



# **Synthesis and optimisation of energy integrated advanced distillation sequences**

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## Abstract

The synthesis of heat-integrated distillation sequences for energy-efficient separation of zeotropic multicomponent mixtures is complex due to the many interconnected design degrees of freedom. The synthesis must determine the basic separation configuration, including thermally coupled complex columns, column pressures, reflux ratios, feed conditions, condenser types and heat integration arrangements all simultaneously. The method most often used to address larger problems is to use short-cut distillation models to screen the large number of structural options and determine the best few potential designs, followed by more detailed examination of these designs using rigorous simulation. However, it is not clear whether short cut distillation models have the necessary accuracy for reliable screening, and whether heat integration must be included in the screening.

To solve this generic problem, the novel contribution of this project is to explore the basis on which reliable screening can be carried out. A screening algorithm has been developed using optimisation of a superstructure for the sequence synthesis using short cut models, in conjunction with a transportation algorithm via an incidence matrix for the synthesis of the heat integration arrangement. The best few designs in terms of total operating cost from the screening are evaluated using rigorous simulations. The overall problem is solved by a decomposed simulation-based optimisation, achieved by a mixed-integer linear programming (MILP) formulation inside the Simulated Annealing (SA) algorithm.

An industrial case study for the fractionation of natural gas liquids (NGLs) is used to evaluate the proposed approach. It has been found that separation problems of the type explored can be screened with confidence. The best sequences in terms of total operating costs identified by rigorous simulations can be pre-selected by the developed screening approach. Additionally, the non-heat-integrated designs using thermally coupled complex columns show much better performance than the corresponding designs using simple columns. However, once heat integration is included the difference between designs using complex columns and simple columns narrows significantly.

## **Declaration**

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

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# **Chapter 1**

## **General Introduction**

This chapter aims to provide a brief introduction to the background of the research topic, followed by a problem statement and research objectives. The purpose of this chapter is to give readers a general understanding of the research focus and scope before proceeding to the publication in Chapter 2.

## 1.1 Background

Currently, the chemical industry accounts for about one third of all industrial energy usage ([US Energy Information Administration, 2018](#)) with separation accounting for 40% of energy use and 40-70% of plant costs, utilising the most capital-intensive equipment. Among the separation technologies, distillation is the most widely used in the chemical industry due to its ability to handle a wide range of throughputs from very low to very high, to separate mixtures with a wide range of feed concentrations, and to produce high purity products ([Kiss, 2013](#)), achieving about 95% of all separations but consuming nearly half of the industry energy usage in the process. The thermodynamic efficiency (the quotient of the minimum amount of work needed for this process and the total energy input to achieve the process ([Henley and Seader, 1981](#)) of the distillation processes) is low, ranging from 18% in air separation and 12% in crude oil separation to just 5% for C2 and C3 splitting ([Kiss, 2014](#)). Therefore, tackling the energy efficiency of the distillation process holds the promise of the largest energy savings potential in the chemical industry. The use of distillation for the separation of multicomponent (four or more components) mixtures is significant in chemical and process industries as it relates to some of the largest applications, such as crude oil fractionation, hydrocarbon chemical separations from steam cracking and natural gas liquid (NGL) separations. A sequence of simple distillation columns is required to effectively separate multicomponent mixtures into more than two product streams, but at the same time, the large scale of the project also results in a significant energy demand. Furthermore, another problem in multicomponent distillation is the remixing of non-key components within the separation, which increases energy usage and vapour rates compared with separating two-component mixtures ([Triantafyllou and Smith, 1992](#)). The use of complex thermally coupled configurations (e.g. dividing-wall columns, side-stripper, side-rectifier, prefractionator) can overcome the drawbacks associated with remixing ([Triantafyllou and](#)

[Smith, 1992](#)) and enhance energy efficiency, and is potentially able to reduce both operating and capital costs.

A systematic synthesis method could assist with identifying possible distillation configurations and can then calculate the energy usage, operating costs and investment costs by determining the best operating conditions of sequences. These include different types of heat integration opportunities (direct or indirect), column internal parameters (efficient trays or feed locations), adjusting operating conditions (operating pressure, feed conditions, condenser types, etc.) and heat transfer enhancement in heat exchangers ([Kiss and Smith, 2020](#)). Even for a single distillation column with a fixed product specification, design optimisation still targets a trade-off between the number of stages (related to capital cost) and the reflux ratio (related to condenser and reboiler operating cost) ([Smith, 2016](#)). It means that when the degrees of freedom generated by distillation sequences (topology of the distillation sequence, heat integration, each pressure optimisation, etc.) are taken into account simultaneously, these factors result in an exponential increase in design complexity. These degrees of freedom are also interconnected, which makes the optimisation even more complicated, but they provide opportunities for engineers to create distillation systems that are cost-effective and energy efficient as well ([Jain et al., 2012](#)). Therefore, finding the optimal distillation sequence while considering operating conditions and trade-offs by an optimisation tool, can provide significant benefits in terms of costs and reducing greenhouse gas emissions.

## **1.2 The synthesis of distillation sequences**

Distillation sequences are classified in terms of their use of simple and complex column configurations. Simple columns involve one feed entering the column and two products, with a condenser at the top and the reboiler at the bottom; complex columns have either more feeds or a side product ([Christiansen et al., 1997](#)).

Generating a synthesis framework screening all possible sequences including simple and complex column configurations is difficult, particularly in the case of multicomponent separation, because of the computational difficulties raised by the large problem size and the

vast array of options. Different approaches have been proposed to address this issue, such as applying heuristic rules for distillation sequencing, superstructure optimisation, separation matrix methods, and simultaneous heat and mass integration methods (Bertran et al., 2017; Kong and Maravelias, 2020; Shenvi et al., 2012; Lee et al., 2022; Chia et al., 2021).

The number of possible sequences for separating multicomponent mixtures is large. For simple columns only, the number of sequences for separating a mixture of  $N$  products are  $S = [2(N - 1)]! / N! (N - 1)!$ . For a mixture of 5 products, there are 14 possible sequences of 4 simple columns - 56 columns to be designed in total. These numbers increase exponentially with the increase of the number of components. For example, a 10-product separation would require 4862 sequences (Thompson and King, 1972).

The earliest studies of the distillation sequence synthesis considered only simple columns (Andreovich and Westerberg, 1985). With the development of distillation technologies to improve energy efficiency, complex configurations are now well known as energy effective options (Kiss and Smith, 2020; Smith, 2016). However, the introduction of complex column arrangements makes the sequence synthesis and modelling even more complicated.

Therefore, some methodologies aiming to synthesise a full search space for all simple and complex configurations. Initial selections are based on heuristic rules (Lockhart, 1947) from experience or intuition. Applying heuristic rules (Hendry et al., 1973) to reduce the search space is one way, but these heuristic rules could be unclear and contradictory. Sargent and Gaminibandara (1976) first propose a superstructure approach to the distillation synthesis problem including complex columns. The superstructure-based synthesis method has been used extensively for distillation network synthesis. By definition, a distillation superstructure should contain all the alternative configurations to be considered. Many researchers contributed to the development of superstructures. Agrawal (1996) introduces a stepwise procedure to obtain the simple column configurations; the method was later extended to consider complex column configurations (Agrawal, 2003). Caballero and Grossmann (2006) propose a mixed integer programming model to generate different configurations. More recently, Shah et al. (2010) propose a matrix method for efficiently enumerating all the basic

and thermally-coupled configurations. In terms of representing and modelling of the distillation superstructure, Sargent (1998) proposes a state task network representation to model the distillation superstructure. Yeomans and Grossmann (1999) later formalize the state task network representations for the optimisation of distillation systems, and Caballero and Grossmann also use a state task network for thermally coupled distillation sequences design (Caballero and Grossmann, 2001; 2004) and dividing wall columns (Caballero and Grossmann, 2013). Some researchers consider superstructure-based models, building a large number of sequences, and come up with a “task based” method (Hendry and Hughes, 1972; Shah, 1999; Shah and Kokossis, 2001) considering the separation in each column separation as a separation “task”, and the design conditions are fixed in each column, then these several separation tasks are combined to form a distillation sequence. The task-based method does not allow operating conditions to be changed in different sequences, and is not feasible in a practical design.

Overall, the above studies only consider the distillation network, focusing on generating distillation sequence configurations. No column operating details and subsequent heat integration opportunities are considered. Thus, other studies explore new approaches to considering sequence synthesis together with heat recoveries to save energy.

### 1.3 Heat-integrated distillation sequences

To minimise the energy requirement of the process after exploring all distillation sequence configurations, heat integration including inter-column heat recovery, heat exchange with utility, and feed pre-heating or pre-cooling, as shown in Figure 1, also need to be considered when designing and optimising the sequences.

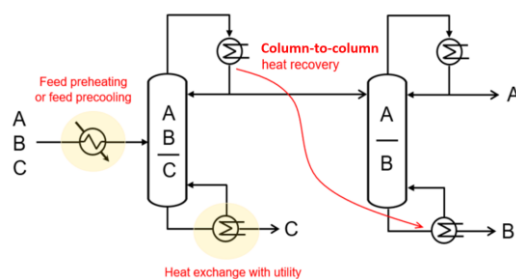


Figure 1 Options illustration in a process (Samanta, 2001)

In process-to-process heat recovery, heat can be exchanged between a reboiler (heat sink) of one column and a condenser (heat source) of another one (i.e. inter-column heat recovery), or between reboilers and condensers, or the heaters or coolers before columns. The operating pressure of the column can be adjusted to enable column-to-column heat recovery without violating the minimum approach temperature ( $\Delta T_{\min}$ ). For feed pre-heating or pre-cooling, feeds can be preheated or precooled by transferring heat between condensers, reboilers or other process streams to achieve its target temperatures. Heat could be provided by hot utilities (e.g. steam, hot oil) if heat obtained by the heat recovery system is not sufficient, practical or economically feasible. Surplus heat could be disposed of to a cold utility (e.g. cooling water) or used in steam generation, boiler feed water heating, etc. The choice of utilities and decisions associated with matching utilities take into account the cost and availability.

The difficulties raised by heat integration options for distillation systems are that since the process design emphasises the whole process, heat integration opportunities are screened and optimised simultaneously with all the following options: column types (simple and complex column configurations), operating conditions (condenser types, column pressure, operating temperature, feed quality, heat flow rates, etc.), number of stages and feed locations of columns and practical limitations or constraints (e.g. the maximum number of heat exchangers allowed for the condensation of reflux). These operations interact with each other, for example, the choice of operating conditions for the columns also affects thermodynamic properties of process streams (heat capacities, temperatures), but the interaction between different operations is expected to be considered from the outset to identify overall insights into the process, which brings more complexity than optimising them separately.

The systematic studies of heat integrated distillation sequences were originally performed by Rathore et al. (1974a, b), who present an algorithm for fixed pressures of the distillation columns. Applying heat integration options for distillation systems causes computational difficulties as the design complexity significantly increases when heat integration is considered simultaneously due to the greater difficulty of structural representation and the

more complex combinatorial problem. For example, the choice of operating conditions for the columns (pressure, feed conditions and reflux ratio), affects not only the design of a column (e.g. size, number of stages, etc.) but also its thermodynamic characteristics (i.e. operating temperature and heat flow rates). Therefore, an optimal solution should take into account the trade-off between operating conditions (affecting column capital cost and energy cost) and potential heat integration (affecting energy cost). For example, increasing column operating pressure could increase the condenser temperature which may create heat integration opportunities. Consequently, consideration of heat integration opportunities and operating conditions for the columns simultaneously is a key but complicated part of the distillation sequencing optimisation.

Researchers have explored simultaneous optimisation of distillation sequence synthesis and direct heat integration opportunities. An et al. (2009) synthesise heat-integrated distillation sequences, but only simple columns and heat integration between columns are considered. Zhang et al. (2019; 2021) enhance this method to synthesise more complex processes considering heat-integrated and thermally coupled distillation sequences. However, there are several limitations of their work, for example, there are no constraints to limit the number of heat exchangers for a condenser or a reboiler; feeds are fixed to be saturated liquid, and all column pressures in one sequence are fixed to be the same. A natural gas liquid distillation sequence proposed by Tamuzi et al. (2020) and a very similar work for the gas to liquid mixture proposed by Louhi et al. (2021) enumerated distillation sequences based on a separation matrix and optimized the distillation sequence based on simulation. However, only Petlyuk and side-draw columns are considered as complex column configurations in their work, and no heat integration is included in their optimisation.

Yoo et al. (2015) propose a shortcut-based heat integrated distillation sequence model, including the optimisation of column pressure, but they consider simple columns sequences only; the feed and products of the columns are saturated liquid; and only total condensers are used. Additionally, the heat integration in their study is carried out after the sequence generation with column design, which may miss the better solution compared with optimising heat integration with sequence generation and columns design simultaneously.

Ramapriya et al. (2018) also use a shortcut distillation model, considering complex column options (but only 18 configurations are considered in order to reduce search space). The limitations of their work are: heat integration is not included in their study; only partial condensers are considered; column pressures are not optimised (all columns are operated at 3 atm); and the relative volatility of the feed stream is used for all column sequences.

Therefore, there are lack of studies attempting to integrate distillation sequence synthesis, including simple and complex configurations together with heat integration in an integral, albeit challenging optimisation. To address this issue, the next chapter presents a decomposed simulation-optimisation approach aiming to develop a screening method for the synthesis and optimisation of the advanced energy integrated distillation sequences.

### **1.3 Problem statement**

Although there have been research investigations to study both the generation of distillation sequence configurations and heat integrated distillation columns, few studies focus on heat integrated distillation sequences together with the optimisation of column types (simple and complex columns) and column operating conditions (column pressure, feed quality, condenser type, reflux ratio and column geometric parameters, such as number of stages and feed locations), which will influence the sequence performance as well, due to the large problem size. Even using simplified shortcut distillation models to reduce the optimisation complexities for the heat integrated distillation sequence, it still proves to be challenging. (Yoo et al., 2015; Ramapriya et al., 2018; Duanmu et al., 2022).

