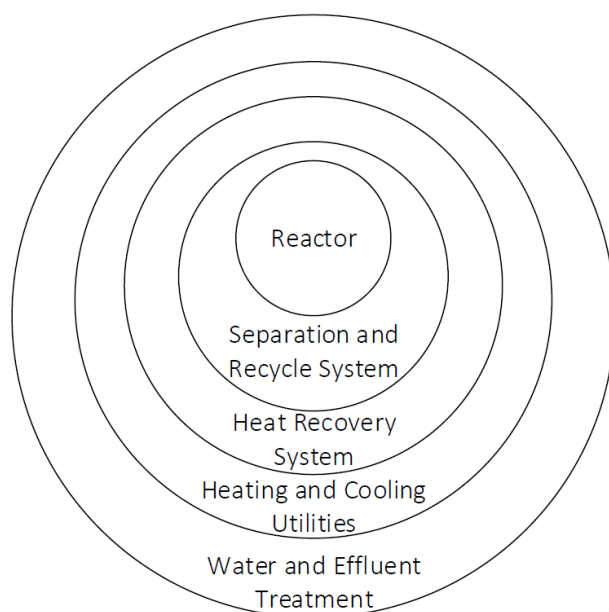


Figure 1: The Onion model of process design. (Smith 2016)

The reason for this is that the characteristics of the separation and recycle system will depend on what is required to be separated and recycled, which is determined by the reactor network outlet, hence the reactor network itself. The same happens with the rest of the subsystems or “layers” of the onion: one always depends on the inner ones. (Smith 2016)

Approaches to the synthesis and design of chemical processes are broadly classified in two main types: (1) hierarchical, decomposition-based, heuristic approaches and (2) mathematical optimization, programming-based approaches. (Li et al. 2018; Yeomans and Grossmann 1999a; Cremaschi 2015) They may be used separately or can also be combined.

The first approach is based on the hierarchy presented by the onion diagram, and the solving strategy is sequential, involving a series of local decisions. In this way, the reactor design is addressed first and is followed by the design of the external layers, from the

separation and recycle system to the water, emissions and effluent treatment (Smith 2016). Well-established examples of this methodology are the 5-level decision hierarchy to conceptual design developed by Douglas (Cremaschi 2015; Blanco and Bandoni 2003; Douglas 1988) and the means-ends analysis developed by Siirola and Rudd (Siirola and Rudd 1971). At each stage alternative designs are proposed using heuristic rules, which are an organised way of knowledge acquired from long-term experience of engineering practice (Li et al. 2018). Then, an economic evaluation of the options is performed, and decisions are made on the basis of available information. The disadvantage of this approach is that this information does not show the complete picture for the process, but only for the present and previous levels, while the consequences of these decisions for the rest of the chemical process are neglected (Smith 2016; Cremaschi 2015). It does not consider the complex interactions occurring between the different parts of the system, and it misses their benefits, leading to near-optimal designs (Smith 2016). However, the advantages of this procedure are that it is relatively easy to apply (Yeomans and Grossmann 1999a) and that the engineer or design team is in control of the intermediate decisions, which allows to easily include the intangibles such as process safety and layout (Smith 2016).

Optimisation-based approaches were developed to incorporate the mentioned interactions between different parts of the system, and their benefits (Cremaschi 2015), which is accomplished by the simultaneous optimisation of the different levels. Their development has been closely related to the improvement of optimisation techniques and computational power (Cremaschi 2015). Among the optimisation methods, the use of superstructures has received the most attention (Yeomans and Grossmann 1999a; Smith 2016); this approach involves the creation of a reducible structure known as superstructure, which represents the set of all possible alternatives for the optimal design structure. Initially it is built including redundant features, both in terms of equipment and their interconnections (Smith 2016; Li et al. 2018). The most common superstructure representations are the state-task network (STN) and the state-equipment network (SEN) (Chen and Grossmann 2017).

The superstructure approach follows three main steps: (1) creation of the superstructure; (2) mathematical modelling of the superstructure, usually as a mixed-integer non-linear programming (MINLP) problem, including the definition of the objective function that will

be minimised or maximised and a series of constraints in the form of equalities and inequalities; (3) implementation of a solving strategy to yield the optimal process flowsheet (Smith 2016; Chen and Grossmann 2017). The objective function used may vary according to the aspect of the process that is desired to optimise, and may include control, yield and economic aspects. Selecting an appropriate superstructure is a critical step because, in the first place, the optimal flowsheet configuration can only be found if it is included in the superstructure (Agrawal 1996); and secondly, because the same process flowsheet can be represented by different superstructures, that may yield mathematical formulations of different complexities, hence facilitating or not the solving process of the problem (Chen and Grossmann 2017; Li et al. 2018). Consequently, the superstructure should be sufficiently rich to contain the optimal flowsheet and simple enough to avoid unnecessary complexities (C. A. Schweiger and Floudas 1999).

The main advantage of the superstructure optimisation approach is the possibility to consider the complex interactions between different parts of the process; these interactions usually result in trade-offs, for example between operation and capital costs, and between the quantity of heat provided and the temperature levels at which heat exchange occurs (Smith 2016). In addition, the superstructure approach determines the objective function value and the structure and characteristics of the optimal process at the same time (C. A. Schweiger and Floudas 1999). However, these benefits are gained at the expense of using complex models and removing the design engineer or team from the decision-making process; hence, in contrast with the hierarchical approach, it becomes more difficult to consider the intangibles satisfactorily (Smith 2016). In addition, the question always remains whether a better process could have been design had the initial superstructure been richer (Feinberg and Hildebrandt 1997).

As mentioned in Chapter 1 the complexity of the complete model and the accuracy of the results will also depend on the type of models that are used for the unit operations, which can be shortcut or rigorous (Chen and Grossmann 2017; Smith 2016). The complexity of the complete model is reflected on the non-linearities that are introduced, as they complicate the solution process. However, complex models can provide more precise representations of reality, yielding more accurate complete models and more practical, valuable results (Smith 2016).

Optimising different parts of a flowsheet simultaneously is a mathematically complex task, and tools for the synthesis of process flowsheet continue to be hierarchical, decomposition-based approaches (Chen and Grossmann 2017). As a consequence, available studies have been developed mostly on the study of subsystems, such as reactor, separation, mass transfer, heat exchanger, steam and power, and water networks (Chen and Grossmann 2017; C. A. Schweiger and Floudas 1999). As the mathematical tools advance, so do the process synthesis and design capabilities. Nowadays, it is possible to address problems that optimise simultaneously the reactor and separation networks, as the present study proposes.

2.1.1. Reactor network synthesis and design

In reactor network synthesis, the aim is to determine the best possible reactor network to transform the raw materials into the required products. The problem statement is assumed to provide information about the mechanisms and stoichiometry of the reactions, their kinetic data, the inlet streams data, the enthalpic data, the constraints of the system and the selected performance objective (C. A. Schweiger and Floudas 1999; Balakrishna and Biegler 1996). Based on this information, the solution to the synthesis problem is the type, number and size of the reactor units selected, the interconnections between the units, the flowrates, temperatures, pressures and compositions of streams, and the heating and cooling duties required (C. A. Schweiger and Floudas 1999).

Three approaches have been proposed to address the reactor network synthesis problem: the use of heuristics, the targeting approach and optimisation techniques (Kokossis et al. 2016). In reactor network design, heuristics emphasize the effects of different degrees of mixing according to the kinetics of the reactions, more specifically, the reaction orders; and the effects of providing or removing heat according to the reaction being endothermic or exothermic. Due to their simplicity, heuristics are usually limited to the study of systems with single reactions or with simple parallel or series reactions (Balakrishna and Biegler 1996).

The targeting approach is based on the concept of the “attainable region” in concentration space (Lakshmanan and Biegler 1996). The attainable region is defined as the convex hull of all attainable (possible) reactants and products concentrations that can be reached from a defined feed stream by steady-state operations of reaction and mixing (Lakshmanan and Biegler 1996; Feinberg and Hildebrandt 1997). It is considered an

elegant and rigorous method, but it is difficult to apply to problems with more than three dimensions (Lakshmanan and Biegler 1996); the number of dimensions refer to the number of concentrations of different species that are involved in the system. Several studies of reactor networks design were developed with this methodology (Balakrishna and Biegler 1996; Lakshmanan and Biegler 1996; Feinberg and Hildebrandt 1997), mainly before the year 2000.

Optimisation techniques for reactor networks are divided in the ones that use superstructures and the ones using dynamic programming (Xie and Freund 2018; Peschel et al. 2010). The former has been presented in the first part of Section 2.1. The latter includes the method of “elementary process function” developed by Freund and Sundmacher (Freund and Sundmacher 2008); this technique searches for the optimal manipulation of a fluid element by internal and external material and energy fluxes, in order to follow the optimal path in the thermodynamic state space and arrive to the desired point (Feinberg and Hildebrandt 1997). The result is an innovative reactor design that follows the optimal flux profiles (Peschel et al. 2010).

An advantage of this approach is that it does not require the pre-selection of reactor types, as will be seen in Section 2.2 that is required for the use of a superstructure. In addition, it allows to include process intensification elements in an early stage of the design process (Xie and Freund 2018). Nevertheless, it has been observed that this approach is not able to achieve certain configurations that are possible when adopting the superstructure and attainable region approaches; additionally, solutions obtained with the elementary process function approach may be near-optimal and include impracticalities (Xie and Freund 2018). This is a relatively recent approach, and studies have been developed in the last decade (Xie and Freund 2018; Peschel et al. 2010; Freund and Sundmacher 2008).

2.1.2. Separation network synthesis and design

A critical task in chemical process synthesis and design is the effective design of separation systems (Caballero and Grossmann 2004). Even though there have been advances in new separation technologies such as PSA and membranes, distillation continues to be the most important separation operation in chemical processes (Caballero 2015; Zou et al. 2012): it has been estimated that distillation is used in 90% of all separation operations performed in the industry (Felbab et al. 2013). However,

distillation is an energy intensive unit operation (Calzon-McConville et al. 2006; Caballero and Grossmann 2014; Dünnebier and Pantelides 1999); according to a report by the Department of Energy of the United States (DOE 2005), in the chemical and petroleum refining industries, which are the first and second largest industrial consumers of energy, distillation accounts for approximately 57% of their total energy consumption. In addition, it states that this corresponds to approximately 14% and 6%, respectively, of the total U.S. manufacturing energy consumption (DOE 2005). These figures translate into high operation costs, which together with the high investment costs required, make distillation an expensive operation to perform (Chen and Grossmann 2017; Grossmann et al. 2004; Yeomans and Grossmann 2000a). These have been the driving forces for distillation to be one of the most studied unit operations for the last 30 years (Caballero et al. 2005; Yeomans and Grossmann 2000a; Zou et al. 2012).

The simplest type of problem that can be formulated for the distillation column synthesis is with a fixed number of trays, where the objective is to select the optimal feed tray location. This problem was addressed in 1976 by Sargent and Gaminibandara (Sargent and K. Gaminibandara 1976). Since then, the problem formulation has evolved to the design of sequences of columns, including different types of them. Nowadays, the synthesis and design problem can be formulated as follows: provided a multicomponent feed or set of feeds, with known composition, flowrate and thermodynamic properties (temperature and pressure could be fixed or not), the specifications of desired products, the economic data for raw materials, products, utilities and equipment, and the maximum number of trays (Yeomans and Grossmann 2000a; Barttfeld et al. 2004; Zou et al. 2012); the objective is to select the operating conditions and the structure of the distillation system (type of columns, number of columns, number of trays per column, feed location, reflux ratio, column diameter, condenser and reboiler duties, and their areas) to accomplish the desired separation while minimising the operating and investment cost, usually represented in the total annualised cost (Barttfeld et al. 2004; Caballero and Grossmann 2013; Caballero and Grossmann 2004; Yeomans and Grossmann 2000a; Caballero and Grossmann 2001; Zou et al. 2012). The formulation of the problem also includes a series of assumptions which state, for example, if the components that form azeotropes are included or not, since the solution procedure is different; it is also specified which of the components require a complete, or sharp separation, and which ones do not (Zou et al. 2012; Caballero and Grossmann 2013).

The type of column refers to the possibility of using simple columns as well as complex configuration distillation columns, which include: columns with side rectifiers, columns with side strippers and prefractionation arrangements. The latter include the use of prefractionator without thermal coupling, Petlyuk columns and dividing wall columns (Barttfeld et al. 2004). Mentioned configurations are shown in Figure 2. Except for the prefractionator arrangement (A), these complex configurations are thermally coupled distillation systems (TCDS). These have been proposed as a promising alternative to conventional distillation systems, because of the significant energy and capital savings that can be achieved in comparison to the conventional sequences (Calzon-McConville et al. 2006; Caballero and Grossmann 2004; Dünnebier and Pantelides 1999).

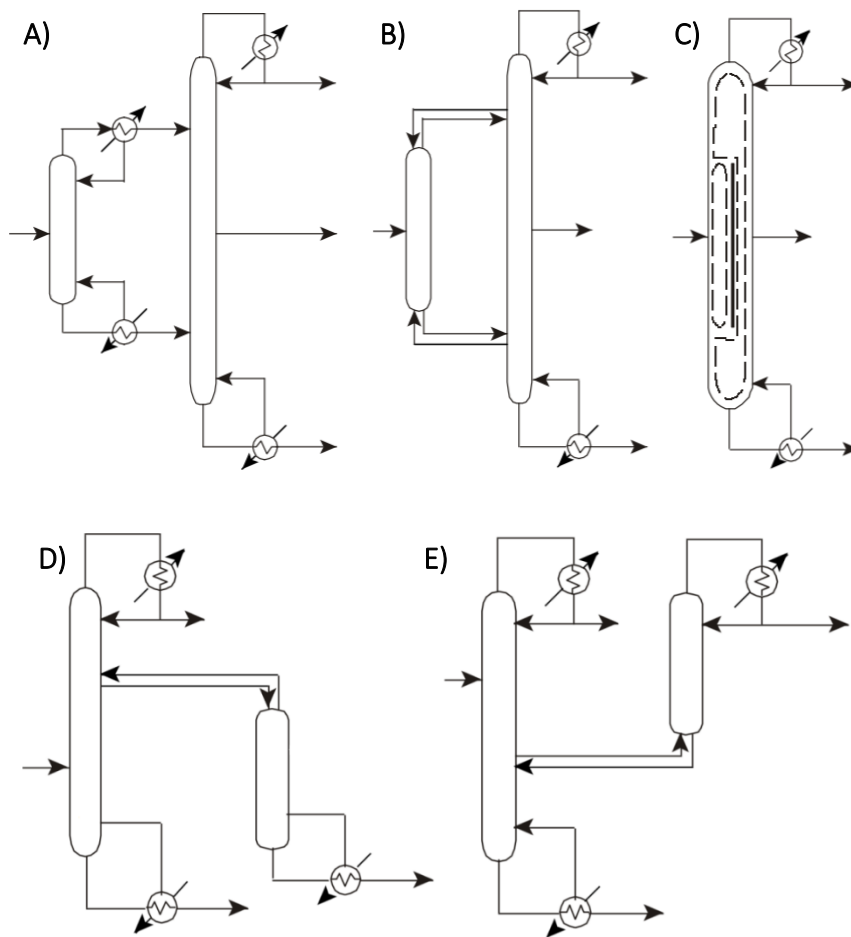


Figure 2: Complex configuration distillation columns. A) Prefractionation without thermal coupling; B) Petlyuk column; C) Dividing wall column; D) Side stripper; E) Side rectifier. (Jobson 2019)

Even though TCDS have the minimum energy consumption, it cannot be concluded that these configurations are always superior. Reasons for this could be: (1) the energy is supplied and removed at more extreme temperature levels, using the highest temperature in the reboiler and lowest at the condenser, as shown in Figure 3; (2) columns may require larger diameters in some sections; (3) a higher number of trays

could be needed; (4) due to the increased number of interconnections between the columns, operation is more difficult. (Caballero and Grossmann 2014) Therefore, it is desired to adopt a solution approach that considers the use of both simple and complex columns.

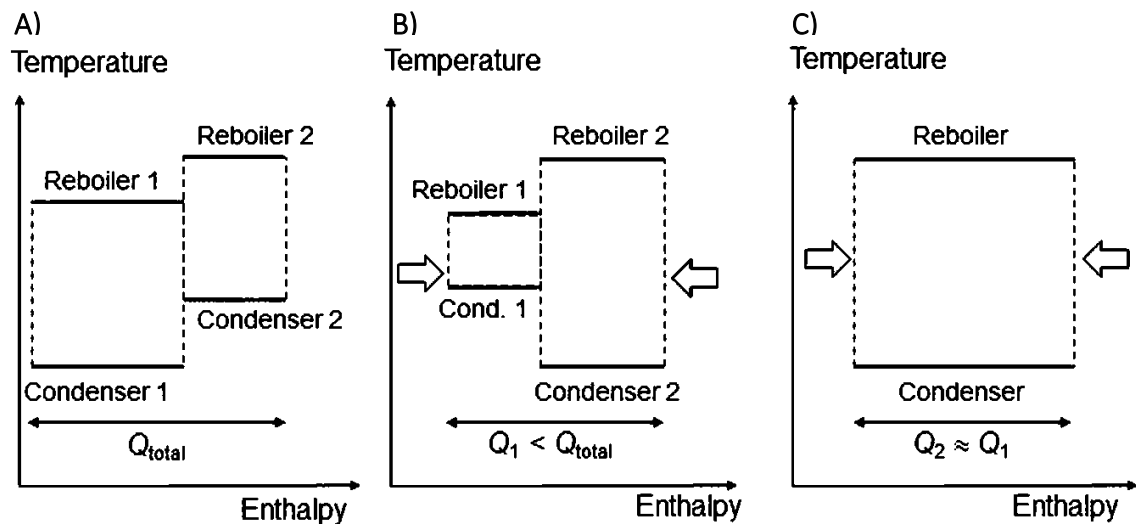


Figure 3: Temperature-enthalpy effects of thermal coupling. A) Conventional sequence (direct); B) Prefractionator arrangement; C) Thermally coupled prefractionation. (Jobson 2019)

Approaches employed for the synthesis and design of distillation systems include hierarchical decomposition (Douglas 1988), heuristics methods (Seader and Westerberg 1977), implicit enumeration (Johns and Romero 1979), evolutionary methods (Stephanopoulos and Westerberg 2002) and mathematical programming methods (Grossmann et al. 2004). Among these, the approach of mathematical programming using superstructures has been receiving much attention (Chen and Grossmann 2017); in fact, distillation systems synthesis was one of the first synthesis problems addressed with this technique.

2.1.3. Simultaneous reaction-separation network synthesis and design

As the separate synthesis of reactor and separation networks evolved and improved, studies started to address the simultaneous synthesis of reaction-separation networks (Pibouleau 1988; Kokossis and Floudas 1991). The simultaneous synthesis allows to exploit the synergies between the reaction and separation subsystems, at the expense of having to solve a more complex problem than the ones addressed separately.

Approaches used for the simultaneous synthesis of reaction-separation networks include: heuristics (Recker et al. 2015), the attainable region concept (Linke and Kokossis 2003; Nisoli et al. 2004) and optimisation techniques (Ma et al. 2018; Zhang et al. 2018; Smith and Pantelides 1995).

2.2. Construction of superstructures

2.2.1. Construction of reactor network superstructure

The construction of the superstructure is developed considering that it should be sufficiently rich to contain the optimal reactor network and simple enough to avoid unnecessary complexities (C. A. Schweiger and Floudas 1999). For reactor networks the richness of the superstructure is determined by the type and number of reactor units included and the interconnections proposed between them. Consequently, it is critical to determine which reactors should be included and how they should be connected (C. A. Schweiger and Floudas 1999).

Feinberg and Hildebrandt (C. A. Schweiger and Floudas 1999) have proposed that the only reactor types required to achieve all possible compositions are the ideal reactors: continuous stirred-tank reactor (CSTR), plug flow reactor (PFR) and differential side-stream reactors. The latter include the maximum mixed reactor (MMR), the segregated flow reactor (SFR) and the cross-flow reactor, usually referred as side-stream reactor (DSR). These reactor models are shown in Figure 4.

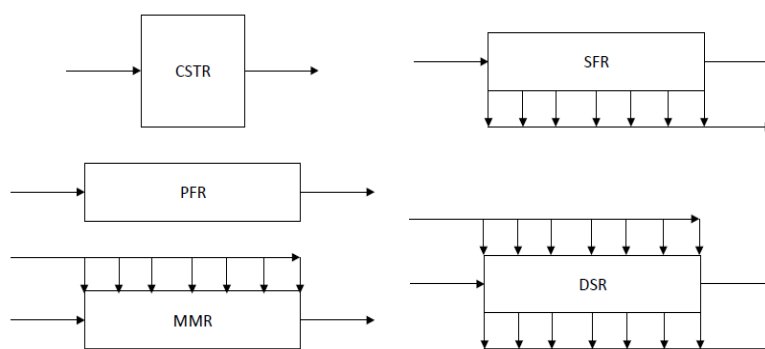


Figure 4: Reactor types of CSTR, PFR and differential side-stream reactors (SFR, MMR and DSR). (C. A. Schweiger and Floudas 1999)

Models of PFR, MMR, SFR and DSR are differential models that include the same assumptions of no mixing in the axial direction and total mixing in the radial direction (Levenspiel et al. 1999). The difference between these models is the inclusion or not of inlet and outlet side-streams. Inlets are present in the MMR and DSR, outlets are in the SFR and DSR and the PFR presents none of them. Because of the characteristics of the models, the PFR, SFR and MMR can be seen as special cases of the DSR, where either the inlets and/or outlets are zero. Because of this, Schweiger and Floudas (C. A. Schweiger and Floudas 1999) concluded that only the CSTR and the DSR models are required. (C. A. Schweiger and Floudas 1999; Lakshmanan and Biegler 1996) However, the reactor models are only one of the elements required to build the superstructure; the other are

the interconnections between the reactor units. If the interconnections are considered, then it is also possible to represent the DSR as a series of PFRs, as shown in Figure 5. Hence, a priori either the PFR or DSR model could be used, together with the CSTR model.

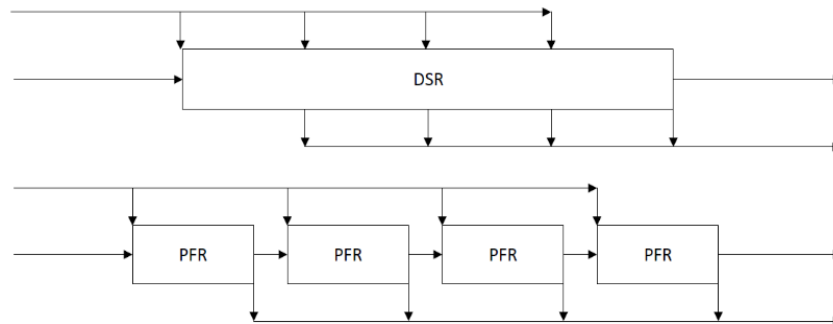


Figure 5: Representation of a DSR with PFR in series. (C. A. Schweiger and Floudas 1999)

Even though the reactor models are equivalent in the way that they can both be used to represent the same superstructure and produce the same results, the modelling and solving of the synthesis problems would not have the same formulation using one reactor model or the other. For example, this decision influences the number of reactor units and streams to be considered in the superstructure, since one DSR is represented by more than one PFR. At the same time, the number of reactor units and streams determine the number of variables and equations that are included in the model. Consequently, it would be beneficial to understand which one of the reactor models, PFR or DSR, is better to use together with the CSTR in order to obtain more accurate and faster results. Nevertheless, to the best of the author's knowledge there has been no study to evaluate which reactor model may present the most benefits.

Previous studies have used CSTRs and PFRs (Kokossis et al. 2016; Pahor et al. 2000; Diaconescu et al. 2002; Zhang et al. 2018), CSTRs and DSRs (C. A. Schweiger and Floudas 1999; C.A. Schweiger and Floudas 1999), CSTRs together with either PFRs or DSRs depending on the situation (Lakshmanan and Biegler 1996), only CSTRs where some of them are used in series to represent PFRs (Kokossis and Floudas 1994) and CSTRs with recycle reactors, which is a PFR with a recycle (Pahor et al. 2002).

