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Multi-objective optimisation: algorithms and application to computer-aided molecular and process design

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Declaration of Authorship

I, Ye Seol Lee, declare that this thesis titled, "Multi-objective optimisation: algorithms and application to computer-aided molecular and process design" and the work presented in it are my own. I confirm that where I have used the works of others, it is clearly stated and referenced accordingly.

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Dedicated to my family

Abstract

Computer-Aided Molecular Design (CAMD) has been put forward as a powerful and systematic technique that can accelerate the identification of new candidate molecules. Given the benefits of CAMD, the concept has been extended to integrated molecular and process design, usually referred to as Computer-Aided Molecular and Process Design (CAMPD). In CAMPD approaches, not only is the interdependence between the properties of the molecules and the process performance captured, but it is also possible to assess the optimal overall performance of a given fluid using an objective function that may be based on process economics, energy efficiency, or environmental criteria. Despite the significant advances made in the field of CAM(P)D, there are remaining challenges in handling the complexities arising from the large mixed-integer nonlinear structure-property and process models and the presence of conflicting performance criteria that cannot be easily merged into a single metric. Many of the algorithms proposed to date, however, resort to single-objective decomposition-based approaches.

To overcome these challenges, a novel CAMPD optimisation framework is proposed, in the first part of thesis, in the context of identifying optimal amine solvents for carbon dioxide (CO₂) chemical absorption. This requires development and validation of a model that enables the prediction of process performance metrics for a wide range of solvents for which no experimental data exist. An equilibrium-stage model that incorporates the SAFT- γ Mie group contribution approach is proposed to provide an appropriate balance between accuracy and predictive capability with varying molecular design spaces. In order to facilitate the convergence behaviour of the process-molecular model, a tailored initialisation strategy is established based on the inside-out algorithm. Novel feasibility tests that are capable of recognising infeasible regions of molecular and process domains are developed and incorporated into an outer-approximation framework to increase solution robustness. The efficiency of

the proposed algorithm is demonstrated by applying it to the design of CO_2 chemical absorption processes. The algorithm is found to converge successfully in all 150 runs carried out.

To derive greater insights into the interplay between solvent and process performance, it is desirable to consider multiple objectives. In the second part of the thesis, we thus explore the relative performance of five multi-objective optimisations (MOO) solution techniques, modified from the literature to address nonconvex MINLPs, on CAM(P)D problems to gain a better understanding of the performance of different algorithms in identifying the Pareto front efficiently. The combination of the sandwich algorithm with a multi-level single-linkage algorithm to solve nonconvex subproblems is found to perform best on average. Next, a robust algorithm for bi-objective optimisation (BOO), the SDNBI algorithm, is designed to address the theoretical and numerical challenges associated with the solution of general nonconvex and discrete BOO problems. The main improvements in the development of the algorithm are focused on the effective exploration of the nonconvex regions of the Pareto front and the early identification of regions where no additional Pareto solutions exist. The performance of the algorithm is compared to that of the sandwich algorithm and the modified normal boundary intersection method (mNBI) over a set of literature benchmark problems and molecular design problems. The SDNBI found to provide the most evenly distributed approximation of the Pareto front as well as useful information on regions of the objective space that do not contain a nondominated point. The advances in this thesis can accelerate the discovery of novel solvents for CO₂ capture that can achieve improved process performance. More broadly, the modelling and algorithmic development presented extend the applicability of CAMPD and MOO based CAMD/CAMPD to a wider range of applications.

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Chapter 1

Introduction

"If I have ever made any valuable discoveries, it has been due more to patient attention, than to any other talent."

- Issac Newton

1.1 Motivation and objectives

Carbon dioxide (CO_2) is one of the primary anthropogenic greenhouse gases that directly contributes to a negative impact on environmental and human lives. A significant reduction in total CO_2 emissions is essential to limit the rise in the global average temperature to 2°C (IPCC, 2007). In December 2015, the 21st conference of the parties (COP21) agreement set out the highly ambitious aspiration of limiting the temperature increase to 1.5 °C by 2050 (UNFCCC, 2015). In response to this, there have been growing efforts to develop and adopt low-carbon technologies to reduce the release of CO_2 to the atmosphere. Carbon Capture and Storage (CCS) technologies are widely accepted as having a vital role to play in a portfolio of net-zero emissions, expecting to contribute approximately 20% of the reduction in greenhouse gas emissions by 2035. Among the variety of available CCS technologies, post-combustion capture based on the chemical absorption processes with amine solvents is regarded as one of the most promising technologies in terms of technological maturity, applicability and capability of handling exhaust streams from large point industrial sources (Rochelle, 2009). A typical amine-based solvent that has been widely used for the process is an aqueous monoethnaolamine (MEA) solution due to its high reaction rate with CO₂, moderate absorption capacity and low solvent cos. However, the main disadvantages of using this conventional solvent include intensive energy requirements associated the solvent regeneration, which takes up to 50% of the total energy use of the process; harmful environmental and health impacts; and high operational costs resulting from limited CO₂ solubility. To counter these shortcomings, considerable efforts have been expended on the search for alternative amine-based solvents that have better thermal, economic and environmental performance.

The identification of potential solvents is very challenging due to the combinatorial complexity derived from both solvent parameters and the significant influence of the choice of solvent on the process objectives, meaning that optimal solvents that are best in overall process performance can only be realised by capturing the interactions between the molecular- and process-level decisions simultaneously. One possible research direction is to investigate the solvent candidates based on extensive experimental program at a laboratory or pilot plant scale. However, experimental investigation often involves the deployment of significant resources, and it is often difficult to translate experimental results to the scale of process performance, hindering the exploration of the space of potentially superior amine-based solvents. Therefore, it is essential to develop systematic methodologies to explore many possibilities efficiently and evaluate the overall performance of the process as a function of solvent choice.

In this context, Computer-aided molecular and process design (CAMPD) has emerged as a promising route that offers a systematic framework to evaluate a very wide range of molecular structures in terms of system metrics, given a desirable set of physicochemical properties and process performance criteria (Adjiman et al., 2014). A variety of solution strategies have been developed for CAMPD problems, focusing on handling the numerical complexity arising from the inherent non-convexity of structure-property and process models. Yet, most algorithms encounter computational difficulties with a large-scale mixed-integer nonlinear formulations. This is mainly because 1) the relationship between the process and molecular property models exhibits a highly nonlinear behaviour and thus it is usually prohibitively expensive to solve such models simultaneously; 2) the integrated solvent-process model is characterised by the number of infeasible regions in the search space, as it is not possible to generate a feasible solution for particular solvent structures. Thus, developing a novel CAMPD algorithm that allows one to avoid infeasibilities during the exploration of a large design space is significantly important.

Another important consideration in the formulation of CAMPD problems is the treatment of the inherent trade-offs between conflicting performance criteria that cannot be easily placed on the same quantitative footing. For example, the economical, safety, and environmental impacts of the solvents cannot be easily merged into a single metric or objective function. In view of the pressing need to capture multiple objective functions, multi-objective optimisation (MOO) techniques have been applied to a range of process design problems and are increasingly being deployed on molecular design problems (CAM(P)D). In practice, it is not possible to construct the entire set of trade-offs known as the "Pareto front" or to derive an analytical expression of this front (Deb et al., 2000b) and thus most MOO algorithms focus on generating an accurate approximation of the Pareto front such that the set of Pareto optimal solutions are well-spaced and close to the true Pareto front assuming that the Pareto front is continuous. However, the true Pareto front may consist of many disconnected parts or entirely isolated points for which the well-distributed Pareto points cannot be attained. Some of the most widely used MOO algorithms in
the area of CAM(P)D are the weighted-sum approach, epsilon-constraints method, multi-objective genetic algorithm and sandwich algorithm. Each method, however, have limited applicability because molecular design problems are very difficult to solve given that they are usually formulated as mixed-integer nonlinear problems (MINLPs) and the algorithms often suffer from limitations that prevent them from reliably producing optimal solutions along the nonconvex or discrete regions of the Pareto front. Despite the fact that significant efforts have been devoted to addressing such challenges, there is a lack of systematic studies that assess the performance of MOO algorithms for CAM(P)D, and hence a lack of guidance on which approach is particularly suited for this class of problems. The improvement of MOO algorithms in terms of on the exploration of nonconvex regions is also an important task to ensure diverse the solutions are obtained without compromising the quality of the Pareto front or incurring significant additional computational cost.

This thesis is therefore organised around into two main aims: developing a robust¹ optimisation framework for the integrated design of optimal aqueous solvent and CO_2 chemical absorption processes and developing a MOO optimisation framework for mixed-integer nonlinear programming that is suited for application to general CAM(P)D problems. The specific objectives of this thesis are:

- To establish a process modelling approach that offers broad predictive capabilities of overall process performance as a function of molecular structure without exhaustive reliance on experimental data and pilot plant data.
- To study the reliability and applicability of the developed model over a set of process specifications and solvent types.
- To develop a robust CAMPD algorithm that can simultaneously optimise molecular and process variables by incorporating tailored feasibility tests such that

¹Note that 'robust' or 'robustness' is used to describe the ability of an algorithm to converge to a solution regardless of the initial point provided by the user but not to indicate the research field of robust optimisation.

infeasible process conditions and solvent properties are automatically detected.