Therefore, it is necessary to develop a systematic method to optimise the distillation sequence, heat integration, as well as column pressure, feed quality, condenser type, reflux ratio and column geometric parameters, such as number of stages and feed locations simultaneously, which can lead to a more energy efficient sequence design.



## **1.4 Objectives**

The specific objectives of this project are:

- (1) Develop a systematic optimisation-based screening approach that considers sequence synthesis, simple and complex configurations, heat integration, column operating conditions and column geometric parameters, all simultaneously, based on shortcut distillation models.
- (2) Demonstrate the proposed screening approach using an industrially relevant case study. Then evaluate the generated sequences using rigorous simulations by comparing the rank-list of sequences in terms of total operating cost.
- (3) Analyse the design and economics of the most economically attractive sequences generated from the screening methods, compare the performance among different configurations, i.e., (non) heat integrated simple/complex distillation sequences.

## **1.5 Outline of the report**

This MPhil thesis uses a journal-based format that is structured according to the thesis policy regulated by the University of Manchester. The journal-based format allows the incorporation of published and submitted scientific papers in different chapters. As a master level research, there is one paper published listed in Chapter 2.

Therefore, the contents of the next chapters in the present thesis are presented as follows. Chapter 2 lists the publication based on the identified research gaps with the detailed methodology developed during the MPhil research, and the approach is evaluated by an industrially relevant case study. Chapter 3 summarises the findings of this work and gives recommendations for the directions of future work that may improve and complement the present work.

## **Chapter 2**

### **Synthesis and optimisation of energy integrated advanced distillation sequences**

This section is based on the following publication:

**Li, Q.**, Finn, A.J., Doyle, S.J., Smith, R. and Kiss, A.A. (2023). ‘Synthesis and optimisation of energy integrated advanced distillation sequences’, *Separation and Purification Technology*, pp.123717.

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**Qing Li:** Conceptualization, Methodology, Software, Data curation, Validation, Visualization, Writing – original draft, Writing – review & editing.

**Adrian J. Finn:** Conceptualization, Methodology, Validation, Writing – review & editing.

**Stephen J. Doyle:** Methodology, Formal analysis, Investigation, Validation.

**Robin Smith:** Conceptualization, Methodology, Formal analysis, Investigation, Validation, Supervision, Writing – review & editing.

**Anton A. Kiss:** Conceptualization, Methodology, Formal analysis, Investigation, Resources, Visualization, Validation, Supervision, Project administration, Writing – original draft, Writing – review & editing.

The US English spelling in the original publication has been changed here to the UK English spelling to fulfil the requirements of the PhD theses policy regulated by the University of Manchester.

# Synthesis and optimisation of energy integrated advanced distillation sequences

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## **Abstract**

This paper explores the basis on which reliable screening of distillation sequences for energy-efficient separation of zeotropic multicomponent mixtures can be carried out. A case study for the separation of natural gas liquids is used to demonstrate the approach. To solve this generic problem, a screening algorithm has been developed using optimisation of a superstructure for sequence synthesis using shortcut models, in conjunction with a transportation algorithm for the synthesis of the heat integration arrangement. Different approaches for the inclusion of heat integration are explored and compared. The best few designs from this screening are then evaluated using rigorous simulation. It has been found that separation problems of the type explored can be screened reliably using shortcut distillation models in conjunction with the synthesis of heat exchanger network designs. Non-integrated designs using thermally coupled complex columns show much better performance than the corresponding designs using simple columns. However, once heat integration is included the difference between designs using complex columns and simple columns narrows significantly.

## **Keywords**

Distillation sequencing; process synthesis; process design; energy integration; process optimisation

## **Highlights**

- Novel effective routes for eco-efficient separation by distillation sequences
- Simultaneous optimisation of all design degrees of freedom in distillation sequences
- Optimal arrangement of complex columns sequencing for NGL separation

## 1. Introduction

The rise in worldwide energy usage has increased interest in cost-effective ways of reducing energy use. Distillation is by far the most widely applied separation technology, but it is recognized as the most energy-intensive operation in the chemical industries due to its inevitable energy degradation. Distillation processes can use one or more distillation columns. For instance, to efficiently separate multicomponent mixtures into more than two product streams using distillation, a sequence of distillation columns is required, which results in significant energy demand and associated CO<sub>2</sub> emissions. Because of its configuration complexities related to process energy efficiency, studies of distillation synthesis have been developed over the past decades to bring cost-efficient solutions. Early work was carried out by [Seader and Westerberg \(1977\)](#) and [Andreovich and Westerberg \(1985\)](#).

### *1.1 Distillation sequence synthesis*

The number of possible sequences is large. For example, for a five-product mixture separation using simple columns only, there are 14 possible sequences, but this number rises to 4862 when the number of products is 10. The number of possible sequences is greatly increased with the number of products from fractionation units. The increase in the number of fractionation products leads to extensive sequence options when only simple columns are used, but this number grows exponentially if thermally coupled complex column options are further considered.

Mathematical programming has been developed to achieve automated distillation sequence synthesis. It commonly formulates the design problem through representing the number of possible sequences to separate multicomponent mixtures, and obtaining the optimal sequence with detailed process design. Due to the non-linearity, non-convexity and increased problem sizes for large-scale distillation sequence synthesis problems, it is challenging to find an optimal sequence configuration solution with an acceptable computational time. Different studies focus only on attempting to synthesise all possible distillation configurations for a multicomponent separation problem using superstructure optimisation,

separation matrix methods, or simultaneous heat and mass integration methods ([Frauzem et al., 2017](#); [Kong and Maravelias, 2020](#); [Shenvi et al., 2012](#)).

Applying distillation sequencing heuristic rules to reduce the search space would be one way of solving the issue. For example, [Lee et al. \(2022\)](#) removed plentiful components at the end of the sequence to narrow the sequence possibilities. But promising solutions could be missed because simultaneous optimisation cannot be achieved based on all possibilities. Other work handled this large problem by retrofitting of an existing distillation system ([Yang, 2022](#); [Long 2016](#)) or by sensitivity analysis in which one variable is changed parametrically while other variables are fixed ([Premkumar and Rangaiah, 2009](#)). But these methods are based on fixed operating conditions, and thus cannot obtain the optimal operational solutions and may miss optimal operating parameters. [Zhang et al. \(2022\)](#) proposed a task-based program method followed by a simulation-optimisation model to carry out optimal design for distillation sequences. However, the task-based method does not allow operating conditions to be changed in different sequences and thus loses design degrees of freedom. [Leeson et al. \(2017\)](#) presented an MILP optimisation to determine the optimum separation sequence within a reduced process superstructure at a conceptual design stage, but only simple columns are considered in their work.

The method most often used to address larger problems is to use shortcut distillation models to screen the large number of structural options and determine the best few potential designs to reduce the search space, followed by more detailed examinations of the best few designs using rigorous simulation ([Ramapriya, 2018](#); [Yoo, 2016](#)). Convergence guaranteed shortcut methods are developed to fast screen the search space of non-heat integrated distillation sequences and their efficacy is further rigorously evaluated. However, excess stages were introduced to the Aspen Plus rigorous model when it was used to evaluate their shortcut method by comparing the heat duty requirements of the two methods ([Ramapriya et al., 2018](#)). To simplify the models, there are also some assumptions made on key operating variables. For example, all column pressures are assumed to be the same throughout the sequence, using relative volatilities of the initial feed for all columns. It is therefore unclear whether shortcut distillation models have the necessary accuracy for reliable screening.

The thermally coupled complex columns based on the principle of process intensifications are then applied to distillation sequences to reduce the remixing of non-key components, and thus lead to a more energy efficient separation sequence and are potentially able to reduce both operating and capital costs (Triantafyllou and Smith, 1992; Flores et al., 2003). Among the complex columns, dividing-wall columns (DWC) are the most common options studied as a complex column application in distillation sequence synthesis cases (Lee et al., 2022; Halvorsen et al., 2016; Long and Lee, 2011; Lestak and Collins, 1997). Their results show the use of DWC can bring energy savings and capital cost savings (up to 50%) compared with simple columns. Nevertheless, the use of DWCs may also require distillation at non-optimal column pressures, and thus may cause more expensive cooling media costs if for example refrigerant is required. Halvorsen et al. (2016) reported that using a DWC to substitute the original two simple columns for a natural gas liquid process might reduce the size of the columns as well as the carbon footprint, but it will increase the refrigerant requirement at an even lower temperature than in simple columns. Therefore, whether or not to apply DWC to replace simple columns should be decided based on an optimisation. There are also other complex column options which may benefit the distillation sequences in terms of energy savings. For example, Agrawal and Fidkowski (1998) reported that the side columns may provide efficient configuration more often when compared with the fully coupled column configuration. Thus, the use of all complex column options should be determined within the sequence synthesis, but few have been studied in a distillation sequence systematically. Waltermann and Skiborowski (2019) and Skiborowski (2018a) proposed optimisation approaches for the synthesis of energy integrated distillation processes including various simple and complex column options. But in their work, the processes include only three products, meaning that either two simple columns or one complex column is needed without demanding a distillation sequence, thus the problem size is reduced.

### ***1.2 Integration of sequence synthesis with complex options***

Heat integration and column operating conditions generate design degrees of freedom and they interact with each other. In distillation sequences, the large amount of energy required by the system creates a wide temperature range and significant quality of heat sources in the



columns, which can provide potential heat integration opportunities. The energy requirements and heat sources in the sequence affects column operating conditions and column geometries and the choice of operating conditions for the columns affects not only the design of a column but also influences columns thermodynamic characteristics (i.e. operating temperature and heat flow rates) and thus influences heat integration opportunities. For instance, the column operating pressures might be increased to create heat integration opportunities (e.g. to increase the condenser temperature). In turn, the heat integration also affects the column operating conditions (e.g. feed conditions and reflux ratio). Therefore, the operating conditions and heat integration opportunities should be optimized simultaneously together with the distillation sequence synthesis.

The other reason for the simultaneous heat integration is that if heat integration is introduced based on a previously fully designed process, which may result in the omission of competitive solutions and unfair process comparisons ([Rathore et al., 1974](#)). Potential heat integrated structures prior to parameter optimisation require an exhaustive enumeration which is time-consuming. Therefore, to enhance the energy efficiency of the distillation systems, it is required to manipulate not only the arrangements of sequences, but also the heat integration with operating conditions and column configurations simultaneously. [An et al. \(2009\)](#) generated a method to search heat-integrated distillation sequences, but only simple columns are considered. [Zhang et al. \(2019; 2021\)](#) enhanced this method to synthesise more complex processes considering heat-integrated and thermally coupled distillation sequences. However, some key operating conditions, e.g. feed conditions and column pressures, are not included. [Zhang et al. \(2022\)](#) proposed a sequence optimisation without heat integration considering the number of stages, feed stage locations, and operating conditions. So far, the previous approaches still cannot provide a solution that considers these complex options concurrently.

Overall, the greater number of interconnected design variables in distillation columns increases the design complexities significantly in terms of structural representation and the more complex combinatorial problem when sequence synthesis, column operating conditions and heat integration are all considered, and produce a more challenging non-linear

optimisation problem (Kiss and Smith, 2020). To find a solution for any process design problem, many sequences with different operating conditions must be examined from a process integration perspective, and therefore an integrated systematic approach is required to provide reliable distillation sequence synthesis and design optimisation. A recent paper (Gooty et al., 2022) developed mathematical programming based approaches to identify the most energy-efficient distillation configuration sequence for a given separation, and a more detailed review on introducing thermally coupled columns into distillation sequences can be found (Jiang and Agrawal, 2019). However, these studies focus on the perspective of generating more efficient thermally coupled column possibilities, rather than optimizing the whole distillation sequence together with allowing changes of condenser types, feed qualities, heat pumping (refrigeration), etc. at a flowsheet level. It is so far not clear whether shortcut models have the required accuracy for reliable screening of sequences. Furthermore, it is also unclear whether the heat integration can be represented by the energy targets of pinch analysis with maximum heat recovery, or whether it is necessary to produce detailed heat exchanger network designs for screening. Additionally, although the thermally coupled complex columns have the possibility to bring energy savings, the combination of the two simple columns also loses degrees of freedom by heat integration between different columns. When heat integration is taken into account, the potential heat integration possibilities for complex columns decrease as the combination of heat sinks and sources are constrained. It is not clear how much difference the benefit of heat integration makes to complex columns and simple columns, and thus it is difficult to make an optimal selection for using complex columns if heat integration is considered.

The novel contribution of the present research is to develop a systematic approach (using a quick screening method combined with optimisation) for the advanced distillation sequences used on combinations of energy-efficient complex columns (side-strippers, side-rectifiers, side-stream columns; and prefractionation arrangements, including Petlyuk columns and dividing wall columns) by eliminating simplifying assumptions and simultaneously including all degrees of freedom, such as column design parameters and operating conditions (feed condition; pressure; condenser type). Furthermore, for the first time this work addresses heat integration explicitly for a complex sequence optimisation by generating a

heat exchanger network (HEN) configuration that accounts for practical constraints, via a matrix representation (rather than using Pinch Analysis). An industrial case study, NGL fractionation system optimisation, is used to demonstrate the methodology proposed in this work.

## **2. Problem statement and motivation**

The optimisation of the distillation sequence systems is motivated by the benefits of energy savings in reducing costs and CO<sub>2</sub> emissions. Its design requires many interconnected design degrees of freedom, which lead to a challenging optimisation problem. Reaching high quality distillation sequences from mathematical optimisation, including integration with complex options, simple columns, complex columns, heat integration with heat exchanger network design, adjustment of operating conditions, has been shown to be complicated and time-consuming for large-scale problems. Using heuristics in the past often led to an economically viable solution, but may miss promising sequences, particularly for updating new and complex options. Complex column options that overcome remixing effects do have value but have not been studied in detail. Thermal integration has been studied, but not with so many column options nor with a methodical and robust optimisation approach.