Since the superstructure is a finite structure, the number of reactor units included has to be specified and will be the maximum number of reactors that the network may use. It is worth noticing that the number of reactor units should be decided according to the type of reactors that are selected, PFR or DSR; this is because, as previously mentioned, one

DSR may be represented by several PFRs. Also, if the DSR is used, the number of side streams employed has to be specified.

In addition, a series of features must be included in the superstructure in the form of interconnections between the units. Previous studies have been found to include: series and parallel operation of the units; split of feed to enter at all units and split of all unit outlet streams; bypass of every unit; mixing points prior to all unit inlets and mixing points to inlet of side streams (in the case that DSR is used); recycle of all unit outlets to mixing points prior to inlets and of side streams to mixing points (in the case that DSR is used); mixing of all unit outlet and side streams (if present) to yield the final product. Apart from these, previous studies have included other two features that are not necessary: the recycle in the CSTR unit and the bypass of feed to the final product. These are examples of features that only increase the complexity of the complete mathematical model, because none of them can be part of the optimal reactor network, but still they have associated variables and equations. In the first case, because the outlet has the same characteristics than the mixture inside the CSTR, so there is no point in recycling it to the inlet; this would only increase the inlet feed and consequently the volume of the reactor in order to have a specific residence time. In the second case, because the raw material would not be used if it is bypassed to the final product. Therefore, these two features should be avoided.

Various superstructures for reactor networks have been proposed in previous studies. The study by Schweiger and Floudas (C. A. Schweiger and Floudas 1999) proposes a superstructure to be used for processes in general, using one CSTR and one DSR. All the interconnections described above are included, but it does not allow for possibilities that come with having more than one reactor of each type, such as CSTRs in parallel or series, and the same for the PFRs.

In the study by Zhang et al. (Zhang et al. 2018) two different superstructures are proposed for the reactor network. The first one is constituted by a series of N modules, where each one has the possibility of selecting a CSTR or a bypass. This superstructure allows the representation of the extreme cases: a CSTR and a PFR if enough CSTRs are selected in series; and it can also represent flow patterns in between the extremes. However, several of the features above mentioned as desired in a superstructure are not present, such as the use of PFRs or CSTRs in parallel and the recycle of streams. Consequently, it is

considered that the superstructure is not sufficiently rich. In order to solve an example, ten modules are used in the superstructure ($N=10$). The second superstructure proposes the use of a different module, including the selection of a PFR, a CSTR or a bypass. This module is used to create a triangular superstructure: $(M+N)$ modules are arranged in parallel, this arrangement is in series with $(M+N-1)$ parallel modules, in series at the same time with $(M+N-2)$ parallel modules and so on until the arrangement of modules in parallel is constituted by only one module. M and N are the maximum number of PFRs and CSTRs that can be used, respectively. The example solved using this superstructure uses a maximum of one reactor of each type, hence allowing for the parallel operations missing in previous works. However, interconnection features are not as rich as in the study by Schweiger and Floudas (C. A. Schweiger and Floudas 1999); for example, no recycles are considered in the superstructure.

The study by Ma et al. (Ma et al. 2018) and the study by Ma et al. (Ma et al. 2019) use the reactor network superstructure shown in Figure 6.

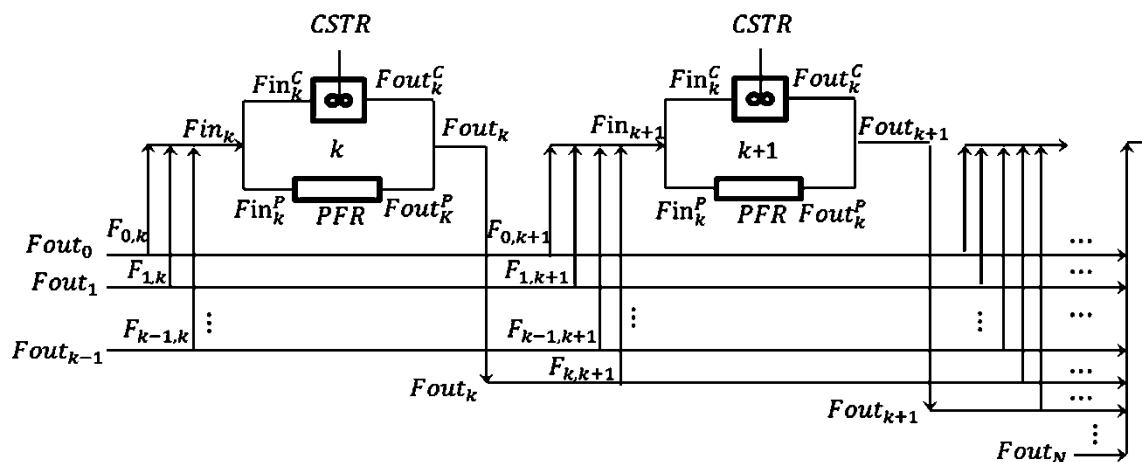


Figure 6: Reactor network superstructure used by Ma et al. (Ma et al. 2018).

In this case the module used is constituted by a CSTR and a PFR, and only one of them can be selected at a time. Although recycles are not present in the superstructure, several of the desired interconnection features are included, such as the splitting of the feed and of the outlet streams of each module, and the mixing of several streams to the inlet of each module. Consequently, it is considered that the superstructure is rich and not as simple as in other studies, but that it could still be improved.

From the analysis of reported studies, it is concluded that considerable advances have been made. However, none of the them was found to present all the possible features

for reactor networks. Consequently, there is still a possibility to improve the superstructures used for the reactor network synthesis.

2.2.2. Construction of separation network superstructure

As mentioned for the reactor network in Section 2.2, the first step of this approach is the construction of a superstructure of alternatives for the separation system (Grossmann et al. 2004). In the area of separation networks it is particularly useful the classification of superstructures into state-equipment networks (SEN) and state-task networks (STN) (Grossmann et al. 2004; Caballero and Grossmann 2004).

SEN representations were motivated by work of Smith and Pantelides (Smith and Pantelides 1995); in this case both states and equipment represent nodes and the solution procedure decides which tasks are performed by the given equipment. States are defined as all the feasible intermediates and products of the superstructure, and tasks are the transformations that connect two states. This representation can lead to more compact problem formulations, and is considered appropriate for conventional columns, but not for the synthesis of complex configurations (Grossmann et al. 2004).

STN representations were inspired by studies in scheduling by Kondili et al. (Kondili et al. 1993); in this case, nodes represent states and tasks, and the solution provides the association between tasks and different separation sections, or group of trays. The resulting equipment is given by the union of the active separation sections and interconnections that exist between them. (Yeomans and Grossmann 2000b) This approach is considered intuitive and more practical for the synthesis of complex configurations, but its disadvantage is that the size of the model created increases quickly with the number of components in the system. (Caballero and Grossmann 2004)

Prior to solving a separation network synthesis problem, it is not known whether complex or conventional configurations are the best option. Consequently, it is desired that the superstructure created may consider both possibilities.

In previous studies regarding separation networks that include thermally coupled distillation configurations, the superstructure proposed by Sargent and Gaminibandara (Sargent and K. Gaminibandara 1976) has been the most widely used (Yeomans and Grossmann 2000b; Grossmann et al. 2004; Barttfeld et al. 2004; Caballero and Grossmann 2004; Dünnebier and Pantelides 1999). Different versions of this superstructure have been used to address the sharp distillation of mixtures with three,

four and five components, as well as mixtures that form azeotropes (Sargent 1998). Figure 7 (left) presents the superstructure used for the separation of mixtures of three components in the STN form. Figure 7 (right) shows an equipment superstructure based on the STN formulation, where each task has been assigned to a particular section of a distillation column; it also shows the possible locations for heat exchange (Yeomans and Grossmann 2000b).

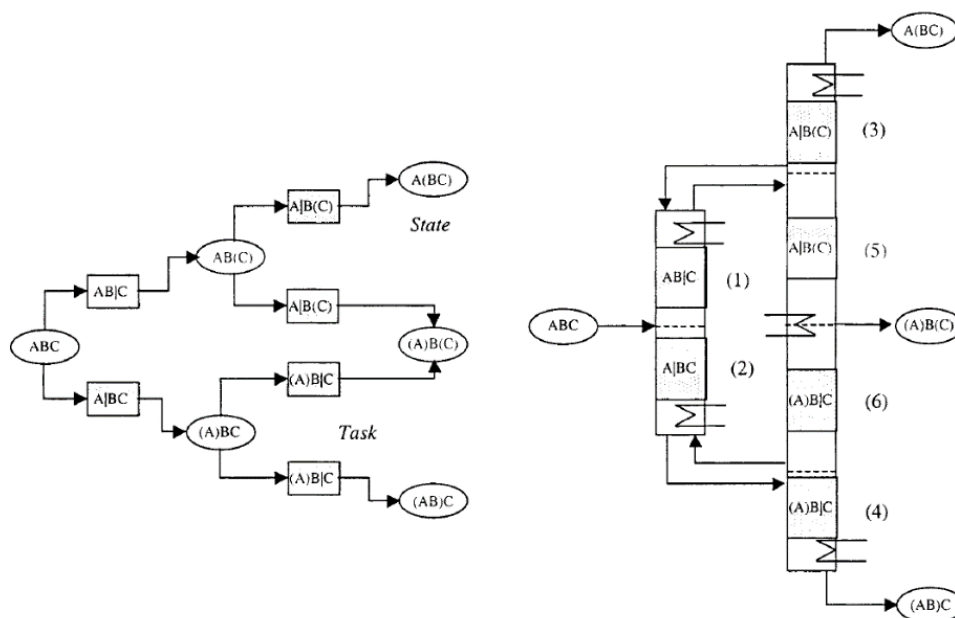


Figure 7: Representation of STN formulation and equivalent superstructure (Yeomans and Grossmann 2000b).

Differently to the case of reactor networks, where the reactor units and features included in the superstructures change between different studies, in separation networks the same elements are always present: feed tray, condenser trays, reboiler trays, and extraction trays. In contrast, the main problem in the superstructure optimisation approach for the synthesis of separation systems is that the procedure involves the elimination of trays from the superstructure in order to obtain the optimal configuration (Yeomans and Grossmann 2000b). Because of this, differences between studies of separation networks are mainly encountered in the modelling and solving stages.

2.2.3. Construction of reaction-separation network superstructure

There are two possibilities for the construction of the reaction-separation network superstructure: (1) reactor and separation networks are created independently, and they are connected afterwards by two streams: one stream that leaves the reactor network to feed the separation network, and another stream that recycles unreacted material from the outlet of the separation network to the inlet of the reactor network (Zhang et al.

2018; Ma et al. 2018; Ma et al. 2019); (2) a superstructure is constructed using reaction and separation units alternated in such a manner that it is not possible to identify reaction and separation subnetworks (Kong and Shah 2016); for example, the feed stream may enter a reaction stage, followed by a separation stage, then another reaction stage and so on. The former approach has been more widely used than the latter, which may produce more complex problems. In addition, it has been found that no study addresses the synthesis of simultaneous reaction-separation systems that include complex configurations for the separation stage.

2.3. Formulation of optimisation problem

Once the superstructure is created, the next step is to formulate it into a mathematical programming model (Chen and Grossmann 2017). The formulation may be performed in one stage, which results in a model already suitable to be solved with optimisation algorithms for NLP, MINLP or MILP problems. Alternatively, it may be first formulated as a logical model using GDP and then transformed into an NLP, MINLP or MILP optimisation problem. In addition to modelling the superstructure itself, the formulation of the optimisation problem includes proposing an objective function and equations that can relate the superstructure with it. For example, if the objective function is economic in nature, an economic model is required to relate the superstructure variables with economic variables.

Before describing the possible formulations in depth, Section 2.3.1 presents concepts and tools that are widely used and required to understand the formulation of optimisation problems.

2.3.1. Mathematical modelling and programming concepts

2.3.1.1. Classes of optimisation problems

Optimisation problems may be linear programming (LP), mixed-integer linear programming (MILP), nonlinear programming (NLP) or mixed-integer nonlinear programming (MINLP) problems. The difference between them lays in the characteristics of the objective function and constraints, as well as the types of variables. Both LP and MILP problems present linear objective functions and constraints, but while LP problems have only continuous variables, MILP problems have some continuous and some integer variables. The case of NLP and MINLP problems is analogue: they present an objective function and/or at least one of the constraints that is non-linear; and while NLP problems

include only continuous variables, MINLP problems include both continuous and integer variables (Li 2018). Generic formulation for LP and NLP problems is presented in Eq. 1, as well as for MILP and MINLP problems in Eq. 2.

$$\begin{aligned}
 \min \quad & z = f(x) \\
 \text{s. t.} \quad & g(x) \leq 0 \\
 & x \in X
 \end{aligned}
 \tag{Eq. 1}$$

$$\begin{aligned}
 \min \quad & z = f(x, y) \\
 \text{s. t.} \quad & g(x, y) \leq 0 \\
 & x \in X \\
 & y \in Y
 \end{aligned}
 \tag{Eq. 2}$$

They represent the minimisation (*min*) of an objective function (z) subject to (*s. t.*) equality and inequality constraints ($g(x), g(x, y)$). In both cases $f: \mathbb{R}^n \rightarrow \mathbb{R}^1$ and $g: \mathbb{R}^n \rightarrow \mathbb{R}^m$ are twice continuously differentiable functions. The continuous and integer variables are represented by x and y respectively. X is assumed to be a convex compact set given by $X = \{x \in \mathbb{R}^n \mid Dx \leq d; x^{lo} \leq x \leq x^{up}\}$, where x^{lo} and x^{up} are the lower and upper bounds respectively. Y represents the set of integer variables, given by $Y = \{y \in \mathbb{Z}^m \mid Ay \leq a; y^{lo} \leq y \leq y^{up}\}$, where y^{lo} and y^{up} are the lower and upper bounds respectively. (Trespalcios and Grossmann 2014)

Process synthesis and design problems usually result in MINLP problems. However, they may be formulated as NLP or MILP problems, and their solving strategies may include the use of MILP, NLP and/or MINLP subproblems.

2.3.1.2. Generalised Disjunctive Programming (GDP)

GDP was proposed by Yeomans and Grossmann (Yeomans and Grossmann 2000a) as a modelling framework that overcomes difficulties encountered with MINLP formulations (Yeomans and Grossmann 2000b). This logic model uses Boolean variables, that can take the values “True” or “False”, and continuous variables; also, the objective function is subject to three types of constraints: (1) constraints in the form of algebraic expressions; (2) conditional constraints included in the disjunctions; (3) logical constraints involving Boolean variables exclusively (Yeomans and Grossmann 2000b).

$$\begin{aligned}
 \min \quad & z = f(x) \\
 \text{s. t.} \quad & g(x) \leq 0 \\
 & \bigvee_{i \in D_k} \left[r_{ki}(x) \leq 0 \right] \quad k \in K \\
 & \bigvee_{i \in D_k} Y_{ki} \quad k \in K \\
 & \Omega(Y) = \text{True} \\
 & x^{lo} \leq x \leq x^{up} \\
 & x \in \mathbb{R}^n \\
 & Y_{ki} \in \{\text{True}, \text{False}\} \quad k \in K, i \in D_k
 \end{aligned}$$

Eq. 3

A generic GDP model is shown in Eq. 3; this represents the minimisation (*min*) of the objective function (z), subject to (*s. t.*): (1) global constraints $g(x)$, equalities and inequalities, that must be fulfilled independently of the Boolean variables Y ; (2) $k \in K$ disjunctions, each one including $i \in D_k$ terms, linked by an “OR” (\vee) operator. Each disjunctive term is associated with a Boolean variable Y_{ki} and a set of equality and inequality constraints $r_{ki}(x)$ that apply only when the corresponding Boolean variable is “True”; (3) logical prepositions, represented by $\Omega(Y) = \text{True}$. (Trespalcios and Grossmann 2014; Li 2018) In order to be solved, a GDP expression of a problem has to be reformulated as a MINLP problem, which can be done using the big-M or convex hull methods (Trespalcios and Grossmann 2014; Li 2018).

2.3.1.3. Big-M and convex hull reformulations

Reformulation using big-M and convex hull methods are shown in Eq. 4 and Eq. 5.

$$\begin{aligned}
 \min \quad & z = f(x) \\
 \text{s. t.} \quad & g(x) \leq 0 \\
 & r_{ki}(x) \leq M^{ki}(1 - y_{ki}) \quad k \in K, i \in D_k \\
 & \sum_{i \in D_k} y_{ki} = 1 \quad k \in K \\
 & Hx \geq h \\
 & x \in \mathbb{R}^n \\
 & y_{ki} \in \{0,1\} \quad k \in K, i \in D_k
 \end{aligned}$$

Eq. 4

$$\begin{aligned}
\min \quad & z = f(x) \\
\text{s. t.} \quad & g(x) \leq 0 \\
& x = \sum_{i \in D_k} v^{ki} \quad k \in K \\
& y_{ki} r_{ki}(x) (v^{ki}/y_{ki}) \leq 0 \quad k \in K, i \in D_k \\
& \sum_{i \in D_k} y_{ki} = 1 \quad k \in K \\
& Hx \geq h \\
& x^{lo} y_{ki} \leq v^{ki} \leq x^{up} y_{ki} \quad k \in K, i \in D_k \\
& x^{lo} \leq x \leq x^{up} \\
& x \in \mathbb{R}^n \\
& y_{ki} \in \{0,1\} \quad k \in K, i \in D_k \quad \text{Eq. 5}
\end{aligned}$$

Both reformulations transform Boolean variables Y_{ki} into binary variables y_{ki} , given that when $Y_{ki} = \text{True}$, $y_{ki} = 1$ and when $Y_{ki} = \text{False}$, $y_{ki} = 0$. Hence, previous logic relations ($\Omega(Y) = \text{True}$) are substituted by integer linear constraints ($Hx \geq h$), and the equation $\sum_{i \in D_k} y_{ki} = 1$ ensures that only one disjunctive term is valid per disjunction.

The big-M reformulation uses parameters M^{ki} so that when a term is selected ($y_{ki} = 1$), the associated constraints $r_{ki} \leq 0$ are applied, and when it is not selected ($y_{ki} = 0$) and M^{ki} is large enough, the constraint $r_{ki} \leq M^{ki}$ is redundant.

The convex hull reformulation disaggregates the continuous variables x into variables v^{ki} for each disjunctive term, in each disjunction. Also, lower and upper bound constraints are added in the way of $x^{lo} y_{ki} \leq v^{ki} \leq x^{up} y_{ki}$, so when a term is selected ($y_{ki} = 1$) the associated disaggregated variable complies with the lower and upper bounds of the continuous variable x , and when it is not selected ($y_{ki} = 0$) it is equal to zero $v^{ki} = 0$. In addition, the constraint $x = \sum_{i \in D_k} v^{ki}$ attributes the value of the activated v^{ki} variable to the original value x , and the constraints of disjunctive terms are expressed as $y_{ki} r_{ki}(v^{ki}/y_{ki})$.

Big-M method results in a smaller MINLP model, as the number of variables is lower. In comparison, the convex hull method generates a tighter formulation. The tightness refers to the comparison of the feasible region of a problem in comparison to that of the big-M

and convex hull relaxations. This is shown in Figure 8 for the example presented by Vecchietti et al. (Vecchietti et al. 2003).

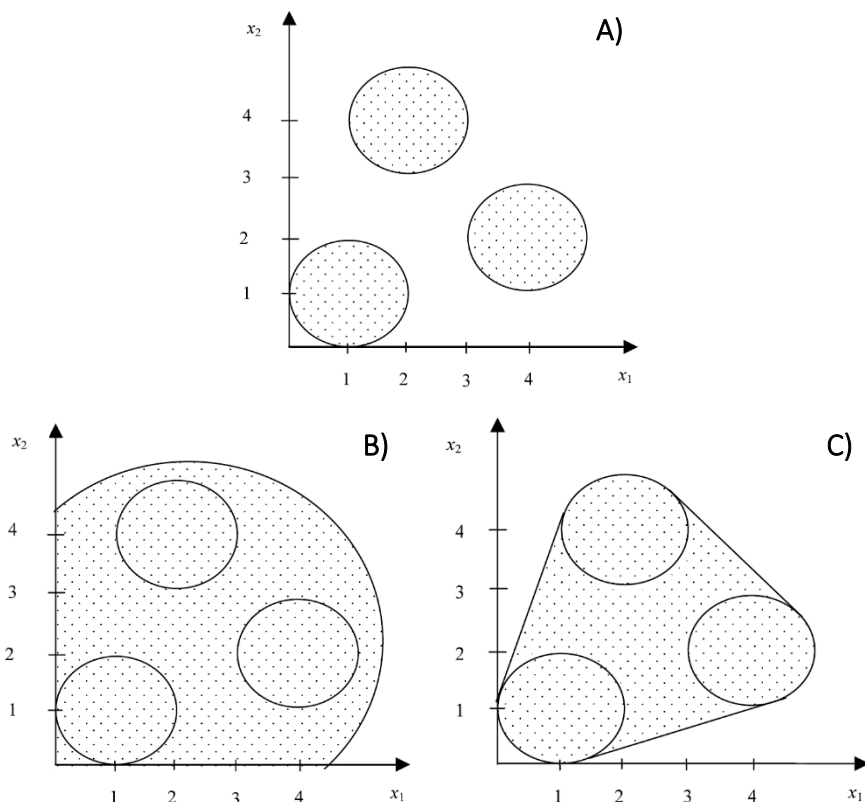


Figure 8: Representation of feasible regions for A) the original problem; B) the big-M reformulation; C) the convex hull reformulation. (Vecchietti et al. 2003)

According to the work of Vecchietti et al. (Vecchietti et al. 2003), different types of disjunctions respond differently to big-M and convex hull reformulations. However, for the analysed cases it is found that convex hull is generally preferred, because of the tighter formulation.

2.3.2. Formulation strategies for reactor networks

Mathematical modelling of reactor networks in previous studies has been majorly performed with MINLP models (Lakshmanan and Biegler 1996; Pahor et al. 2000; Pahor et al. 2002; Lakshmanan et al. 1999; C.A. Schweiger and Floudas 1999; Kokossis and Floudas 1994), although one case decided on the use of an NLP model (Achenie and Biegler 1990) and some employed the use of GDP models (Zhang et al. 2018; Pahor et al. 2002; Ma et al. 2019; Ma et al. 2018).

For reactor networks the models are constituted by equations of material and energy balances around each splitter, mixer and reactor in the superstructure; equations of summation of mole fractions in every stream; logical, non-negativity and integrality constraints (Lakshmanan and Biegler 1996; Kokossis and Floudas 1994). Material and

energy balances around reactors use the appropriate models for the type of reactor, and according to whether the PFR is modelled as such or as a series of CSTRs, the problem may have only algebraic equations or differential equations as well.

The models include parameters and variables, which may be only continuous (NLP formulation) or continuous and discrete (MINLP and GDP formulations). Continuous variables are related to the properties of streams and reactor units, while discrete variables are related to the existence or not of each reactor unit in the solution network.

In the studies where GDP models were implemented, their reformulation to MINLP problems is performed using Big-M (Zhang et al. 2018) and convex-hull (Ma et al. 2018) techniques. The study by Pahor et al. does not specify the reformulation strategy (Pahor et al. 2002).

The objective functions that have been used in previous studies include yield and selectivity (Lakshmanan and Biegler 1996; Kokossis and Floudas 1994), profit (Lakshmanan et al. 1999; Pahor et al. 2000; Pahor et al. 2002) and controllability (C. A. Schweiger and Floudas 1999).