- To demonstrate the efficiency of the proposed algorithm on case studies of CO₂ chemical absorption-desorption process.
- To investigate the relative performance of a variety of MOO algorithms on molecular design problems to provide insights of their reliability and computational efficiency in generating Pareto-optimal solutions over the MINLP search space.
- To develop a novel bi-objective optimisation (BOO) algorithm design to address the numerical challenges associated with the solution of general nonconvex and discrete BOO problems.
- To access the effectiveness of the proposed BOO algorithm by applying it to benchmark problems that span general nonlinear programming and MINLPs, and extend the validation study to CAM(P)D problems.

1.2 Thesis overview

In chapter 2, we provide a review of solution approaches to CAMPD, with a brief mention of a predictive thermodynamic model, the statistical associating fluid theory (SAFT)- γ Mie equation of state (EOS), that is needed throughout this work. The physical treatment of the chemical reactions between CO₂ and the aqueous amine solvent is described in the context of the application of the SAFT- γ Mie model to the molecular design problem. We also set out the fundamentals of MOO theories and relevant definitions that will be used throughout this thesis.

In chapter 3, we present an equilibrium-based CO_2 absorption-desorption process and cost model. A process model is developed with the SAFT- γ Mie group contribution EOS to facilitate the reliable prediction of physical properties and fluid phase behaviour of the water-amine- CO_2 mixtures. The accuracy of the process model is demonstrated using a specific set of pilot plant data. A robust initialisation strategy that incorporates the inside-out algorithm is developed to overcome the numerical complexities arising from the complex mass– and heat–balance equations and the highly non-ideal behaviour of water-solvent- CO_2 mixtures. Next, we identify the relative influence of operating parameters on key performance indicators through a comprehensive parametric study, with the aim to formulate a process optimisation problem that can be integrated into the CAMPD framework.

After establishing the process modelling approach, in Chapter 4, we present a robust CAMPD technique for the design of optimal amine solvents for CO_2 chemical absorption. The study focuses on the development of feasibility tests based on an outer-approximation algorithm (Duran & Grossmann, 1986), with which feasible process and molecular domains are recognised prior to evaluating the molecule in the process. The efficiency of the proposed algorithm is highlighted through three case studies of CO_2 chemical absorption processes. The robustness of the approach is further demonstrated by comparing it to conventional molecular design approaches: CAMD and decomposition-based CAMPD method.

Due to the conflicting nature of performance criteria, we take a closer look at the application of the MOO algorithms within the area of the molecular design in Chapter 5. In order to understand the suitability of different MOO algorithms for CAM(P)D problems, we present a systematic comparison of the performance of five MINLP MOO algorithms on the selection of CAM(P)D problems. The five methods are designed to address the discrete and nonlinear nature of the problem, with the aim of generating an accurate approximation of the Pareto front. They include: a weighted-sum approach without global search phases (SWS), a weighted-sum approach with simulated annealing (SA), a weighted-sum approach with multi-level single-linkage (MLSL), the sandwich algorithm (SD) with MLSL and the non dominated sorting genetic algorithm-II (NSGA-II). In order to test these five optimisation techniques, two CAMD and one CAMPD problems of varying dimensionality are formulated as case studies.

In Chapter 6, we present a novel algorithm (SDNBI) that combines the SD and modified normal boundary intersection (mNBI) method to tackle the numerical challenges associated with the solution of bi-objective mixed-integer nonlinear programming. The main improvements we introduce are the identification of regions where no nondominated solution exist and the exploration of nonconvex parts of the Pareto front. The performance of the algorithm in terms of its ability to construct an accurate approximation of the Pareto front is compared to two MOO approaches: the SD algorithm and mNBI method. The features of the MOO algorithms are evaluated using a published benchmark model.

Following the work presented in Chapter 6, in Chapter 7 the effectiveness of the proposed algorithm is investigated through the CAM(P)D problems in an attempt to examine the applicability and reliability of the method in the practical mixed-integer nonlinear problem domain. Several modifications of the SDNBI method are introduced to adapt it to a mNBI subproblem. The resulting algorithm is first applied to computer-aided solvent design for CO₂ capture, where two molecular properties are optimised simultaneously. The SDNBI algorithm is then tested on the integrated design of pure-component working fluids and Organic Rankine Cycle processes, where thermal performance and economic value are taken as two objective functions. Finally, we compare the performance of the algorithm with SD algorithm and mNBI method.

We conclude the thesis in Chapter 8 by summarising the key results and contributions, which also provide some avenues for future research and model improvement.

CHAPTER 2

Background

The goal of this thesis is to develop optimisation frameworks for the study of the integrated solvent and CO_2 chemical absorption process design and multi-objective optimisation algorithms that can accurately approximate the Pareto front in the solution of molecular design problems. In this chapter the fundamentals of solution approaches of computer-aided molecular and process design (CAMPD) in relation to the objectives of this work are summarised.

2.1 Predictive thermodynamic models for the formulation of molecular design

In the search for new molecules, it is imperative to develop thermodynamic methodologies capable of calculating the physical properties and describing the phase behaviour of fluids from molecular structural information, without the need for extensive experimental data. Given the importance of the predictive capability of the thermodynamic model to describe wide ranges of molecules, we use the SAFT- γ Mie (Papaioannou et al., 2014) equation of state (EOS) in this work. SAFT- γ approach is a well-established group contribution (GC) (Lydersen, 1955; Joback, 1984; Joback & Reid, 1987; Constantinou & Gani, 1994) EOS initially derived by Lymperiadis et al. (2007, 2008) from earlier SAFT-VR (Gil-Villegas et al., 1997) and SAFT-VR Mie (Lafitte et al., 2013). The underlying assumption of GC-based approaches is that a given chemical compound can be broken down into chemically distinct functional groups such that the thermodynamic properties of a given molecule can be determined from contributions of each functional group to the molecular properties. The main advantage of this concept is that it can significantly reduce the number of parameters required to represent the thermodynamic behaviours and the properties of new molecules are readily assessed by means of the parameters assigned to the functional groups even in the absence of the experimental data. GC approaches are thus well suited to molecular design problems where the exploration of the physical properties as a function of molecular structures are essential part of the problems.

Within the SAFT- γ Mie approach, molecules are represented as associating heteronuclear chain of fused spherical segments. These segments interact via intermolecular potentials that determine the force between segments and between association sites. The total Helmholtz free energy A of a fluid system is written in dimensionless form as the sum of different perturbative contributions to a reference free energy,

$$\frac{A}{k_BT} = \frac{A^{\text{ideal}}}{Nk_BT} + \frac{A^{\text{mono.}}}{Nk_BT} + \frac{A^{\text{chain}}}{Nk_BT} + \frac{A^{\text{assoc.}}}{Nk_BT}$$
(2.1)

where N is the total number of molecules, k_B is the Boltzmann constant, and T is the absolute temperature. A^{ideal} is the free energy of an ideal gas, A^{mono.} is the term accounting for the Mie segment-segment interactions derived by perturbing from a reference hard-sphere fluid, A^{chain} represents the free energy for the formation of molecules from Mie segments. A^{assoc.} is the term accounting for the free energy contribution due to interactions between association sites. A complete review of literature covering this area is beyond the scope of the thesis. The reader is referred to Papaioannou et al. (2014); Dufal et al. (2014) for the description of the SAFT- γ Mie EOS for more details and McCabe & Galindo (2010); Haslam et al. (2020) for an overview of SAFT.

Of particular interest in the context of the chemical absorption of carbon dioxide (CO_2) is that treatment of the reactions between CO_2 and aqueous amine solutions within a group-contribution framework. A key concept used within the SAFT- γ Mie EOS is that the reactions involved in a mixture of CO_2 and aqueous amines are modelled by a physical association scheme (Rodriguez et al., 2012), rather than treating the chemical reactions explicitly. In the physical association scheme, the reaction products are treated as aggregates physically bounded due to strong intermolecular forces exerted between the molecular segments. Such aggregation process is mediated by incorporating a number of short-range "sticky" association sties in appropriate functional groups, by which the main reaction pathway of CO₂ can be posed effectively. The type and concentration of the bonded products are determined by choosing the number of association sites, the strength of their interactions and association ranges. One important aspect of the physical approach is that it does not require explicit specification of a reaction scheme and ionic species. In Figure 2.1, an example of implicit reactions used to describe the formation of carbamate and bicarbonate products resulting from the reactions occurring when CO₂ is absorbed in an aqueous monoethanolamine (MEA) solution is illustrated. The MEA is represented as two spherical segments (NH_2 and CH_2OH) with 3 e sites, e H sites. Note that the superscript * of e and H site as shown in Figure 2.1 is used to distinguish the association cites of NH_2 segment from those of CH_2OH . The CO_2 model comprises two fused (heteronuclear) segments and has 1 α_1 site and 1 α_2 site (acceptor sites) that interact only with the e^{*} sites of the nitrogen atom in MEA. The α_1 -e^{*} and $\alpha_2 - e^*$ characterises two types of chemical association. A carbamate pair is formed when both α_1 and α_2 on CO₂ are bonded to two molecules of MEA, whereas the bicarbonate pair is formed when $\alpha_1 - e^*$ or $\alpha_2 - e^*$ are associated. The concentration

of bicarbonate can be calculated as the probability that α_1 is bonded and not α_2 , plus the probability that α_2 is bonded and not α_1 , while the concentration of bicarbonate is a probability that α_1 or α_2 is bonded (Rodriguez et al. (2012) and Chremos et al. (2016)).