This study addresses this problem by combining process synthesis and optimisation to evaluate all the fractionation process alternatives, as illustrated by a natural gas liquids (NGL) separation case study. Shortcut distillation models are used for fast screening, which determines which possible sequences are likely to achieve the desired separation, eliminating simplifications on key design variables. A process optimisation procedure is then used (based on simulated annealing) to find and rank the best configurations in terms of total operating cost (TOC).

## **3. Methodology and optimisation approach**

### ***3.1 Superstructure sequences synthesis approach***

Taking advantages of a superstructure, all possible separation sequences for a given multi-component mixture can be derived, and the basic superstructure can also be extended with advanced options in mathematical ways. For a given mixture of (P) products, the number of

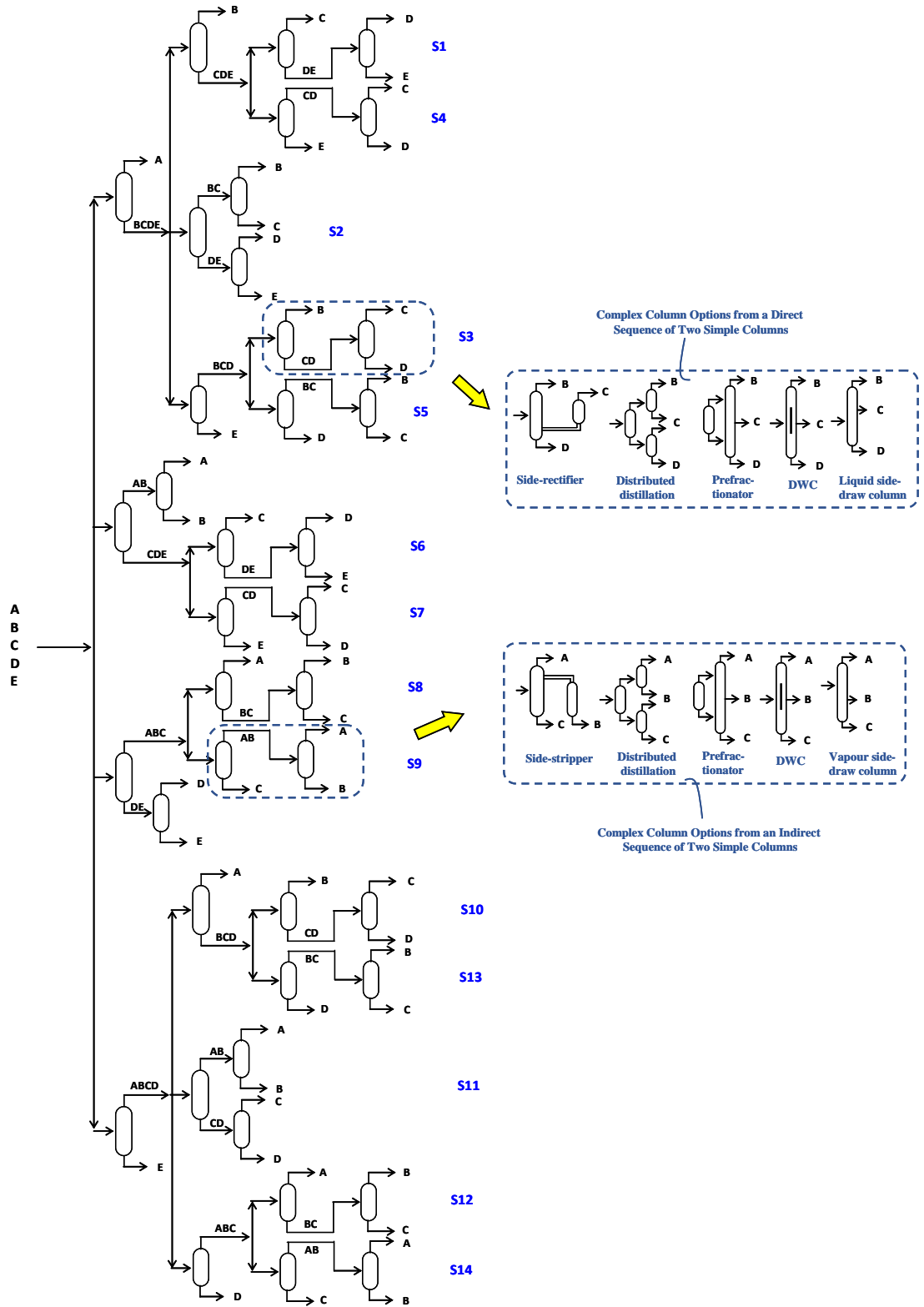
simple column sequences (S) is given by the formula:  $S = [2(P-1)]! / P!(P-1)!$  (Seider et al., 1999). This basic superstructure is then extended to handle complex column options. In principle, any two column tasks in the superstructure can be merged to give different complex column arrangements. As shown in Figure 1, a three components mixture separation task represented by the circled two simple columns has the potential be achieved by alternative thermally coupled composite columns with a single feed and three product streams (side-stripper, side-rectifier, pre-fractionators, and thermally coupled pre-fractionators, liquid side draw, vapour side draw) (Smith, 2016).

The appropriate complex column arrangement options depend on whether the two simple columns in the series are in the direct or indirect sequence. For a 5 component mixture, there are  $S=14$  simple column sequence possibilities. Taking simple column sequence 1 (S1) as an example. The separation task order is: A/BCDE, B/CDE, C/DE, D/E. Based on this separation task, the optimizer tries several paths to select various complex columns, and finally when the optimisation converges, the optimal complex column sequence is produced based on the sequence 1 separation task. The simple column sequences and the corresponding complex column sequences are optimized based on the same starting defaults. Therefore, this generated optimal complex sequence is actually not the only configuration possible or evaluated, but rather it is the optimal solutions found by the optimiser after optimising all the possible combinations of complex columns, based on the simple column sequence 1 structure (i.e. performing the same separation tasks).

Other optimal complex column sequences are also determined in the same way. Each simple sequence has 4 simple columns, and each complex column could contain 2 complex columns or 1 complex column and 2 simple columns. The shortcut Fenske-Underwood-Gilliland (FUG) models (see Appendix C) are used to design the columns and can screen very many options. These models can avoid dramatic computational difficulties created by nonlinear, large tray-based combinations of rigorous design formulation and provide an efficient screening for a large number of separation sequences (Fenske, 1932; Gilliland, 1940; Underwood, 1949). Rigorous simulation can then be carried out based on the attractive sequences, as screened and selected by shortcut models.

### **3.2 *Process heat integration***

During operations in the chemical process sector, a large amount of heat is consumed in separation systems, which brings considerable heat across the processes with a wide range of temperatures under different operating pressures, and thus creates potential opportunities for heat recovery. Before optimisation can be applied to the superstructure, the energy cost is evaluated for each structure and set of conditions. Energy integration options are thus applied to each sequence during the optimisation process to enhance process energy efficiency. This requires optimisation of the matches between heat sources (defined as hot streams discharging energy) and heat sinks (defined as cold streams absorbing energy) throughout the process to be determined. The match between a heat source and a heat sink can be considered through a heat exchanger with a feasible temperature difference. Heat integration opportunities including feed preheating or precooling and column to column heat recovery (between column condensers and reboilers) are optimized with sequence synthesis simultaneously. As shown in Figure 2, all heat sinks and heat sources are compiled into an incidence matrix, and are solved by using an MILP transportation model ([Cerdea et al., 1983](#); [Jain et al., 2012](#)). A heat exchanger network can be synthesised for each separation sequence. Binary variables are introduced to make discrete decisions for each match between rows and columns of the matrix. Closed cycle heat pumping is also taken into account in this optimisation to divert heat to above ambient cooling water to further achieve energy savings when a sub-ambient utility media is required ([Kiss and Infante Ferreira, 2016](#); [Farrokpanah, 2009](#)).



**Figure 1.** Superstructure for the optimisation of distillation sequences (Smith, 2016)

		Row: available heat sinks					
		R1	R2	R3	CU1	CU2	...
Column: available heat sources	C1	0	1	1	1	0	
	C2	0	0	1	1	0	Feasible match
	C3	0	0	0	1	0	Infeasible match
	HU1	0	1	1	0	0	
	HU2	1	1	1	0	0	No match between utilities
	⋮						

**Figure 2.** Heat integration model embedded into superstructure

### 3.3 Design variables and interactions

To eliminate the assumptions on key design decision variables in the previous literature, the proposed approach allows adjustment of the column pressure, condenser type, reflux scale-up, reflux ratios, feed conditions, and complex column options, together with heat integration opportunities to achieve an integral optimisation and find the optimum operating conditions, as listed in Table 1.

- Sequence number. Each sequence number represents a different order of separation tasks, the optimisation of which can lead to different outcomes. For example, heuristic rules suggest doing the most difficult separation last, because a difficult separation requires a high reflux ratio. However, the most difficult separation can also be carried out earlier. This is because separating the most difficult binary pair in the presence of non-critical components greatly increases the vapour and liquid flow rates in the column and correspondingly increases the energy required for separation. However, when the relative volatility is small between a binary pair, the relative volatility between the components can be enhanced by the addition of a third component to increase the relative volatility between the close boiling binary pair through differential molecular interactions. The relative volatility between the components is not constant throughout the separation, and is influenced by the change of mixtures to separate and by the change of conditions. Of these opposing effects, whichever is dominant depends on the details of the individual separation, and thus an optimisation is needed to find the best conditions.

**Table 1.** Key decision variables (degrees of freedom) in the distillation sequence optimisation

Type	Variables	Constraints / Bounds
Integer variables	Sequence number	n/a
	Column merge (to form complex columns)	n/a
	Column merge type	n/a
	Condenser type	Total or Partial
	Side stream quality	Liquid or Vapour
	Number of stages	n/a
	Feed stage	n/a
Continuous variables	Column feed pressure	1bar – 0.95×feed critical pressure
	Column feed quality	0 – 1
	Reflux ratio	n/a
	Column pressure	n/a

- For column pressure, an increase in the column pressure increases the stream (column distillate or bottom product) temperatures. If a stream that needs to be condensed is only matched by a low-temperature refrigerant, increasing the column operating pressure may be optimized to increase the temperature so that cooling water can be used instead. Thus, the operating pressure can be determined to match the available utilities or the hot and cold utilities for the condenser and reboiler can be assigned for fixed pressure. In addition, the change of operating pressure should be optimized together with heat integration. Heat integration by closed-loop heat pumps is used simultaneously to investigate its association with the sequence energy efficiency.
- For reflux ratio and reflux scale up (the ratio between the actual reflux ratio and the minimum reflux ratio): reflux ratio not only affects the individual column, but also impacts heat integration by affecting condenser and reboiler duties. The relative volatility varies accordingly with the column pressure. In this study, we assume the reflux scale up to be 1.1.



- For condenser type and feed conditions: either partial or total condensers are selected. The feed conditions (including pressures, temperatures and feed quality) for each column are optimized, and are considered independently of the column pressures, depending upon the permitted feed quality, which could be sub-cooled, two phase or super-heated. No additional pressure drop is considered for any feed stream heat exchangers.