2.3.3. Formulation strategies for separation networks

To model the separation network superstructure, it must be first decided on the model for the distillation operation itself, which can be shortcut or rigorous. Most of the studies developed on this subject of separation networks use the Fenske-Underwood-Gilliland equations (Caballero and Grossmann 2004; Dünnebier and Pantelides 1999; Caballero and Grossmann 2014; Caballero and Grossmann 2001; Caballero and Grossmann 2013; Calzon-McConville et al. 2006), which is a shortcut model; this is because of the non-linearity and convergence difficulty problems already encountered without the rigorous models (Caballero and Grossmann 2013). Nevertheless, it has been acknowledged that the accuracy of results increases with the use of rigorous models, which could increase the industrial relevance of the approach and the scope of application; therefore, it is highly desirable to include rigorous models (Yeomans and Grossmann 2000a). For the distillation operation, these are constituted by material and energy balances, equilibrium relations and summation equations, known as MESH equations. Some studies have been developed using rigorous models (Yeomans and Grossmann 2000b; Grossmann et al. 2004; Dünnebier and Pantelides 1999; Yeomans and Grossmann 2000a). Particularly, for the modelling of superstructures that include the possibility of thermally coupled

distillation columns, slightly more studies have been developed using shortcut models (Caballero and Grossmann 2004; Calzon-McConville et al. 2006; Caballero and Grossmann 2014; Caballero and Grossmann 2001; Caballero and Grossmann 2013) than rigorous models (Yeomans and Grossmann 2000b; Grossmann et al. 2004; Dünnebier and Pantelides 1999).

Regarding the mathematical representation of the superstructure, major alternatives are MINLP and GDP formulations (Grossmann et al. 2004). Both of them were first applied for systems with simple, conventional columns, and were then extended for complex configurations (Yeomans and Grossmann 2000a). For the MINLP formulation there are two possibilities, depending on the use of binary variables. The first option is to use binary variables to identify the existence or absence of each tray (Viswanathan and Grossmann 1993) and the second one is to use them to establish the location of the reflux, reboiler or both (Aguirre et al. 2001; Bauer and Stichlmair 1998; Viswanathan and Grossmann 1993), defining in this way the trays that exist (those in between the condenser and the reboiler) (Yeomans and Grossmann 2000b). However, both MINLP models present an important drawback: the non-existence of trays results in their associated streams flows to become zero, which may cause certain equations to be discontinuous or undefined for some values, presenting numerical difficulties to achieve convergence (Grossmann et al. 2004; Yeomans and Grossmann 2000b).

These are the difficulties that can be overcome with the use of GDP formulations (Yeomans and Grossmann 2000b). With this model the trays are considered as “permanent” and “conditional”. Permanent trays are considered those that have one or more of the following functions: feed, condenser, reboiler, liquid or vapour extraction; for them, MESH equations are enforced. Conditional trays are the rest of the trays, and they are always located between two permanent trays (Yeomans and Grossmann 2000b); in addition, conditional trays have two options: vapour-liquid equilibrium equations can be enforced, or the streams can only pass through, without mass nor heat transfer. These are the equivalents of an existing and non-existing trays, respectively, as the existence of a stage is defined as the streams achieving the equilibrium.

The model presented by Yeomans and Grossmann (Yeomans and Grossmann 2000b) is shown in Figure 9, and can be applied both for simple columns and thermally coupled

configurations (Yeomans and Grossmann 2000b). In particular, it can be used together with the superstructure presented in Figure 7.

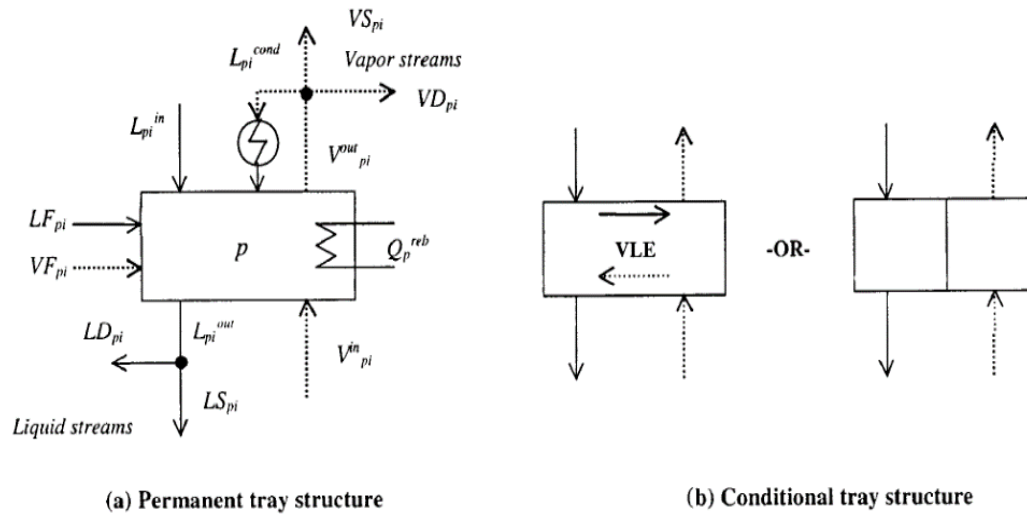


Figure 9: Tray structures for the modelling of complex columns (Yeomans and Grossmann 2000b).

The use of GDP and its reformulations in studies that consider only conventional distillation configurations is extended (Caballero et al. 2005; Yeomans and Grossmann 2000a; Yeomans and Grossmann 1999b). However, only some studies developed on the synthesis of separation networks including complex configurations use this representation (Caballero and Grossmann 2004; Yeomans and Grossmann 2000b; Caballero and Grossmann 2001; Caballero and Grossmann 2013). Among these, two works (Yeomans and Grossmann 2000b; Grossmann et al. 2004) do not mention a reformulation strategy and propose logic-based algorithms to solve the GDP model directly. In contrast, other two studies (Caballero and Grossmann 2004; Caballero and Grossmann 2013), including the latest one of 2013, use the big-M reformulation.

Several studies on the synthesis of separation networks have also developed MINLP models directly. Most of them considering only conventional distillation columns (Giridhar and Agrawal 2010; Novak et al. 1994; Smith and Pantelides 1995; Viswanathan and Grossmann 1993) and one considering also complex configurations (Dünnebier and Pantelides 1999), despite the drawbacks above mentioned. However, only one of them (Dünnebier and Pantelides 1999) was able to include rigorous distillation models, as were the ones using GDP, because of the non-linearities and non-convexities added with them.

2.3.3.1. Bypass efficiency method

The formulation of separation networks as MINLP problems using MESH equations may result in intractable optimisation problems when using several separation units. Even

more so, if it is desired to include this network into a flowsheet with a reactor network. This has been the motivation of works focused on the reformulation of MINLP distillation column models to remove the integer variables. (Dowling and Biegler 2015) These works include revised shortcut models for distillation (Kamath et al. 2010), the relaxation of integer to continuous variables (Kraemer et al. 2009) and the most recent one, a MESH model that considers a bypass efficiency for each tray (Dowling and Biegler 2015).

Modelling of a tray with the bypass efficiency method is shown in **Figure 10**. In this model a fraction of the inlet streams to tray “n”, L_{n+1} and V_{n-1} , enters the tray and the remaining fraction is bypassed to the outlet of the tray, creating the streams L_n^* and V_n^* .

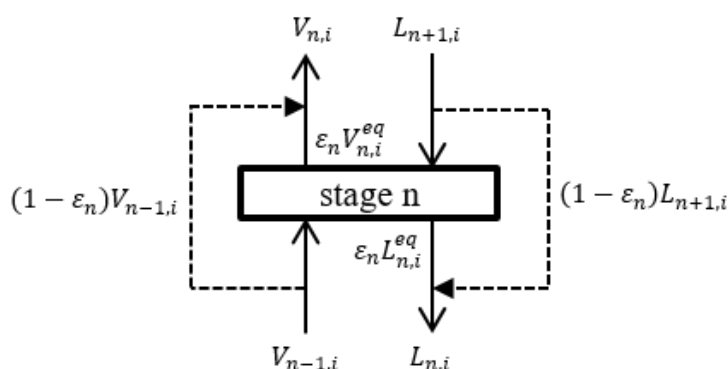


Figure 10: Bypass efficiency model (Ma et al. 2018).

Inside the tray, the standard MESH equations are fulfilled. The bypass efficiency is then the fraction that effectively enters the tray, ϵ_n . Consequently, if there is no bypass ($\epsilon_n = 1$) then the tray is active, and the outlet streams are in equilibrium. However, if the bypass is complete ($\epsilon_n = 0$) then the tray is inactive and the flows remains unchanged. Cases in between are possible and well defined, using continuous feasible regions. (Dowling and Biegler 2015)

Bypass efficiency method presents the benefit of modelling conditional trays without using integer variables, resulting in an NLP model. It has been used in several works since it was proposed (Dowling and Biegler 2015; Ma et al. 2018; Ma et al. 2019; Pattison et al. 2016) because of this advantage.

2.3.4. Formulation strategies for reaction-separation networks

As mentioned in Section 2.2.3, the synthesis and design of reaction-separation networks may be addressed in two different ways. In the first case, where reaction and separation networks are created independently, the same happens with the modelling of the superstructures: models are developed to represent each one, and equations are added

to represent the streams connecting them. Studies developed using this approach have used both shortcut (Kokossis and Floudas 1991) and rigorous (Zhang et al. 2018; Ma et al. 2018; Smith and Pantelides 1995) methods to represent the unit operations. In addition, their formulation as optimisation problems has involved the direct proposition of MINLP models (Smith and Pantelides 1995; Kokossis and Floudas 1991) and the use of GDP (Zhang et al. 2018; Ma et al. 2018). It is observed that the use of GDP is followed in both cases by the Big-M reformulation technique. The second case, where a new reaction-separation networks is created using a superstructure approach, consists of one study that has proposed the formulation as a MILP model (Kong and Shah 2016). However, none of the studies developed has proposed the use of separation networks that include thermally coupled distillation columns.

In previous studies of the formulation of reaction-separation synthesis problems, the most common objective is the total annualised cost (Zhang et al. 2018; Ma et al. 2018).

2.4. Solving strategies for superstructure optimisation

Solving optimisation problems formulated in Section 2.3. involves the use of modelling environments; the two most established platforms are General Algebraic Modelling System (GAMS) and A Mathematical Programming Language (AMPL) (Chen and Grossmann 2017). In these environments, different algorithms, or solvers, can be used according to the class of optimisation problem to be solved. Also, according to this, solvers may be able to achieve a globally or locally optimal solution.

LP and MILP problems are usually solved with branch and bound technique, and solvers include Linear, Interactive, and Discrete Optimizer (LINDO), ZOOM and Optimization Subroutine Library (OSL).

NLP solvers rely on successive quadratic programming (SQP) or reduced-gradient strategies. Available codes for SQP include Sparse Nonlinear Optimiser (SNOPT), and for reduced-gradient CONOPT and Modular In-core Nonlinear Optimisation System (MINOS).

MINLP solutions rely on decomposition in NLP, MILP and/or LP subproblems. Major methods for MINLP include: branch and bound (BB) which is an extension of the linear case that solves NLP subproblems at each node (Gupta and Ravindran 1985), Generalised Benders Decomposition (GBD) (Benders 1962) and Outer-Approximation (OA) (Duran and Grossmann 1986). The last two methods are iterative and solve a sequence of alternated NLP and MILP problems; NLP subproblems have fixed integer variables and MILP master

problem is used to predict lower bounds and new sets of integer variables. The difference between the GBD and OA methods lies in the definition of the MILP master problem: OA uses accumulated linearization of the functions, while GBD uses accumulated Lagrangean functions. The main codes available for the solution of MINLP problems include DICOPT, (Viswanathan and Grossmann 1990) MINLP_BB and SBB.

All the proposed methods guarantee convergence to the global optimum if the problems are convex. In the presence of nonlinearities of NLP and MINLP problems the above solvers yield locally optimal solutions, and rigorous global optimisation techniques are required to guarantee convergence to the global optimum. Most used codes for global optimisation of NLP and MINLP problems include Algorithms for coNTinuous / Integer Global Optimization of Nonlinear Equations (ANTIGONE) (Misener and Floudas 2014), Branch-And-Reduce Optimization Navigator (BARON) (Tawarmalani and Sahinidis 2005) and Solving Constraint Integer Programs (SCIP) (Vigerske and Gleixner 2018).

2.4.1. Solving strategies for reactor networks

Strategies adopted to solve reactor networks problems formulated as MINLP models involve several steps that vary between studies. Works start with the proposition of initial conditions and are followed by the implementation of an appropriate algorithm in a specific software and the verification of results. Some of the works verify results according to the Kuhn Tucker conditions, and if they are not realised, new initial conditions are proposed (Diaconescu et al. 2002; Achenie and Biegler 1990). Diaconescu et al. (Diaconescu et al. 2002) mention that for their work the Kuhn-Tucker method is directly applied with a routine of MATLAB Optimisation Toolbox. In contrast, Achenie and Biegler (Achenie and Biegler 1990) further explain the followed procedure, stating that a quadratic programming algorithm was implemented before verifying the Kuhn-Tucker conditions; additionally they state that as this method does not guarantee global optimality, several initial conditions should be tested in order to arrive to a global optimum. Two other studies report the use of hierarchical MINLP solver in the software MIPSYN (Pahor et al. 2000; Pahor et al. 2002); also one work reports the use of MI-NOS5.2 and ZOOM/XMP in GAMS, specifying that each one was used to solve NLP and MILP subproblems respectively (Kokossis and Floudas 1994).

In general, it is found that approaches used for the mentioned studies are not in line with more elaborate strategies used today, as will be described in the next two sections. In

comparison, reactor networks are not as difficult to solve as separation networks, given the non-convexities and nonlinearities found in distillation systems. In the last decade more studies have been focused on the simultaneous synthesis of reaction-separation networks, hence the lack of studies on this period involving reaction networks exclusively.

2.4.2. Solving strategies for separation networks

Once the optimisation problem has been formulated, as described in Section 2.3.3, the usual case is to have a MINLP problem. The alternative, presented in two studies, is to have a GDP problem (Yeomans and Grossmann 2000b; Grossmann et al. 2004).

For the case of an MINLP problem, there are standard solvers that can be used. However, separation networks problems are highly non-convex and present a large number of local solutions, leading to suboptimal solutions (Caballero and Grossmann 2013). This is the reason why, even though the studies use tools in common, each one presents a particular set of observations or guides that are suitable for the addressed problem and improve the efficiency of the solution procedure. The efficiency may refer to the computational time used for convergence, the tendency of the problem to get trapped in a poor locally optimal solution or the confidence in the solution achieved.

For example, the study by Caballero and Grossmann (Caballero and Grossmann 2004) that addresses the synthesis of separation networks for a mixture of “N” components, and focuses on mixtures with more than three components, proposes that in the first step all the alternative configurations are identified. In mixtures with more than three components, the number of possible configurations increases considerably with the number of components; consequently, the first step of the solution is of particular importance to this study. After the most prominent configurations have been identified, the solution is found using DICOPT in GAMS.

Studies have used the following solvers: CONOPT in GAMS (Caballero and Grossmann 2013; Smith and Pantelides 1995) and in gPROMS (Dünnebier and Pantelides 1999), DICOPT in GAMS (Viswanathan and Grossmann 1993; Caballero and Grossmann 2001), SBB in GAMS (Caballero and Grossmann 2013) and CPLEX in GAMS (Giridhar and Agrawal 2010).

In the two previous studies where GDP models are obtained from the formulation stage, modified logic-based outer approximation algorithms were used to solve the problems (Yeomans and Grossmann 2000b; Grossmann et al. 2004). One of the works (Yeomans

and Grossmann 2000b) reports to have used CONOPT 2.0 and CPLEX 4.5 as solvers in GAMS, while the other does not comment on that.

According to Grossmann et al. (Grossmann et al. 2004) both GDP and MINLP formulations present complexities due to nonlinearities in distillation models, and considers essential for the solution procedure to develop initialisation and bounding methods for the variables involved.

2.4.3. Solving strategies for reaction-separation networks

The simultaneous synthesis of reaction-separation systems leads to the formulation of highly nonlinear and nonconvex MINLP models. With these characteristics, even when the class of optimisation problem allows for the use of solvers above mentioned, arbitrary initial values usually result in a considerable number of infeasibilities. Hence, it has been observed that refined initialisation procedures are required. (Dowling and Biegler 2015) iBecause of the mentioned difficulties, the work of Recker et al. (Recker et al. 2015) proposes to first screen for the most promising configurations using shortcut models and to optimize those configurations in a second step. The one by Zhang et al. (Zhang et al. 2018) proposes to use the standard solvers SBB and CONOPT in GAMS, but does not refer to the difficulty of the initialization procedure. In contrast, the work by Ma et al. (Ma et al. 2018) proposes a clear solution approach to solve the problem, shown in Figure 11 consisting of a pseudo-transient continuous model. The initialization step consists on solving the reactor network using GAMS and using the product stream leaving this

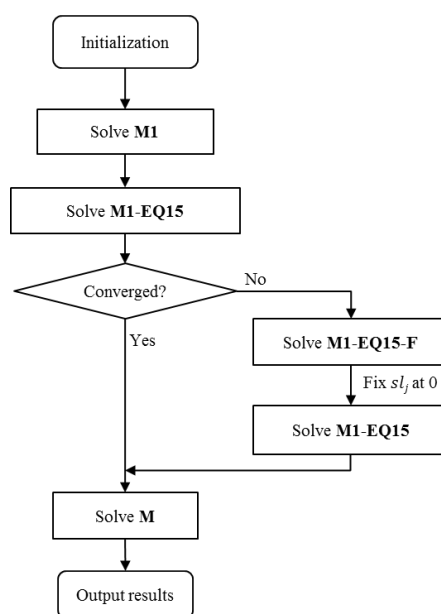


Figure 11: Solution strategy proposed by Ma et al. (Ma et al. 2018).

network as the feed to a model of the separation networks, implemented in Aspen Custom Modeler.

This generates the initial solution for the model, but this point may produce infeasibilities if directly used in model M due to its highly nonlinear and nonconvex character. Consequently, model M1 is created, that allows for some flexibility in the purities and bypass efficiency values, by allowing them to take values between 0 and 1. After M1 is solved, the constraint for purity is added, and if the model M1-EQ15 is converged, then the constraint of binary bypass efficiencies is also added and M is solved using as initial solution the values obtain in the previous step. If M1-EQ15 is not converged, then another auxiliary model, M1-EQ15-F is created. This model uses a modified version of the purity constraints by adding slack variables. M1-EQ15-F model has the objective to minimise the slack variables, and once they are all zero, M1-EQ15 is solved, followed by the solution of M. Finally, for this work it is specified that all models were solved using SBB in GAMS (Ma et al. 2018).

In the work by Ma et al. (Ma et al. 2019) a different pseudo-transient continuous (PTC) modelling approach is proposed, based on the work by Pattison and Baldea (Pattison and Baldea 2014). The complete procedure, which includes two options, is presented in Figure 12. (Ma et al. 2019)

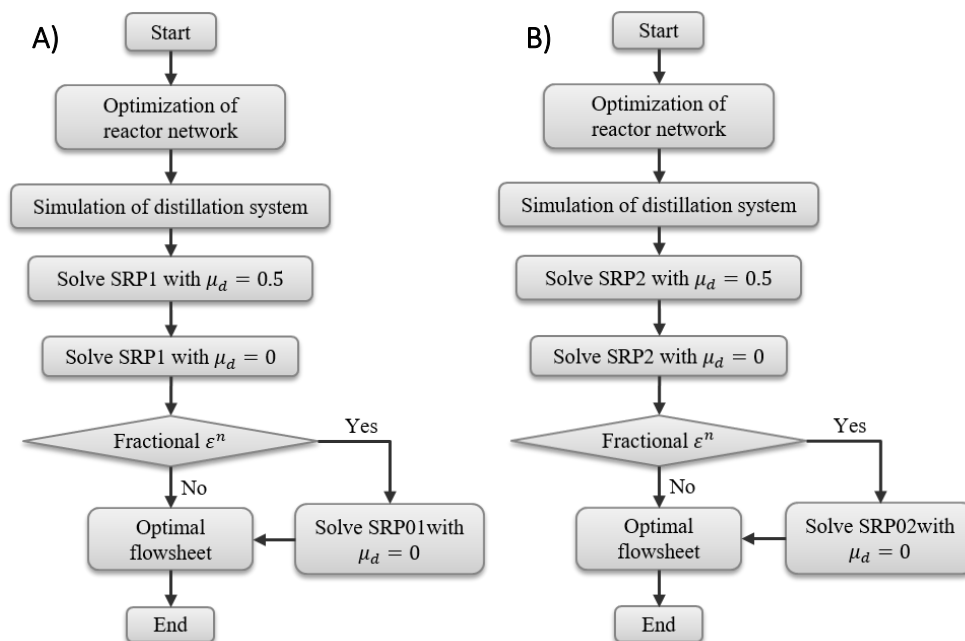


Figure 12: Solution strategy proposed by Ma et al. (Ma et al. 2019)

In contrast with the procedure in the previous work, here the reactor network is optimised first, and the resulting product stream is used as feed for the simulation of the

distillation system, performed in Aspen Custom Modeler. The results of these simulation are used as initial values to solve a model named SRP1, which includes all the equations but relaxes the values of binary variables that influence on the purity specifications in the separation system. However, according to the complexity of the reactor network, it might be necessary to solve a model named SRP2, which includes all the equations but relaxes binary variables related to the reactor network as well as the ones related with purity specifications. If fractional bypass efficiencies are obtained in the result after solving SRP1 or SRP2, another problem SRP01 or SRP02 has to be solved, where bypass efficiency variables are constrained to binary variables.

It is reported that the optimisation models were solved using SBB in GAMS, because it is considered to have a better convergence performance than DICOPT for the model. In addition, it is stated that the method proposed significantly improves the convergence performance. (Ma et al. 2019)

2.5. Conclusions

It is concluded from the literature review that the synthesis and design of processes has considerably advanced in the last decades. Several approaches have been proposed, and the superstructure optimisation one has been widely used. Improvements have been made in moving from the synthesis of subsystems towards the synthesis of simultaneous reaction-separation processes. In addition, progress has been made in the use of rigorous models in the design, in order to improve the accuracy and reliability of the results.

For the synthesis of separation systems and simultaneous reaction-separation systems, the solving strategy is of critical importance. This is because the tools most commonly used achieve locally optimum solutions and if the solution procedure is not appropriate, the result may be a bad local optimum.

Finally, no study has been developed on the synthesis of simultaneous reaction-separation systems that include the use of complex configurations for distillation systems, such as thermally coupled distillation columns. These configurations have shown improvements in the economic aspect compared with the use of conventional distillation columns. Consequently, it is concluded that including complex configurations in the synthesis of simultaneous reaction-separation systems can present advantages, and studies should be developed to this purpose.

Chapter 3: Methodology

In order to achieve the objectives proposed in Section 1.1, and based on the literature review present in Chapter 2: Background, a methodology is developed in the present Chapter. Using an optimisation-based superstructure approach, the present study procures to develop on the works by Zhang et al. (Zhang et al. 2018) and Ma et al. (Ma et al. 2019) by studying the influence on the result of considering the use of complex configuration columns including thermally coupled distillation columns. To be able to study this influence, the methodology is considerably similar to that presented by Ma et al. (Ma et al. 2019) which is the most developed and best supported. Differences are found mostly in the sections related to the separation network, where a different superstructure is used. In addition, to be able to compare results for the case study, the same kinetic, economic and specifications data is used. All the required data is presented in Appendix A. Despite the similarities that are required, all the steps of the methodology are discussed in order to either propose changes or recommendations for future work.

The present Chapter includes the construction of the superstructure, its modelling using GDP, the reformulation into a MINLP problem and the solving strategy. This procedure is applied to the case study of benzene chlorination, presented also in the works by Zhang et al. (Zhang et al. 2018) and Ma et al. (Ma et al. 2019).

3.1. Construction of superstructures

Reaction and separation superstructures are constructed separately and connected as shown in Figure 13. According to the case under study, the stream going from the reactor network to the separation network may require heating or cooling and can be added.

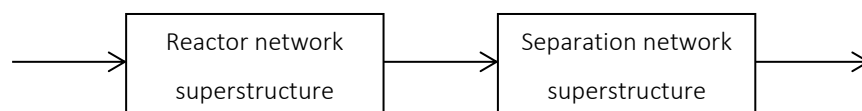


Figure 13: Connection of reactor and separation network superstructures.