The effectiveness and validity of this approach within the SAFT formalism have been highlighted across the research area including process modelling (Mac Dowell et al., 2013; Bui et al., 2018; Brand et al., 2016), molecular design (Papadopoulos et al., 2016, 2019; Mac Dowell et al., 2010; Lee et al., 2021). Here, we do not aim to provide a detailed discussion on the modelling approaches and advancement of the SAFT models. Instead, we make use of the same version of the SAFT formalism and physical association scheme described in Papaioannou et al. (2014); Rodriguez et al. (2012); Khalit (2019) and all of the data of the parameters used in the current work can be found in Haslam et al. (2020)



Figure 2.1: Schematic representation of the physical association scheme between MEA and CO₂ in aqueous solution within SAFT- γ Mie showing two reaction products: the bicarbonate pair [HO(CH₂)₂NH₃⁺ + HCO₃⁻] and carbamate pair [HO(CH₂)₂NHCOO⁻ + HO(CH₂)₂NH₃⁺]. The large spheres represent the monomeric segments which interact via Mie potential. The smaller spheres are association sites: e represents a lone pair of electrons, H represents a hydrogen atom and the superscript * is used to distinguish between the different association site types assigned to MEA. This figure is an adaptation of Figure 57 in Graham (2020).

2.2 Computer-aided molecular and process design

The discovery of new molecules, such as solvents, refrigerants, and pharmaceutical products is important in achieving high performance, including greater efficiency, favourable process economics, and low environmental impact (Adjiman et al., 2014). For example, the selection on appropriate solvent has a critical effect on separation efficiency (Pretel et al., 1994; Odele & Macchietto, 1993; Pereira et al., 2011; Folić et al., 2008), and that of an appropriate working fluid facilitates the design of power cycles to extract work from a range of heat sources (Papadopoulos et al., 2010a; Linke et al., 2015; Cignitti et al., 2017; Schilling et al., 2017; White et al., 2017; Bowskill et al., 2020). Computer-aided molecular design (CAMD) has emerged as a powerful and systematic technique that can accelerate the identification of such molecule candidates by making it possible to explore in silico a very large space of possibilities (Harper & Gani, 2000; Gani et al., 2006). Given the benefits of CAMD, the concept has been extended to integrated molecular and process design, usually referred to as Computer-aided molecular and process design (CAMPD). In CAMPD approaches, not only is the inter-dependency between the properties of the molecule and the process performance captured, but it is also possible to assess the optimal overall performance of a given fluid using an objective function that may be based on economics (Pereira et al., 2011; Gopinath et al., 2016; Ahmad et al., 2018), process performance (Bardow et al., 2010; Eden et al., 2004; Bowskill et al., 2020), or environmental criteria (Hostrup et al., 1999; Pistikopoulos & Stefanis, 1998).

The CAMD and CAMPD problem is often posed as Mixed-integer nonlinear programming (MINLP) due to the presence of discrete decisions and a large number of nonlinear equations that involve the molecular property prediction model and the representation of process units. Here, we denote the CAMD or CAMPD problem as CAM(P)D. The generic mathematical formulation of the design problem can be defined by:

$$egin{aligned} \min_{m{x},m{n}} & f(m{x},m{n}) \ & ext{s.t.} & m{g}(m{x},m{n}) \leq m{0} \ & m{h}(m{x},m{n}) = m{0} \ & m{C}m{n} \leq m{d} \ & m{x} \in \mathbb{R}^n, \ m{n} \in m{N} \subset \mathbb{Z}^q \end{aligned}$$
 (MINLP)

where x is a n-dimensional vector of continuous variables, n is a q-dimensional vector of integer variables that define a molecular space, g(x, n) is a vector of inequality constraints that represent design constraints and feasibility constraints, h(x, n) is a vector of equality constraints that include structure-property models, process models and a set of linear equations $Cn \leq d$ represent molecular constraints such as the octet rule (Odele & Macchietto, 1993) and bounds on vector n.

In general it is well-known that MINLP CAM(P)D problems are NP-hard and remain very challenging to solve due to the difficulties of optimising over the combinatorial explosion of the decision space coupled with the handling of (highly) nonlinear functions. Furthermore, when the design of optimal processes and molecular structures is considered simultaneously, the feasible domains with respect to the process constraints varies for each combination of discrete variables and it may involve many infeasible operating regions, leading to numerical failure in the absence of a good initial guess.

One strategy that can handle the complexities inherent in the MINLP formulation is to reformulate the problem as continuous Nonlinear programming (NLP) or Mixed-integer linear programming (MILP) to render the problem more tractable. Maranas (1996) presented a systematic CAMD framework that reformulates the MINLP problem into an equivalent MILP problem by substituting the linearised structure-property constraint function for the bilinear term. The proposed approach was applied to the design of polymers where thermo-physical properties were calculated using the group contribution method proposed by Gani et al. (1991). Siddhaye et al. (2000) used the similar approach for the design of pharmaceutical products, by which the molecular representation model was linearised using the Glover transformation (Glover, 1975). Hamad & El-Halwagi (1998) introduced a simplified model in the solution of simultaneous design of synthesising solvents and separation networks. The original MINLP formulation was reduced to MILP by linearising the thermodynamic properties model and the overall material balance equations. Struebing et al. (2013) also formulated a reactive solvent design problem as MILP by employing a linear surrogate model for reaction kinetics. Such reformulation approach is advantageous as existing MILP solvers are readily available and a global solution to the MILP is guaranteed within a practical computational time. The linearisation approach however maybe cumbersome when the transformation involves a large number of additional variables or when the original problem is highly nonconvex and thus the linearised functions cut off the original feasible domain.

With a view to maintain a problem more tractable compared to MINLP problems, Pereira et al. (2011) solved a simplified version of the CAMPD problem for the design of solvents for the physical CO₂ absorption processes. The problem was posed as a continuous optimisation problem in which solvent mixtures of n-alkanes were represented with their average chain length. The need for binary variables for the representation of molecules was avoided by choosing the thermodynamic parameters as optimisation variables and restricting the solvent design space. Bardow et al. (2010) proposed the continuous molecular targeting CAMD (CoMT-CAMD) method to solve the integrated process and fluid design problem for CO₂ capture. The approach employed the perturbed-chain statistical associating fluid theory (PC-SAFT) model (Gross & Sadowski, 2001) in which each molecule was characterised by a set of continuous parameters. The key idea of the method was the decomposition of the design into two steps: a continuous targeting step, in which the process variable and the molecular parameters are optimised in a continuous fashion; and a structure mapping step, in which the optimal properties of the hypothetical molecule are mapped onto the discrete molecular design space. The method has been extended to incorporate an integer optimisation in the structure mapping step and it has been applied to the design of working fluids for the organic Rankine cycle (ORC) processes (Schilling et al., 2017) and in solvent design for the physical absorption of CO₂ (Lampe et al., 2015). The main advantage of the NLP reformulation is that it is much easier to solve compared to the MINLP problem and it can significantly reduce computational time. However, the relaxation of integer variables may lead to a loss of detail on the molecular information and therefore the optimal molecular properties or group parameters may not necessarily translate into a physically meaningful molecule. Furthermore, the representation of a molecule with continuous variables is not always justified and specific to particular type of structure-property models.

Due to the advancement made in the development of MINLP algorithms that can explore large and complex search spaces, several methodologies have been put forward to solve CAM(P)D problems in the presence of both discrete and continuous variables. The solution strategies can be categorised as deterministic optimisation approaches, stochastic optimisation approaches, and hybrid of those. Within the deterministic approaches, the application of the outer approximation (Duran & Grossmann, 1986) has been widely recognised in the design of refrigerant blends for a single evaporator cycle (Duvedi & Achenie, 1997), working fluids for ORC processes (White et al., 2017), extractive fermentation solvents (Wang & Achenie, 2002), solvents for a physical absorption of CO_2 (Gopinath et al., 2016), optimal solvents that enhance the solubility of solutes (Sheldon et al., 2006), solvent mixture for liquid-liquid extraction (Karunanithi et al., 2005) and many others. As alternatives to the deterministic method, various stochastic methods such as genetic algorithm (GA) and simulated annealing (SA) method have been adopted in order to solve a complex set of highly nonlinear equations efficiently by avoiding the necessities of calculating first-order and second-order derivatives. Diwekar & Xu (2005) developed a solution approach based on GA to identify the optimal solvents that encoded a molecular structure based on functional group identities. A similar approach was employed in the study of liquid-liquid extraction (Scheffczyk et al., 2017) based on COSMO-RS thermodynamics. An SA-based CAMD approach was proposed by Marcoulaki & Kokossis (2000) and its performance was demonstrated to the design of solvents and refrigerants. The proposed approach was extended to the design of working fluids (Papadopoulos et al., 2010b) and environmentally friendly solvents for separation processes (Song & Song, 2008). For an overview of these methods and their applications to the molecular-design domain, the reader is referred to Ng et al. (2015), Papadopoulos et al. (2018), and references therein.

Although the algorithms developed up to date are useful to solve the MINLP CAM(P)D problems, the solution of the full MINLP remains prone to failing, in particular in the application to the simultaneous design of molecular and process design problems. A Key challenge of the application of such algorithms is the difficulty to postulate feasible bounds of the process domain as they vary from each combination of molecular variables. Therefore, many algorithms resort to the decomposition of the problem where a series of "less difficult" subproblems are solved. Note that the term "decomposition" in this chapter does not refer to the numerical solution approach of mixed-integer nonlinear problems (MINLPs) but to the overall strategy for solving molecular design problem. For example, potential molecular candidates are identified as a first step and then the performance of the process for the reduced feasible set of molecular candidates is explored (Papadopoulos & Linke, 2006a,b). Alternatively, a simplified process model that approximates the strong interactions between the process performance and molecule choice can be introduced in order to avoid the inclusion of significant numerical difficulties. The main disadvantage of using such decomposition or simplification approaches is that they may result in sub-optimal solutions. The goal is thus to develop a robust framework that can solve the original CAMPD formulation without limiting the level of details in the representation of molecular structures, thermodynamic models, and process models. The motivation of this study is based on Buxton et al. (1999); Gopinath et al. (2016); Bowskill et al. (2020), which we will discuss in Chapter 4.