### **3.4 Process optimisation**

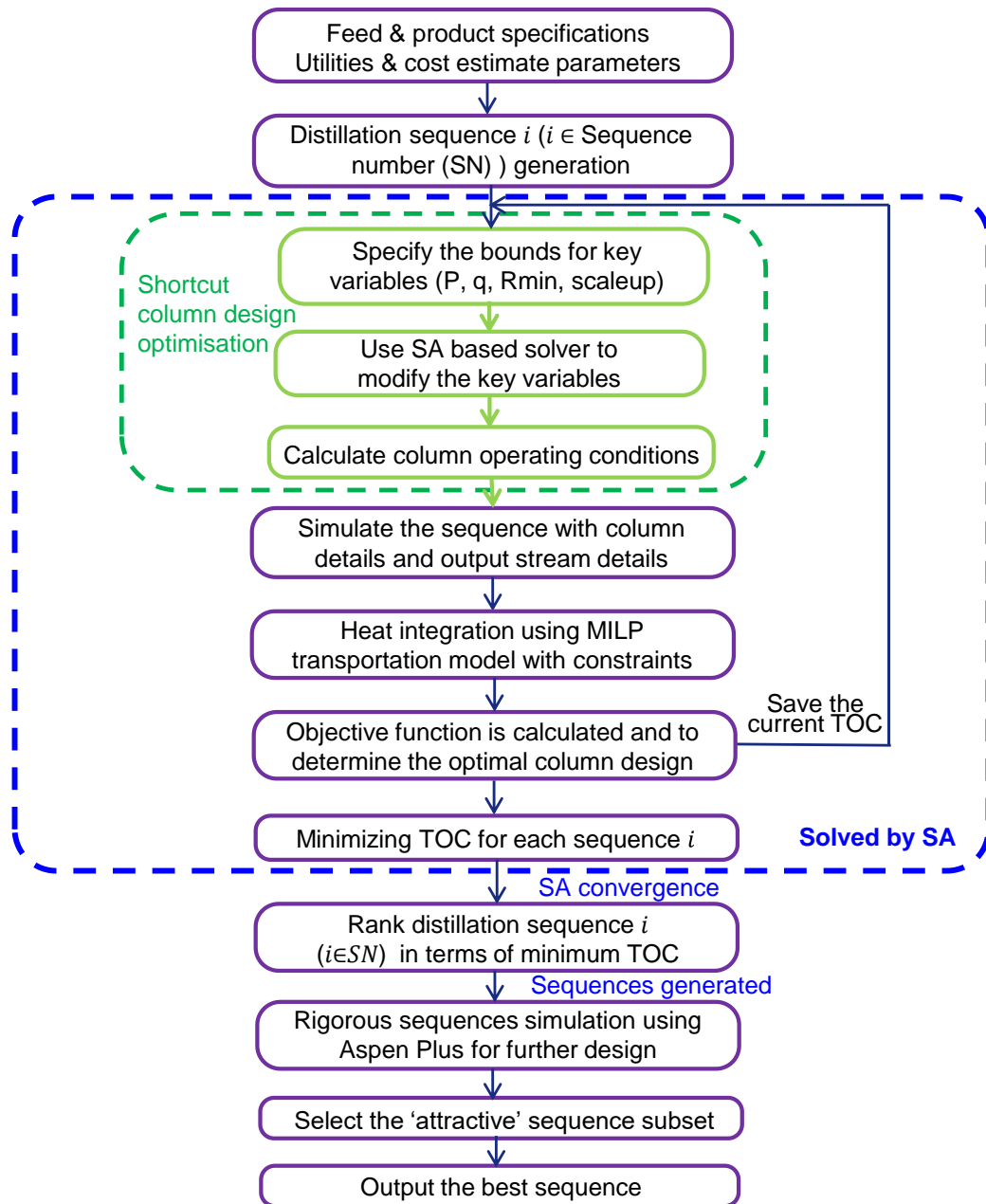
#### *3.4.1 Optimisation approach*

In this work, a decomposition method is proposed to solve this complex optimisation problem, as shown in Figure 3. For the given feed mixtures, distillation sequences are first generated by the proposed superstructure with defined operating conditions. The key decision variables are specified within their bounds and are then optimized by the optimizer to design the distillation columns in sequences using the shortcut models. The sequences with specific design operating conditions are then generated with column details and the stream details are then outputted for heat exchanger network synthesis. The outputs of stream temperatures, heat capacities, heat integration opportunities are explored, and the optimal heat exchanger network structure is conducted in terms of the energy target. Heat exchangers are assumed to connect in parallel without a series of exchangers in an individual stream, which means that multiple exchangers acting as a condenser or reboiler have the same inlet and outlet temperatures, i.e. for a total condenser,  $T_{in} = T_{dew}$ ,  $T_{out} = T_{bub}$ . Heat exchangers connecting in parallel also avoids the high non-linearity introduced by the intermediate temperature because of the log mean temperature difference (LMTD) calculation for each HEX in the series. The shortcut distillation model equations are embedded in a column sequence simulator, rather than the optimizer, with operating conditions adjusted by the optimizer. The overall decomposed simulation-based optimisation is achieved using a mixed-integer linear programming (MILP) formulation inside the Simulated Annealing (SA) algorithm.

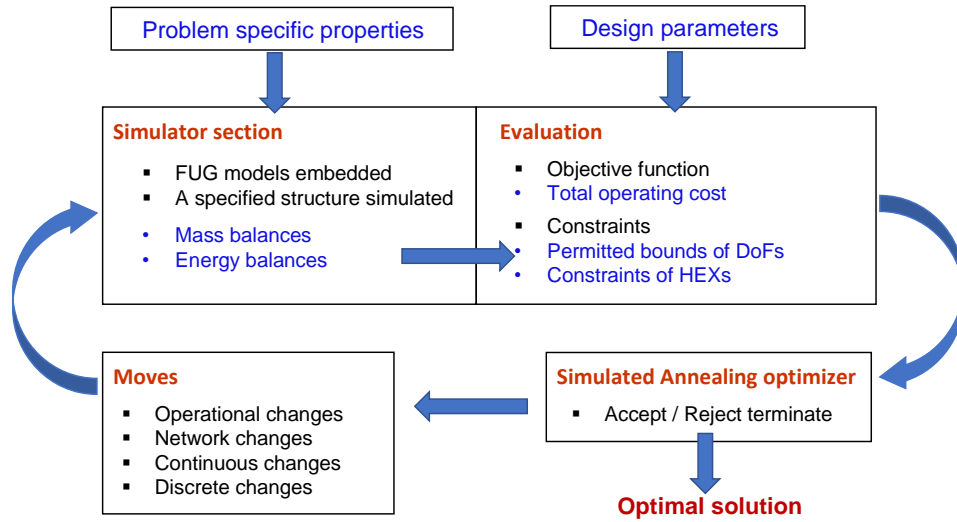
The optimisation framework is given in Figure 4. The SA optimizer creates ‘moves’ in the optimisation that allow for changes in the distillation structure (e.g. changing two adjacent

column tasks to be a complex column task) and the decision variables (e.g., P, q, Rmin, reflux scale-up) within their permitted bounds. They are taken as inputs for the shortcut distillation models. After each move, the sequence is then simulated, the objective function is evaluated, constraints violation checked, HEN designed, and the corresponding total operating cost is estimated. The objective function value is then sent back to the optimizer. The optimisation method then changes the decision variables and repeats the process until convergence is obtained, based on annealing parameters. A hierarchy of sequences can be determined by repeating the optimisation using additional constraints to reject any previous solutions. This hierarchy can be used to identify promising sequences that can be further evaluated. The annealing parameters used are: random number generator seed (2); initial and final annealing temperatures ( $10^9$  and  $10^{-8}$ ); Markov chain length (70); maximum iterations (25,000); maximum consecutive failed chains (10); maximum unsuccessful moves (300); cooling parameter ( $5 \times 10^{-3}$ ) and move acceptance criterion (Metropolis).

The objective function of the optimisation in this work is the minimum operating cost, which is directly proportional to the energy used in the process. A fair question at this point is: why not the total annual cost? This is because taking into account the capital cost requires using the same correlations for both simple and complex columns, without any inconsistencies. There are no generally accepted simple capital cost correlations available for different complex column arrangements to allow a consistent comparison. Another problem is that of using the annualized capital cost to obtain a total annual cost. For example, assuming an annualization of 5 years versus 10 years will give a completely different balance between capital and operating costs. Thus, simply adjusting the annualization factor can lead to different results in the optimisation. Whilst we can be reasonably scientific about utility costs, which are directly proportional to the energy used in the process, capital cost cannot be dealt with in the same rational way. When the capital costs need to be taken into account, the top results of the optimal designs (minimal TOC) can be considered by adding also the annualized capital costs and then checking the total annualized costs to see if the ranking changes. For the sake of completeness, a rough indication of the total investment cost - estimated using the IChemE method ([Gerrard, 2000](#)) - is also provided for the optimal distillation sequences.



**Figure 3.** Framework of the optimisation method for distillation sequences design



**Figure 4.** Framework for Simulated Annealing optimisation procedure

### 3.4.2 Design specifications

The options used in the optimisation calculations are shown in Table 2. The separation is assumed to be sharp split. Liquids and gases are pressurized by pumps and multistage-compressors and depressurized by valves and turbo expanders. The flowchart of the models of multistage-compressors and turbo expanders are given in Appendix A.

**Table 2.** Design specifications in the optimisation calculations

Parameters	Value / unit
Heat transfer coefficient in the reboiler and condenser	600 W/m <sup>2</sup> K
Minimum temperature difference	10 °C
Ambient temperature	20 °C
Sub-ambient minimum temperature difference	4 °C
Default feed quality	q = 1
Compressor maximum size	20,000 kW
Maximum compression ratio P <sub>out</sub> /P <sub>in</sub>	5
Isentropic efficiency	87%
Liquid pump efficiency	90%
Refrigeration critical pressure fraction	0.8
Annual operating hours	8400 h
Pressure decreasing in columns	0 bar

### 3.4.3 *Optimisation tool*

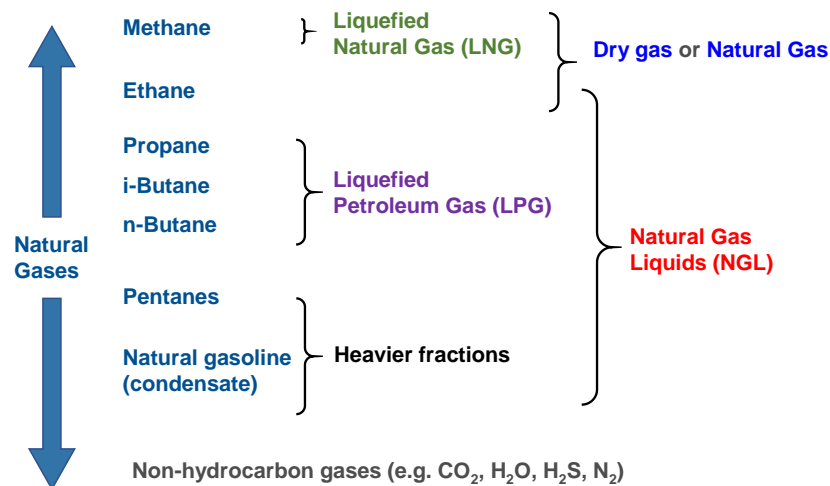
This optimisation methodology can be carried out within the ColSeq software developed and available at the Centre for Process Integration of The University of Manchester ([CPI Suite, 2022](#)). This stores the “best” N sequences with the ability to ignore similar structures so that a set of promising sequences can be identified for further evaluation, which can reduce the effects of inaccuracy led by shortcut design models. To the best of our knowledge, the ColSeq software is one of the most advanced available for this task. It can be used not only for process optimisation but also for the simulation of each distillation column unit, which closes the gap where previous algorithms did not provide unit operations that were accepted by process engineers in the chemical industry ([Franke, 2019](#)). All complexity options have been included in the process synthesis and optimisation panel, e.g. total or partial condenser, feed quality optimisation, reflux ratio optimisation, pre-fractionator recovery optimisation, pressure optimisation, multi-stage intercooled compressors, closed cycle heat pumping, dephlegmators, side-strippers, side-rectifiers, (thermally coupled) pre-fractionators, sloppy pre-fractionators, and also dividing-wall columns. These are all optimized simultaneously and systematically. It is the only software we are aware of that is capable of achieving this feat.

## 4. **Case study: Natural Gas Liquids separation**

As the energy use of industry and society moves to a more sustainable basis, it is projected that there will be a significant reduction in the use of coal and oil, but a significant growth in the use of natural gas. The International Energy Agency projects that between 2017 and 2040 there will be a 44% increase in the use of natural gas ([IEA, 2018](#)). This growth will be realized by a significantly greater proportion of the natural gas being traded as liquefied natural gas. The raw natural gas typically contains a small, but economically very significant, portion of heavier hydrocarbons. The heavier hydrocarbons have a value significantly greater than the methane as chemical plant and refinery feedstock, and as liquid fuels. These heavier components are separated from the predominantly methane fuel gas as Natural Gas Liquids (NGL), as defined in Figure 5, composed of ethane, propane, i-butane, n-butane, and a gasoline fraction (pentane and other heavier components). The NGL fractionation is one of the most energy-demanding processes in the oil and gas industry. Once the NGL mixture

is recovered from the natural gas stream, it must be separated into relatively pure components to be useful.

The NGL fractionation process typically uses a train of four distillation columns that separates in the order of 2.5 million tons per year of NGL feed, requiring approximately 77 GJ per barrel (0.4 MJ/liter) energy, and is equivalent to 4.65 tons of CO<sub>2</sub> emissions per barrel (Manley, 1998). Considering the massive scale of operations in NGL fractionation (e.g. 100,000 BPD for a single plant), any energy savings are important and would contribute to fewer greenhouse gas (GHG) emissions because of long-term pressure to move energy production to a more sustainable basis.



**Figure 5.** Difference between NGL, LNG, LPG and NG

Although many improved conceptual designs of NGL recovery processes have been introduced to date to enhance the economics and efficiency (Tamuzi, 2020; Yoo et al., 2016), these designs are still much more complex and far from suitable for industrial practice (Qyyum et al., 2022). Qyyum et al. (2022) also carried out an assessment of the NGL recovery processes to provide references and help process design engineers choose conceptual design for further enhancement. Overall, there are still significant improvements that can be made for the synthesis of energy-integrated distillation sequences.

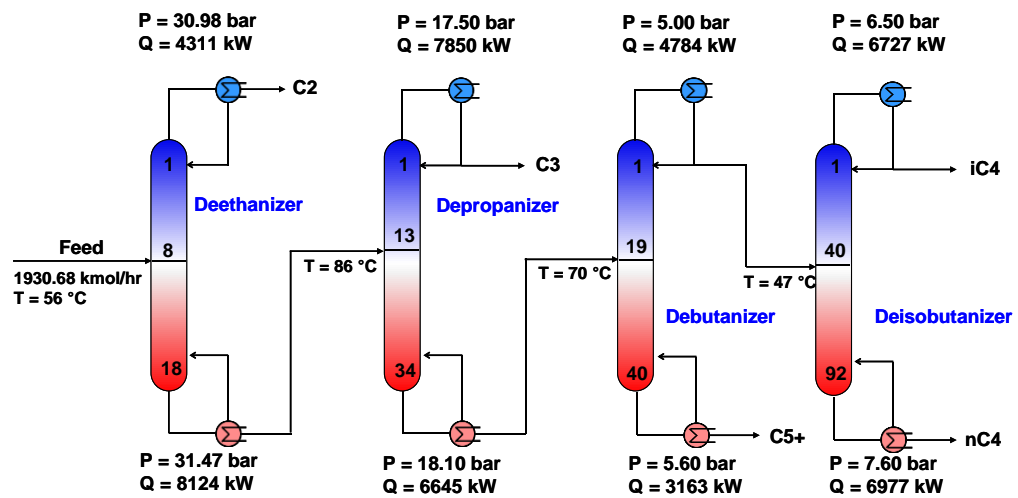
The design details of the conventional NGL fractionation process given in Figure 6 are the rigorous simulation results obtained from Aspen Plus, based on the reported data in the

literature (Manley, 1998; Long et al., 2016). The feed composition is the same as in our current study, and the feed is fed at saturated liquid (56°C at 31.18 bar). In this study, the details of the feed composition and properties of the components that are involved (see

Table 3) are taken from Long et al. (2016). The feed stream considered in this work is fed at 41.36 bar as saturated liquid, with a temperature of 85 °C. The feed flow is chosen to be 1.7641 kmol/s (which is equivalent to 100,000 BPD). The relative volatility of the feed at these conditions is shown in Table 4. It can be observed that the most difficult separation is between i-butane and n-butane. Several utilities are used for heating, cooling, and refrigeration, as listed in Table 5. The prices of utilities are taken from Turton et al. (2018).