The reactor network superstructure from the study of Ma et al. (Ma et al. 2018) is used in the present study as well. The generic superstructure, shown in Figure 6, uses CSTR and isothermal PFR units, and it is considered rich in features although it does not consider all the possibilities that would be desired. From these features, mentioned in Section 2.2, the superstructure presents the possibility of series and parallel operation, split of feed and outlet streams, bypass of every unit, and mixing points prior to unit inlets

and for the final product. However, it is missing the recycle feature, which could allow for the recycle of a unit outlet to the inlet of all previous units, and to its own inlet. The present study uses the same superstructure, without the recycles, to avoid changing the complete superstructure, and being able to evaluate only the influence of the separation network. In addition to this, the inclusion of recycles increases the complexity of the model, and the complexity is already increased due to the presence of complex configurations in the separation; hence, it appears sensible to increase the complexity gradually, leaving the introduction of recycles for a future study.

For the separation network the Sargent-Gaminibandara (Sargent and K. Gaminibandara 1976) superstructure is selected, shown in Figure 7. This superstructure is the most popular one that includes the synthesis of conventional and complex configuration distillation systems, for the separation of mixtures with three components that form no azeotrope; in addition, it has been the starting point to studies constructing superstructures for the separation of mixtures with more components, with and without the formation of azeotropes (Sargent 1998). The separation superstructure is constituted by eight “permanent trays” and six stacks of “conditional trays”, numbered as shown in Figure 14. It allows the possibility of both liquid and vapour feeds, and the outlet of products in both phases as well, as recommended by Dünnebier and Pantelides (Dünnebier and Pantelides 1999).

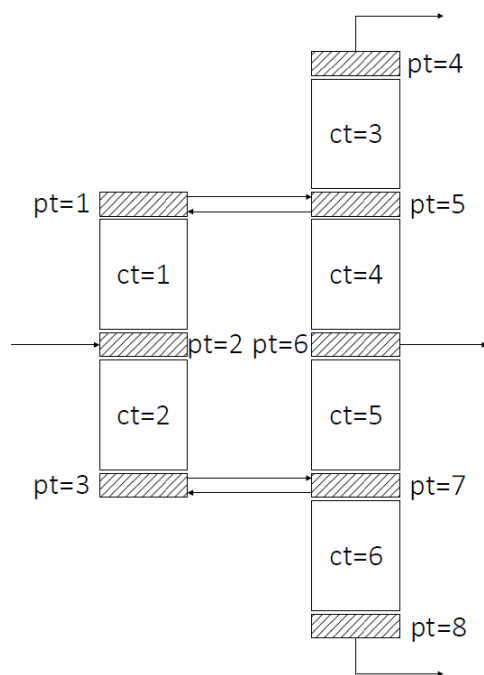


Figure 14: Arrangement of permanent and conditional trays in the separation network superstructure.

3.2. GDP model of superstructure

From the literature review presented in Section 2.3.3, it is found that the most efficient modelling strategy is to develop a GDP model and reformulate it into a MINLP problem. In addition, this is the approach taken by both Zhang et al. (Zhang et al. 2018) and Ma et al. (Ma et al. 2019).

3.2.1. Reactor network modelling

As mentioned in Section 2.2, the model is comprised of the material and energy balance around the reactor units and at mixing and splitting points of the superstructure. The model is developed for a system including $i \in 1, 2, \dots, I$ components, and $k \in 0, 1, \dots, K + 1$ stages, where the stages 0 and $K + 1$ represent the feed inlet and product outlet, respectively. A system of $m \in 1, 2, \dots, M$ chemical reactions is considered, and the stoichiometric data is represented by matrix R , shown in Eq. 6, of dimensions $M \times I$ where element $R_{m,i}$ represents the stoichiometric coefficient of component i in the reaction m . The nomenclature used to develop the reactor network model is shown in Appendix B.

$$R = \begin{bmatrix} R_{1,1} & \dots & R_{1,I} \\ \vdots & \ddots & \vdots \\ R_{M,1} & \dots & R_{M,I} \end{bmatrix} \quad \text{Eq. 6}$$

For each reaction a reference component is defined, $Ref = (Ref_1 \dots Ref_M)$, and the kinetic expressions for the reference component of each reaction is given by r , as shown in Eq. 7 as function of temperature and components compositions. The heat of reactions $\Delta H = (\Delta H_1 \dots \Delta H_M)$ are also assigned for the reference component.

$$r = f_1(C, T) \quad \text{Eq. 7}$$

Based on these data organisation, the reactor network model is represented with Eq. 8 to Eq. 17. Prior to module k there is a mixing point of fractions of outlets of all the previous modules. Eq. 8 and Eq. 9 represent the global and component material balances at this mixing point, where the inlet molar flowrate to module k is the sum of the outlets of previous modules j that inlet module k .

$$F_k^{in} = \sum_{j=0}^{k-1} F_{j,k}^{out} \quad \forall k / 0 < k < K + 1 \quad \text{Eq. 8}$$

$$F_{k,i}^{in} = v_k^{in} \cdot C_{k,i}^{in} = \sum_{j=0}^{k-1} (v_{j,k}^{out} \cdot C_{j,i}^{out}) \quad \forall i \quad \text{Eq. 9}$$

The total and component molar flowrate outlets of a module k are defined in Eq. 10 and Eq. 11 respectively.

$$F_k^{out} = \sum_{i=1}^I F_{ki}^{out} \quad \forall k \quad \text{Eq. 10}$$

$$F_{k,i}^{out} = v_k^{in} \cdot C_{k,i}^{out} \quad \forall k, i \quad \text{Eq. 11}$$

The fraction of the molar flowrate outlet from module j that inlets module k is defined in Eq. 12, constrained to Eq. 13 and Eq. 14. The latter states that fractions of the inlet may go to modules 1 to K , but cannot form part of the product stream, which would be a bypass of raw material.

$$F_{j,k}^{out} = F_j^{out} \cdot \alpha_{j,k} \quad \forall k, j, 0 < k < K + 1, j < k \quad \text{Eq. 12}$$

$$\sum_{k=j+1}^{K+1} \alpha_{j,k} = 1 \quad \forall j, 1 \leq j \leq K \quad \text{Eq. 13}$$

$$\sum_{k=1}^K \alpha_{0,k} = 1 \quad \text{Eq. 14}$$

Eq. 15 represents the energy balance at the mixing point.

$$v_k^{in} \cdot h_k^{in} = \sum_{j=0}^{k-1} (v_{j,k}^{out} \cdot h_j^{out}) \quad \forall k, 0 < k < K + 1 \quad \text{Eq. 15}$$

Eq. 16 represents energy balances and global energy balances for both units in module k .

$$\left[\begin{array}{l} v_k^{in} \cdot C_{k,i}^{out} = v_k^{in} \cdot C_{k,i}^{in} - \sum_{m=1}^M \left(r_m(C_k^{out}, T_k^{out}) \cdot \frac{R_{m,i}}{R_{m,Ref_m}} \right) \cdot V_k^C \quad \forall i \\ v_k^{in} \cdot \rho \cdot h_k^{out} = v_k^{in} \cdot \rho \cdot h_k^{in} - \sum_{m=1}^M (r_m(C_k^{out}, T_k^{out}) \cdot \Delta H_m) \cdot V_k^C + Q_k^{reac} \end{array} \right]^{Y_{C,k}}$$

$$\forall \left[\begin{array}{l} v_k^{in} \cdot dC_{k,i} = - \sum_{m=1}^M \left(r_m(C_k, T_k) \cdot \frac{R_{m,i}}{R_{m,Ref_m}} \right) \cdot dV_k^P \quad \forall i \\ v_k^{in} \cdot \rho \cdot dh_k = - \sum_{m=1}^M (r_m(C_k, T_k) \cdot \Delta H_m) \cdot dV_k^P + dQ_k^{reac} \end{array} \right]^{Y_{P,k}} \quad \forall k, 0 < k < K + 1$$

Eq. 16

Note that in the energy balances the heat may be positive or negative according to whether it needs to be supplied or removed to perform the reactions at the optimum temperature.

The outlet of stage $K + 1$, the product stream leaving the reactor network, is defined in the mass balance of Eq. 17.

$$F_{K+1}^{out} = \sum_{k=1}^K (F_k^{out} \cdot \alpha_{k,K+1}) \quad \text{Eq. 17}$$

3.2.2. Separation network modelling

The model for the separation network superstructure is tray by tray and based on the model proposed by Yeomans and Grossmann (Yeomans and Grossmann 2000b), shown in Figure 9. Given that the superstructure is constituted by two types of trays, “permanent” and “conditional” trays, two models are required for the trays, one for each type.

Permanent trays may have one or more of the following functions: reboiler, partial or total condenser, feed tray, vapour or liquid side extraction. For them, the MESH equations are always enforced. In the model proposed by Yeomans and Grossmann (Yeomans and Grossmann 2000b) the reboiler and condenser functions are treated differently without any mentioned advantage. Instead of allowing the tray to be supplied or removed heat, only the former is allowed and the removing of heat, which is the condenser function, is performed on a separate stream that is recycled in the tray, symbolised $L_{p,i}^{cond}$. In addition, using this auxiliary stream includes more variables into the mathematical model and additional complexities in its implementation in GAMS. Consequently, it is decided to change this model to treat the reboiler and condenser functions in the same way, as shown in Figure 15.

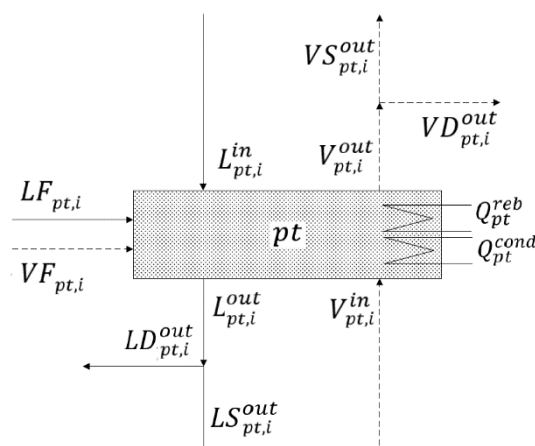


Figure 15: Proposed model for permanent trays.

The model for conditional trays is the same as the one proposed by Yeomans and Grossmann (Yeomans and Grossmann 2000b). For these trays the material, energy and summation equations are always enforced, and the enforcement of equilibrium equations is conditional, determining if the tray is active or not.

As well as for the reactor network, for the modelling of the separation network $i \in 1, 2, \dots, I$ components are considered. The nomenclature used to develop the model for the separation network is presented in Appendix C.

3.2.2.1. Permanent trays

The model for permanent trays is constituted by Eq. 18 to Eq. 36. In this model $pt \in [1:8]$ is used to represent variables related to a permanent tray.

Eq. 18 represents the mass balance for component i in tray pt , while Eq. 19 and Eq. 20 are mass balances relating the vapour and liquid streams of component i that leave tray pt , respectively.

$$LF_{pt,i} + VF_{pt,i} + L_{pt,i}^{in} + V_{pt,i}^{in} = L_{pt,i}^{out} + V_{pt,i}^{out} \quad \forall pt, i \quad \text{Eq. 18}$$

$$V_{pt,i}^{out} = VD_{pt,i} + VS_{pt,i} \quad \forall pt, i \quad \text{Eq. 19}$$

$$L_{pt,i}^{out} = LD_{pt,i} + LS_{pt,i} \quad \forall pt, i \quad \text{Eq. 20}$$

Eq. 21 represents the energy balance of tray pt . Note that the same convention with the heat supplied and removed is used than in the reactor network.

$$\sum_{i=1}^I \left(LF_{pt,i} \cdot h_{LF_{pt,i}} + VF_{pt,i} \cdot h_{VF_{pt,i}} + L_{pt,i}^{in} \cdot h_{L_{pt,i}^{in}} + V_{pt,i}^{in} \cdot h_{V_{pt,i}^{in}} + L_{pt,i}^{out} \cdot h_{L_{pt,i}^{out}} - V_{pt,i}^{out} \cdot h_{V_{pt,i}^{out}} \right) + Q_{pt}^{reb} + Q_{pt}^{cond} = 0 \quad \forall pt \quad \text{Eq. 21}$$

Eq. 22 and Eq. 23 represent summation equations for fraction in the liquid and vapour streams leaving tray pt in equilibrium, respectively.

$$\sum_{i=1}^I x_{pt,i} = 1 \quad \forall pt \quad \text{Eq. 22}$$

$$\sum_{i=1}^I y_{pt,i} = 1 \quad \forall pt \quad \text{Eq. 23}$$

Eq. 24 represent the equilibrium equation for component i in tray pt .

$$y_{pt,i} \cdot P_{pt} = \gamma_{pt,i} \cdot P_{pt,i}^{sat} \cdot x_{pt,i} \quad \forall pt, i \quad \text{Eq. 24}$$

Complementary Eq. 25 and Eq. 26 relate the outlet vapour and liquid flowrates of a component with the fraction of the component in the vapour and liquid, respectively, for component i and tray pt .

$$V_{pt,i}^{out} = V_{pt}^{out} \cdot y_{pt,i} \quad \forall pt, i \quad \text{Eq. 25}$$

$$L_{pt,i}^{out} = L_{pt}^{out} \cdot x_{pt,i} \quad \forall pt, i \quad \text{Eq. 26}$$

Complementary Eq. 27 and Eq. 28 relate the vapour and liquid side draws as fractions of the vapor and liquid outlets, respectively, for component i and tray pt .

$$VD_{pt,i} = \beta_{pt} \cdot V_{pt,i}^{out} \quad \forall pt, i \quad \text{Eq. 27}$$

$$LD_{pt,i} = \delta_{pt} \cdot L_{pt,i}^{out} \quad \forall pt, i \quad \text{Eq. 28}$$

Complementary Eq. 29 and Eq. 30 establish the equality of enthalpies at the splitting point of vapour stream leaving tray, for component i and tray pt . Eq. 31 and Eq. 32 establish the same relations for the liquid stream leaving tray pt .

$$h_{VD_{pt,i}} = h_{V_{pt,i}^{out}} \quad \forall pt, i \quad \text{Eq. 29}$$

$$h_{VS_{pt,i}} = h_{V_{pt,i}^{out}} \quad \forall pt, i \quad \text{Eq. 30}$$

$$h_{LD_{pt,i}} = h_{L_{pt,i}^{out}} \quad \forall pt, i \quad \text{Eq. 31}$$

$$h_{LS_{pt,i}} = h_{L_{pt,i}^{out}} \quad \forall pt, i \quad \text{Eq. 32}$$

Complementary Eq. 33 and Eq. 34 establish the enthalpy of streams leaving tray pt as functions of the temperature of the tray.

$$h_{L_{pt,i}^{out}} = f_2(T_{pt}) \quad \forall pt, i \quad \text{Eq. 33}$$

$$h_{V_{pt,i}^{out}} = f_3(T_{pt}) \quad \forall pt, i \quad \text{Eq. 34}$$

Eq. 35 calculates the activity coefficient of component i in the conditions of tray pt , while Eq. 36 calculates the vapour pressure of component i in the same conditions.

$$\gamma_{pt,i} = f_4(T_{pt}, P_{pt}, C_{pt}) \quad \forall pt, i \quad \text{Eq. 35}$$

$$P_{pt,i}^{sat} = f_5(T_{pt}) \quad \forall pt, i \quad \text{Eq. 36}$$

Given that permanent trays are always part of the solution, vapour and liquid flowrates leaving the tray are greater than zero in every possible scenario, as established by Eq. 37 and Eq. 38

$$L_{pt}^{out} > 0 \quad \forall pt, i \quad \text{Eq. 37}$$

$$V_{pt}^{out} > 0 \quad \forall pt, i \quad \text{Eq. 38}$$

The modelling of permanent trays could also include disjunctions for each one of them, establishing which functions are expected for each one considering the usual conventional and complex configurations. For example, a priori it is not expected to have a reboiler and a condenser at the same time, and it is expected that permanent trays 4 and 8 present a condenser and a reboiler, respectively. However, the disjunctions should not be necessary for the optimisation process to avoid the first situation, nor to result in the second one. In addition, the inclusion of disjunctions may eliminate configurations outside of the usual conventional and complex configurations of distillation systems, and it requires considerable additional effort for their modelling. For these reasons, disjunctions for each of the permanent trays are not included, and it is left to the optimisation algorithm to decide the optimum function or functions of each tray.

3.2.2.2. Conditional trays

Conditional trays are organised in stacks $ct \in [1:6]$, each one with trays $t \in 1, 2, \dots, T$ where the top tray is assigned $t = 1$. The model for conditional trays consists of Eq. 39 to Eq. 43.

Eq. 39 represents the mass balance of component i for tray t of stack ct .

$$L_{t-1,i}^{ct} + V_{t+1,i}^{ct} - L_{t,i}^{ct} - V_{t,i}^{ct} = 0 \quad \forall i, t, ct \quad \text{Eq. 39}$$

Eq. 40 represents the energy balance for tray t of stack ct .

$$\sum_{i=1}^I \left(L_{t-1,i}^{ct} \cdot h_{L_{t-1,i}^{ct}} + V_{t+1,i}^{ct} \cdot h_{V_{t+1,i}^{ct}} - L_{t,i}^{ct} \cdot h_{L_{t,i}^{ct}} - V_{t,i}^{ct} \cdot h_{V_{t,i}^{ct}} \right) = 0 \quad \forall t, ct \quad \text{Eq. 40}$$

Eq. 41 and Eq. 42 represent the summation equations for tray t of stack ct .

$$\sum_{i=1}^I x_{t,i}^{ct} = 1 \quad \forall t, ct \quad \text{Eq. 41}$$

$$\sum_{i=1}^I y_{t,i}^{ct} = 1 \quad \forall t, ct \quad \text{Eq. 42}$$

Eq. 43 represents the disjunction for tray t of stack ct .

$$\left[\begin{array}{l} W_t^{ct} \\ y_{t,i}^{ct} \cdot P_t^{ct} = \gamma_{t,i}^{ct} \cdot P_{t,i}^{ct,sat} \cdot x_{t,i}^{ct} \\ \gamma_{t,i}^{ct} = f_3(TL_t^{ct}, P_t^{ct}, C_t^{ct}) \\ P_{t,i}^{ct,sat} = f_4(TL_t^{ct}) \\ L_{t,i}^{ct} = L_t^{ct} \cdot x_{t,i}^{ct} \\ V_{t,i}^{ct} = V_t^{ct} \cdot y_{t,i}^{ct} \\ TL_t^{ct} = TV_t^{ct} \end{array} \right] \vee \left[\begin{array}{l} -W_t^{ct} \\ y_{t,i}^{ct} = y_{t+1,i}^{ct} \\ x_{t,i}^{ct} = y_{t-1,i}^{ct} \\ L_{t,i}^{ct} = L_{t-1,i}^{ct} \\ V_{t,i}^{ct} = V_{t+1,i}^{ct} \\ TL_t^{ct} = TL_{t-1}^{ct} \\ TV_t^{ct} = TV_{t+1}^{ct} \end{array} \right] \quad \forall ct, t \quad \text{Eq. 43}$$

Complementary Eq. 44 and Eq. 45 establish the enthalpy of streams leaving tray t of stack ct as functions of the temperature of the tray.

$$h_{L_{t,i}^{ct}} = f_6(TL_t^{ct}) \quad \text{Eq. 44}$$

$$h_{V_{t,i}^{ct}} = f_7(TV_t^{ct}) \quad \text{Eq. 45}$$

3.2.2.3. Interconnections between permanent and conditional trays

In order to effectively construct the separation network superstructure, stacks of conditional trays must be connected appropriately with permanent trays, and in some cases connections between permanent trays are also required.

Eq. 46 to Eq. 49 establish the connection between the stack of conditional trays 1 ($ct = 1$) and permanent tray 1 ($pt = 1$).

$$V_{1,i}^{in} = V_{1,i}^1 \quad \forall i \quad \text{Eq. 46}$$

$$h_{V_{1,i}^{in}} = h_{V_{1,i}^1} \quad \forall i \quad \text{Eq. 47}$$

$$L_{0,i}^1 = LS_{1,i} \quad \forall i \quad \text{Eq. 48}$$

$$h_{L_{0,i}^1} = h_{LS_{1,i}} \quad \forall i \quad \text{Eq. 49}$$

Eq. 50 to Eq. 53 establish the connection between the stack of conditional trays 1 ($ct = 1$) and permanent tray 2 ($pt = 2$).

$$L_{2,i}^{in} = L_{NT,i}^1 \quad \forall i \quad \text{Eq. 50}$$

$$h_{L_{2,i}^{in}} = h_{L_{NT,i}^1} \quad \forall i \quad \text{Eq. 51}$$

$$V_{NT,i}^1 = VS_{2,i} \quad \forall i \quad \text{Eq. 52}$$

$$h_{V_{NT,i}^1} = h_{VS_{2,i}} \quad \forall i \quad \text{Eq. 53}$$

Eq. 54 to Eq. 57 establish the connection between the stack of conditional trays 2 ($ct = 2$) and permanent tray 2 ($pt = 2$).

$$V_{2,i}^{in} = V_{1,i}^2 \quad \forall i \quad \text{Eq. 54}$$

$$h_{V_{2,i}^{in}} = h_{V_{1,i}^2} \quad \forall i \quad \text{Eq. 55}$$

$$L_{0,i}^2 = LS_{2,i} \quad \forall i \quad \text{Eq. 56}$$

$$h_{L_{0,i}^2} = h_{LS_{2,i}} \quad \forall i \quad \text{Eq. 57}$$

Eq. 58 to Eq. 61 establish the connection between the stack of conditional trays 2 ($ct = 2$) and permanent tray 3 ($pt = 3$).

$$L_{3,i}^{in} = L_{NT,i}^2 \quad \forall i \quad \text{Eq. 58}$$

$$h_{L_{3,i}^{in}} = h_{L_{NT,i}^2} \quad \forall i \quad \text{Eq. 59}$$

$$V_{NT,i}^2 = VS_{3,i} \quad \forall i \quad \text{Eq. 60}$$

$$h_{V_{NT,i}^2} = h_{VS_{3,i}} \quad \forall i \quad \text{Eq. 61}$$

Eq. 62 to Eq. 65 establish the connection between the stack of conditional trays 3 ($ct = 3$) and permanent tray 4 ($pt = 4$).

$$V_{4,i}^{in} = V_{1,i}^3 \quad \forall i \quad \text{Eq. 62}$$

$$h_{V_{4,i}^{in}} = h_{V_{1,i}^3} \quad \forall i \quad \text{Eq. 63}$$

$$L_{0,i}^3 = LS_{4,i} \quad \forall i \quad \text{Eq. 64}$$

$$h_{L_{0,i}^3} = h_{LS_{4,i}} \quad \forall i \quad \text{Eq. 65}$$

Eq. 66 to Eq. 69 establish the connection between the stack of conditional trays 3 ($ct = 3$) and permanent tray 5 ($pt = 5$).

$$L_{5,i}^{in} = L_{NT,i}^3 \quad \forall i \quad \text{Eq. 66}$$

$$h_{L_{5,i}^{in}} = h_{L_{NT,i}^3} \quad \forall i \quad \text{Eq. 67}$$

$$V_{NT,i}^3 = VS_{5,i} \quad \forall i \quad \text{Eq. 68}$$

$$h_{V_{NT,i}^3} = h_{VS_{5,i}} \quad \forall i \quad \text{Eq. 69}$$

Eq. 70 to Eq. 73 establish the connection between the stack of conditional trays 4 ($ct = 4$) and permanent tray 5 ($pt = 5$).

$$V_{5,i}^{in} = V_{1,i}^4 \quad \forall i \quad \text{Eq. 70}$$

$$h_{V_{5,i}^{in}} = h_{V_{1,i}^4} \quad \forall i \quad \text{Eq. 71}$$

$$L_{0,i}^4 = LS_{5,i} \quad \forall i \quad \text{Eq. 72}$$

$$h_{L_{0,i}^4} = h_{LS_{5,i}} \quad \forall i \quad \text{Eq. 73}$$

Eq. 74 to Eq. 77 establish the connection between the stack of conditional trays 4 ($ct = 4$) and permanent tray 6 ($pt = 6$).