2.3 Multi-objective optimisation

One other focus of this thesis lies on the development of a multi-objective optimisation (MOO) algorithm to capture the conflicting nature of objective functions within the molecular design problem. In this section, basic concepts, definitions, and the notation used throughout this thesis, particularly focusing on the general NLP MOO problems, are outlined. We refer the reader to Chapter 5 for a detailed insight with an eye towards MOO applications in the area of CAM(P)D and to Chapter 6 for a general review of scalarisation-based MOO methods.

The generic mathematical formulation of MOO is defined as follows:

$$\begin{array}{ll} \text{minimize} & (f_1(\boldsymbol{x}), \dots, f_m(\boldsymbol{x}))^\top \\ \text{subject to} & \boldsymbol{x} \in X := \{ \boldsymbol{x} \in \mathbb{R}^{n_1} \times \mathbb{N}^{n_2} \mid \boldsymbol{g}(\boldsymbol{x}) \leq \boldsymbol{0}, \boldsymbol{h}(\boldsymbol{x}) = \boldsymbol{0} \}, \end{array}$$
(MOP)

where objective functions $f_j : \mathbb{R}^n \to \mathbb{R}, j = 1, 2, ..., m$, x is an n-dimensional vector of variables $(n = n_1 + n_2)$, which consists of n_1 continuous variables and n_2 integer variables, $X \neq \emptyset$ is an nonempty feasible set, g(x) is a p-dimensional vector of inequality constraints and h(x) is a q-dimensional vector of equality constraints, $q \leq n$. we assume that all $f_j(x), j = 1, 2, ..., m$ are bounded by some upper bound $U \in \mathbb{R}$ and lower bound $L \in \mathbb{R}$ for any instance of an MOO problem. Note that, we use \mathbb{R} to denote the set of real numbers, \mathbb{R}_+ to denote the set of nonnegative real numbers, and \mathbb{R}_{++} to denote the set of positive real numbers. The set of real nvectors is denoted \mathbb{R}^n . For the special cases m = 2, MOP is also called a bi-objective optimisation (BOO) problem.

In contrast to single-objective optimisation, when the objective functions conflict

with each other, no single solution can simultaneously minimise all scalar objective functions. Hence, it is necessary to introduce a new notion of optimality or Pareto efficiency (Ehrgott, 2005a).

Definition 1. The *objective space* is defined as the set of all feasible combinations of the objective function values, i.e., $Z = \{f(x) \mid x \in X\}$

Definition 2. A point $x^* \in X$ is called *weakly efficient (weakly Pareto-optimal)* if there exists no feasible point $x \in X$ such that $f_j(x) < f_j(x^*)$ for all j = 1, ..., m. A point $x^* \in X$ is called an *efficient solution (Pareto-optimal)* if there exists no feasible point $x \in X$ such that $f_j(x) \le f_j(x^*)$ for all j = 1, ..., m and $f_{j'}(x) < f_{j'}(x^*)$ for at least one $j' \in \{1, ..., m\}$. If x^* is an efficient solution, the point in objective space $z = f(x^*)$ is referred to as a *nondominated solution* or *Pareto point* in the objective space Z. The set of efficient solutions $x^* \in X$ is the Pareto set and is denoted by X_E .



Figure 2.2: Schematic representation of bi-objective space and Pareto optimal set. The area *Z* enclosed by a solid black line represents feasible region of the problem (MOP). The thick black solid line represents a complete set of the Pareto front Ψ^* . Points A, B and C are different Pareto (nondominated) points.

All Pareto optimal points lie on the boundary of the feasible objective space Z as shown in Figure 2.2. Each Pareto optimal solution cannot be improved (see points A, B, C in Figure 2.2) in one objective without a sacrifice in the other objectives. Focusing on a posteriori method where the Pareto optimal set is generated first then,

a decision-maker selects the most preferred, the Pareto front approach provides useful information about the trade-offs by accounting for the varying importance of the objectives simultaneously. It is desirable to generate a set of Pareto optimal solutions as accurate as possible such that the alternatives are not biased towards certain criteria. The complete set of the Pareto optimal solutions is known as the (true) Pareto front and the definition is as follows:

Definition 3. (Marler & Arora, 2004) The set of efficient solutions Ω^* is the *complete set of efficient solutions* if it contains all possible efficient solutions x^* . The set Ψ^* is the *efficient frontier (or Pareto front)* formed by all nondominated solutions $f(x^*) \in \Psi^*$ which have corresponding feasible solutions $x^* \in \Omega^*$. We denote an approximation of the efficient frontier by $Z_E \subseteq \Psi^*$ where the k^{th} row of Z_E corresponds to the k^{th} nondominated point $z^k = f(x^{k,*})$. The corresponding approximation of efficient solutions of Z_E, x^* is denoted as $X_E \subseteq \Omega^*$.

Definition 4. The ideal objective vector or utopia point f^{id} is defined as the objective vector whose components are the optimal objective function values of each single-objective problem, i.e., $f_j^{id} = \min_{\boldsymbol{x}\in\Omega^*} f_j(\boldsymbol{x}), \ j = 1, ..., m$. The objective vector f^{nd} is defined as the nadir objective vector and is such that $f_j^{nd} = \max_{\boldsymbol{x}\in\Omega^*} f_j(\boldsymbol{x}), \ j = 1, ..., m$

Definition 5. Let $x^* \in X_E$. If there is a $\lambda \in \mathbb{R}^m_{++}$ such that x^* is an optimal solution to $\min_{x \in X} \lambda^\top z$, then x^* is called a *supported efficient solution* and $z = f(x^*)$ is called a *supported nondominated objective vector*.

Definition 6. A set of Pareto points is said to be *convex*, if all nondominated point $z \in \Psi^*$ is on the boundary of the convex envelope of Z, which is the smallest convex set that contains z. Note this does not imply that the Pareto front is continuous, but rather it is a relaxed concept of *convex* introduced to distinguish between a supported and unsupported nondominated objective vector where only supported nondominated point is attainable by means of a weighted-sum scalarisation approach.

Definition 7. A true Pareto front is said to be *disconnected* or *discrete*, if there exist empty regions of the boundary of the Pareto front or if the Pareto front consists of disjoint nondominated points. Note that *disconnected* or *discrete* Pareto is defined as *convex* Pareto front if all nondominated Pareto points is $z \in \Psi^*$ is on the boundary of the convex envelope of Z according to Definition 6.

In practice, an analytical expression of the true Pareto front is not available and it is hard to establish a complete set of Pareto solutions given the complexities of underlying engineering problems (Ehrgott, 2005a), as for example in the work of Marler (2005) and Rangaiah & Bonilla-Petriciolet (2013). In the solution of MOO problems, the numerical complexities arises not only from the number of evaluations of the original problem (or single-objective optimisation if the scalarisation approach is introduced), but also from the additional equations derived from the MOO algorithm. Consequently, critical to MOO approaches is that the computation of the approximation of the Pareto front with "good" quality guarantees within a reasonable computational time. The quality of this approximation depends upon: 1) the proximity of the approximation to the true Pareto front, i.e., the convergence of the approximation, and 2) the diversity (or spreadness) of the solutions over the approximated Pareto front. A key motivation of this thesis study is the evaluation of the performance of existing MOO algorithms in application to the molecular design domain. From the conclusions derived by the comparative study presented in Chapter 5, we will also develop improved MOO algorithms that may be used in a CAM(P)D context.

2.4 Conclusions

In this chapter a brief review of the SAFT- γ Mie framework has been provided to describe the physical association concept in the context of CO₂ chemical absorption. After presenting the SAFT- γ Mie approach, the formulation of general CAMPD problems, i.e., MINLPs and the difficulties encountered in the solution of these problems has discussed. The basic concepts and notation used for the development of MOO techniques have been also defined to provide an consistency thorough out the thesis.

CHAPTER 3

Modelling a CO_2 chemical absorption process

In Chapters 1 and 2, we set out the context for the importance of developing a robust optimisation framework that can provide a systematic way of identifying optimal solvent candidates to enhance the economic and environmental performance of CO_2 capture processes. One of challenges in developing such a framework is to establish a process modelling approach that can capture the interactions between process performance and solvent properties without significantly increasing numerical complexity. Our focus in this chapter is to develop an equilibrium-stage model of the absorption-desorption of CO_2 with the aim of being as predictive as possible in terms of the properties of the solvents involved in the process, such that the performance of various solvents can be assessed without the need for extensive experimental data. We also investigate initialisation strategies for the solution of the process model in order to facilitate the evaluation of the complex phase behaviour of many solvents within the process. A detailed parametric study is then carried out for the key process variables, leading to the development of an optimisation oriented model that can be integrated into the solvent design problem is then be developed after carrying out a detailed parametric study for key process variables.

The main contributions of this work include: 1) the introduction of the SAFT-

 γ Mie (Papaioannou et al., 2014) equation of state (EOS) in the development of CO₂ chemical absorption-desorption process models such that the economic, thermal, and environmental performance of the process can be assessed as a function of amine solvent structures; 2) validation of the process model developed focusing on whether it can provide a quantitative agreement in the behaviour of the process using the SAFT- γ Mie EOS; 3) the development of an tailored initialisation algorithm to handle increased numerical complexities arising from the complex thermodynamic model equations and the many combinations of process conditions and solvent structures; 4) the development of an optimisation model that is suited for integrating into CAMPD frameworks.