There are 5 product streams with various recoveries (given in %, listed in Table 6) taken from Long et al., (2016). It is assumed that demethanization (separation of methane and later components) has already taken place.

- *Product A* – ethane (94.57% recovery), propane (4.96%) and methane (100%)
- *Product B* – propane (94.97%), ethane (5.43%), i-butane (7.44%)
- *Product C* – i-butane (83.62%), propane (0.07%) and n-butane (0.27%)
- *Product D* – n-butane (98.93%), i-pentane (3.11%) and i-butane (8.94%)
- *Product E* – i-pentane (96.89%), n-butane (0.8%), n-pentane (100%), C6&C7 (100%)



**Figure 6.** NGL fractionation in a conventional process (Manley, 1998; Long et al., 2016)

**Table 3.** Feed and product compositions in percentage of liquid volume (Long et al., 2016)

Component	n.b.p. (°C)	Feed mol%	Ethane (A)	Propane (B)	I-butane (C)	N-butane (D)	Gasoline (E)
Methane	-161.5	0.5	1.36				
Ethane	-88.5	37.0	95.14	7.32			
Propane	-42.2	26.0	3.50	90.18	2.00		
i-Butane	-11.7	7.2		2.50	96.00	4.50	3.00
n-Butane	-1.0	14.8			2.00	95.00	
i-Pentane	27.8	5.0					33.13
n-Pentane	35.9	3.5				0.50	23.52
n-Hexane	68.5	4.0					26.90
n-Heptane	98.3	2.0					13.45

**Table 4.** Relative volatilities calculation examples for the NGL feed

	Component	Relative volatilities
C1	Methane	372.98
C2	Ethane	101.55
C3	Propane	38.66
i-C4	i-Butane	19.16
n-C4	n-Butane	14.78
	i-Pentane	7.26
	n-Pentane	5.88
C5+	n-Hexane	2.39
	n-Heptane	1.00

**Table 5.** Heating and cooling utilities used in the NGL fractionation (Turton et al., 2018)

Utility	Supply T (°C)	Return T (°C)	Price (\$/GJ)
HP steam	255	254	5.66
MP steam	185	184	4.77
LP steam	161	160	4.54
Cold water	20	25	0.378
Chilled water	5	15	4.77
Refrigerant 1	-21	-20	8.49
Refrigerant 2	-51	-50	14.12
Electricity	-	-	18.72



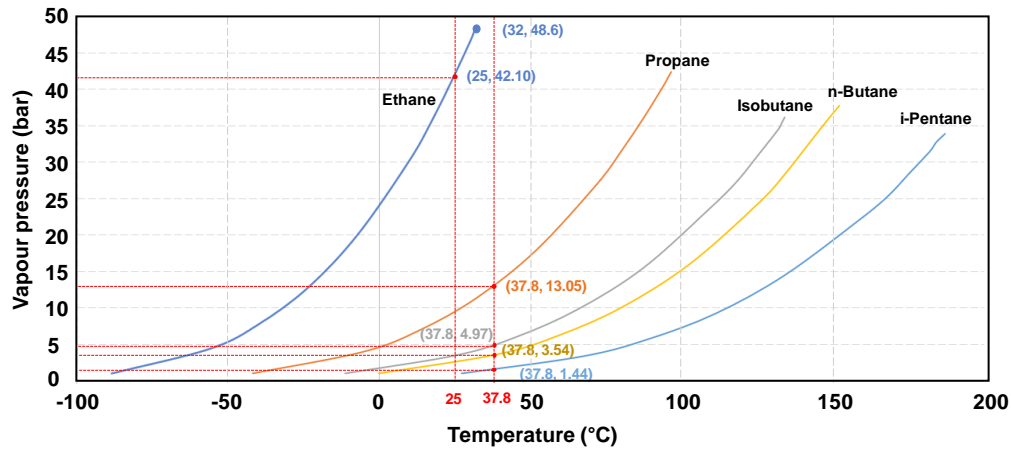
Product storage conditions are well considered in this study. All products are obtained in the liquid phase with the pressure at 3.5 bar (50 psi) above respective vapour pressure: Ethane at a temperature of -30°C, 14.16 bar; Propane at 38°C, 16.55 bar; i-Butane at 38°C, 8.47 bar; n-Butane at 38°C, 7.04 bar; Condensate at 38°C, 4.94 bar ([GPSA Standard 2140](#); [GPSA Engineering Data Book, 2017](#)). Figure 7 shows the vapour pressure – temperature profile for pure ethane, propane, isobutane, n-butane and i-pentane products taken from Aspen Plus.

**Table 6.** Component recoveries (%) in NGL products

Component	Ethane	Propane	i-Butane	n-Butane	Gasoline	Recovery
Recoveries %	product	product	product	Product	product	sum
Methane	100					100
Ethane	94.57	5.43				100
Propane	4.96	94.97	0.07			100
i-Butane		7.44	83.62	8.94		100
n-Butane			0.27	98.93	0.8	100
i-Pentane				3.11	96.89	100
n-Pentane					100	100
n-Hexane					100	100
n-Heptane					100	100

For optimisation, there are 14 possible sequences of 4 simple columns (counting from S1=direct to S14=indirect, as listed in Figure 1) when fixing the topology of the base sequence in each case. Afterwards, the complex cases are optimized from the same simple starting point and defaults, leading to another set of 14 sequences (C1 to C14) generated for a mixture of 5 products. These sequences are generated by three optimisation routes: 1) sequences without heat integration; 2) heat integrated sequences based on Pinch Analysis; and 3) heat integrated sequences with heat exchanger network design. The optimisation is carried out using a desktop PC with *CPU - Intel(R) Core i7-10700 CPU 2.90GHz* (8 cores), with an average time resource of 19 hours. (The sensitivity analysis of the SA parameters shows that the computational time increases with the increase in the Markov chain length,

for example, with the Markov chain length of 100, the computational time goes to ~30 hours, but the results in terms of TOC ranking in this study remains the same)

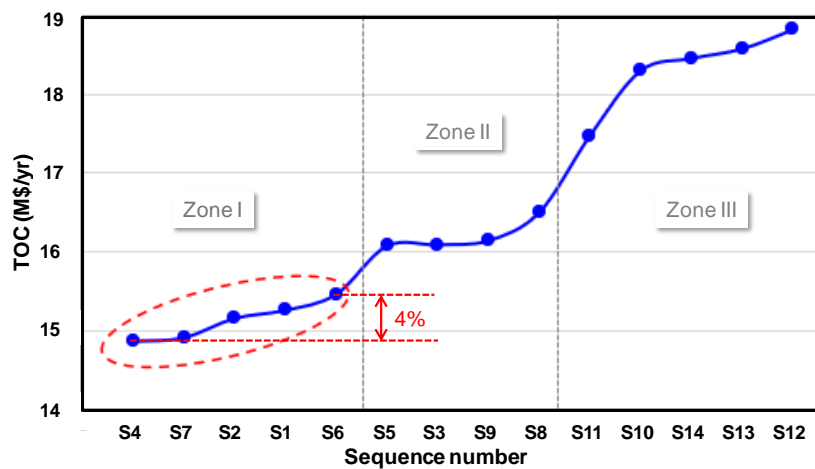


**Figure 7.** Vapour pressure – Temperature profile for NGL products

## 5. Results and discussion

### 5.1 Optimisation results evaluation and analysis

A series of optimisations was carried out to explore the optimal arrangement for the NGL separation. Firstly, the non-energy integrated sequences are carried out by optimizing the operating design variables using simple columns. Figure 8 provides the total operating cost rankings of the 14 sequences in descending order. Taking into account the actual operating conditions and the operational flexibility, the best few sequences should be kept for further detailed design rather than the best single sequence (Smith, 2016).



**Figure 8.** Total operating costs ranking of simple column sequences

In this case, the first sequence family, which are the 5 top ranked sequences (Zone-I), are considered the most economically attractive sequence family identified by the screening method based on shortcut models. To evaluate the performance of these proposed sequences and the ability to find reliable economically attractive sequences with the shortcut-based screening method, the simple column sequences are validated by rigorous simulations carried out using the Aspen Plus RadFrac model, with the short-cut design details (reflux ratio, trays, condenser temperatures and distillate rate) extracted as the initialization parameters for the rigorous simulations. Defining the best few sequences within a 10% difference in the total operating costs as the most economically attractive sequences subset (Ramapriya et al., 2018), S7 is the most economically attractive sequence identified by rigorous simulations, followed by S6 and then S4. It should be noted that in the economically attractive S6, the most difficult pair to separate, C/D, is not separated as a binary pair, but is separated as C/DE. This is because the presence of other components increases the relative volatility between the key components, making the separation between the close boiling binary pair easier, and reducing the energy required. When getting benefits from the presence of other non-key components, the column pressure should not be very high as increasing column pressure decreases the relative volatilities. The column pressure of the C/DE column is 4.62 bar.

Table 7 provides details of the rigorous simulation results and a comparison with the shortcut methods of sequence 7 as an example. Additional information on the real relative volatility ( $\alpha$ ) values at the top and bottom stage of the columns by rigorous simulations versus the geometric mean  $\alpha$  in shortcut models of sequence 7 is provided in Table 8, which shows the actual variation of the  $\alpha$  across stages. The relevant details of sequence 6 and sequence 4 can be found in

**Appendix B.** The three most promising sequences identified by rigorous simulations have all been preselected within the attractive families by the pre-screening based on the developed approach, indicating that despite the deviation between shortcut and rigorous models, the developed fast screening method using shortcut models is validated. The following comparisons are given based on the developed screening results.

**Table 7.** Comparison between shortcut models and rigorous simulation results of sequence

7

	Column 1		Column 2		Column 3		Column 4	
	(AB/CDE)		(A/B)		(CD/E)		(C/D)	
	SC*	R*	SC	R	SC	R	SC	R
Vapour fraction	0.39	0.39	0.98	0.98	0.65	0.65	0.99	0.99
Pressure (bar)	21.28	21.28	17.15	17.15	4.61	4.61	4.62	4.62
T <sub>feed</sub> (°C)	51.44	51.04	21.49	22.26	68.22	67.94	44.36	44.34
Condenser type	Partial		Total		Partial		Total	
T <sub>conden</sub> (°C)	30.2	31.0	-17.0	-17.0	44.4	44.4	34.4	34.9
T <sub>reb</sub> (°C)	133.2	132.9	43.3	43.7	97.7	97.2	47.1	47.1
Condenser duty								
(MW)	18.78	16.31	20.36	22.63	10.30	10.52	25.29	26.75
Reboiler duty (MW)	30.16	27.73	5.91	8.04	10.03	10.23	18.51	20.14
Minimum reflux ratio	0.94	-	1.36	-	1.22	-	11.86	-
Reflux ratio	1.22	1.05	1.59	1.88	1.50	1.56	13.15	13.97
Number of stages**	39	39	15	15	27	27	67	67
Feed stage**	9	9	9	9	13	13	51	51

Note: \* SC refers to shortcut models, R refers to rigorous model; \*\* Theoretical stages

**Table 8.** Comparison between real relative volatilities\* versus the geometric mean  $\alpha$  in the shortcut models of sequence 7

	Column 1		Column 2		Column 3		Column 4	
	(AB/CDE)		(A/B)		(CD/E)		(C/D)	
	SC	R	SC	R	SC	R	SC	R
Top stage	1.98	2.08	3.65	3.62	2.22	2.13	1.34	1.34
Bottom stage	1.46	1.49	2.46	2.47	1.87	1.89	1.33	1.33
Log mean $\alpha^{**}$	1.70	n/a	3.00	n/a	2.04	n/a	1.34	n/a

Note: \* Real relative volatilities between LK and HK components at the top and bottom stage of the columns generated by rigorous simulations; \*\* Log mean  $\alpha = (\text{top } \alpha \times \text{bottom } \alpha)^{-0.5}$

## 5.2 Energy integrated distillation sequences

Energy intensified sequences using complex columns and heat integration bring significant energy benefits. Table 9 provides the TOC comparison between non-heat integrated simple and complex columns. It shows that all the non-heat integrated simple sequences benefit, in terms of total operating cost savings, from introducing complex columns within the range of 7-21%. The sequence with the lowest TOC is now the complex sequence 6, which separates isobutane by a side rectifier, followed by two simple columns separating ethane/propane and n-butane/C5+, with the TOC of 12.78 M\$/yr. Compared with its corresponding simple sequence S6, the requirement of the refrigerant remains the same, but the reboiler duty (LP steam requirement) decreased from 68 MW to 51 MW, and the condenser duty (required of cooling water) decreased from 59 MW to 37 MW.