$$L_{6,i}^{in} = L_{NT,i}^4 \quad \forall i \quad \text{Eq. 74}$$

$$h_{L_{6,i}^{in}} = h_{L_{NT,i}^4} \quad \forall i \quad \text{Eq. 75}$$

$$V_{NT,i}^4 = VS_{6,i} \quad \forall i \quad \text{Eq. 76}$$

$$h_{V_{NT,i}^4} = h_{VS_{6,i}} \quad \forall i \quad \text{Eq. 77}$$

Eq. 78 to Eq. 81 establish the connection between the stack of conditional trays 5 ($ct = 5$) and permanent tray 6 ($pt = 6$).

$$V_{6,i}^{in} = V_{1,i}^5 \quad \forall i \quad \text{Eq. 78}$$

$$h_{V_{6,i}^{in}} = h_{V_{1,i}^5} \quad \forall i \quad \text{Eq. 79}$$

$$L_{0,i}^5 = LS_{6,i} \quad \forall i \quad \text{Eq. 80}$$

$$h_{L_{0,i}^5} = h_{LS_{6,i}} \quad \forall i \quad \text{Eq. 81}$$

Eq. 82 to Eq. 85 establish the connection between the stack of conditional trays 5 ($ct = 5$) and permanent tray 7 ($pt = 7$).

$$L_{7,i}^{in} = L_{NT,i}^5 \quad \forall i \quad \text{Eq. 82}$$

$$h_{L_{7,i}^{in}} = h_{L_{NT,i}^5} \quad \forall i \quad \text{Eq. 83}$$

$$V_{NT,i}^5 = VS_{7,i} \quad \forall i \quad \text{Eq. 84}$$

$$h_{V_{NT,i}^5} = h_{VS_{7,i}} \quad \forall i \quad \text{Eq. 85}$$

Eq. 86 to Eq. 89 establish the connection between the stack of conditional trays 6 ($ct = 6$) and permanent tray 7 ($pt = 7$).

$$V_{7,i}^{in} = V_{1,i}^6 \quad \forall i \quad \text{Eq. 86}$$

$$h_{V_{7,i}^{in}} = h_{V_{1,i}^6} \quad \forall i \quad \text{Eq. 87}$$

$$L_{0,i}^6 = LS_{7,i} \quad \forall i \quad \text{Eq. 88}$$

$$h_{L_{0,i}^6} = h_{LS_{7,i}} \quad \forall i \quad \text{Eq. 89}$$

Eq. 90 to Eq. 93 establish the connection between the stack of conditional trays 6 ($ct = 6$) and permanent tray 8 ($pt = 8$).

$$L_{8,i}^{in} = L_{NT,i}^6 \quad \forall i \quad \text{Eq. 90}$$

$$h_{L_{8,i}^{in}} = h_{L_{NT,i}^6} \quad \forall i \quad \text{Eq. 91}$$

$$V_{NT,i}^6 = VS_{8,i} \quad \forall i \quad \text{Eq. 92}$$

$$h_{V_{NT,i}^6} = h_{VS_{8,i}} \quad \forall i \quad \text{Eq. 93}$$

Eq. 94 to Eq. 101 establish the connection between permanent tray 1 ($pt = 1$) and permanent tray 5 ($pt = 5$).

$$LF_{1,i} = LD_{5,i} \quad \forall i \quad \text{Eq. 94}$$

$$h_{LF_{1,i}} = h_{LD_{5,i}} \quad \forall i \quad \text{Eq. 95}$$

$$VF_{1,i} = VD_{5,i} \quad \forall i \quad \text{Eq. 96}$$

$$h_{VF_{1,i}} = h_{VD_{5,i}} \quad \forall i \quad \text{Eq. 97}$$

$$LF_{5,i} = LD_{1,i} \quad \forall i \quad \text{Eq. 98}$$

$$h_{LF_{5,i}} = h_{LD_{1,i}} \quad \forall i \quad \text{Eq. 99}$$

$$VF_{5,i} = VD_{1,i} \quad \forall i \quad \text{Eq. 100}$$

$$h_{VF_{5,i}} = h_{VD_{1,i}} \quad \forall i \quad \text{Eq. 101}$$

Eq. 102 to Eq. 109 establish the connection between permanent tray 3 ($pt = 3$) and permanent tray 7 ($pt = 7$).

$$LF_{3,i} = LD_{7,i} \quad \forall i \quad \text{Eq. 102}$$

$$h_{LF_{3,i}} = h_{LD_{7,i}} \quad \forall i \quad \text{Eq. 103}$$

$$VF_{3,i} = VD_{7,i} \quad \forall i \quad \text{Eq. 104}$$

$$h_{VF_{3,i}} = h_{VD_{7,i}} \quad \forall i \quad \text{Eq. 105}$$

$$LF_{7,i} = LD_{3,i} \quad \forall i \quad \text{Eq. 106}$$

$$h_{LF_{7,i}} = h_{LD_{3,i}} \quad \forall i \quad \text{Eq. 107}$$

$$VF_{7,i} = VD_{3,i} \quad \forall i \quad \text{Eq. 108}$$

$$h_{VF_{7,i}} = h_{VD_{3,i}} \quad \forall i \quad \text{Eq. 109}$$

3.2.2.4. Closing relations

To finish the construction of the superstructure, relations are required to establish the boundaries of the superstructure.

Eq. 110 to Eq. 113 establish the inlet streams to the separation network, through permanent tray 2 ($pt = 2$).

$$LF_{2,i} = LFeed_i \quad \forall i \quad \text{Eq. 110}$$

$$h_{LF_{2,i}} = h_{LFeed_i} \quad \forall i \quad \text{Eq. 111}$$

$$VF_{2,i} = VFeed_i \quad \forall i \quad \text{Eq. 112}$$

$$h_{VF_{2,i}} = h_{VFeed_i} \quad \forall i \quad \text{Eq. 113}$$

Eq. 114 and Eq. 115 establish that no liquid flows into permanent trays 1 ($pt = 1$) and 4 ($pt = 4$) from a tray above, since there is none.

$$L_{1,i}^{in} = 0 \quad \forall i \quad \text{Eq. 114}$$

$$L_{4,i}^{in} = 0 \quad \forall i \quad \text{Eq. 115}$$

Eq. 116 and Eq. 117 establish that no vapour flows into permanent trays 3 ($pt = 3$) and 8 ($pt = 8$) from a tray below, since there is none.

$$V_{3,i}^{in} = 0 \quad \forall i \quad \text{Eq. 116}$$

$$V_{8,i}^{in} = 0 \quad \forall i \quad \text{Eq. 117}$$

Eq. 118 and Eq. 119 establish that no vapour flows out from permanent trays 1 ($pt = 1$) and 4 ($pt = 4$) to a tray above, since there is none.

$$VS_{1,i} = 0 \quad \forall i \quad \text{Eq. 118}$$

$$VS_{4,i} = 0 \quad \forall i \quad \text{Eq. 119}$$

Eq. 120 and Eq. 121 establish that no liquid flows out from permanent trays 3 ($pt = 3$) and 8 ($pt = 8$) to a tray above, since there is none.

$$LS_{3,i} = 0 \quad \forall i \quad \text{Eq. 120}$$

$$LS_{8,i} = 0 \quad \forall i \quad \text{Eq. 121}$$

Eq. 122 represents the global material balance of component i between the inlet and outlets of the complete superstructure.

$$LF_{2,i} + VF_{2,i} = VD_{4,i} + LD_{4,i} + VD_{6,i} + LD_{6,i} + VD_{8,i} + LD_{8,i} \quad \forall i \quad \text{Eq. 122}$$

3.3. Model reformulation

The formulated GDP model presents disjunctions for both the reactor and the separation networks. For the reactor network disjunction, presented in Eq. 16, convex hull is used. In the case of the separation network disjunction, presented in Eq. 43, bypass efficiency method is applied. They are selected because they are considered the most efficient representations for each case, as explained in Sections 2.3.1.3 and 2.3.3.1 for convex hull and bypass efficiency, respectively.

3.3.1. Reformulation of reactor network disjunction using convex hull

As mentioned in Section 2.3.1.3, convex hull technique uses variable disaggregation to reformulate the GDP problem. However, not all variables need to be disaggregated, but only the ones that are involved in the disjunction.

A priori the present study could propose to disaggregate the same variables as in the work by Ma et al. (Ma et al. 2019), given that the reactor model is the same. Nevertheless, it has been observed that it is possible to disaggregate only some of them and avoid disaggregating the variables related to the inlet of each module, since they do not change according to the selection of the CSTR or PFR unit. Consequently, disaggregated variables are the outlet concentration of component i , the reactor volume, the outlet temperature and the heat required for every module k . Outlet enthalpy could be disaggregated but since it is a function of temperature, that is already disaggregated, it is not necessary. Eq. 123 to Eq. 159 represent the disaggregation of mentioned variables.

$$y_k^C + y_k^P = 1 \quad \forall k, 0 < k < K + 1 \quad \text{Eq. 123}$$

$$C_{k,i}^{out} = C_{k,i}^{out,C} + C_{k,i}^{out,P} \quad \forall k, 0 < k < K + 1 \quad \text{Eq. 124}$$

$$0 \leq C_{k,i}^{out,C} \leq C_{k,i}^{out,U} \cdot y_k^C \quad \forall k, 0 < k < K + 1 \quad \text{Eq. 125}$$

$$0 \leq C_{k,i}^{out,P} \leq C_{k,i}^{out,U} \cdot y_k^P \quad \forall k, 0 < k < K + 1 \quad \text{Eq. 126}$$

$$V_k = V_k^C + V_k^P \quad \forall k, 0 < k < K + 1 \quad \text{Eq. 127}$$

$$0 \leq V_k^C \leq V_k^U \cdot y_k^C \quad \forall k, 0 < k < K + 1 \quad \text{Eq. 128}$$

$$0 \leq V_k^P \leq V_k^U \cdot y_k^P \quad \forall k, 0 < k < K + 1 \quad \text{Eq. 129}$$

$$T_k^{out} = T_k^{out,C} + T_k^{out,P} \quad \forall k, 0 < k < K + 1 \quad \text{Eq. 130}$$

$$0 \leq T_k^{out,C} \leq T_k^{out,U} \cdot y_k^C \quad \forall k, 0 < k < K + 1 \quad \text{Eq. 131}$$

$$0 \leq T_k^{out,P} \leq T_k^{out,U} \cdot y_k^P \quad \forall k, 0 < k < K + 1 \quad \text{Eq. 132}$$

$$Q_k^{reac} = Q_k^{reac,C} + Q_k^{reac,P} \quad \forall k, 0 < k < K + 1 \quad \text{Eq. 133}$$

$$0 \leq Q_k^{reac,C} \leq Q_k^{reac,U} \cdot y_k^C \quad \forall k, 0 < k < K + 1 \quad \text{Eq. 134}$$

$$0 \leq Q_k^{reac,P} \leq Q_k^{reac,U} \cdot y_k^P \quad \forall k, 0 < k < K + 1 \quad \text{Eq. 135}$$

In previous equations y_k^C and y_k^P represent the binary variables for the CSTR and PFR, respectively. The superscript U refers to the upper bound of the variables.

Eq. 136 and Eq. 137 represent the reformulated material and energy balances for the CSTR unit and are valid $\forall k, 0 < k < K + 1$. Note that concentrations and temperature used in the kinetic expressions are the real values, and not the disaggregated variables. This is done to avoid possible indeterminations due to dividing zeros.

$$v_k^{in} \cdot C_{k,i}^{out,C} = \left[v_k^{in} \cdot C_{k,i}^{in} - \sum_{m=1}^M \left(r_m(C_k^{out}, T_k^{out}) \cdot \frac{R_{m,i}}{R_{m,Refm}} \right) \cdot V_k^C \right] \cdot y_k^C \quad \forall i \quad \text{Eq. 136}$$

$$v_k^{in} \cdot \rho \cdot h_k^{out} = \left[v_k^{in} \cdot \rho \cdot h_k^{in} - \sum_{m=1}^M (r_m(C_k^{out}, T_k^{out}) \cdot \Delta H_m) \cdot V_k^C + Q_k^{reac,C} \right] \cdot y_k^C \quad \text{Eq. 137}$$

Eq. 138 and Eq. 139 represent the reformulated material and energy balances for the PFR unit, in their integrated form and are valid for $\forall k / 0 < k < K + 1$. As for the CSTR unit, concentrations and temperature used in the kinetic expressions are the real values.

$$v_k^{in} \cdot C_{k,i}^{out,P} = INTEG \left[- \sum_{m=1}^M \left(r_m(C_k, T_k) \cdot \frac{R_{m,i}}{R_{m,Refm}} \right) \cdot dV_k^P \right] \cdot y_k^P \quad \forall i \quad \text{Eq. 138}$$

$$v_k^{in} \cdot \rho \cdot h_k^{out} = INTEG \left[- \sum_{m=1}^M (r_m(C_k, T_k) \cdot \Delta H_m) \cdot dV_k^P + dQ_k^{reac,P} \right] \cdot y_k^P \quad \text{Eq. 139}$$

3.3.2. Reformulation of reactor network disjunction using bypass efficiency

The separation model is composed of the permanent and the conditional trays. The permanent trays present the possibility of all the functions and the equilibrium equations are always enforced. However, for conditional trays whether the equilibrium equations are enforced or not will determine if the tray is active or not. Consequently, only the conditional trays equations need to be reformulated. The reformulated model consists of Eq. 140 to Eq. 149.

$$L_{t,i}^{ct} = \varepsilon_t^{ct} \cdot L_{t,i}^{eq,ct} + (1 - \varepsilon_t^{ct}) \cdot L_{t-1,i}^{ct} \quad \forall i, t, ct \quad \text{Eq. 140}$$

$$V_{t,i}^{ct} = \varepsilon_t^{ct} \cdot V_{t,i}^{eq,ct} + (1 - \varepsilon_t^{ct}) \cdot V_{t+1,i}^{ct} \quad \forall i, t, ct \quad \text{Eq. 141}$$

$$h_{L_{t,i}^{ct}} = \varepsilon_t^{ct} \cdot h_{L_{t,i}^{eq,ct}} + (1 - \varepsilon_t^{ct}) \cdot h_{L_{t-1,i}^{ct}} \quad \forall i, t, ct \quad \text{Eq. 142}$$

$$h_{V_{t,i}^{ct}} = \varepsilon_t^{ct} \cdot h_{V_{t,i}^{eq,ct}} + (1 - \varepsilon_t^{ct}) \cdot h_{V_{t-1,i}^{ct}} \quad \forall i, t, ct \quad \text{Eq. 143}$$

$$y_{t,i}^{ct} \cdot P_t^{ct} = \gamma_{t,i}^{ct} \cdot P_{t,i}^{sat,ct} \cdot x_{t,i}^{ct} \quad \forall i, t, ct \quad \text{Eq. 144}$$

$$\gamma_{t,i}^{ct} = f_3(T_t^{ct}, P_t^{ct}, C_t^{ct}) \quad \forall i, t, ct \quad \text{Eq. 145}$$

$$P_{t,i}^{sat,ct} = f_4(T_t^{ct}) \quad \forall i, t, ct \quad \text{Eq. 146}$$

$$L_{t,i}^{eq,ct} = L_{t,i}^{eq,ct} \cdot x_{t,i}^{ct} \quad \forall i, t, ct \quad \text{Eq. 147}$$

$$V_{t,i}^{eq,ct} = V_{t,i}^{eq,ct} \cdot y_{t,i}^{ct} \quad \forall i, t, ct \quad \text{Eq. 148}$$

$$TL_t^{ct} = TV_t^{ct} = T_t^{ct} \quad \forall t, ct \quad \text{Eq. 149}$$

3.4. Economic model and other equations

Equations are needed also to establish the specifications of production required from the reactor network and purity and recovery in the separation system. This vary according to the case to be studied. In addition, equations are required for the economic model and evaluation of the complete superstructure. In order to compare results with the works by Zhang et al. (Zhang et al. 2018) and Ma et al. (Ma et al. 2019), it is important to use the same economic model and parameters.

3.4.1. Economic equations for reactor network

Eq. 150 and Eq. 151 are used to calculate the length and diameter of each reactor.

$$Lg_k^R = 4 \cdot D_k^R \quad \forall k, 0 < k < K + 1 \quad \text{Eq. 150}$$

$$D_k^R = \left(\frac{V_k}{\pi} + 10^{-10} \right)^{1/3} \quad \forall k, 0 < k < K + 1 \quad \text{Eq. 151}$$

Eq. 152 and Eq. 153 calculate the capital cost of each reactor unit and the total capital cost of reactors, respectively.

$$Bcost_k^R = 1000. \left(\frac{D_k^R}{0.9144} + 10^{-10} \right)^{1.05} \cdot \left(\frac{Lg_k^R}{1.2192} + 10^{-10} \right)^{0.81} \quad \forall k, 0 < k < K + 1$$

Eq. 152

$$Bcost^R = \left(\frac{0.75 \times 585 \times 4.23}{115} \right) \cdot \sum_{k=1}^K Bcost_k^R \quad \forall k, 0 < k < K + 1$$

Eq. 153

Utility costs are calculated according to the case in study, analysing whether cold or hot utilities would be required. The total cost of the reaction network is then calculated as the sum of capital and utility costs.

3.4.2. Economic equations for separation network

In this case the equations are analogue to those used by Zhang et al. (Zhang et al. 2018) and Ma et al. (Ma et al. 2019); their use is adapted to consider conventional and complex configuration. To do so, the costs of permanent trays and stacks of conditional trays are calculated separately. The only real difference with the economic equations used in these two works is in the calculation of the capital cost of heat exchangers required for the distillation columns. This is because in the case of Zhang et al. (Zhang et al. 2018) and Ma et al. (Ma et al. 2019) the cost of heat exchangers is calculated per distillation column, using the sum of the reboiler and condenser areas, to the power of 0.65. In contrast, the present study uses the same equation per tray, as the columns are not yet defined prior to the solution result. Consequently, the powers of 0.65 of each area are summed, and the cost for the same area is higher. Because of this, for the same solution, the present work would have a slightly higher cost than those reported by Zhang et al. (Zhang et al. 2018) and Ma et al. (Ma et al. 2019).

3.4.2.1. Permanent trays

Eq. 154 to Eq. 156 are used to calculate the reboiler duties and steam flowrates required for each permanent tray pt .

$$\Delta T_{pt}^{reb} = T_{st} - T_{pt} \quad \forall pt$$

Eq. 154

$$Q_{pt}^{reb} = A_{pt}^{reb} \cdot \Delta T_{pt}^{reb} \cdot HTC^{reb} \quad \forall pt$$

Eq. 155

$$Q_{pt}^{reb} = M_{pt}^{st} \cdot \lambda_{st} \quad \forall pt$$

Eq. 156

Eq. 157 to Eq. 159 are used to calculate the condenser duties and cooling water flowrate required for each permanent tray pt .

$$\Delta T_{pt,ML}^{cond} \cdot \text{Ln} \left(\frac{T_{pt} - T_{CW}^{in}}{T_{pt} - T_{CW}^{out}} \right) = T_{CW}^{out} - T_{CW}^{in} \quad \forall pt \quad \text{Eq. 157}$$

$$-Q_{pt}^{cond} = A_{pt}^{cond} \cdot \Delta T_{pt,ML}^{cond} \cdot HTC^{cond} \quad \forall pt \quad \text{Eq. 158}$$

$$-Q_{pt}^{cond} = M_{pt}^{CW} \cdot Cp_{CW} \cdot (T_{CW}^{out} - T_{CW}^{in}) \quad \forall pt \quad \text{Eq. 159}$$

Eq. 160 and Eq. 161 are used to calculate the diameter of permanent tray pt .

$$D_{pt}^S = \sqrt{\frac{2 \cdot V_{pt}^{out}}{\pi}} \sqrt{\frac{R \cdot T_{pt} \cdot MW_{pt}^{av}}{P_{pt}}} \quad \forall pt \quad \text{Eq. 160}$$

$$MW_{pt}^{av} = \sum_{i=1}^I y_{pt} \cdot MW_i \quad \forall pt \quad \text{Eq. 161}$$

Eq. 162 to Eq. 167 are used to calculate costs related to permanent tray pt : shell, internal fittings, heat exchangers, cooling water, steam and total operating cost.

$$C_{pt}^{shell} = C_1 \cdot D_{pt}^S \cdot dH \quad \forall pt \quad \text{Eq. 162}$$

$$C_{pt}^{int} = C_2 \cdot D_{pt}^S \cdot dH \quad \forall pt \quad \text{Eq. 163}$$

$$C_{pt}^{hex} = C_3 \cdot (A_{pt}^{cond} + A_{pt}^{reb})^{0.65} \quad \forall pt \quad \text{Eq. 164}$$

$$C_{pt}^{CW} = M_{pt}^{CW} \cdot C^{CW} \cdot hours \quad \forall pt \quad \text{Eq. 165}$$

$$C_{pt}^{st} = M_{pt}^{st} \cdot C^{st} \cdot hours \quad \forall pt \quad \text{Eq. 166}$$

$$C_{pt}^{op} = C_{pt}^{CW} + C_{pt}^{st} \quad \forall pt \quad \text{Eq. 167}$$

3.4.2.2. Conditional trays

Eq. 168 calculates the number of active trays for each stack of conditional trays ct .

$$NT_{ct} = \sum_{t=1}^T \varepsilon_t^{ct} \quad \forall ct \quad \text{Eq. 168}$$

Eq. 169, Eq. 170 and Eq. 171 calculate the dimensions, diameter and height, for stack of conditional trays ct . Note that the diameter is calculated for the lowest tray because the vapour flow is the greatest in that tray, which is conservative.

$$D_{ct}^S = \sqrt{\frac{2 \cdot V_T^{ct}}{\pi}} \sqrt{\frac{R \cdot T_V^{ct} \cdot MW_{ct,T}^{av}}{P_T^{ct}}} \quad \forall ct \quad \text{Eq. 169}$$

$$MW_{ct,T}^{av} = \sum_{i=1}^I y_{T,i}^{ct} \cdot MW_i \quad \forall ct \quad \text{Eq. 170}$$

$$H_{ct}^S = NT_{ct} \cdot dH \quad \forall ct \quad \text{Eq. 171}$$

Eq. 172 and Eq. 173 represent shell and internal fittings costs for stack of conditional trays ct .

$$C_{ct}^{shell} = C_1 \cdot D_{ct}^S \cdot H_{ct}^S \quad \forall ct \quad \text{Eq. 172}$$

$$C_{ct}^{int} = C_2 \cdot D_{ct}^S \cdot dH \cdot NT_{ct} \quad \forall ct \quad \text{Eq. 173}$$

3.4.3. Total costs and objective function

The model presents costs related to supplying or removing heat from reactor units, and before feeding the product stream to the separation network. These values, in \$/yr, are calculated according to the case studied and are represented by $C1$ and $C4$ respectively.

Additionally, based on the economic model three other terms, also in \$/yr, are calculated: $C2$ represents the capital cost of the reactor network, $C5$ the costs associated to the permanent trays and $C6$ the costs associated to the conditional trays (first term) and the space without trays in the columns (second term). The cost of the permanent trays includes the cost of reboilers and condensers required, as well as their operating costs. Both permanent and conditional trays include the capital cost of shell and internal fittings.

$$C2 = Bcost^R \quad \text{Eq. 174}$$

$$C5 = \sum_{pt=1}^8 (C_{pt}^{shell} + C_{pt}^{int} + C_{pt}^{hex} + C_{pt}^{op}) \quad \text{Eq. 175}$$

$$C6 = \sum_{ct=1}^6 (C_{ct}^{shell} + C_{ct}^{int}) + 4 \cdot C_1 \cdot (D_3^S + D_8^S) \quad \text{Eq. 176}$$

Eq. 177 shows the objective function, which is the total annualised cost of the process.

$$TAC = C1 + C2 + C3 + C4 + C5 + C6 \quad \text{Eq. 177}$$

At this point, the mathematical formulation is completed; the model is denoted M0 and comprises Eq. 8 to Eq. 177, except for Eq. 16 and Eq. 43. The result is a large-scale complex nonconvex MINLP problem.

3.5. Solution strategy

All the data and equations are implemented in GAMS, as well as lower and upper bounds for the variables. Sets are used to implement the equations for the corresponding components, stages, stacks of conditional trays, conditional trays and permanent trays.