3.1 Introduction

Carbon capture and storage (CCS) technologies are set to play a central role in responding to the growing demand for carbon dioxide (CO₂) removal in the mitigation of anthropogenic climate change. Currently, chemical absorption-desorption processes using amine-based solvents have been regarded as one of the most effective and mature technologies for some time, due to the versatility of the implementation of the process across a wide range of industrial applications (Rochelle, 2009). In an absorption process unit, the amine solvent reacts with CO₂ in the feed gas stream, forming weakly bonded intermediate compounds. The CO₂ captured is reclaimed from the solvent solution usually by heating the solvent to elevated temperature, thereby regenerating the solvent by reducing the concentration of CO₂. A relatively high selectivity towards CO₂ can be achieved with appropriate selection of the amine solvent, making it possible to remove the CO₂ from diluted sources with high separation efficiency (Bui et al., 2018). Conventional amine-based solvents used for these processes are monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA). There remain, however, a number of

challenges to the use of such solvents in CO₂ capture processes that limit their performance. Among these are the high energy requirements associated with solvent regeneration; the low cyclic capacity of many solvents; the high environmental and health impacts associated with solvent degradation, corrosivity, and solvent loss. To overcome these drawbacks, substantial research efforts (Singh et al., 2007, 2009; Oexmann & Kather, 2010; Chemmangattuvalappil & Eden, 2013; Liang et al., 2015; Papadopoulos et al., 2016; Singto et al., 2016; Zhang et al., 2017) have been undertaken to develop new solvents that may improve the overall performance of the process.

A promising research direction in the identification of new solvents is the application of computer-aided molecular and process design (CAMPD) techniques. CAMPD offers systematic methodologies to explore a very large molecular design space in which the overall performance of a process is evaluated by capturing interactions between molecular properties and process performance. In any CAMPD framework, essential elements are: the development of thermodynamic methodologies that can provide predictions of fluid phase behaviours and physical properties of solvents; and the development of accurate and robust mathematical models for describing the performance of the absorption-desorption process as a function the thermophysical properties and the phase behaviour of the (unknown) amine solvents. Owing to the recent advances in group contribution version of SAFT, in particular SAFT- γ Mie (Papaioannou et al., 2014) and its predictive capabilities, it becomes possible to reliably predict physical properties and fluid phase behaviour of a wide ranges of molecular structures and their mixtures. The adoption of the SAFT- γ Mie EOS has been increasingly recognised in the area of CAMPD (Gopinath et al., 2016; Bowskill et al., 2020; Watson et al., 2021). The use of SAFT- γ Mie EOS in the context of CAMPD however may present specific challenges due to the increased complexities inherent in the model equations compared to conventional cubic EOSs. Moreover, the simulation and optimisation of the CO₂ chemical absorption-desorption process can be prohibitively expensive when it needs to solve the process models under a wide ranges of operating conditions and solvent candidates due to the the highly nonlinear nature of the process and physical property equations. There is, however, limited understanding of the suitability of process modelling approaches for the solution of the CAMPD problems using the SAFT γ Mie EOS.

For the modelling and simulation of the chemical absorption process, two approaches are typically used to describe the phenomena of simultaneous heat and mass transfer in the presence of chemical reactions: equilibrium-stage and rate-based approaches. Equilibrium-stage models assume that each theoretical stage is composed of well-mixed vapour and liquid phases, and that these phases are at phase equilibrium (Taylor & Krishna, 1993). The equilibrium-stage model may be inaccurate when mass and heat transfer are kinetically-limited due to the presence of chemical potential and temperature gradients (Henley & Seader, 1981). Rate-based models account for heat and mass transfer limitations by considering mass and heat mass balances for each phase (Seader, 1989) separately.

For CO₂ chemical absorption processes, the application of a rate-based model has been shown to provide better predictions of the temperature and composition profiles of the column than the equilibrium-stage approach (Lawal et al., 2009; Mac Dowell et al., 2013; Afkhamipour & Mofarahi, 2013; Oko et al., 2015; Sherman et al., 2016; Norouzbahari et al., 2016; Dutta et al., 2017). However, the results of the rate-based model strongly depend on the choice of approaches to treat heat and mass transfer phenomena, and on the availability of model parameters such as transport properties, kinetic models and mass transfer correlations. To avoid such difficulties, equilibrium-stage models have been chosen over the rigorous rate-based models in simulation or optimisation studies (Alhajaj et al., 2016b; Soltani et al., 2017) owing to their relative simplicity, flexibility and fast convergence. The equilibrium-stage models proposed by Abu-Zahra et al. (2007b); Alhajaj et al. (2016a,b); Soltani et al. (2017) have been shown to provide useful insights into the viability of solvent candidates within the CO₂ capture process.

Given a robust and systematic approach for describing the CO₂ capture process, modelling studies can play a vital role in identifying the optimal operating conditions that yield the best techno-economic performance for a specific amine solvent. However, this remains a difficult task since the complex relationship between optimal process variables and molecular properties affects the overall performance of the absorption process. In this regard, there have been research efforts to develop approaches for process design and techno-economic analysis to arrive at optimal process conditions. A number of authors (Mariz, 1998; Rao & Rubin, 2002; Abu-Zahra et al., 2007b; Mofarahi et al., 2008; Qiu et al., 2014; Soltani et al., 2017) have carried out parametric studies of the process variables with the aim to maximise absorption efficiency, while process optimisation was employed to capture the effect of the process operating conditions on energy demand (Dave et al., 2011; Karimi et al., 2011) and economic performance (Nuchitprasittichai & Cremaschi, 2011; Lee et al., 2013; Sharifzadeh et al., 2016; Mores et al., 2012; Schach et al., 2010). Although parametric studies provide invaluable insights into the effect of key operating parameters on performance criteria such as energy requirement, environmental impact, and the overall cost, optimisation-based approaches enable the evaluation of the performance of the absorption process using the operating conditions best suited for the amine solvent examined. This results in a more realistic assessment of the suitability of novel solvents.

Here, we focus on the development of detailed mathematical models of the CO_2 chemical absorption process and economic models using the SAFT- γ Mie EOS that are sufficiently accurate and robust over a wide range of operating conditions for various types of amine solvents. Given the advantages of equilibrium-stage models in section 3.2, we first describe the model equations, and validated the model using pilot-plant data (CASTOR, 2004). In section 3.3, an initialisation strategy is presented to improve the convergence behaviour during the solution of the com-

plex nonlinear process model. The initialisation method presented in this chapter includes several modifications over the traditional inside-out algorithm (Boston, 1980), leading to enhanced convergence as well as model reliability. To formulate the process optimisation problem to be integrated into the CAMPD framework, a parametric study is conducted in Section 3.4 motivated by the work of Alhajaj et al. (2016a) and Abu-Zahra et al. (2007b). The aim is to investigate the effect of the key operating parameters on overall process performance, such that suitable process variables and constraints are introduced in the optimisation problem. The suitability of the formulation is studied by performing the process optimisation for selected amine solvents.

3.2 Development of the chemical process model



Figure 3.1: Process overview of the CO₂ absorption-desorption

The process model developed in this work is based on a standard regenerative absorption-desorption concept as shown in the process flow diagram in Figure 3.1. The flue gas coming out from a direct contact cooler is fed into the bottom of the absorber. The gas stream flows upward through the packing bed inside the absorber,

against a countercurrent stream of a selected aqueous amine solvent. The gaseous CO_2 is chemically absorbed into the amine solution and the clean gas stream leaving the top of the absorber is emitted to the atmosphere. The CO_2 rich solution leaving the bottom of the absorber passes thorough the rich-lean heat exchanger (HE) where the rich amine solution is heated by the hot CO_2 lean amine solution. It then enters the top of the desorber for solvent regeneration. The rich amine solution flows downward against a counter-current flow of water-rich vapour generated in the reboiler until CO_2 concentration in the solvent solution is reduced to the target level. Finally, the lean amine solution passes through the rich-lean HE and lean amine cooler to achieve a pre-defined operating temperature and then returns to the top of the absorber.

The CO_2 loading indicates the absorption capacity of a solvent, i.e., how many moles of CO_2 can be dissolved into 1 mole of solvent at given conditions of pressure and temperature. The lean loading is calculated based on the liquid composition of the lean solvent stream going into the top of the absorber, while rich loading is measured at the liquid composition of the rich solvent stream coming out of the bottom of the absorber.

In the modelling of the CO_2 capture processes with amine solutions, there have been several efforts to describe the phenomena of simultaneous heat and mass transfer in the presence of chemical reactions. Although rate-based process simulations may provide a more precise representation of the absorption process, we adopt here an equilibrium-stage model, as discussed in the previous section. The following assumptions are made in the modelling of the process.

- The model is steady state.
- Each tray of the column is considered as having complete mixing, with thermodynamic equilibrium is reached. Thus, there are no concentration and temperature gradients.

- Pressure drops across the process units are neglected.
- The isentropic efficiency for the pump is assumed to be $\eta_{pump} = 0.8$
- The minimum approach temperature in the heat exchanger is set to 10 K to ensure feasible heat transfer.