**Table 9.** Cost comparison between non-heat integrated simple and complex columns (with breakdown costs in Appendix D)

Seq. No.	Simple sequences		Complex sequences		TOC Savings %
	TOC (M\$/yr)	TIC* (M\$/yr)	TOC (M\$/yr)	TIC* (M\$/yr)	
1	15.26	5.05	12.79	5.49	16%
2	15.15	6.10	12.97	4.13	14%
3	16.09	5.72	14.82	4.40	8%
4	14.86	5.00	12.79	5.49	14%
5	16.07	6.68	14.27	6.33	11%
6	15.46	6.35	12.78	5.53	17%
7	14.91	6.23	12.78	5.50	14%
8	16.50	7.57	14.78	10.65	10%
9	16.14	9.20	12.78	5.56	21%
10	18.30	7.81	15.01	4.54	18%
11	17.47	8.34	16.28	7.62	7%
12	18.82	9.21	15.50	11.26	18%
13	18.58	7.71	14.84	4.51	20%
14	18.46	10.66	15.88	11.02	17%

\* **Note:** TIC is the annualized total investment cost, estimated relative to the end of year 2021 (CEPCI index = 776.9), assuming a loan repayment period of 10 years and interest rate of 5%

To achieve further energy savings, heat integration is applied, achieved by optimizing the heat exchanger network with column operating conditions simultaneously for both simple and complex sequences. Table 10 lists the optimal heat integrated column sequences based on simple (S) and complex (C) columns. The total operating cost saving brought by heat integration on the optimized non-heat integrated simple columns is up to 26%, and the operating cost saving from optimizing both heat integration and complex columns can achieve up to 38%. It should be noted that the heat integration between heat sources and heat sinks used for the sequences in this table is constrained such that each source of heat was matched with a maximum of two heat sinks and each heat sink was matched with a maximum of two heat sources. This constraint avoids the heat exchanger network becoming overly complex. Removing the constraint will decrease the utility cost at the expense of increased capital cost. However, the increase in capital cost will not be reflected accurately in approximate capital cost estimation methods used for calculation. Restricting the heat sources and sinks to a maximum of two matches is considered to be a practical constraint for the majority of cases.

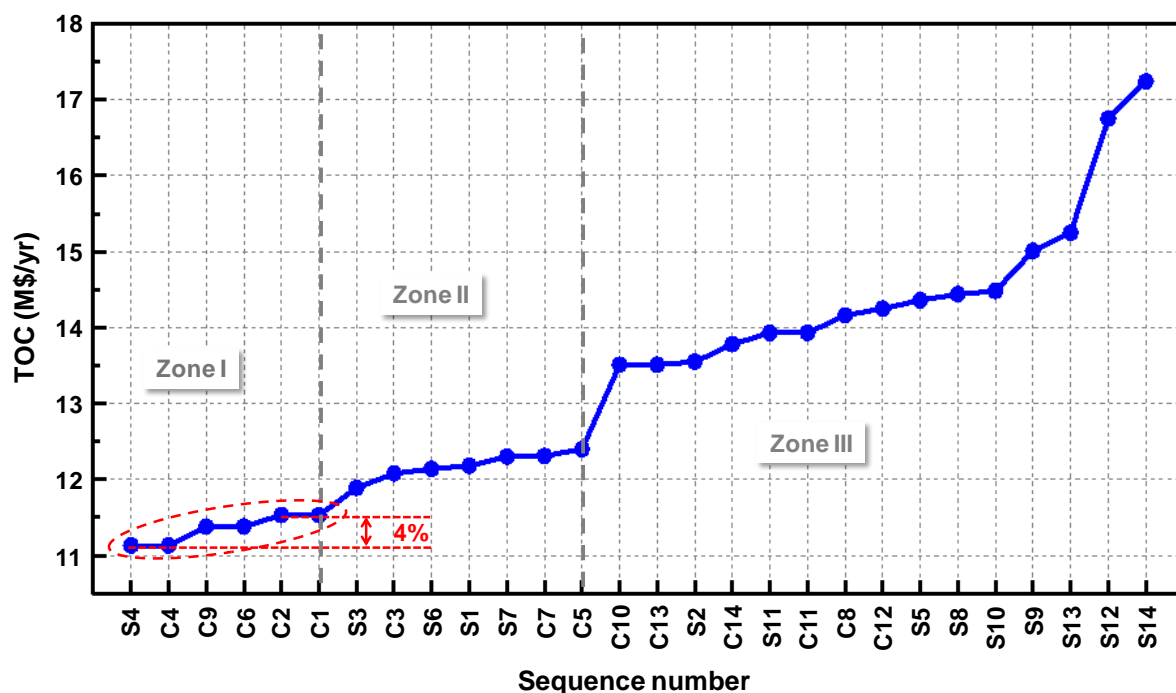
Figure 9 shows the overall ranking of heat integrated simple and complex column sequences in terms of total operating costs. Simple sequence 4 is ranked the best (with the detailed design in Figure 10) when optimizing heat integration and complex column arrangements, with the total operating cost of 11.13 M\$/yr, and a 25% total operating cost saving is achieved compared to the optimum non-heat integrated simple sequence, as shown in Figure 11 and Figure 12. Based on the results, simple column sequences benefit to a larger extent from heat integration compared to complex column sequences, which can achieve an average energy saving of 16% by introducing heat integration, but complex columns gain an average 11% energy saving compared to the optimum non-heat integrated complex columns sequences in this case study. This is because complex columns reduce the number of design degrees of freedom compared with the non-combined two adjacent simple columns, for

example, the column pressures do not need to be the same for two simple columns if they are not to be merged into one complex column. Complex columns therefore lose some potential heat integration possibilities after merging simple columns as the combination of heat sinks and sources are constrained. The potential benefits of lower capital costs that could be obtained from using complex columns are not taken into account in the optimisation (which focused on minimizing TOC), as the capital costs may not be reflected accurately using cost correlations methods. Nonetheless, the potential advantages in terms of capital cost can be also evaluated based on the additional TIC data provided in Table 10 for each of the optimal sequences.

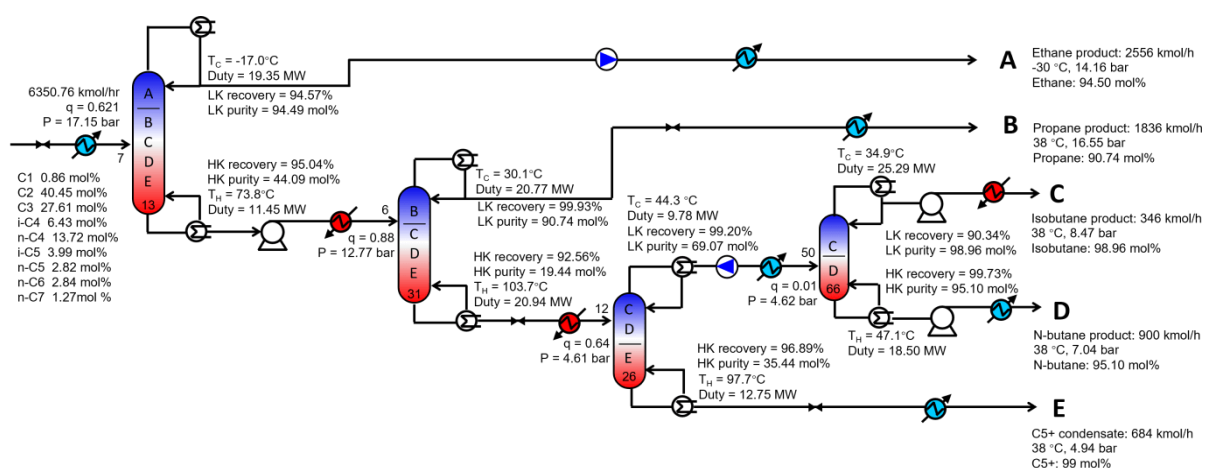
**Table 10.** Optimal column sequences based on simple (S) and complex (C) columns

Seq.	Rate <sub>vap</sub> (kmol/s)	TOC (M\$/yr)	Sav <sup>1</sup> (%)	TOC Ranking	Sav <sup>2</sup> (%)	TIC* (M\$/yr)
S1	6.51	12.18	20%	10	n/a	14.25
S2	6.61	13.55	11%	16		14.32
S3	6.56	11.89	26%	7		14.72
S4	4.83	11.13	25%	1		5.68
S5	4.21	14.36	11%	22		8.12
S6	5.08	12.14	22%	9		9.56
S7	5.09	12.30	17%	11		6.78
S8	5.06	14.44	12%	23		9.12
S9	6.64	15.01	7%	25		14.07
S10	6.50	14.48	21%	24		11.99
S11	7.43	13.93	20%	18		20.64
S12	5.41	16.75	11%	27		9.46
S13	6.05	15.25	18%	26		12.55
S14	5.37	17.24	7%	28		10.48
C1	3.69	11.54	10%	6	5%	4.36
C2	3.76	11.53	11%	5	15%	4.28
C3	3.69	12.08	18%	8	-2%	5.98
C4	4.84	11.13	13%	1	0%	5.68
C5	4.93	12.40	13%	13	14%	6.98
C6	3.87	11.38	11%	3	6%	5.49
C7	5.10	12.30	4%	11	0%	6.78
C8	5.92	14.16	4%	20	2%	11.62
C9	3.84	11.38	11%	3	24%	5.47
C10	5.38	13.51	10%	14	7%	10.04
C11	7.43	13.93	14%	18	0%	20.64
C12	4.43	14.25	8%	21	15%	11.45
C13	5.38	13.51	9%	14	11%	10.04
C14	4.38	13.78	10%	17	20%	7.30

**Note:** Sav<sup>1</sup> (%) represents the savings of the heat integrated sequences compared to the non-heat integrated sequences, while Sav<sup>2</sup> (%) represents the savings of heat-integrated complex sequences compared to the heat-integrated simple sequences. TIC is the annualized total investment cost, estimated relative to the end of year 2021 (CEPCI index = 776.9), assuming a loan repayment period of 10 years and interest rate of 5%.



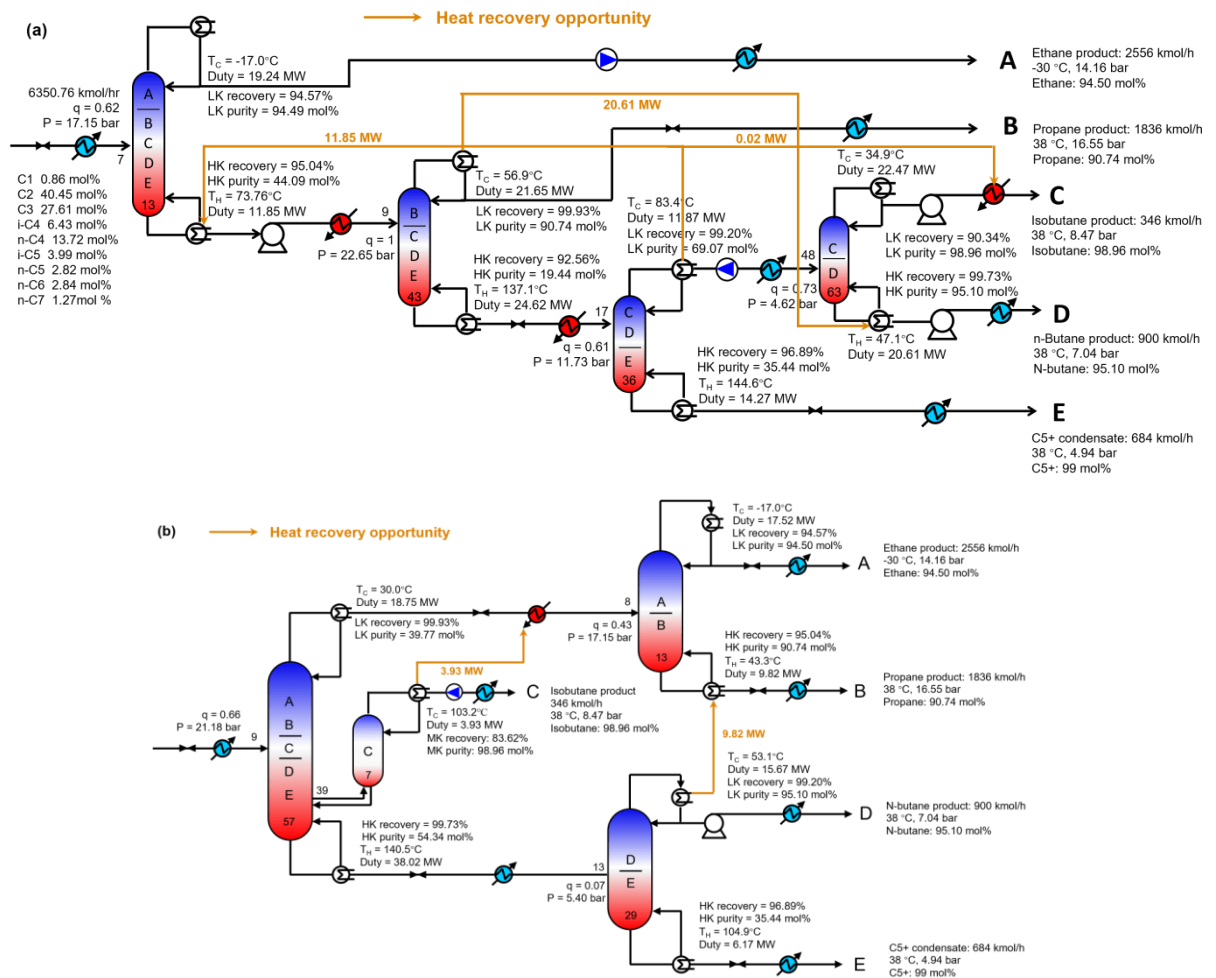
**Figure 9.** Sequence rankings of simple and complex columns in terms of total operating cost