Considering that the problem to be solved is a large-scale complex nonconvex MINLP problem, there are four MINLP solvers that can be used, including BARON, ANTIGONE, DICOPT and SBB. The first two, which are global optimisation solvers, failed to solve this problem. Between DICOPT and SBB, the latter has been reported to perform better than the former (Zhang et al. 2018; Ma et al. 2019). Consequently, SBB solver is used to solve the present problem.

SBB uses the branch and bound algorithm; a Relaxed Mixed Integer Nonlinear Programming (RMINLP) model is first solved with the introduced initial guess. At this point the solver stops if variables are unbounded or infeasibilities are found. If all the discrete variables are integer, then the solver reports the solution as the optimal integer solution; otherwise, the solution is saved, and the branch and bound procedure starts.

In order to generate a feasible starting point for the solver, and avoid the mentioned problems, the initialisation strategy suggested by Ma et al. (Ma et al. 2019) is used. This strategy proposes to solve the reaction network first and use its outlet stream as feed to the distillation system, which is modelled using pseudo-transient continuous (PTC) approach in Aspen Custom Modeler. This simulation is performed with conventional distillation columns from Ma et al. (Ma et al. 2019). Results from the optimised reactor network and the simulated distillation system with conventional distillation columns are feasible to the complex columns used in the work. Consequently, it is an appropriate initial point for the solver.

After the initialisation step, the entire model is solved using the SBB solver in GAMS. Then it is necessary to verify that the bypass efficiency variables (ε_t^{ct}) are zero or one. If that is not the case, then an additional constraint is introduced to model, now denoted M1. This M1 model is solved again to guarantee that all bypass efficiencies are zero or one.

$$\varepsilon_t^{ct} \cdot (1 - \varepsilon_t^{ct}) \leq 1 \tag{Eq. 178}$$

The solution approach is shown in Figure 16.

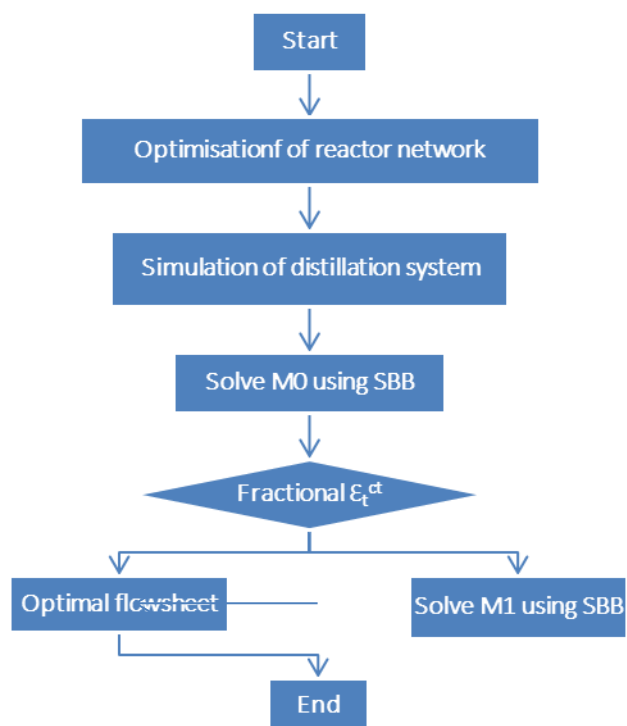


Figure 16: Solution approach for the present study.

3.6. Case study: benzene chlorination process

This case study is used to illustrate the solution strategy proposed, and to assess if improvements are found by including complex configurations in the separation system, by comparing the results with the works by Zhang et al. (Zhang et al. 2018) and Ma et al. (Ma et al. 2019).

3.6.1. Description

Benzene chlorination, one of the first industrialised processes for the production of organic chemicals (Zhang et al. 2018), produces chlorobenzene and p-dichlorobenzene, as shown in Figure 17.

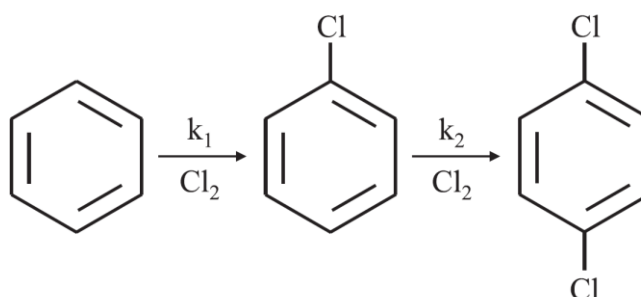


Figure 17: Benzene chlorination. (Zhang et al. 2018)

In the present study, as in those by Zhang et al. (Zhang et al. 2018) and Ma et al. (Ma et al. 2019), chlorobenzene is considered as the main product and p-dichlorobenzene as the by-product.

Physical properties of the components, kinetic and economic data required are used from mentioned previous works. They are presented in Appendix A. Kinetic data is provided at a fixed temperature; consequently, the temperature is not optimised. Two simplifications are made: activity coefficients are not used, and pressure is fixed to atmospheric pressure, as previous works have included them.

3.6.2. Superstructures specifications

Although the superstructures have already been defined, it is necessary to specify that for the reactor networks three modules are used. This is selected to have the same reactor superstructure as in the work by Ma et al. (Ma et al. 2019).

Regarding the utilities required for the reactor network, mentioned in Section 3.2.1 cooling water is found to be required. This is because of the exothermic nature of reactions. In addition, this case benefits from a preheating stage between the reactor and the separation network, as the reaction temperature is low in relation to the boiling point range of the product mixture. Consequently, a heat exchanger is used to heat the product stream to its saturated liquid condition, as proposed by Ma et al. (Ma et al. 2019).

3.6.3. Modelling specifications

The proposed model is used for the present case study, constituted by Eq. 8 to Eq. 178, except for Eq. 16 and Eq. 43 that represent the disjunctions; these are not required because they were reformulated into Eq. 123 to Eq. 139 and Eq. 140 to Eq. 150, respectively.

It is required to add equations to this model to consider the cooling of the reactor network (Eq. 179 and Eq. 180) and the preheating stage between the reactor and separation networks (Eq. 81 to Eq. 194), as anticipated in Section 3.4.3.

$$Q_k^{react} = M_k^{react,CW} \cdot Cp_{CW} \cdot (T_{CW}^{out} - T_{CW}^{in}) \quad \forall k, 0 < k < K + 1 \quad \text{Eq. 179}$$

$$C1 = \sum_{k=1}^K C_k^{react,CW} = M_k^{react,CW} \cdot C^{CW} \cdot hours \quad \text{Eq. 180}$$

Eq. 181 calculates the required heat, knowing the boiling point temperature of the mixture and the outlet temperature from the reactor network.

$$Q_{preheat} = \sum_{i=1}^I (Cp_i^{liq} \cdot F_{i,K+1}^{out}) \cdot (T_{eb} - T_{K+1}^{out}) \quad \text{Eq. 181}$$

Eq. 182 to Eq. 185 are used to calculate the boiling point temperature of the mixture.

$$P_i^{sat} = f_5(T_{eb}) \quad \forall i \quad \text{Eq. 182}$$

$$\sum_{i=1}^I (K_i \cdot z_i^R) = 1 \quad \text{Eq. 183}$$

$$K_i = \frac{P_i^{sat}}{P_{atm}} \quad \forall i \quad \text{Eq. 184}$$

$$F_{i,K+1}^{out} = F_{K+1}^{out} \cdot z_i^R \quad \forall i \quad \text{Eq. 185}$$

Eq. 186 and Eq. 187 define the inlets to the separation network considering the saturated liquid condition. Since there is no vapour fraction, the associated enthalpy is defined as zero, as shown in Eq. 188. The enthalpy of the feed stream to the separation network is that of saturated liquid, as shown in Eq. 189.

$$L_{Feed_i} = F_{i,K+1}^{out} \quad \forall i \quad \text{Eq. 186}$$

$$V_{Feed_i} = 0 \quad \forall i \quad \text{Eq. 187}$$

$$h_{V_{Feed_i}} = 0 \quad \forall i \quad \text{Eq. 188}$$

$$h_{L_{Feed_i}} = h_i^{sat,l} \quad \forall i \quad \text{Eq. 189}$$

Eq. 190 to Eq. 194 are used to calculate the operation and capital cost of preheating.

$$\Delta T_{ML}^{pre} \cdot \ln \left(\frac{T_{st} - T_{K+1}^{out}}{T_{st} - T_{eb}} \right) = (T_{eb} - T_{K+1}^{out}) \quad \text{Eq. 190}$$

$$Q_{preheat} = HTC \cdot A_{pre} \cdot \Delta T_{ML}^{pre} \quad \text{Eq. 191}$$

$$Q_{preheat} = M_{pre}^{st} \cdot \lambda_{st} \quad \text{Eq. 192}$$

$$C_{pre}^{hex} = C_3 \cdot A_{pre}^{0.65} \quad \text{Eq. 193}$$

$$C_{pre}^{st} = C_{st} \cdot M_{pre}^{st} \cdot \text{hours} \quad \text{Eq. 194}$$

Additionally, equations are included to account for the reactor network production (Eq. 195 for chlorobenzene) and specifications of purity and recovery for benzene and chlorobenzene in the separation network (Eq. 196 to Eq. 205).

$$F_{i,K+1}^{out} = 50 \text{ kmol} \cdot \text{h}^{-1} \quad / i = \text{chlorobenzene} \quad \text{Eq. 195}$$

Eq. 196 and Eq. 197 define the distillate and intermediate product streams from the possible outlets of permanent trays 4 ($Pt = 4$) and 6 ($Pt = 6$), respectively.

$$Dist_i = VD_{4,i} + LD_{4,i} \quad \forall i \quad \text{Eq. 196}$$

$$Int_i = VD_{6,i} + LD_{6,i} \quad \forall i \quad \text{Eq. 197}$$

Eq. 198 and Eq. 199 establish the total flowrates, and Eq. 200 and Eq. 201 the molar fractions in those streams.

$$Dist_i^T = \sum_{i=1}^I Dist_i \quad \forall i \quad \text{Eq. 198}$$

$$Int_i^T = \sum_{i=1}^I Int_i \quad \forall i \quad \text{Eq. 199}$$

$$Dist_i^T \cdot Df_i - Dist_i = 0 \quad \forall i \quad \text{Eq. 200}$$

$$Int_i^T \cdot Mf_i - Int_i = 0 \quad \forall i \quad \text{Eq. 201}$$

Eq. 202 and Eq. 203 represent recovery specifications, while Eq. 204 and Eq. 205 represent purity specifications.

$$Dist_i - LF_{2,i} \cdot R_i \geq 0 \quad / i = \textit{benzene} \quad \text{Eq. 202}$$

$$Int_i - LF_{2,i} \cdot R_i \geq 0 \quad / i = \textit{chlorobenzene} \quad \text{Eq. 203}$$

$$Df_i \geq Pur_i \quad / i = \textit{benzene} \quad \text{Eq. 204}$$

$$Mf_i \geq Pur_i \quad / i = \textit{chlorobenzene} \quad \text{Eq. 205}$$

The final model presents 224 blocks of equations and 3996 equations in total, that use 3822 variables, 6 of which are binary.

3.6.4. Solution strategy

All the data and equations were introduced in GAMS, together with lower and upper bounds. The initial guess is also introduced, adapted from the initial guess produced by Ma et al. (Ma et al. 2019) with Aspen Custom Modeler for the same case study. This is a difference between the solution approach used by Ma et al.: given that the same case study is solved, the complexity of using Aspen Custom Modeler to generate the initial guess and the limited time for the completion of the present work, Aspen Custom Modeler is not used directly. After the initialisation step, the solution procedure follows the diagram shown in Figure 12 A), using SBB solver from GAMS, as recommended by Ma et al. (Ma et al. 2019).

Chapter 4: Results and discussion

4.1. Results

4.1.1. Flowsheet

The resulting flowsheet for the reactor separation process is shown in Figure 18. For the reaction stage only one PFR unit is used; its residence time and dimensions are shown in Figure 18. The required production of 50 kmol/h of chlorobenzene is achieved, for which 89.20 kmol/h of benzene are required. However, the process leaves 35.57 kmol/h of benzene unreacted. From the separation network 35.53 kmol/h of benzene can be recirculated, given the established specifications of a 99% recovery and 99% purity. This accounts for 39.8% of the indicated raw material required. Chlorobenzene is also separated with 99% of recovery and 99% of purity, as specified, and dichlorobenzene is separated as a product with 87.2% purity. The three products are obtained in liquid phase.

4.1.2. Separation system

The separation system is constituted by a complex configuration, with partially thermally coupled distillation columns. The structure of the separation system is shown in Figure 19. The structure presents a total of 46 trays, divided in two sections. The three product streams are extracted from trays 1, 22 and 39 of section 2, as shown in Figure 19. The two sections are connected from tray 1 of section 1 to tray 9 of section two, and from tray 7 of section 2 to tray 33 of section 2.

The first connection involves both vapour and liquid from section 1 to section 2, and liquid in the opposite direction. The fact that both liquid and vapour are taken from one tray to another is not usual in complex configurations. Usually, when the top of section 1 presents no condenser, vapor flow would be expected from section 1 to section 2, and liquid flow in the opposite direction; the usual configuration corresponds with Figure 2, B), where the vapour flows to section 2 and liquid into section 1 presents the function of a reflux. The result is the type of configuration that would have been left out had disjunctions for each permanent tray been used. On the one hand, it is positive to obtain a configuration that is suited for the case under study, without restrictions to usual configurations. However, it presents the challenge of evaluating whether it can be realised in practice without too much inconvenience. Both liquid streams involved in this

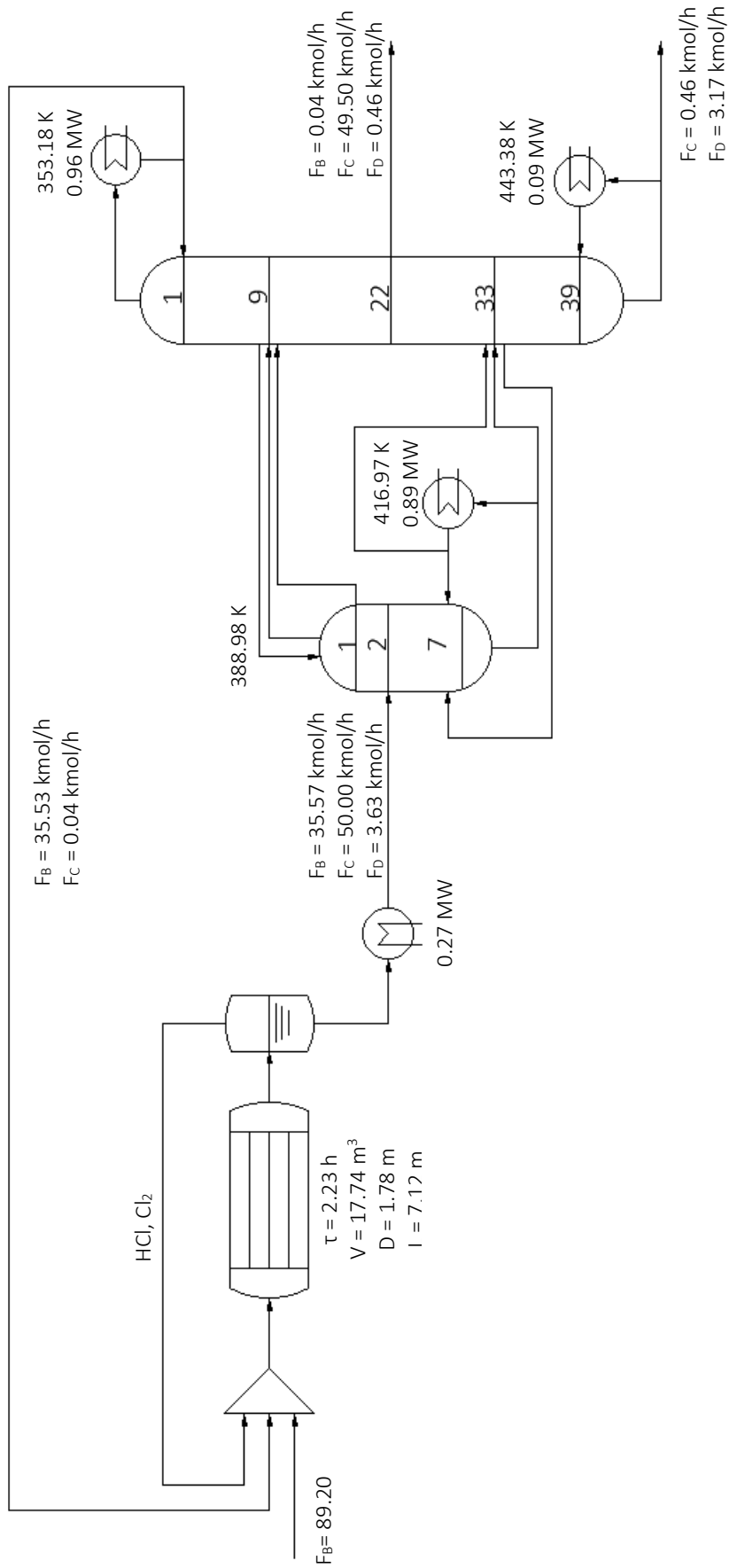


Figure 18: Optimal process configuration.

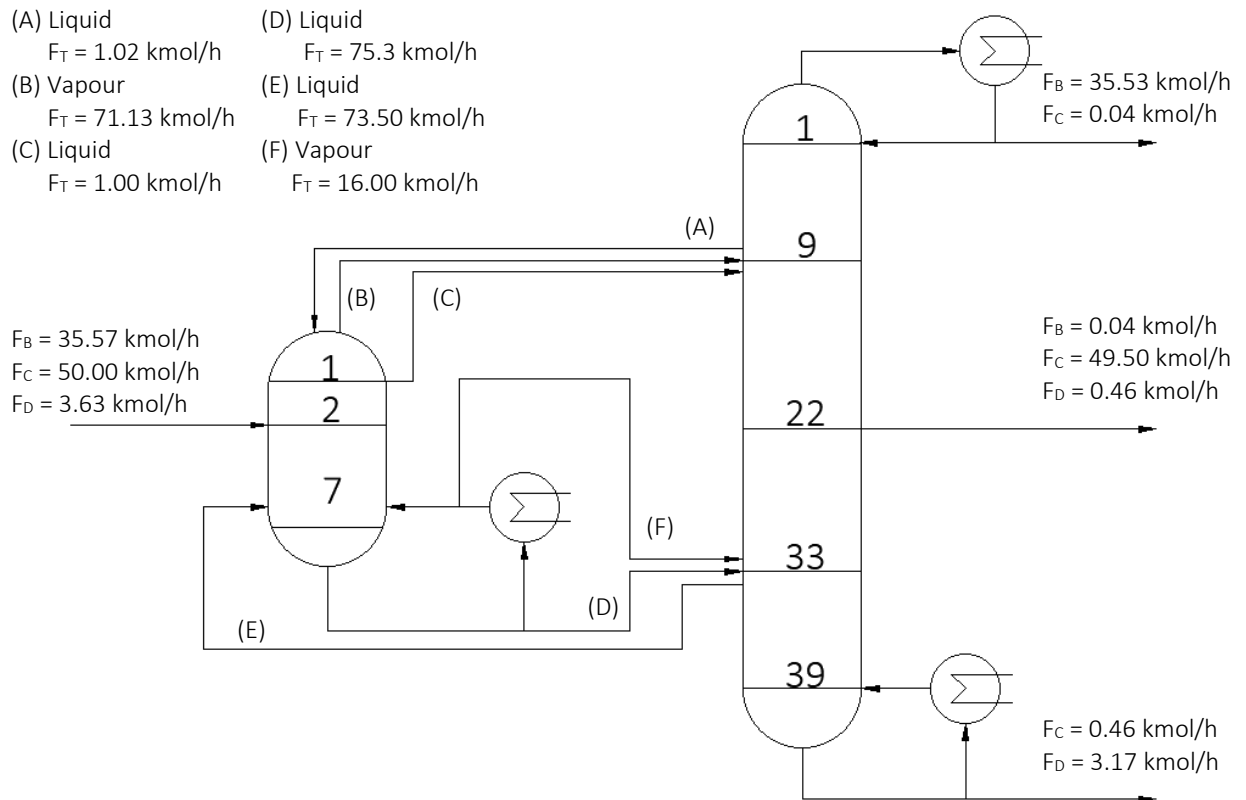


Figure 19: Optimal distillation system.

connection have small flowrates in comparison with the vapour flowrate: approximately 1.0 kmol/h each one, which represents 1.4% of the vapour flowrate. In addition, their composition is considerably similar given the small temperature difference between the trays. This may suggest that, if practical difficulties should arise, a second design could be produced with the additional constraints of these two liquid flowrates being zero, and the result should not be considerably different. Regarding the liquid flowrate that would usually constitute a reflux, in the result it is not present but is substituted by the feed to the separation system, which enters section 1 in the second tray.

In the case of the second connection between the sections, the same arrangement is present: both vapour and liquid flow from section 1 to section 2, while liquid goes from section 2 to section 1. In contrast, the flowrates involved are not small: both liquid flowrates are 73.5 and 75.3 kmol/h, while the vapour flowrate is 16.0 kmol/h. Additionally, the temperatures are almost identical: 416.9 and 416.8 K for the tray in section 1 and 2 respectively. Consequently, the compositions of the liquids are almost identical as well, which brings the question of why both these streams are necessary, and with such high flowrates when they seem to be interchanging the same composition. The

written model does not present constraints for this interchange to be avoided, given that the interchange does not reflect in any of the costs involved in the objective function. However, in practice it presents piping and insulation cost, and additional complexity which could be prevented. As in the case of the first connection, this arrangement could have been avoided with the disjunctions for the particular trays.

The solution structure includes two reboilers, one at the bottom tray of each section, and a condenser in the top tray of section 2, with a reflux ratio of 2.04. In addition, considerably small condenser and reboilers are present in each one of the permanent trays, with duties lower than 0.4 kJ/h. Their cost is negligible in comparison with the two reboilers and the condenser, but since they are not needed, they should not be present in the solution. The simultaneous presence of a reboiler and a condenser can be avoided using disjunctions. However, having one of them with a considerably low duty is not avoided with disjunctions; if this was the case, the model could be run again with constraints of zero duty for the permanent trays involved, and the previous solution as a starting point. Figure 20 and Figure 21 show the temperature profiles for both sections.

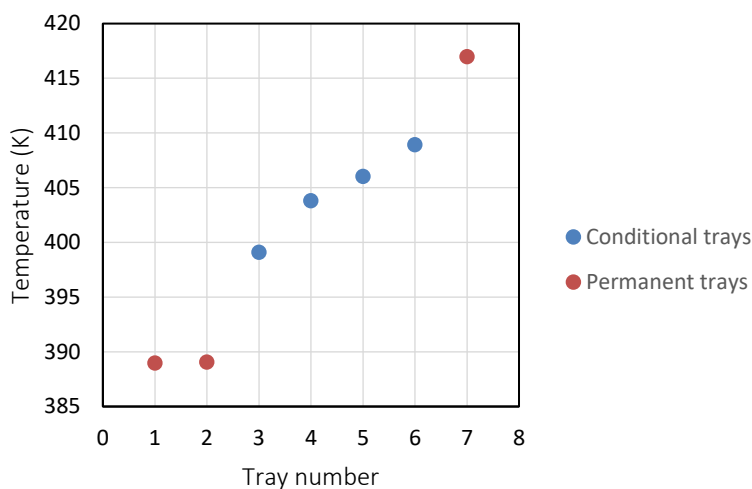


Figure 20: Temperature profile - section 1.

Temperature profiles show continuity as expected, even though trays were treated with different models. Considering that tray number one is at the top of each section, it is expected that the temperature increases with the number of trays, as the reboiler, which provides the heat for the system, is at the bottom. In section 2, trays where benzene chlorobenzene and dichlorobenzene are extracted present temperatures of 353.28 K,

405.02 K and 443.38 K, respectively. These temperatures are determined by the product compositions that have been specified for each component.