3.2.1 Model equations

Figure 3.2: Schematic of an equilibrium stage of the absorber or desorber

The absorption/desorption column comprises N theoretical stages, with $N = N_a$ for the absorber and $N = N_d$ for the desorber, respectively. As an initial assumption, the absorber and desorber are modelled with ten theoretical stages. In Figure 3.2 the general model of a stage j in a counter-current cascade of N equilibrium stages is represented, where F_j is the feed molar flowrate to stage j, $z_{i,j}$ is the mole fraction of component i in the feed, L_j and V_j are the total liquid and vapour molar flowrates (mol s⁻¹) coming out of the jth theoretical stage, respectively, $x_{i,j}$ and $y_{i,j}$ are the liquid and vapour mole fractions of component i on stage j, U_j and W_j are the liquid and vapour sidestream molar flowrates leaving stage j, h_j^L , and h_j^V (J mol⁻¹) are the molar enthalpies of streams L_j and V_j , respectively, Q_j is the total heat rate (J s⁻¹) transferred from stage j, and T_j and P_j are the temperature and pressure of stage j, respectively. The resulting MESH (mass balance, equilibrium, summation of mole fractions, energy balance) equations for each equilibrium stage for the absorber and desorber are outlined below:

$$L_{j-1}x_{i,j-1} + V_{j+1}y_{i,j+1} + F_j z_{i,j}$$

$$- (L_j + U_j) x_{i,j} - (V_j + W_j) y_{i,j} = 0, \quad i = 1, \dots, NC, \quad j = 1, \dots N$$
(3.1)

$$L_{j-1}h_{j-1}^{L}(T_{j-1}, P_{j-1}, \boldsymbol{x}_{j-1}) + V_{j+1}h_{j+1}^{V}(T_{j+1}, P_{j+1}, \boldsymbol{y}_{j+1}) + F_{j}h_{j}^{F}(T_{j}, P_{j}, \boldsymbol{z}_{j}) - (L_{j} + U_{j})h_{j}^{L}(T_{j}, P_{j}, \boldsymbol{x}_{j}) - (V_{j} + W_{j})h_{j}^{V}(T_{j}, P_{j}, \boldsymbol{y}_{j}) - Q_{j} = 0, \ j = 1, \dots N$$
(3.2)

where x_j and y_j (in bold) are vectors of the liquid and vapour component mole fractions in the streams leaving stage j. The mole fractions in the stream leaving each stage must sum to unity:

$$\sum_{i=1}^{NC} x_{i,j} = 1 \quad \text{and} \quad \sum_{i=1}^{NC} y_{i,j} = 1; \quad j = 1, 2, \dots, N$$
(3.3)

The phase equilibrium relation for each component can be expressed as:

$$y_{i,j} - K_{i,j} x_{i,j} = 0$$
, $i = 1, \dots, NC, j = 1, \dots N$ (3.4)

where $K_{i,j} = K_{i,j}(T_j, P_j, \boldsymbol{x}_j, \boldsymbol{y}_j)$ is a partition coefficient for component *i* on stage *j*.

All other process units such as the cooler, pump, reboiler, heat exchanger and condenser are modelled as equilibrium stages in which the mass and heat balance equations in conjunction with the phase equilibria are solved simultaneously.

3.2.2 Sizing and cost model

A key objective of this work is to link the cost of the CO_2 capture process to the properties of the solvent. The cost model herein is based on the method developed in Alhajaj et al. (2016a,b). For the techno-economic evaluation of the integrated process and solvent model, the total annualised cost (TAC) is considered as an objective function of Problem (MINLP), where,

$$TAC = \frac{(TCI)CRF + FOM}{CF} + VC + CP\dot{m}_{CO_2}^{ven}.$$
 (3.5)

Here, FOM is the fixed operation and maintenance cost (smillion year⁻¹), VC is the variable cost, the sum of the utility cost and the solvent makeup cost, CP is the carbon price (\$million per ton of CO_2 emitted), $\dot{m}_{CO_2}^{ven}$ is the amount of CO_2 emitted to the atmosphere (ton year⁻¹), i.e., the amount of CO_2 in the clean gas stream, CRF is the capital recovery factor that takes into account the depreciation of the plant and interest rate through the plant lifetime and CF is the capacity factor. We choose CRF, CF, CP to be 0.15, 0.7 and 4, respectively. TCI is the total capital cost of investment (\$million year⁻¹), which is calculated by summing the purchased equipment cost of the individual process units, after a sequence of multipliers have been applied to represent various indirect and direct costs such as engineering, taxes, and labour. The economic lifetime of the process for the costing is assumed to be 25 years. The cost of MEA is chosen as \$1.2/kg (Alhajaj et al., 2016b). Note that we assume the cost for all amine-based solvents is same as that of MEA throughout the thesis. As discussed in Mores et al. (2012), once the solvent is loaded into the system, the most solvent is regenerated in the desorber and the impact of MEA make-up cost is indeed insignificant taking up to 5.8 % of the total utility cost.

The first step of the cost evaluation, given the results of the process simulation, is to estimate the equipment size so that the purchased equipment cost can be calculated, and followed by other elements of the cost. The purchased equipment cost of

Table 3.1: Equipment type and materials used for each process unit of the absorptiondesorption process modelled in the current work. SS and CS denote stainless steel and carbon steel, respectively.

Equipment	Туре	Material	
Column	Vertical vessel	SS	
Column internal	Plate - Sieve	SS	
Rich-Lean HE	Shell and tube, 20 ft tube length	shell: SS / tube: SS	
Condenser	Shell and tube, 20 ft tube length	shell: CS / tube: SS	
Reboiler	Shell and tube, 20 ft tube length	shell: SS / tube: CS	
Lean amine cooler	Shell and tube, 20 ft tube length	shell: CS / tube: SS	
Pump	Centrifugal, 3600rpm shaft	SS	

 Table 3.2: Types and overall heat transfer coefficient (U) for the heat exchangers

Heat exchanger	Туре	$U (W m^{-2}K^{-1})$
Rich-lean HE	Floating head	710
Condenser	Fixed-head	425
Reboiler	Kettle vaporiser	850
Lean amine cooler	Fixed head	425

each process unit is calculated using the method described in Seider et al. (2009). The size factors and parameters that are used for the cost evaluation are listed in Table 3.1. The overall heat transfer coefficients used for each heat exchanger are listed in Table 3.2.

Columns

We assume that the absorber and desorber are designed as tray columns to avoid having to prediction additional properties, such as diffusivity and mass transfer coefficients, associated with packing design. We employ the approach described by Pereira et al. (2011) for the calculation of the column diameter and the empirical correlation proposed by O'Connell (1946) for the column height. Here, we summarise key aspects of each method. The calculation of the diameter of the absorber and desorber is performed based on 80% flooding, which is typical for a gas absorber (Kister et al., 1992). The minimum velocity at which entrainment flooding occurs, i.e., flooding velocity, $U_{n,\text{flood}}$ (m s⁻¹), is obtained from the balance between droplet weight and drag force defined by:

$$U_{n,\text{flood}} = C_{sb,\text{flood}} \cdot \left(\frac{\sigma_L}{20}\right)^{0.2} \cdot \sqrt{\frac{\rho_L - \rho_V}{\rho_V}},\tag{3.6}$$

where σ_L is the liquid surface tension (mN m⁻¹), ρ_L is the liquid density (kg m⁻³), and ρ_V is the gas density (kg m⁻³). $C_{sb,flood}$ is the ultimate capacity parameter. It can be obtained from a correlation established by Lygeros & Magoulas (1986), and is expressed as a function of the tray spacing TS (inches) and ratio of liquid to vapour kinetic energy F_{LV} :

$$C_{sb,\text{flood}} = 0.0105 + 8.127 \times 10^{-4} (25.4 \ TS)^{0.755} \exp\left(-1.463 F_{LV}^{0.842}\right), \qquad (3.7)$$

where $C_{sb,flood}$ has units of (m s⁻¹), and F_{LV} is dimensionless and defined as:

$$F_{LV} = \sqrt{\frac{\rho_L}{\rho_V}} \frac{q_L}{q_V}.$$
(3.8)

The gas velocity U_n (m s⁻¹) through the net column area A_n is obtained at a flowrate of about 80% of the maximum, i.e.,

$$U_n = 0.8U_{n,\text{flood}}.$$
 (3.9)

Finally, the column diameter, D (m), is calculated based on the total cross section of the column A_t :

$$D = 2\sqrt{\frac{A_t}{\pi}}, \ A_t = 1.2A_n.$$
 (3.10)

The column height is deduced from the actual number of trays N_{actual} , provided that a tray spacing TS has been chosen. We take 24 inches as tray spacing. Some additional space at the top and at the bottom of the column is required for the flow, equivalent to 15% of the total height of tray stack. The column height H (m) is given by

$$H = 1.15N_{\text{actual}}TS = 1.15\frac{N}{\eta_0}TS,$$
(3.11)

where *N* is the calculated number of theoretical stages taken from the simulation and η_0 is an overall stage efficiency, usually less than 1.0, which is determined by the following empirical equation proposed by O'Connell (1946):

$$\log \eta_o = 1.597 - 0.199 \left[\log \left(\frac{KM_L \mu_L}{\rho_L} \right) \right] \quad -0.0896 \left[\log \left(\frac{KM_L \mu_L}{\rho_L} \right) \right]^2, \tag{3.12}$$

where μ_L is the liquid viscosity (cP), M_L is the average molecular weight of the liquid mixture, ρ_L is the density of the liquid (lb ft⁻³) and *K* is a partition coefficient of a species being absorbed or stripped, i.e., CO₂. The values of μ_L , M_L , and ρ_L are calculated to be an average over all stages of the column. Note that the efficiency calculated is known to deviate from operational data about 15% for water-hydrocarbon system (Seader, 1989 and Seider et al., 2009).