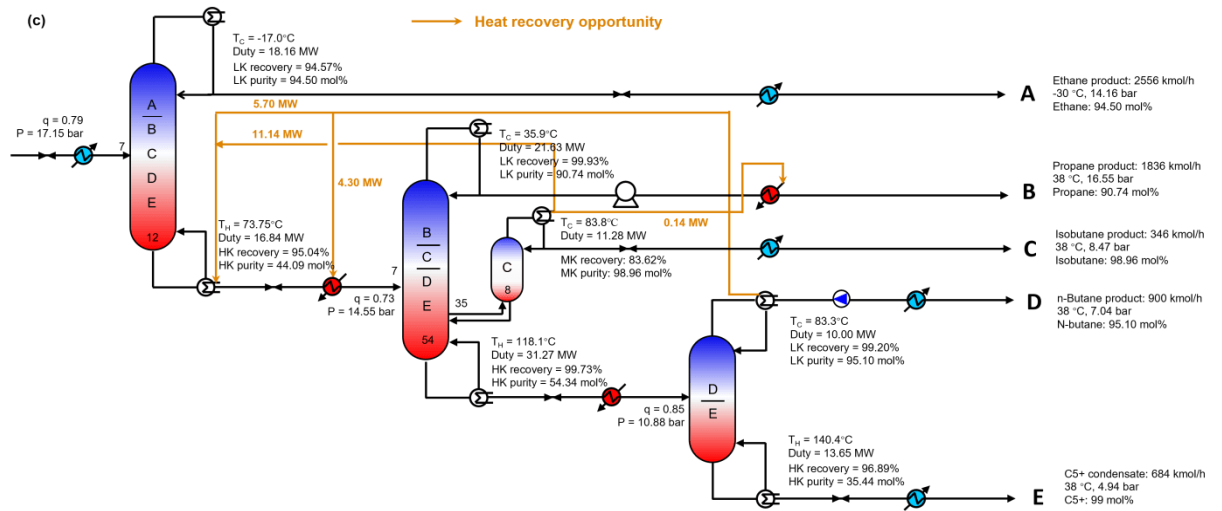


**Figure 10.** Optimised operating conditions of the non-heat integrated simple sequence 4



The top 6 sequences with rather small operating cost differences (within 5%) are considered the most economically attractive sequence family. This most economically attractive sequences family remains the same, even when TIC is also factored in along with the TOC. It should be noted that when introducing heat integration, applying complex columns cannot provide benefits for sequence 4, and thus the optimum design for S4 and C4 are the same. The final designs of heat integrated C6 and C9 are the same, C1 and C2 are the same, by merging different columns in S6 and S9; S1 and S2. Overall, the recommended economic attractive sequences for the NGLs fractionation process in terms of total operating cost are, in order: S4 (C4), C6 (C9), and C1 (C2). The optimum configurations with design details of these three sequences are shown in Figure 11. Depending on the parameters used for optimisation, there might be slight changes in the ranking of these sequences. It is worth noting that the complex distillation sequences proposed involve indeed highly integrated thermally coupled columns or dividing-wall columns, but these can be effectively well controlled provided that an appropriate control structure is used (Kiss and Bildea, 2011).

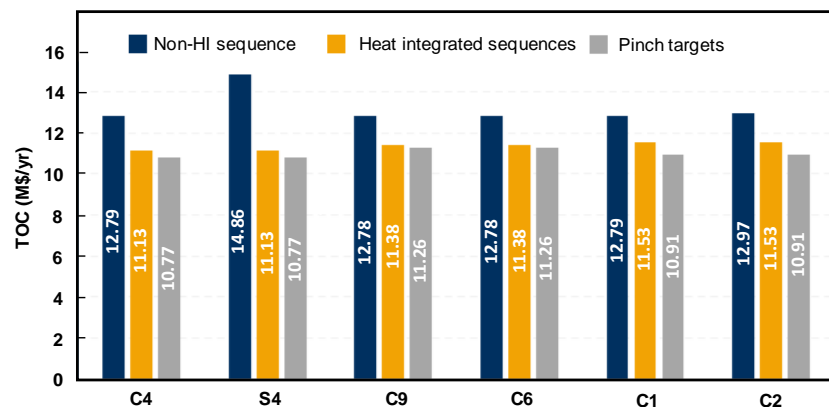




**Figure 11.** Details of the Top 3 attractive distillation sequence designs (a) S4, (b) C9, (c)

C2

In order to compare the difference between the heat integration achieved by actual heat exchanger network design and the Pinch Analysis targets, the heat integration of simple and complex sequences is also carried out. Figure 12 presents the operating cost details for the three most attractive heat-integrated sequences, and their non-heat integrated sequences, as well as the difference between heat exchanger network design with practical constraints and the heat integration targets achieved by Pinch Analysis. It should be noted that the column pressure will increase if process to process heat integration is introduced. For example, according to the operating details given in Figure 11, the pressures of column 2 (B/CDE) and 3 (CD/E) are increased from 12.77 bar to 22.65 bar and from 4.61 bar to 11.73 bar respectively, compared to the non-heat integrated column in order to achieve hot enough condenser temperatures to transfer heat to other heat sinks.



**Figure 12.** Comparison of total operating costs among different design scenarios

Overall, the design of S4 (Figure 11) is the best sequence and consists of a simple column that splits A/BCDE, followed by a simple column that separates B/CDE, and then two columns that separate CD/E and C/D, respectively, with heat integration opportunities. The design of C6 (Figure 11) is the next best and consists of a side-rectifier separating AB/C/DE, followed by two simple columns that splits A/B and D/E. Then is the design of C1 that consists of a simple column splitting A/BCDE, followed by a side-rectifier separating B/C/DE, and then another simple column separates D/E.

### 5.3 Sustainability metrics

The sustainability of the process can be evaluated using several metrics: material and energy intensity, water consumption, toxic and pollutant emissions, greenhouse gas (GHG) emissions – with lower values meaning better performance (Schwarz, et al., 2002). The following evaluations are carried out based on the best heat integrated distillation sequence S4 (C4).

- *Material intensity* expresses the mass of wasted materials per unit of output. In this separation process, there are five outlet streams, and all five are product streams. Therefore, there is zero kg waste in this process.
- *Energy intensity* represents the primary energy consumed per unit of output (i.e. per kg of all NGL products). The heat integrated process S4 and C4 requires total heating of  $41,786 \text{ kW} / 284,679 \text{ kg/h} = 0.15 \text{ kWh/kg NGL products}$  ( $0.53 \text{ MJ/kg NGL products}$ ) and total cooling of  $-55,330 \text{ kW} / 284,679 \text{ kg/h} = -0.19 \text{ kWh/kg NGL products}$  ( $0.70 \text{ MJ/kg NGL products}$ ).
- *Water consumption* expresses the amount of water used per unit of output. The temperature range from process to cooling tower is  $5 \text{ }^{\circ}\text{C}$ , from  $20 \text{ }^{\circ}\text{C}$  to  $25 \text{ }^{\circ}\text{C}$ . The cooling capacity of water is  $4.187 \text{ kJ/kgK}$ . The flowrate of CW is  $6052 \text{ m}^3/\text{h}$ . As water cooling is obtained by evaporation in cooling towers, the loss must be compensated by a make-up with fresh water. Following the 7% rule (Schwarz, et al., 2002), the total water loss is  $0.07 \times 6052 = 423.6 \text{ m}^3/\text{h}$  (or  $0.0015 \text{ m}^3/\text{kg NGL}$ ).
- *Greenhouse gas (GHG) emissions* expresses the total GHG emitted per unit of output. This amount is proportional to the energy used in the process. Based on the US-EPA-RULE-E9-5711 method, the  $\text{CO}_2$  emission factor given by Aspen Plus for

natural gas is  $5.589 \times 10^{-8}$  kg CO<sub>2</sub> / J, and the default CO<sub>2</sub> energy source efficiency factor is 1. Considering the energy intensity (0.53 MJ/kg NGL products), the specific CO<sub>2</sub> emissions are 0.030 kg CO<sub>2</sub> / kg NGL products, translated to 8,432.68 kg/h CO<sub>2</sub>.

## 6. Conclusions

The systematic screening approach developed in this study was successfully used for simultaneously optimizing sequence structures, accounting for all design degrees of freedom and heat integration in the distillation sequences. By optimizing the whole sequencing process, novel NGL fractionation sequences have been explored and ranked techno-economically. The generated economically attractive sequences (ranked by the operating costs) are shown to be comparable with those of rigorous simulations using the Aspen Plus RadFrac model. For a given feed composition and product requirements, the ranking of the designed energy integrated complex sequences for the NGL fractionation are listed, and the most energy efficient economically attractive sequence family has been selected. The best sequences in terms of total operating costs are presented, with total operating costs of 11.13, 11.38 and 11.53 M\$/yr, respectively, for a processed NGL feed rate of 6,350.76 kmol/hr (2,500 kton per year). These results demonstrate that screening of the search space of energy-efficient distillation sequences considering synthesis and optimisation of all the design degrees of freedom is achievable with the newly proposed approach.

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## Appendix A. Flow charts on the models of multistage-compressors and turbo expanders

### A.1 Multi-stage isentropic compressor

#### A.1.1 Inputs:

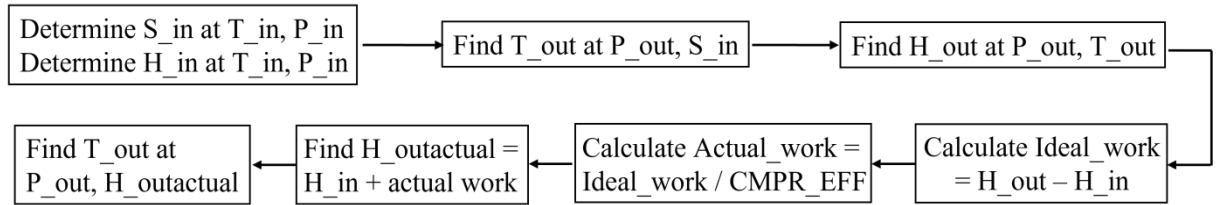
- 1)  $P_{in}$  / bar – inlet pressure
- 2)  $P_{out}$  / bar – outlet pressure
- 3)  $T_{in}$  / K – inlet temperature
- 4) Molar Composition (in molar fraction)
- 5) CMPR\_EFF – stage isentropic efficiency
- 6)  $Pr_{max}$  – maximum stage pressure ratio

#### A.1.2 Number of stages - $N_{stage}$

$$N_{stage} = \log(P_{out}/P_{in})/\log(Pr_{max})$$

$$Pr_{max} > (P_{out}/P_{in})^{(1/N_{stage})}$$

#### A.1.3 The flowchart of the method



If  $T_{out}$  for the stage  $> T_{ambient} + DT_{min}$ , then the vapour stream is cooled to  $T_{ambient} + DT_{min}$ .

$$P_{in\_stage}(n+1) = P_{out\_stage}(n)$$

$$T_{in\_stage}(n+1) = T_{out\_stage}(n)$$

Any liquid form is separated and compressed using an isentropic liquid pump, and the vapour flowrate of the remaining stages is subsequently reduced. The liquid is combined with the final outlet vapour to give the over composition and temperature.

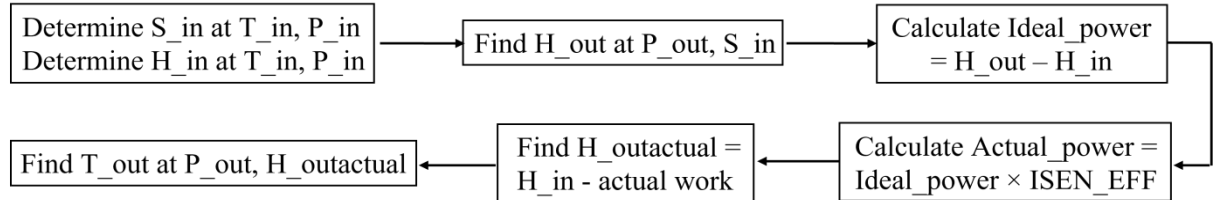
### A.2 Turbo expander – generates power from pressure reduction

#### A.2.1 Inputs:

- 1)  $P_{in}$  / bar – inlet pressure

- 2)  $P_{out}$  / bar – outlet pressure
- 3)  $T_{in}$  / K – inlet temperature
- 4) Molar Composition (in molar fraction)
- 5) ISEN\_EFF – stage isentropic efficiency

#### A.2.2 The flowchart of the method



#### Appendix B. Operating condition details of sequence 6 and sequence 4

**Table B1.** Comparison between shortcut models and rigorous simulation results of S6

	Column 1		Column 2		Column 3		Column 4	
	(AB/CDE)		(A/B)		(C/DE)		(D/E)	
	SC*	R*	SC	R	SC	R	SC	R
Vapour frac	0.39	0.39	0.98	0.98	0.64	0.64	0.10	0.10
Pressure (bar)	21.20	21.20	17.15	17.15	4.62	4.62	3.27	3.27
$T_{feed}$ (°C)	51.3	50.9	21.5	22.3	68.1	67.8	50.6	50.2
Condenser type	Partial		Total		Total		Total	
$T_{conden}$ (°C)	30.0	30.8	-17.0	-17.0	34.9	35.0	34.6	34.6
$T_{reb}$ (°C)	133.0	132.7	43.3	43.7	62.9	62.5	83.1	82.5
Cond duty (MW)	18.76	16.28	20.37	22.63	27.25	29.91	12.97	12.32
Reboiler duty (MW)	30.12	27.69	5.91	8.04	19.50	22.25	12.68	12.02
Reflux ratio	1.22	1.04	1.59	1.88	14.24	15.74	1.50	1.42
Number of stages**	39	39	15	15	68	68	24	24
Feed stage**	9	9	9	9	50	50	12	12

Note: \* SC refers to shortcut models, R refers to rigorous model; \*\* Theoretical stages

**Table B2.** Comparison between real relative volatilities\* versus the geometric mean  $\alpha$  in shortcut models of S6

	Column 1 (AB/CDE)		Column 2 (A/B)		Column 3 (C/DE)		Column 4 (D/E)	
	SC	R	SC	R	SC	R	SC	R
Top stage	1.99	2.09	3.65	3.62	1.34	1.34	2.34	2.23
Bottom stage	1.46	1.49	2.46	2.47	1.30	1.28	1.98	2.00
Log mean $\alpha^{**}$	1.71	n/a	3.00	n/a	1.32	n/a	2.15	n/a

Note: \* Real relative volatilities between LK and HK components at the top and bottom stage of the columns generated by rigorous simulations; \*\* Log mean  $\alpha = (\text{top } \alpha \times \text{bottom } \alpha)^{-0.5}$