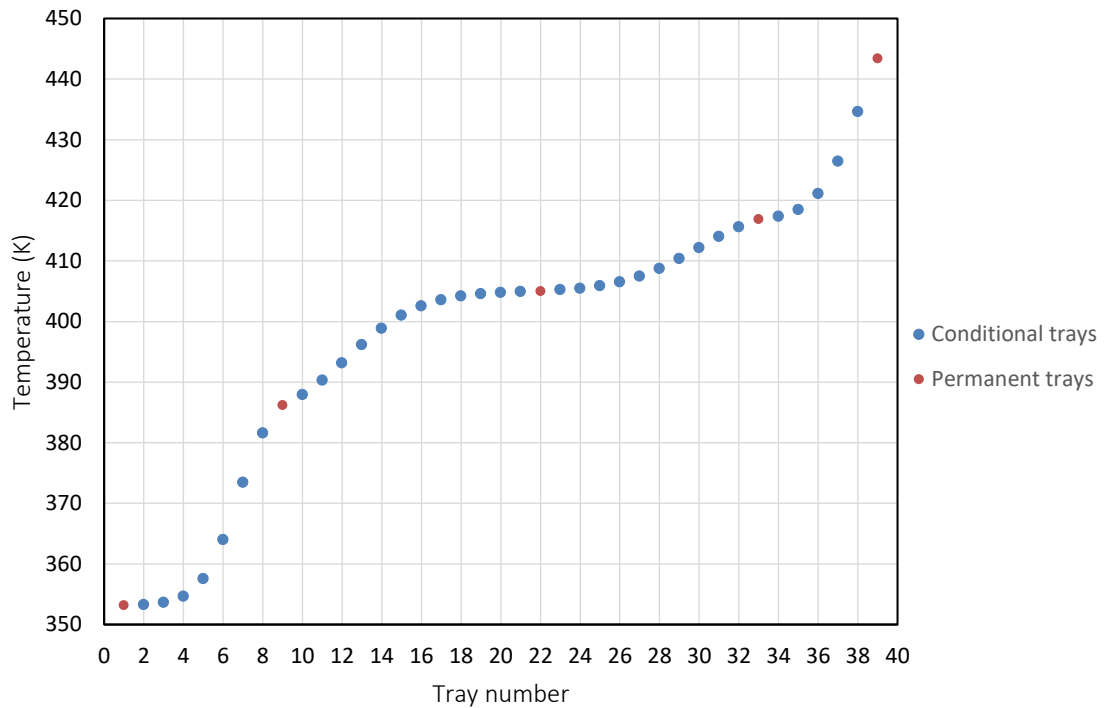


Figure 21: Temperature profile - section 2.

Composition profiles for the liquid phase are shown in Figure 22 and Figure 23, while for the vapour phase they are shown in Figure 24 and Figure 25.

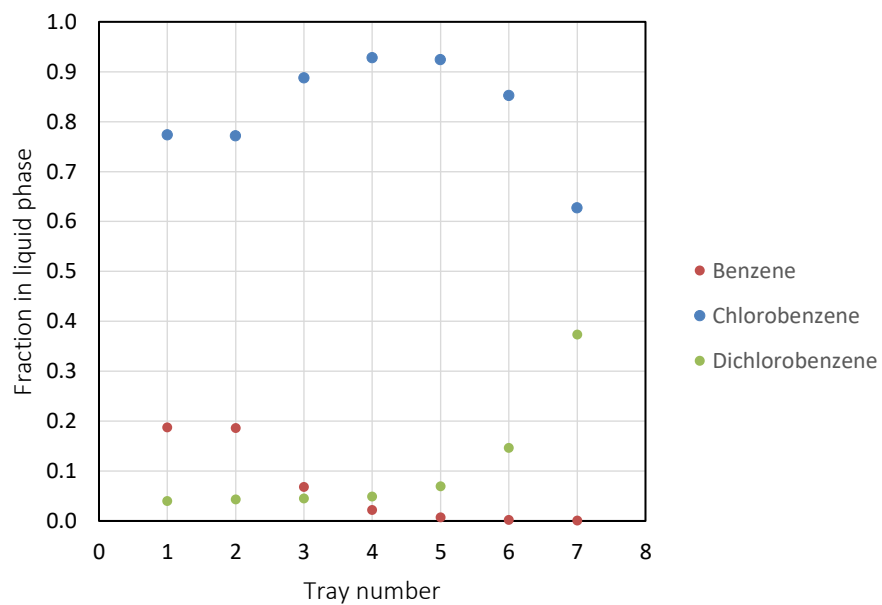


Figure 22: Liquid composition - section 1.

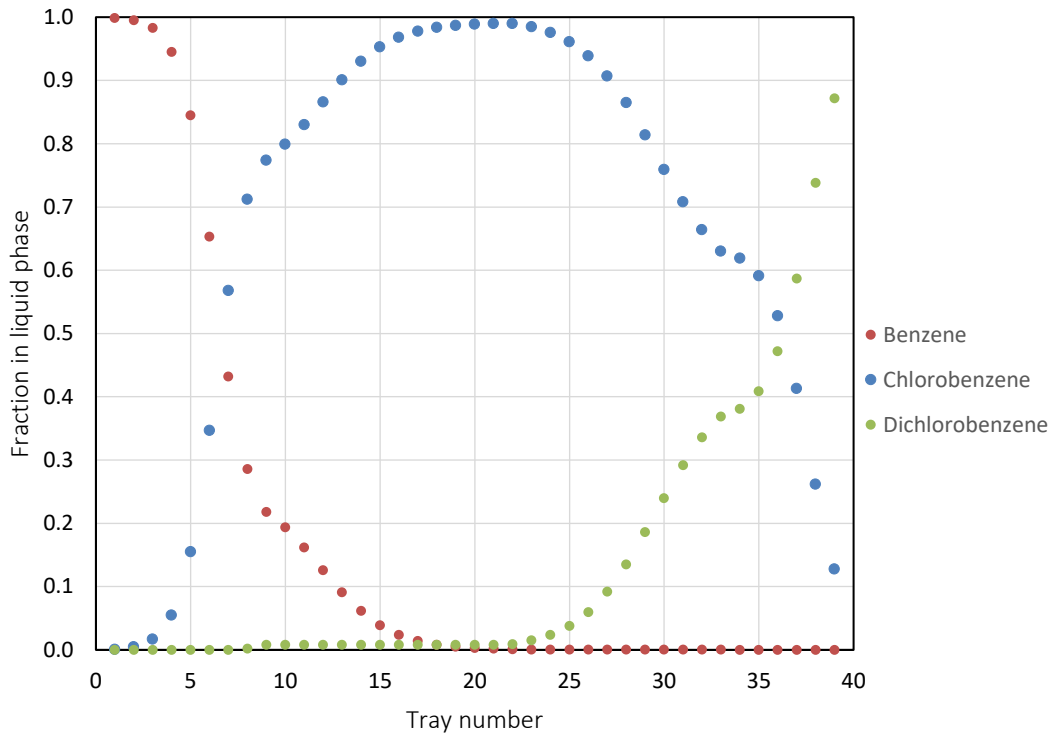


Figure 23: Liquid composition - section 2.

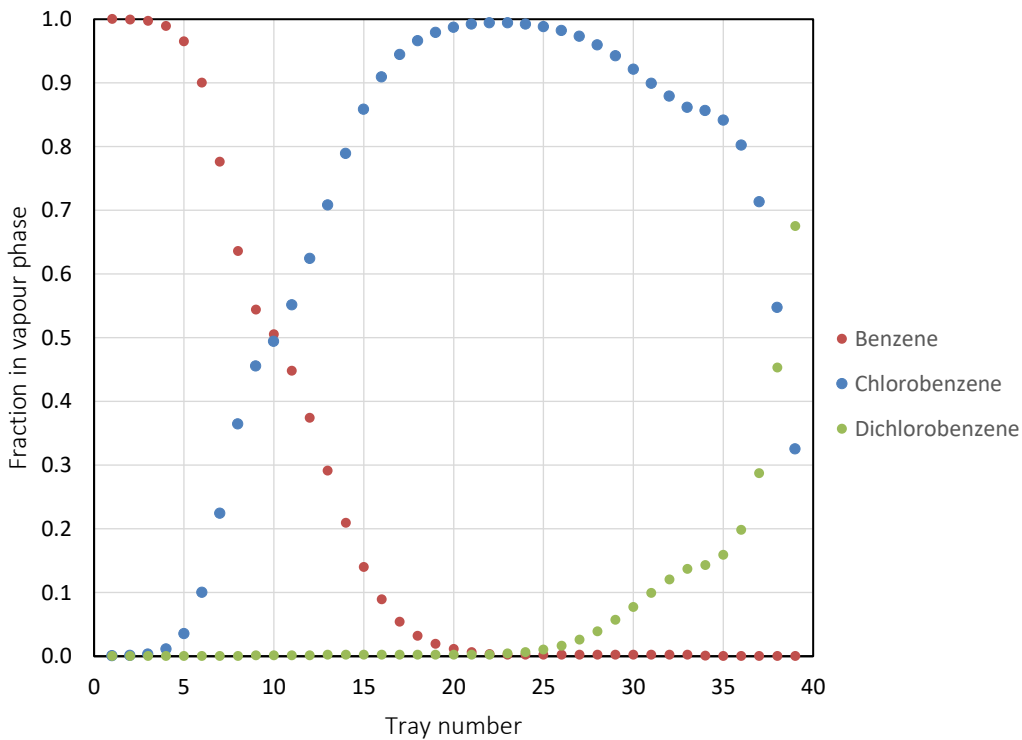


Figure 24: Vapour composition - section 1.

The figures presented allow to see the continuity of the composition profiles, as expected given the continuity in the temperature profiles. The concentration of benzene is the highest at the top of section 2 which is its extraction point, while for chlorobenzene and

dichlorobenzene the highest concentration happens at tray 22 and bottom tray, respectively, also their extraction points.

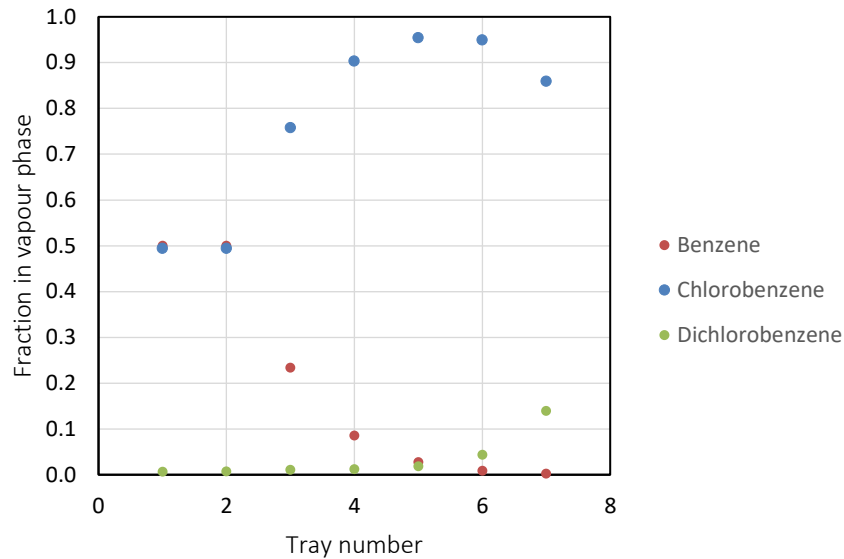


Figure 25: Vapour composition - section 2.

It is observed that in the first section it is already achieved a good separation of the distillate and bottom products: at the top the fraction of dichlorobenzene is lower than 0.04 and at the bottom the benzene fraction is lower than 0.005, in both liquid and vapour phases. The composition profiles indicate that the remixing effects on chlorobenzene are avoided, given that the purification of chlorobenzene is performed on the second section. In addition, it is possible to match considerably well the compositions and temperatures of the trays that are connected.

The dimensions of the distillation system are shown in Table 1.

Table 1: Diameters calculated for different sections.	
Trays	Diameter (m)
Section 1	
1-2	0.83
3-7	0.99
Section 2	
1-8	0.98
9-21	0.56
22-33	0.52
34-39	0.31

Diameters are calculated for each permanent tray and stack of conditional trays, according to the vapour flowrate in the tray, or in the lowest tray in the second case. It is

interesting to notice that the bottom tray of section 1, which presents a reboiler, has the highest diameter of the configuration. This is because the highest vapour flowrate is present in this point. In addition, first part of section 2 presents almost the same diameter, given that vapour flowrates from both sections are united there, presenting a larger vapour flowrate, hence a larger diameter. Section 1 presents a height of 7.5 m while section 2 has a height of 23.5 m.

4.1.3. Economic results

Economic results for the final flowsheet are presented in Table 2.

Table 2: Economic results.	
Section	Cost (\$/yr)
Reactor system	
Capital cost	135,710
Operating cost	77,862
Total	213,572
Preheating	
Capital cost	7,936
Operating cost	37,250
Total	45,186
Distillation system	
Section 1	
Capital cost of shell	12,762
Capital cost of internals	12,773
Capital cost of heat exchangers	30,556
Subtotal	56,091
Section 2	
Capital cost of shell	48,241
Capital cost of internals	21,179
Capital cost of heat exchangers	54,459
Subtotal	123,879
Operating cost	146,179
Total	326,149
Total annualised cost (TAC)	584,907

The most significant cost of the process is from the distillation system, representing 56% of the total annualised cost. From this cost, 55% corresponds to the capital cost whereas the rest is given by operating costs related to steam and cooling water. The capital cost

of the reactor is slightly more than 23% of the total annualised cost, and comparable to the capital cost of the distillation system.

4.2. Comparison of results with previous studies

As previously mentioned, the case study of benzene chlorination has been previously used by Zhang et al. (Zhang et al. 2018) and Ma et al. (Ma et al. 2019) to evaluate their optimisation approach to the synthesis of reaction-separation systems. Their most significant results are presented in Table 3 (Ma et al. 2019).

Table 3: Results from the present and previous works.			
	Design by Zhang et al.	Design by Ma et al.	New design
Reactor network	One PFR	One PFR	One PFR
Residence time (h)	2.82	2.85	2.23
Input flowrate (kmol.h ⁻¹)	79.74	79.36	89.20
Reaction conversion (%)	69	69	60
Reaction selectivity (%)	91	91	93
Separation sequence	Direct	Direct	Complex
First column			
Number of trays	20	18	7
Reboiler duty (MW)	0.50	0.52	0.89
Reboiler temperature (K)	407.15	407.17	416.97
Condenser duty (MW)	1.66	0.48	-
Second column			
Number of trays	14	13	39
Reboiler duty (MW)	0.64	0.64	0.09
Reboiler temperature (K)	445.28	445.39	443.38
Condenser duty (MW)	2.29	0.64	0.96
TAC (\$/yr)	6.24x10⁵	6.14x10⁵	5.85x10⁵

The new design results in a very similar reactor, with 9% lower conversion and slightly higher reaction selectivity, which results in higher benzene input required. This may be due to the smaller residence time, which is 78% of the one in the design by Ma et al. (Ma et al. 2019).

The distillation system of the new design presents significantly higher number of trays, but the capital cost of the system is compensated with the savings in energy costs in the reboiler of column 2. The higher number of trays may be required to avoid the remixing effect for the intermediate product, chlorobenzene in this case. In conventional sequences such section is not present.

Even though the duty of reboiler in column 1 increased by 71% compared with the design by Ma et al. (Ma et al. 2019), the reboiler in column 2 decreased by 86% of the value in the same design. This is even more significant considering that the reboiler in column 2 presents the highest temperature of the system. The increase of duty in reboiler 1 and decrease in reboiler 2 can be explained by the fact that the system has selected the lowest temperature level to heat the system as much as possible, which is in reboiler 1. This implies lower heating requirements at the highest temperature, present in reboiler 2.

Consequently, it is observed that even though capital costs increase in comparison with previous works, the energy savings are significant enough for the optimal solution to be a complex configuration.

Finally, it is observed that the objective function, the total annualised cost, has decreased by 6.3% and 4.7% compared with the results of Zhang et al. (Zhang et al. 2018) and Ma et al. (Ma et al. 2019), respectively. This is considered a positive result, although savings are not as high as reported for thermally coupled distillation columns in literature (Calzon-McConville et al. 2006; Caballero and Grossmann 2004; Dünnebier and Pantelides 1999; Fidkowski and Agrawal 2001). It could be argued whether the economic model adaptation for this type of columns is appropriate and could be worth to develop more specialised economic models.

4.3. Limitations

The present study is limited to the design of continuous processes in which reaction and separation stages are performed in separate equipment; operations such as reactive distillation are not considered. For the reaction network constant density is considered, and for the separation network it is considered the sharp separation of mixtures of three components that do not form azeotrope, performed by distillation columns.

Regarding the solution of the case study, the reactor temperature and pressure are fixed, which limits the evaluation of the solution strategy to these simplified conditions. In addition, the separation network is solved for a fixed pressure, constant throughout the columns, and the activity coefficient is not used. These are simplifications that decrease the complexity of the problem to be solved but may also decrease the accuracy of the solution. For example, neglecting the activity coefficient and using Raoult's Law is considered appropriate when both the liquid and vapour phases can be regarded to have close to ideal behaviour. This happens at low pressures, such as is in the study case, but

when considering the nature of the species involved, it is found that chlorobenzene is a polar molecule, which cannot be regarded as ideal behaviour in the liquid phase. In this occasion the case study has been solved as in previous works (Zhang et al. 2018; Ma et al. 2019), but this simplifications should be re-examined in future studies.

Chapter 5: Conclusions

In the present study a framework was developed for the synthesis of reaction-separation systems including complex configuration distillation columns, using rigorous models. The superstructure was constructed using the reaction superstructure from the study of Ma et al. (Ma et al. 2019) and the separation superstructure created by Sargent and Gaminibandara (Sargent and K. Gaminibandara 1976). The modelling was performed in two stages, using GDP first to produce a logic-based model. To formulate the problem into a MINLP optimisation problem, convex hull and bypass efficiency methods were used for the disjunctions of the reaction and separation networks, respectively. The final model, including 3996 equations and 3822 variables, 6 of which are binary, was successfully solved using the strategy proposed by Ma et al. (Ma et al. 2019), which included its implementation in the software GAMS and solution using the solver SBB.

It was possible to model the complete superstructure using a lower number of binary variables than in the work of Zhang et al. (Zhang et al. 2018), that uses 86. Instead, it was used the same number than in the study by Ma et al. (Ma et al. 2019), despite using a more complex superstructure for the separation network.

Results present a flowsheet with one PFR reactor and complex configuration distillation columns that are partially thermally coupled. This shows that it is both possible and beneficial to consider complex configuration distillation columns, including thermally coupled ones, in the simultaneous synthesis and design of reaction-separation systems using rigorous models. The solution flowsheet presents a total annualised cost of 5.85×10^5 \$/yr, which is 6.3% and 4.7% less than the value achieved by Zhang et al. (Zhang et al. 2018) and Ma et al. (Ma et al. 2019), respectively. However, savings are not as high as reported in literature (Calzon-McConville et al. 2006; Caballero and Grossmann 2004; Dünnebier and Pantelides 1999; Fidkowski and Agrawal 2001).

It was also found that the cost of the reaction network obtained is comparable to the cost of the separation network. However, studies from the last decade suggest that more attention is paid to improvements in the separation network, and not so much in the reaction network. The comparable costs suggest that, even if the separation networks have a higher cost, improving the reaction network could also be considerably beneficial.

The present study is considered a successful continuation of the studies developed by Zhang et al. (Zhang et al. 2018) and Ma et al. (Ma et al. 2019), as it was able to include

the use of complex configuration distillation columns and the results show an improvement in terms of the total annualised cost.

5.1. Future work

Regarding the use of the framework in the present study, it is considered that it should be applied to a case study for which kinetic expressions are available. In this way, it would be possible to optimise the reaction temperature. In addition, it would be desirable to use activity coefficients to improve the accuracy of results, as well as optimise the operation pressure in the separation network. These improvements would increase the complexity of the model, and it would be possible to evaluate whether the solution procedure can manage the increased complexity, or if different strategies are required.

Considering the developed framework, it would be desirable to modify the reaction superstructure by including recycle features, which would increase its richness. Recycles could decrease the cost of the network for the same product specifications or improve conversion and selectivity levels. Also, would be interesting to include the use of disjunctions for each permanent tray, hence restraining the functions that each one may have. This would avoid the result of unusual features in the connectivity of the resulting configuration and limit the options to usual complex configuration distillation columns, in addition to the conventional sequences. Using these disjunctions would considerably increase the complexity of the model, and suitable solving strategies should be proposed not to result in a bad local optimum. It is suggested as well to study available options for economic models that may apply for both conventional sequences and complex configuration columns. Alternatively, different model could be used according to the resulting configuration of the separation network.

Appendix A: Data of case study

Table A.1: Data required to solve the case study of benzene chlorination.

Ambient conditions	
Temperature (K)	298.15
Pressure (kPa)	101.325
Other temperatures	
Reference temperature (K)	273.15
Inlet temperature, cooling water (K)	293.15
Outlet temperature, cooling water (K)	343.15
Reaction data	
Temperature of reaction (K)	303.15
Kinetic constant, reaction 1 (h^{-1})	0.412
Kinetic constant, reaction 2 (h^{-1})	0.055
Reaction enthalpy, reaction 1 (kJ/kmol)	143.09
Reaction enthalpy, reaction 1 (kJ/kmol)	128.55
Latent heat	
Steam for preheating (kJ/kg)	2107.42
Steam for column 1 (kJ/kg)	2021.40
Steam for column 2 (kJ/kg)	1933.10
Molecular weights	
Benzene (kg/kmol)	78.11
Chlorobenzene (kg/kmol)	112.56
Dichlorobenzene (kg/kmol)	147.01
Enthalpy of formation – liquid	
Benzene (kJ/kmol)	48700
Chlorobenzene (kJ/kmol)	11100
Dichlorobenzene (kJ/kmol)	-17400
Enthalpy of formation – vapour	
Benzene (kJ/kmol)	82930
Chlorobenzene (kJ/kmol)	52000
Dichlorobenzene (kJ/kmol)	33000
Heat capacity – liquid	
Benzene (kJ/kmol.K)	134.6
Chlorobenzene (kJ/kmol.K)	161
Dichlorobenzene (kJ/kmol.K)	193
Heat capacity – vapour	
Benzene (kJ/kmol.K)	94.035
Chlorobenzene (kJ/kmol.K)	108
Dichlorobenzene (kJ/kmol.K)	118

Table A.2: Data required to solve the case study of benzene chlorination.