The purchase cost of the column is obtained by summing the cost of column vessel and column internals. The cost of the vessel depends on the type of materials and their weight. For our case, stainless steel is selected for all process units due to the highly corrosive nature of aqueous solutions of amines. The base cost for a vertical column, C_P , is given by:

$$C_P = F_M C_V + C_{PL}, \tag{3.13}$$

where F_M is a material factor, C_V is the empty vessel cost and C_{PL} is the added cost for the column such as ladders and a nominal number of nozzles. C_V is determined by the weight, W (lb), of the column as

$$C_V = \exp\left\{7.2756 + 0.18255[\ln(W)] + 0.02297[\ln(W)]^2\right\}.$$
(3.14)

The correlation for C_{PL} is given by:

$$C_{PL} = 300.9 \left(D_{ft} \right)^{0.63316} (H_{ft})^{0.80161}, \tag{3.15}$$

where D_{ft} and H_{ft} are column diameter and height in ft. The purchase cost of the internals is given by

$$C_T = N_{actual} F_{NT} F_{TT} F_{TM} C_{BT}, aga{3.16}$$

where F_{TT} is a factor accounting for the type of tray and taken as 1.0 for a sieve tray, F_{NT} is a factor accounting for the total number of trays and taken as 1 for $N_{actual} < 20$, F_{TM} is a material correction factor calculated by

$$F_{TM} = 1.401 + 0.0724D_{ft}, \tag{3.17}$$

and C_{BT} is the base cost of the trays expressed as

$$C_{BT} = 468 \exp(0.1739 D_{ft}). \tag{3.18}$$

Heat exchangers

The cooler, condenser, reboiler and rich-lean HE are modelled as shell and tube type heat exchangers with countercurrent flow. The required heat transfer area for a heat duty Q can be calculated as:

$$A_{\text{heat}} = \frac{Q}{U \times LMTD}, \ LMTD = \frac{(T_{hot,in} - T_{cold,out}) - (T_{hot,out} - T_{cold,in})}{\ln(\frac{T_{hot,in} - T_{cold,out}}{T_{hot,out} - T_{cold,in}})}, \quad (3.19)$$

where A_{heat} is the heat transfer area (m²), U is the overall heat transfer coefficient (Wm⁻²K⁻¹) and *LMTD* is the log mean temperature calculated using the temperatures of the inlet and outlet streams of the HE. $T_{m,p}$, where m denotes a hot (m = "hot") or cold (m = "cold") stream and p denotes an inlet (p = "in") or outlet (p = "out") stream. The overall heat transfer coefficient depends on the properties of the fluid, the configuration of the HE and the flow regime inside of the HE. An

alternative to the rigorous calculation of the *U*-value is to make use of typical values published in literature (Green & Perry, 2008; Association et al., 2012) either based on the type of the fluids or the type of HE, assuming that the design of the HEs is optimised such that commonly known *U*-values can be achieved, as shown in Table 3.2.

The cost correlations of the HEs differ based on the type of application. The condenser (*cd*) and cooler (*cl*) are chosen as shell and tube type equipped with a fixed head, the rich-lean heat HEs (*rl*) as shell and tube type with a floating head, and the reboiler (*r*) as a kettle vaporiser. The base cost $C_{B,u}$ for each HE, *u*, is given by:

• Floating head

$$C_{B,rl} = \exp\left\{11.667 - 0.8709[\ln(A_{\text{heat}})] + 0.09005[\ln(A_{\text{heat}})]^2\right\}$$
(3.20)

• Fixed head

$$C_{B,u} = \exp\left\{11.0545 - 0.9228[\ln(A_{\text{heat}})] + 0.09861[\ln(A_{\text{heat}})]^2\right\}, u = cd, cl \quad (3.21)$$

• Kettle vaporiser

$$C_{B,r} = \exp\left\{11.967 - 0.8709[\ln(A_{\text{heat}})] + 0.09005[\ln(A_{\text{heat}})]^2\right\}$$
(3.22)

The purchase cost of each of these three types of HE is determined from:

$$C_{P,u} = F_P F_{M,u} F_L C_{B,u}, \ , u \in \{rl, cd, cl, r\}$$
(3.23)

where F_L is a correction factor that accounts for tube-length. This is taken as 1.00, assuming that typical tube length, 20 ft. F_M is a material factor for various combi-

nations of shell and tube materials given as function of surface area, A_{heat} , i.e.,

$$F_{M,u} = a_u + \left(\frac{0.0929A_{\text{heat}}}{100}\right)^{b_u} u \in \{rl, cd, cl, r\}.$$
(3.24)

The exponents a_u and b_u are determined by the shell-and-tube material and are given by $a_u=1.75$ and $b_u=0.13$ for condenser and lean amine cooler (u = cd, cl), and $a_u=2.70$ ad $b_u=0.07$ for rich-lean HE and reboiler (u = r, rl) (Seider et al., 2009). F_P is a pressure correction factor given by

$$F_P = 0.9803 + 0.018 \left(\frac{P}{100}\right) + 0.0017 \left(\frac{P}{100}\right)^2, \qquad (3.25)$$

where P is operating pressure (psig).

Pumps

The pump is modelled as a centrifugal pump. The cost of the pump is a function of the size parameter, *S*, given as

$$S = Q_{\text{pump}} (H_{\text{head}})^{0.5}, \qquad (3.26)$$

where Q_{pump} denotes the volume flow rate through the pump (gallons per minute) and H_{head} is the pump head (ft). The purchase cost of a centrifugal pump is then given by

$$C_P = F_T F_M C_B, \tag{3.27}$$

where F_M is a material factor and F_T is a pump-type factor and the values are taken as 1.5 and 2.0, respectively, based on the selected material and equipment type (see Table 3.1).

Specification	Units	Value
Lean solvent flow rate	$m^3 h^{-1}$	23
MEA concentration in lean solvent	wt%	30.4
Lean solvent temperature	К	331.9
Absorber inlet flue gas rate	$\mathrm{Nm}^3 \mathrm{h}^{-1}$	4915
Absorber inlet flue gas CO ₂ molar composition	mol%	11.86
Absorber inlet flue gas H_2O molar composition	mol%	11.00
Absorber inlet flue gas N ₂ molar composition	mol%	77.14
Absorber inlet flue gas temperature	К	320.4
Absorber operating pressure	MPa	0.101
Stripper and Reboiler pressure	MPa	0.181
Rich solvent temperature coming out of Rich-lean HE	К	373.1
Degree of capture	%	90

Table 3.3: Main specification of CASTOR pilot plant (CASTOR, 2004) used for the validation study

3.2.3 Model validation

Following the modelling of the process, the simulation results are compared against published pilot plant data (Alhajaj et al., 2016a) in order to assess whether the process model, in which SAFT- γ Mie thermodynamic treatment and an equilibriumstage column models are integrated, can provide a quantitative agreement with the pilot plant data. The performance of the process model is validated for a 30.4 wt% concentration of MEA using the CASTOR pilot plant data (CASTOR, 2004). Note that the concentration of the solvent is calculated only based on water and solvent contents in a liquid stream. This data set is chosen as it has been independently reproduced in previous works (Alhajaj et al., 2016a; Abu-Zahra et al., 2007b). The data used in the simulations of CO₂ absorption is presented in Table 3.3. The water content in the flue gas is taken from Abu-Zahra et al. (2007a) as it is not reported along with the pilot plant data (CASTOR, 2004). The process model is implemented in the gPROMS modelling environment using a SAFT- γ Mie Foreign Object for the physical properties. As a performance criterion, a percentage relative error, δ_{error} , is used to compare the results of the model with plant data:

Item, g	Units	Plant	Simulation	$\delta_{error,g}$
Absorber height	m	18.0	17.9	0.56
Absorber diameter	m	1.10	0.94	14.38
CO_2 mass flowrate in inlet flue gas	$\mathrm{kg}~\mathrm{h}^{-1}$	1145	1136	0.78
CO ₂ mass flowrate captured in absorber	$\mathrm{kg}~\mathrm{h}^{-1}$	1045	1026	1.31
Degree of CO_2 captured	%	90.00	90.35	0.38
Clean gas outlet temperature	K	331.95	343.03	3.34
Rich solvent CO ₂ loading	$mol mol^{-1}$	0.46	0.50	8.39
Rich solvent temperature at the outlet of the absorber	K	327.15	325.98	0.36
Max. solvent temperature in the absorber	К	348.15	344.14	1.15
Desorber height	m	10.00	16.44	64.43
Desorber Diameter	m	1.10	0.75	32.19
Reboiler heat duty	GJ ton- CO_2^{-1}	3.897	4.777	22.58
Reboiler temperature	К	391.65	394.01	0.06
Cooling water requirement	GJ ton- CO_2^{-1}	3.434	2.229	35.00
Lean loading	$mol mol^{-1}$	0.28	0.28	0

Table 3.4: Comparison between the predictions of the performance of CO_2 absorptiondesorption process model and plant data of CASTOR (2004).

$$\delta_{error,g} = \left(\frac{|Y_g^{\text{Sim}} - Y_g^{\text{Plt}}|}{Y_g^{\text{Plt}}}\right) \times 100, \qquad (3.28)$$

where Y_g^{Plt} and Y_g^{Sim} are the values taken from the plant data and the simulation results, respectively, for process parameter g.