**Table B3.** Comparison between shortcut models and rigorous simulation results of S4

	Column 1 (A/BCDE)		Column 2 (B/CDE)		Column 3 (CD/E)		Column 4 (C/D)	
	SC*	R*	SC	R	SC	R	SC	R
Vapour frac	0.45	0.45	0.13	0.13	0.40	0.40	0.99	0.99
Pressure (bar)	17.15	17.15	12.77	12.77	4.61	4.61	4.62	4.62
T <sub>feed</sub> (°C)	44.0	43.6	62.1	61.6	62.3	62.0	44.4	44.4
Condenser type	Total		Total		Partial		Total	
T <sub>conden</sub> (°C)	-17.0	-16.9	30.1	30.6	44.3	44.3	34.9	34.9
T <sub>reb</sub> (°C)	73.8	73.3	103.7	103.5	97.7	97.2	47.1	47.1
Cond duty (MW)	19.35	23.79	20.77	21.78	9.78	9.50	25.29	26.66
Reboiler duty (MW)	11.45	15.86	20.94	21.92	12.75	12.40	18.50	20.08
Reflux ratio	1.46	2.03	1.85	1.93	1.43	1.41	13.15	13.93
Number of stages**	14	14	32	32	26	26	66	66
Feed stage**	8	8	7	7	12	12	50	50

Note: \* SC refers to shortcut models, R refers to rigorous model; \*\* Theoretical stages

**Table B4.** Comparison between real relative volatilities\* versus the geometric mean  $\alpha$  in shortcut models of S4

	Column 1 (A/BCDE)		Column 2 (B/CDE)		Column 3 (CD/E)		Column 4 (C/D)	
	SC	R	SC	R	SC	R	SC	R
Top stage	3.65	3.62	2.14	2.27	2.22	2.13	1.34	1.34
Bottom stage	2.21	2.20	1.69	1.73	1.87	1.89	1.33	1.33
Log mean $\alpha^{**}$	2.84	n/a	1.90	n/a	2.04	n/a	1.34	n/a

Note: \* Real relative volatilities between LK and HK components at the top and bottom stage of the columns generated by rigorous simulations; \*\* Log mean  $\alpha = (\text{top } \alpha \times \text{bottom } \alpha)^{-0.5}$

## Appendix C. Shortcut methods

### 1. For simple columns:

- Fenske equation for minimum number of stages:  $N_{min} = \frac{\log[(F_{L,D}/F_{H,D})(F_{H,B}/F_{L,B})]}{\log \alpha_m}$  (1)

where,

$\alpha_m$ : relative volatility of top and bottom stage of a column

$F_{L,D}$ : light key component flow in the distillate product

$F_{H,D}$ : heavy key component flow in the distillate product

$F_{L,B}$ : light key component flow in the bottom product

$F_{H,B}$ : heavy key component flow in the bottom product

- Underwood equation for minimum reflux ratio:

$$\sum_{i=1}^n \frac{\alpha_i x_{i,F}}{\alpha_i - \theta} = 1 - q \quad (2); \quad R_{min} + 1 = \sum_{i=1}^n \frac{\alpha_i x_{i,D}}{\alpha_i - \theta} \quad (3)$$

where,

n: number of components

q: liquid fraction of feed

$x_{i,F}$ : mole amount fraction of i in feed

$x_{i,D}$ : mole amount fraction of i in distillate

$\alpha_i$ : relative volatility of component i to the heaviest component

$\theta$ : root of Eq. (3)

- Gilliland correlations for actual number of stages:  $Y=1-\exp\left[\frac{1+54.4X}{11+117.2X} \frac{X-1}{X^{0.5}}\right]$  (4)

Where,

$$Y=\frac{N-N_{min}}{N+1}, X=\frac{R-R_{min}}{R+1}$$

R: Actual reflux ratio

- Kirkbride equations for feed stage:  $\log \frac{N_r}{N_s} = 0.206 \log \left[ \frac{z_H}{z_L} \frac{F_B}{F_D} \left( \frac{X_{B,L}}{X_{D,H}} \right)^2 \right]$

where,

$N_r$ : number of stages above feed stage

$N_s$ : number of stages below feed stage

$z_H$ : mole amount fraction of heavy key component in feed

$z_L$ : mole amount fraction of light key component in feed

$F_B$ : molar flowrate of bottom product

$F_D$ : molar flowrate of distillate product

$X_{B,L}$ : mole fraction of light key component in bottom product

$X_{D,H}$ : mole fraction of heavy key component in distillate product

## 2. For complex columns – taking dividing wall column (DWC) as an example

A dividing wall column is considered to have a single feed and a top and bottom product and a side draw, as well as a vertical wall in the column. In this work, it is assume that a DWC is thermally equivalent to a fully thermally coupled prefractionator. To calculate the thermodynamic performance of a dividing wall column, an equivalent three column model is used. The first column (C1) acts as the prefractionator, the second column (C2) acts as the rectifying section of the main column and the third column (C3) acts as the stripping section of the main column.

The calculation steps are a follows

- *Calculate the performance of the prefractionator section (C1)*
  - (1) Given the  $\alpha$  values, light key (LK) and heavy key (HK) components and the feed quality (q), using the Underwood Equation determine the roots ( $\theta$ ). The LK and HK

are for the overall separation. (i.e. if a three component system (ABC) is to be separated, LK = A and HK = C)

- (2) Specify the top product (D) by assuming that all the components above the Light key K ( $1 \rightarrow \text{LK}-1$ ) are in the distillate and there are no components heavier than the heavy key ( $\text{HK}+1 \rightarrow \text{Number of components}$ ) in the distillate. The amount of the LK in the distillate is given by  $\text{Feed}_{\text{LK}} * \text{Rec}_{\text{LK},\text{act}}$  and the amount of HK in the distillate is given by  $\text{Feed}_{\text{HK}} * (1 - \text{Rec}_{\text{HK},\text{act}})$ . The amount of mid-key components in the distillate is determined by the Underwood Equation. The recoveries  $\text{Rec}_{\text{LK},\text{act}}$  and  $\text{Rec}_{\text{HK},\text{act}}$  may be a degree of freedom in the design and can be controlled using the Bias factors.
- (3) The minimum vapour and liquid traffic is then calculated above and below the feed by flow balance. It is assumed all the vapour in the feed goes up the column and all the liquid goes down.
- (4) The minimum reflux above ( $R_{\text{min,above}} = L_{\text{min,above}}/D$ ) and below ( $R_{\text{min,below}} = L_{\text{min,below}}/D$ ) the feed is then calculated.
- (5) The Reflux scaleup is then applied to the column to obtain the actual vapour and liquid traffic. this scaleup can either be applied to the top of the column or to the limiting section
- (6) The minimum number of trays ( $N_{\text{min}}$ ) is then calculated using the Fenske equation. If  $\text{Rec}_{\text{LK}}$  or  $\text{Rec}_{\text{HK}}$  is 1.0 then a tolerance maybe applied to the actual component fractions if the Relax Product Specification for Tray Calculations option has been selected. This will adjust the recovery values used in the Fenske equation in an attempt to give a more practical number of trays.
- (7) The Kirkbride Equation is then applied to the number of trays to obtain the feed tray location.

- *The calculate of the performance of the rectifying section (C2) and the stripping section (C3) are similar to the above.*

- *Others*

➤ The actual number of trays ( $N_{\text{act}}$ ):  $N_{\text{act}} = N_{\text{min}} / \text{Tray efficiency}$

➤ Condenser and reboiler loads:

(1) Total condenser load calculations: Given the distillate composition, pressure and distillate (D) and liquid reflux (L) flowrate, the condenser heat load can be determined. It is assumed that the distillate will be at the bubble temperature ( $T_{bub}$ ) and the overhead vapour at the dew temperature ( $T_{dew}$ ). The molar enthalpies (DH) are obtained from physical property data. The vapour and liquid composition will be the same.  $V=L+D$ ; Condenser Duty =  $V*DH_{T_{dew},v} - L*DH_{T_{bub}} - D* DH_{T_{bub}}$ .

(2) Partial condenser load calculations: Given the distillate composition, pressure and distillate (D) and liquid reflux (L) flowrate, the condenser heat load can be determined. It is assumed that the distillate will be at the dew temperature ( $T_{dew,D}$ ), the liquid return at bubble temperature ( $T_{bub,L}$ ) and the overhead vapour at the dew temperature ( $T_{dew,V}$ ). The molar enthalpies (DH) are obtained from physical property data. The composition of the distillate is known and it is assumed that the liquid return is in phase equilibrium with it. The overhead vapour composition is determined by mass balance.  $V=L+D$ , Condenser Duty =  $V*DH_{T_{dew,V}} - L*DH_{T_{bub,L}} - D*DH_{T_{dew,D}}$ .

(3) Reboiler load calculations Given the bottoms composition, pressure and bottoms (B) and vapour return (V) flowrate the reboiler heat load can be determined. It is assumed that the bottoms will be at the bubble temperature ( $T_{bub,B}$ ), the vapour return at dew temperature ( $T_{dew,V}$ ) and the bottom liquid at the bubble temperature ( $T_{bub,L}$ ). The molar enthalpies (DH) are obtained from physical property data. The composition of the bottoms is known and it is assumed that the vapour return is in phase equilibrium with it. The bottoms liquid composition is determined by mass balance.  $L=V+B$ , Reboiler Duty =  $B*DH_{T_{bub,B}} + V*DH_{T_{dew,V}} - L*DH_{T_{bub,L}}$ .

# **Appendix D.** Breakdown costs of simple and complex distillation sequences

Seq No	CW (M\$/yr)	LP (M\$/yr)	MP (M\$/yr)	Chilled water (M\$/yr)	Ref 1 (M\$/yr)	Ref 2 (M\$/yr )	Electricity (M\$/yr)
S1	0.70	9.20	0.00	0.00	4.97	0.37	0.02
S2	0.67	8.83	0.00	0.00	4.97	0.37	0.31
S3	0.76	9.97	0.00	0.00	4.97	0.37	0.02
S4	0.67	8.84	0.00	0.00	4.97	0.37	0.02
S5	0.74	9.68	0.00	0.00	4.97	0.37	0.31
S6	0.70	9.39	0.00	0.00	5.23	0.37	-0.22
S7	0.66	8.88	0.00	0.00	5.23	0.37	-0.23
S8	0.72	9.82	0.00	0.00	5.57	0.37	0.02
S9	0.74	9.80	0.00	0.00	5.23	0.37	0.00
S10	0.86	11.12	0.00	0.00	5.30	0.37	0.65
S11	0.83	7.30	3.74	0.00	5.23	0.37	0.01
S12	0.86	11.36	0.00	0.01	5.57	0.37	0.64
S13	0.86	11.10	0.00	0.00	5.30	0.37	0.95
S14	0.87	11.23	0.00	0.00	5.23	0.37	0.76
C1	0.47	6.97	0.00	0.00	4.97	0.37	0.01
C2	0.51	7.14	0.00	0.00	4.97	0.37	-0.02
C3	0.66	8.83	0.00	0.00	4.97	0.37	-0.01
C4	0.47	6.97	0.00	0.00	4.97	0.37	0.01
C5	0.60	7.95	0.00	0.00	5.03	0.38	0.31
C6	0.47	7.03	0.00	0.00	5.23	0.37	-0.32
C7	0.47	6.97	0.00	0.00	4.97	0.37	0.01
C8	0.46	1.30	6.15	0.00	6.50	0.37	0.00
C9	0.47	7.03	0.00	0.00	5.23	0.37	-0.32
C10	0.45	6.58	1.31	0.00	6.20	0.38	0.02
C11	0.73	6.32	3.71	0.00	5.23	0.37	-0.09
C12	0.47	1.92	5.92	0.00	6.82	0.37	-0.08
C13	0.52	6.59	1.24	0.00	6.15	0.37	-0.03
C14	0.58	2.90	6.11	0.54	5.11	0.49	0.14

\* **Note:** The negative values of electricity cost means the electricity generated by turbo expander is more than what compressor required.



## **Chapter 3**

### **Conclusions and recommendations for future work**

### **3.1 Conclusions**

This work has developed, demonstrated and evaluated the usefulness of the screening method for the synthesis and optimisation of energy integrated distillation sequences, which is applicable to zeotropic ideal or near ideal mixture. The developed methodology is then applied to an industrial case study for the fractionation of natural gas liquids (NGLs) to evaluate the proposed approach. Through the optimisation of the entire sequencing process, it has been established that the separation problems examined in this study can be effectively screened using shortcut distillation models in combination with the synthesis of heat exchanger network designs. For a given feed composition and product specifications, novel fractionation sequences can be ranked techno-economically, and the most energy-efficient and economically attractive sequence family can be selected. Moreover, the generated economically attractive sequences, ranked based on their operating costs, are demonstrated to be comparable to those obtained through rigorous simulations.

Incorporation of thermally coupled complex columns in non-integrated designs demonstrates better performance when compared to corresponding designs using simple columns. However, the difference in performance between designs of complex and simple columns becomes significantly narrower once heat integration is included.

The results obtained through this study illustrate that screening the search space of energy-efficient distillation sequences, while considering the synthesis and optimisation of all design degrees of freedom is well achieved through the proposed approach.

### **3.2 Recommendations for future work**

The scope of heat integration in this work was limited to direct heat exchange where the temperature of the heat source was higher than that of the heat sink by a minimum temperature difference. High pressures can be assigned to columns to increase the heat source temperature (condenser temperature) until the minimum temperature driving force dictates that no more heat integration opportunities can be generated, but the separation may become difficult with a high reflux ratio and number of stages.

To further extend the development of the screening method, indirect heat integration opportunities such as heat pumps are recommended to be performed in the future. Heat pumps, such as vapour recompression, vapour compression, compression-resorption heat pump, heat-integrated distillation column (HIDiC), etc., can upgrade the heat level by adding extra "work" into a distillation column, and thus have the potential to achieve heat integration within or between columns as well as achieve energy savings.

Moreover, process dynamics and control are also recommended to be studied for the further work to maintain the stability of the intensified process, optimize energy usage, and improve the overall efficiency of the distillation sequence.

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