Antoine equation coefficient A_0	
Benzene	13.7819
Chlorobenzene	13.8635
Dichlorobenzene	14.265
Antoine equation coefficient B_0	
Benzene	2726.81
Chlorobenzene	3174.78
Dichlorobenzene	3798.2
Antoine equation coefficient C_0	
Benzene	217.572
Chlorobenzene	211.7
Dichlorobenzene	213.32
Economic data	
Price of steam (\$/ton)	10
Price of cooling water (\$/ton)	0.05
Coefficient C1 (\$)	4100
Coefficient C2 (\$)	1800
Coefficient C3 (\$)	3100
Other data	
Density of benzene (kg/m ³)	876.5
Operation hours per year (h)	8000
Heat capacity of cooling water(kJ/kg.K)	4.1813
Heat transfer coefficient (W/m ² .K)	800

Appendix B: Nomenclature for reaction network model

Scripts:

C related to CSTR reactor

i component

j stage

k stage

m reaction

P related to PFR reactor

Parameters:

ρ density ($kg.m^{-3}$)

R matrix of stoichiometric coefficients for all components in all reactions

$R_{m,i}$ stoichiometric coefficient of component i in reaction m

Ref vector of reference component for all reactions

Ref_m reference component of reaction m

r function of kinetic expressions for all reactions ($kmol.m^{-3}.h^{-1}$)

r_m kinetic expression for reaction m ($kmol.m^{-3}.h^{-1}$)

ΔH vector of reaction heat for all reactions per kmol of reference component ($kJ.kmol^{-1}$)

ΔH_m heat of reaction for reaction m ($kJ.kmol^{-1}$)

Binary variables:

$Y_{C,k}$ indicates the existence of the CSTR reactor in module k

Continuous variables:

$C_{k,i}^{in}$ concentration of component i in inlet stream of stage k ($kmol.m^{-3}$)

$C_{j,i}^{out}$ concentration of component i in outlet stream of stage j ($kmol.m^{-3}$)

F_k^{in} molar flow of inlet stream of stage k ($kmol.h^{-1}$)

$F_{j,k}^{out}$ molar flow of outlet stream from stage j that goes to stage k ($kmol.h^{-1}$)

h_k^{in} enthalpy of inlet stream of stage k ($kJ.kg^{-1}$)

h_j^{in} enthalpy of inlet stream of stage j ($kJ.kg^{-1}$)

Q_k^{reac} heat supplied to reactor stage k ($kJ.h^{-1}$)

T_k^{in} temperature of inlet stream of stage k ($^{\circ}C$)

v_k^{in} volumetric flow of inlet stream of stage k ($m^3.h^{-1}$)

$v_{j,k}^{out}$ volumetric flow of inlet stream of stage k ($m^3.h^{-1}$)

V_k^C volume of CSTR reactor in stage k (m^3)

V_k^P volume of PFR reactor in stage k (m^3)

$\alpha_{j,k}$ fraction of outlet stream from stage j going to stage k

Appendix C: Nomenclature for separation network model

Scripts:

- i component
- t conditional stage
- ct stack of conditional stages
- pt permanent stage

Streams related with permanent trays

- C_{pt} composition in permanent tray pt
- $h_{L_{pt,i}}^{in}$ molar enthalpy of flow of component i in the liquid stream that inlets permanent tray pt from the tray above ($kJ.kmol^{-1}$)
- $h_{L_{pt,i}}^{out}$ molar enthalpy of flow of component i in the liquid stream that outlets permanent tray pt ($kJ.kmol^{-1}$)
- $h_{LD_{pt,i}}$ molar enthalpy of flow of component i in the liquid stream that is drawn from permanent tray pt ($kJ.kmol^{-1}$)
- $h_{LF_{pt,i}}$ molar enthalpy of flow of component i in the liquid stream that is fed into permanent tray pt ($kJ.kmol^{-1}$)
- $h_{LS_{pt,i}}$ molar enthalpy of flow of component i in the liquid stream that flows from permanent tray pt into the tray below ($kJ.kmol^{-1}$)
- $h_{V_{pt,i}}^{in}$ molar enthalpy of flow of component i in the vapour stream that inlets permanent tray pt from the tray below ($kJ.kmol^{-1}$)
- $h_{V_{pt,i}}^{out}$ molar enthalpy of flow of component i in the vapour stream that outlets permanent tray pt ($kJ.kmol^{-1}$)
- $h_{VD_{pt,i}}$ molar enthalpy of flow of component i in the vapour stream that is drawn from permanent tray pt ($kJ.kmol^{-1}$)
- $h_{VF_{pt,i}}$ molar enthalpy of flow of component i in the vapour stream that is fed into permanent tray pt ($kJ.kmol^{-1}$)

- $h_{VS_{pt,i}}$ molar enthalpy of flow of component i in the vapour stream that flows from permanent tray pt into the tray above ($kJ.kmol^{-1}$)
- $L_{pt,i}^{in}$ molar flow of component i in the liquid stream that inlets permanent tray pt from the tray above ($kmol.h^{-1}$)
- $L_{pt,i}^{out}$ molar flow of component i in the liquid stream that outlets permanent tray pt ($kmol.h^{-1}$)
- $LD_{pt,i}$ molar flow of component i in the liquid stream that is drawn from permanent tray pt ($kmol.h^{-1}$)
- $LF_{pt,i}$ molar flow of component i in the liquid stream that is fed into permanent tray p ($kmol.h^{-1}$)
- $LS_{pt,i}$ molar flow of component i in the liquid stream that flows from permanent tray pt into the tray below ($kmol.h^{-1}$)
- P_{pt} pressure in permanent tray pt (Pa)
- $P_{pt,i}^{sat}$ equilibrium vapour pressure of component i in the conditions of permanent tray pt (Pa)
- Q_{pt}^{cond} heat flow associated with condenser of permanent tray pt ($kJ.h^{-1}$)
- Q_{pt}^{reb} heat flow associated with reboiler of permanent tray pt ($kJ.h^{-1}$)
- T_{pt} temperature in tray pt (K)
- $V_{pt,i}^{in}$ molar flow of component i in the vapour stream that inlets permanent tray pt from the tray below ($kmol.h^{-1}$)
- $V_{pt,i}^{out}$ molar flow of component i in the vapour stream that outlets permanent tray pt ($kmol.h^{-1}$)
- V_{pt}^{out} total molar flow of vapour stream that outlets permanent tray pt ($kmol.h^{-1}$)
- $VD_{pt,i}$ molar flow of component i in the vapour stream that is drawn from permanent tray p ($kmol.h^{-1}$)
- $VF_{pt,i}$ molar flow of component i in the vapour stream that is fed into permanent tray pt ($kmol.h^{-1}$)

$V_{S_{pt,i}}$ molar flow of component i in the vapour stream that flows from permanent tray pt into the tray above ($kmol.h^{-1}$)

$x_{pt,i}$ molar fraction of component i in the liquid stream that leaves permanent tray pt (—)

$y_{pt,i}$ molar fraction of component i in the vapour stream that leaves permanent tray pt (—)

β_{pt} fraction of molar flow of vapour stream that outlets permanent tray pt that leaves as a vapour side draw (—)

$\gamma_{pt,i}$ activity coefficient for component i in the conditions of permanent tray pt (—)

δ_{pt} fraction of molar flow of liquid stream that outlets permanent tray pt that leaves as a liquid side draw (—)

Variables related with conditional trays

$h_{L_{t,i}^{ct}}$ molar enthalpy of flow of component i of liquid stream that outlets tray t from conditional tray stack ct ($kJ.kmol^{-1}$)

$h_{V_{t,i}^{ct}}$ molar enthalpy of flow of component i of vapour stream that outlets tray t from stack of conditional trays ct ($kmol.h^{-1}$)

L_t^{ct} total molar flow of liquid stream that outlets tray t from conditional tray stack ct ($kmol.h^{-1}$)

$L_{t,i}^{ct}$ molar flow of component i of liquid stream that outlets tray t from conditional tray stack ct ($kmol.h^{-1}$)

P_t^{ct} pressure in tray t of stack of conditional trays ct (Pa)

$P_{t,i}^{ct,sat}$ equilibrium vapour pressure of component i in the conditions of tray t of stack of conditional trays ct (Pa)

TL_t^{ct} temperature of liquid stream that outlets tray t of stack of conditional trays ct (K)

TV_t^{ct} temperature of vapour stream that outlets tray t of stack of conditional trays ct (K)

- V_t^{ct} total molar flow of vapour stream that outlets tray t from conditional tray stack ct ($kmol.h^{-1}$)
- $V_{t,i}^{ct}$ molar flow of component i of vapour stream that outlets tray t from conditional tray stack ct ($kmol.h^{-1}$)
- W_t^{ct} logic variable related to the existence of tray t of stack of conditional trays ct (—)
- $x_{t,i}^{ct}$ molar fraction of component i in the liquid stream that leaves tray t of stack of conditional trays ct (—)
- $y_{t,i}^{ct}$ molar fraction of component i in the vapour stream that leaves tray t of stack of conditional trays ct (—)
- $\gamma_{t,i}^{ct}$ activity coefficient for component i in the conditions of tray t of stack of conditional trays ct (—)

References

- Achenie, L.K.E. and Biegler, L.T. (1990). A superstructure based approach to chemical reactor network synthesis. *Computers and Chemical Engineering*, 14(1), pp.23–40.
- Agrawal, R. (1996). Synthesis of Distillation Column Configurations for a Multicomponent Separation. *Industrial and Engineering Chemistry Research*, 35(4), pp.1059–1071.
- Aguirre, P.A., Corsano, G. and Barttfeld, M. (2001). A hybrid method for optimal synthesis of multicomponent distillation processes. *Informacion Tecnologica*, 12(1), p.119.
- Azapagic, A. and Perdan, S. (2011). *Sustainable Development in Practice: Case Studies for Engineers and Scientists: Second Edition*.
- Balakrishna, S. and Biegler, L.T. (1996). Chemical Reactor Network Targeting and Integration: An Optimization Approach. *Advances in Chemical Engineering*, 23, pp.247–300.
- Baliban, R.C., Elia, J.A., Floudas, C.A., et al. (2013). Thermochemical conversion of duckweed biomass to gasoline, diesel, and jet fuel: Process synthesis and global optimization. *Industrial and Engineering Chemistry Research*, 52(33), pp.11436–11450.
- Baliban, R.C., Elia, J.A. and Floudas, C.A. (2013). Novel Natural Gas to Liquids Processes: Process Synthesis and Global Optimization Strategies. *AIChE Journal*.
- Bariani Bremermann, M. (2019). *Dissertation Proposal: Generalized framework for the synthesis and design of heat- integrated reaction-separation system using rigorous models*.
- Barnicki, S.D. and Sirola, J.J. (2004). Process synthesis prospective. *Computers and Chemical Engineering*, 28(4), pp.441–446.
- Barttfeld, M., Aguirre, P.A. and Grossmann, I.E. (2004). A decomposition method for synthesizing complex column configurations using tray-by-tray GDP models. *Computers and Chemical Engineering*, 28(11), pp.2165–2188.
- Bauer, M.H. and Stichlmair, J. (1998). Design and economic optimization of azeotropic distillation processes using mixed-integer nonlinear programming. *Computers and Chemical Engineering*, 22(9), pp.1271–1286.
- Benders, J.F. (1962). Partitioning procedures for solving mixed-variables programming problems. *Numerische Mathematik*, 4(1), pp.238–252.

- Bertran, M.O. et al. (2017). A generic methodology for processing route synthesis and design based on superstructure optimization. *Computers and Chemical Engineering*, 106, pp.892–910.
- Bixby, R. and Rothberg, E. (2007). Progress in computational mixed integer programming - A look back from the other side of the tipping point. *Annals of Operations Research*, 149(1), pp.37–41.
- Blanco, A.M. and Bandoni, J.A. (2003). Interaction between process design and process operability of chemical processes: An eigenvalue optimization approach. *Computers and Chemical Engineering*, 27(8–9), pp.1291–1301.
- Caballero, J.A. (2015). Logic hybrid simulation-optimization algorithm for distillation design. *Computers and Chemical Engineering*, 72, pp.284–299.
- Caballero, J.A. and Grossmann, I.E. (2004). Design of distillation sequences: From conventional to fully thermally coupled distillation systems. *Computers and Chemical Engineering*, 28(11), pp.2307–2329.
- Caballero, J.A. and Grossmann, I.E. (2001). Generalized disjunctive programming model for the optimal synthesis of thermally linked distillation columns. *Industrial and Engineering Chemistry Research*, 40(10), pp.2260–2274.
- Caballero, J.A. and Grossmann, I.E. (2014). Optimal synthesis of thermally coupled distillation sequences using a novel MILP approach. *Computers and Chemical Engineering*, 61, pp.118–135.
- Caballero, J.A. and Grossmann, I.E. (2013). Synthesis of Complex Thermally Coupled Distillation Systems Including Divided Wall Columns. *AIChE Journal*, 59(4), pp.1139–1159.
- Caballero, J.A., Milán-Yañez, D. and Grossmann, I.E. (2005). Rigorous design of distillation columns: Integration of disjunctive programming and process simulators. *Industrial and Engineering Chemistry Research*, 44(17), pp.6760–6775.
- Calzon-McConville, C.J. et al. (2006). Design and optimization of thermally coupled distillation schemes for the separation of multicomponent mixtures. *Industrial and Engineering Chemistry Research*, 45(2), pp.724–732.
- Chen, Q. and Grossmann, I.E. (2017). Recent Developments and Challenges in Optimization-Based Process Synthesis. *Annual Review of Chemical and Biomolecular*

Engineering, 8(1), pp.249–283.

Cremaschi, S. (2015). A perspective on process synthesis. *Computers and Chemical Engineering*, 81, pp.130–137.

Diaconescu, R., Tudose Z., R.Z. and Curteanu, S. (2002). A case study for optimal reactor networks synthesis: Styrene polymerization. *Polymer-Plastics Technology and Engineering*, 41(2), pp.297–326.

DOE. (2005). Hybrid Separations/Distillation Technology: Research Opportunities for Energy and Emissions Reduction. , pp.1–31. [online]. Available from: https://www.energy.gov/sites/prod/files/2013/11/f4/hybrid_separation.pdf [Accessed August 18, 2019].

Douglas, J.M. (1988). *Conceptual design of chemical processes*.

Dowling, A.W. and Biegler, L.T. (2015). A framework for efficient large scale equation-oriented flowsheet optimization. *Computers and Chemical Engineering*, 72, pp.3–20.

Dünnebier, G. and Pantelides, C.C. (1999). Optimal design of thermally coupled distillation columns. *Industrial and Engineering Chemistry Research*, 38(1), pp.162–176.

Duran, M.A. and Grossmann, I.E. (1986). An outer-approximation algorithm for a class of mixed-integer nonlinear programs. *Mathematical Programming*, 36(3), pp.307–339.

Feinberg, M. and Hildebrandt, D. (1997). Optimal reactor design from a geometric viewpoint- I. Universal properties of the attainable region. *Chemical Engineering Science*, 52(10), pp.1637–1665.

Felbab, N. et al. (2013). Vapor recompression for efficient distillation. 1. A new synthesis perspective on standard configurations. *AIChE Journal*, 59(8), pp.2977–2992.

Fidkowski, Z.T. and Agrawal, R. (2001). Multicomponent thermally coupled systems of distillation columns at minimum reflux. *AIChE Journal*, 47(12), pp.2713–2724.

Freund, H. and Sundmacher, K. (2008). Towards a methodology for the systematic analysis and design of efficient chemical processes. Part 1. From unit operations to elementary process functions. *Chemical Engineering and Processing: Process Intensification*, 47(12), pp.2051–2060.

Giridhar, A. and Agrawal, R. (2010). Synthesis of distillation configurations. II: A search formulation for basic configurations. *Computers and Chemical Engineering*, 34(1), pp.84–

95.

Grossmann, I.E., Aguirre, P.A. and Barttfeld, M. (2004). Optimal synthesis of complex distillation columns using rigorous models. *Computer Aided Chemical Engineering*, 18(C), pp.53–74.

Gupta, O.K. and Ravindran, A. (1985). Branch and Bound Experiments in Convex Nonlinear Integer Programming. *Management Science*, 31(12), pp.1533–1546.

Jobson, M. (2019). Chapter 6: Complex distillation configurations.

Johns, W.R. and Romero, D. (1979). The automated generation and evaluation of process flowsheets. *Computers and Chemical Engineering*.

Kamath, R.S., Biegler, L.T. and Grossmann, I.E. (2010). An equation-oriented approach for handling thermodynamics based on cubic equation of state in process optimization. *Computers and Chemical Engineering*, 34(12), pp.2085–2096.

Kokossis, A., Labrador-Darder, C. and Cecelja, F. (2016). Semantically enabled process synthesis and optimisation. *Computers and Chemical Engineering*, 93, pp.64–86.

Kokossis, A.C. and Floudas, C.A. (1994). Optimization of complex reactor networks-II. Nonisothermal operation. *Chemical Engineering Science*, 49(7), pp.1037–1051.

Kokossis, A.C. and Floudas, C.A. (1991). Synthesis of isothermal reactor-separator-recycle systems. *Chemical Engineering Science*, 46(5–6), pp.1361–1383.

Kondili, E., Pantelides, C.C. and Sargent, R.W.H. (1993). A general algorithm for short-term scheduling of batch operations-I. MILP formulation. *Computers and Chemical Engineering*, 17(2), pp.211–227.

Kong, Q. and Shah, N. (2016). An optimisation-based framework for the conceptual design of reaction-separation processes. *Chemical Engineering Research and Design*, 113, pp.206–222.

Kraemer, K., Kossack, S. and Marquardt, W. (2009). Efficient optimization-based design of distillation processes for homogeneous azeotropic mixtures. *Industrial and Engineering Chemistry Research*, 48(14), pp.6749–6764.

Lakshmanan, A. and Biegler, L.T. (1996). Synthesis of Optimal Chemical Reactor Networks. *Industrial and Engineering Chemistry Research*, 35(4), pp.1344–1353.

Lakshmanan, A., Rooney, W.C. and Biegler, L.T. (1999). A case study for reactor network synthesis: The vinyl chloride process. *Computers and Chemical Engineering*, 23(4–5), pp.479–495.

Levenspiel, O., Wiley, J. and Hepburn, K. (1999). *Chemical Reaction Engineering*. Third Edit.

Li, J. (2018). Computer-Aided Process Design.

Li, J., Demirel, S.E. and Hasan, M.M.F. (2018). Process synthesis using block superstructure with automated flowsheet generation and optimization. *AIChE Journal*, 64(8), pp.3082–3100.

Linke, P. and Kokossis, A. (2003). Attainable reaction and separation processes from a superstructure-based method. *AIChE Journal*, 49(6), pp.1451–1470.

Ma, Y. et al. (2018). Simultaneous Synthesis and Design of Integrated Reaction-Separation Systems using Rigorous Models.

Ma, Y. et al. (2019). *Simultaneous Synthesis and Design of Reaction-Separation-Recycle Processes Using Rigorous Models*.

Misener, R. and Floudas, C.A. (2014). ANTIGONE: Algorithms for coNTinuous / Integer Global Optimization of Nonlinear Equations. *Journal of Global Optimization*, 59(2–3), pp.503–526.

Nisoli, A., Malone, M.F. and Doherty, M.F. (2004). Attainable regions for reaction with separation. *AIChE Journal*, 43(2), pp.374–387.

Novak, Z., Kravanja, Z. and Grossmann, I.E. (1994). Simultaneous Optimization Model for Multicomponent Separation. *Computers and Chemical Engineering*, 18, pp.S125–S129. [online]. Available from: [http://dx.doi.org/10.1016/0098-1354\(94\)80021-9](http://dx.doi.org/10.1016/0098-1354(94)80021-9).

Pahor, B., Irsic, N. and Kravanja, Z. (2000). MINLP synthesis and modified attainable region analysis of reactor networks in overall process schemes using more compact reactor superstructure. *Computers and Chemical Engineering*, 24(2–7), pp.1403–1408.

Pahor, B., Kravanja, Z. and Iršič Bedenik, N. (2002). Synthesis of reactor networks in overall process flowsheets within the multilevel MINLP approach. *Computers & Chemical Engineering*, 25(4–6), pp.765–774.

Papadopoulos, A.I. and Seferlis, P. (2009). Generic modelling, design and optimization of

- industrial phosphoric acid production processes. *Chemical Engineering and Processing: Process Intensification*, 48(1), pp.493–506.
- Pattison, R.C. and Baldea, M. (2014). Equation-oriented models of multistream heat exchangers for flowsheet optimization. In *Computer Aided Chemical Engineering*. pp. 1351–1356.
- Pattison, R.C., Gupta, A.M. and Baldea, M. (2016). Equation-Oriented Optimization of Process Flowsheets with Dividing-Wall Columns. , 62(3).
- Peschel, A., Freund, H. and Sundmacher, K. (2010). Methodology for the design of optimal chemical reactors based on the concept of elementary process functions. *Industrial and Engineering Chemistry Research*, 49(21), pp.10535–10548.
- Pibouleau, L. (1988). Optimal Synthesis of Reactor-Separator Systems by Nonlinear Programming Method. , 34(1), pp.163–166.
- Recker, S. et al. (2015). A unifying framework for optimization-based design of integrated reaction-separation processes. *Computers and Chemical Engineering*, 81, pp.260–271. [online]. Available from: <http://dx.doi.org/10.1016/j.compchemeng.2015.03.014>.
- Sargent, R.W.H. (1998). A functional approach to process synthesis and its application to distillation systems. *Computers and Chemical Engineering*, 22(1–2), pp.31–45.
- Sargent, R.W.H. and K. Gaminibandara. (1976). Optimum design of plate distillation columns. In *Optimisation in action*. New York: Academic Press, pp. 267–314. [online]. Available from: https://www.researchgate.net/publication/237128384_Optimum_Design_of_Plate_Distillation_Columns.
- Schweiger, C.A. and Floudas, C.A. (1999). Optimization framework for the synthesis of chemical reactor networks. *Industrial and Engineering Chemistry Research*, 38(3), pp.744–766.
- Schweiger, C.A. and Floudas, C.A. (1999). Synthesis of optimal chemical reactor networks. *Computers & Chemical Engineering*, 23, pp.S47–S50. [online]. Available from: <https://linkinghub.elsevier.com/retrieve/pii/S0098135499800131>.
- Seader, J.D. and Westerberg, A.W. (1977). A combined heuristic and evolutionary strategy for synthesis of simple separation sequences. *AIChE Journal*.

Siirola, J.J. and Rudd, D.F. (1971). Computer-Aided Synthesis of Chemical Process Designs From Reaction Path Data to the Process Task Network. *Industrial and Engineering Chemistry Fundamentals*, 10(3), pp.353–362.

Smith, E.M.B. and Pantelides, C.C. (1995). Design of reaction/separation networks using detailed models. *Computers and Chemical Engineering*.

Smith, R. (2016). *Chemical Process Design and Integration*.

Stephanopoulos, G. and Westerberg, A.W. (2002). Studies in process synthesis—II. Evolutionary Synthesis of Chemical Process Flowsheets. *Chemical Engineering Science*.

Tawarmalani, M. and Sahinidis, N. V. (2005). A polyhedral branch-and-cut approach to global optimization. In *Mathematical Programming*. pp. 225–249.

Trespalacios, F. and Grossmann, I.E. (2014). Review of mixed-integer nonlinear and generalized disjunctive programming methods. *Chemie-Ingenieur-Technik*, 86(7), pp.991–1012.

Vecchietti, A., Lee, S. and Grossmann, I.E. (2003). Modeling of discrete/continuous optimization problems: Characterization and formulation of disjunctions and their relaxations. *Computers and Chemical Engineering*, 27(3), pp.433–448.

Vigerske, S. and Gleixner, A. (2018). SCIP: global optimization of mixed-integer nonlinear programs in a branch-and-cut framework. *Optimization Methods and Software*, 33(3), pp.563–593.

Viswanathan, J. and Grossmann, I.E. (1990). A combined penalty function and outer-approximation method for MINLP optimization. *Computers and Chemical Engineering*, 14(7), pp.769–782.

Viswanathan, J. and Grossmann, I.E. (1993). An alternate MINLP model for finding the number of trays required for a specified separation objective. *Computers and Chemical Engineering*.

Xie, M. and Freund, H. (2018). Fast synthesis of optimal chemical reactor networks based on a universal system representation. *Chemical Engineering and Processing: Process Intensification*, 123(July 2017), pp.280–290. [online]. Available from: <https://doi.org/10.1016/j.cep.2017.11.011>.

Yeomans, H. and Grossmann, I.E. (1999a). A systematic modeling framework of

superstructure optimization in process synthesis. *Computers and Chemical Engineering*, 23(6), pp.709–731.

Yeomans, H. and Grossmann, I.E. (2000a). Disjunctive Programming Models for the Optimal Design of Distillation Columns and Separation Sequences †. *Industrial & Engineering Chemistry Research*, 39(6), pp.1637–1648.

Yeomans, H. and Grossmann, I.E. (1999b). Nonlinear disjunctive programming models for the synthesis of heat integrated distillation sequences. *Computers and Chemical Engineering*, 23(9), pp.1135–1151.

Yeomans, H. and Grossmann, I.E. (2000b). Optimal design of complex distillation columns using rigorous tray-by-tray disjunctive programming models. *Industrial and Engineering Chemistry Research*, 39(11), pp.4326–4335.

Zhang, X., Song, Z. and Zhou, T. (2018). Rigorous design of reaction-separation processes using disjunctive programming models. *Computers and Chemical Engineering*, 111, pp.16–26. [online]. Available from: <https://doi.org/10.1016/j.compchemeng.2017.12.013>.

Zou, X. et al. (2012). Optimal design of complex distillation system for multicomponent zeotropic separations. *Chemical Engineering Science*, 75, pp.133–143. [online]. Available from: <http://dx.doi.org/10.1016/j.ces.2012.02.045>.