As can be seen in Table 3.4, the equilibrium stage model delivers an overall good agreement with the pilot plant data available in terms of the amount of CO_2 captured, the composition and temperature of the rich solvent stream and the operating conditions of the lean stream leaving the reboiler. The predicted diameters of the absorber and desorber are slightly underestimated compared to the experimental data. This is because the lumped hydrodynamic model used in the current study cannot account for the effect of heat- and mass-transfer limitations. The prediction for the height of the desorber column deviates significantly the experimental data by 64.43%. This error is attributed to the fact that each theoretical stage is interpreted as a tray, which often results in a larger column size than in a packed bed column, which is the type of column used in the pilot plant. The purchased cost of the desorber accounts for 24.04% of the total purchased cost. However, the TCI only contributes 3.43 % on TAC and therefore the impact of the purchased cost of
the desorber is much less significant. Similar discussion can be found in Mores et al. (2012) in which a detailed comparison of the distribution of the cost-items on overall cost was studied for the different CO₂ capture levels. Although the reboiler temperature is accurately described, there is an overprediction of approximately 0.9 GJ ton- \mathbf{CO}_2^{-1} in the reboiler duty. This difference may be attributed to the sensitive nature of the SAFT- γ Mie parameters to the prediction of second-order thermodynamic derivative properties such as heat capacity, that have not been taken into account in the model development. It has been shown previously that heat of absorption accuracy can be improved by incorporating caloric properties in model development (Graham, 2020). Nonetheless, the predicted reboiler duty represents well a typical reboiler duty of 3.9-4.2 GJ ton- CO_2^{-1} for coal-fired power plants and 4-5 GJ ton- CO_2^{-1} for combined cycle gas turbine (CCGT) plants as reported in Singh et al. (2003); Kehlhofer et al. (2009); Mac Dowell et al. (2013); Soltani et al. (2017); Bui et al. (2018). The CO_2 loading of the rich solvent stream is overestimated by approximately 8% although a similar amount of CO_2 is removed from the flue gas. This discrepancy may be associated with the assumption made on the water composition in the flue gas stream, as the value is not reported in the pilot plant data. It can also be postulated from the higher flue gas outlet temperature that the evaporative loss of the water content from the lean solvent stream may lead to a higher solvent mole fraction in the rich solvent stream, consequently resulting in a higher CO_2 loading. Additionally, the equilibrium stage model exhibits higher CO_2 capture capacity in the absorber (i.e., a higher degree of CO_2 captured is predicted by the model), allowing more gaseous CO_2 to be dissolved in the liquid solvent solution. The relative difference is however marginal.

In summary, the validation of the model with the use of the SAFT- γ Mie EOS has shown the ability of the equilibrium stage model to predict the overall process performance. It is thus suitable for providing useful insight into the economic performance and energy efficiency of the process for a given solvent. A more refined description of the absorption process could be obtained by using a rate-based process model, but the equilibrium-stage model allows us to focus on system trends as opposed to the detailed behaviour at the individual unit level while achieving computational efficiency and greater flexibility in the choice of process operating conditions and the types of solvents.

3.3 Initialisation strategy

One difficulty in solving the model of the CO₂ chemical absorption process is that it involves the calculation of the highly nonlinear MESH equations coupled with complex thermodynamic property models. Convergence to a solution for such systems strongly depends on the quality of the initial guesses. However, it is notoriously difficult to provide good initial guesses that are universal for all solvent candidates and cover a wide range of operating conditions. Furthermore, equation-oriented solvers that are based on the simultaneous update of all variables can encounter numerical difficulties even with the good initial guesses. It is therefore of interest to develop a robust initialisation algorithm that is capable of accommodating a variety of process specifications and solvent molecular structures as well as one that is insensitive to the initial user-provided estimates.

In this section, we investigate a column solution method that can be adapted to the CO_2 chemical absorption process. An extension of the "inside-out" algorithm is then introduced to provide a reliable way of handling the a highly non-ideal systems under consideration.

3.3.1 Inside-out method

There have been advances made in solution approaches for multistage equilibrium separation processes — for example, the bubble-point method (Wang, 1966), the sum-rates method (Sujata, 1961; Friday & Smith, 1964), the simultaneous correc-

tion techniques (Naphtali, 1965; Naphtali & Sandholm, 1971), which employ the Newton–Raphson method, and the inside-out algorithm (Boston & Sullivan, 1974; Boston, 1980). These methods are based on an equation-decoupling technique to avoid the necessity of enumerating a large matrix of partial derivatives in which the predominant variables in the calculation of heat and mass balances may differ from these in the equilibrium stages and also in the phase equilibrium model. The techniques also allow one to deal with the large variations in the magnitude of the variables, round-off errors, and the sparsity of the Jacobian matrices effectively (Boston, 1980). The solution approaches that have been proposed to date differ in the choice of independent variables, the grouping and arrangement of the equations, and the convergence path.

One of the most widely used methods in practice is the inside-out method (IOM), first proposed by Boston & Sullivan (1974) and further extended by many others (Boston, 1980; Russell, 1983; Jelinek, 1988) to make it applicable to highly nonideal systems as well as ones with extremely narrow or wide boiling ranges. It has also been modified to account for reactive systems (Simandl & Svrcek, 1991; Wang et al., 2020) so that robust convergence behaviour can be achieved in the simultaneous calculation of phase and chemical equilibrium. The IOM has not only been demonstrated to converge rapidly into a solution and to be flexible in the choice of specified variables, but also not to require accurate initial estimates. One important feature of the IOM is that the calculation procedure is divided into two stages: (1) an inner-loop where an approximate (simplified) thermodynamic model is employed to solve the MESH equations, and (2) an outer-loop where the parameters of the approximate thermodynamic model are updated using rigorous thermodynamic calculations for given temperatures, pressure, vapour and liquid compositions, which are obtained from the inner-loop. Another distinctive feature of the IOM is the choice of iteration variables. The iteration variables for the inner-loop are related to stripping factors defined by $S_{b,j}$, for each stage j, and the iteration variables for the outer-loop

are a set of simplified thermodynamic model parameters. Details of each parameter are discussed in later sections. Here, we implement the inside-out methods of Wang et al. (2020) and Jelinek (1988) for the absorber and that of Russell (1983) for the desorber calculation.

3.3.2 Inner-loop property model and MESH equations

The description of the inside-out method begins by defining approximate property models that are designed to facilitate the calculation of stage temperatures and phase equilibrium during execution of the inner-loop. First the stripping factors are defined in terms of an approximate K-value, $K_{b,j}$, as follows:

$$S_{b,j} = K_{b,j}V_j/L_j, \quad j = 1, ..., N.$$
 (3.29)

An approximate K-value model, the a K_b model (Holland, 1963; Boston & Sullivan, 1974), is adopted to capture the temperature dependence of the most significant component equilibrium ratio ($K_{i,j}$, i = 1, ..., NC) values for each stage j, while removing the explicit dependence on component identities:

$$\ln K_{b,j} = A_j - B_j / T_j, \quad j = 1, ..., N,$$
(3.30)

where the coefficients A_j and B_j are model parameters calculated at each outerloop using the rigorous thermodynamic model. To aid subsequent calculations in the outer-loop, it is useful to define, a base K-value $K_{b,j}$, as a weighted average:

$$K_{b,j} = \exp\left(\sum_{i=1}^{NC} w_{i,j} \ln K_{i,j}\right), \quad j = 1, ..., N,$$
(3.31)

where $w_{i,j}$ are weighting factors used to reflect the temperature sensitivity of the individual components in $K_{b,j}$. The definition of theses factors varies depending



in (a) is a procedure where a set of MESH equations are solved simultaneously using a EO solver. standard inside-out algorithm. Red highlighted sections in (a) correspond to the inside-out algorithm of (b). Blue highlighted section **Figure 3.3:** An overview of (a) the initialisation strategy used for the solution of CO_2 absorption-desorption process model and (b) a

on how to make $\partial(\ln K_{b,j})/\partial T_j$ an appropriate weighted average of the individual $\partial(\ln K_{i,j})/\partial T_j$. In our study, we make use two different heuristic definitions of the weighting factors proposed by Boston & Britt (1978) and Russell (1983) for the absorber and Wang et al. (2020) for the desorber, respectively. The equations for each column are as follows:

$$w_{i,j} = \frac{y_{i,j} \left[\partial \ln K_{i,j} / \partial (1/T_j)\right]}{\sum_i y_{i,j} \left[\partial \ln K_{i,j} / \partial (1/T_j)\right]} \ i = 1, ..., NC, \ j = 1, ..., N, \ \text{for the absorber.}$$
(3.32)

$$w_{i,j} = \frac{y_{i,j}/K_{i,j}}{\sum y_{i,j}/K_{i,j}} \ i = 1, ..., NC, \ j = 1, ..., N, \ \text{ for the desorber.}$$
(3.33)

The derivatives in Equation (3.32) are obtained either numerically or analytically by using the rigorous thermodynamic model in the outer-loop iteration. As the $K_{i,j}$ are strongly dependent on the temperature (as well as the compositions for highly nonideal systems), the $K_{b,j}$ values also exhibit a strong dependence on those variables. In the K_b model, however, the coefficients A_j and B_j are much less sensitive to temperature, therefore their use as independent variables leads to improved convergence behaviour. An important aspect of the IOM is the separating temperature and composition effects by partitioning the $K_{i,j}$ values:

$$K_{i,j} = \alpha_{i,j} K_{b,j} \ i = 1, ..., NC, j = 1, ...N,$$
(3.34)

where $\alpha_{i,j}$ is a relative volatility of component *i* on stage *j*. The value of $\alpha_{i,j}$ is much less sensitive to the temperature than that of $K_{i,j}$ because temperature dependence is included in the $K_{b,j}$ parameter. As a result, the iteration procedure with the $\alpha_{i,j}$'s as independent variables presents much better convergence characteristics than a procedure using the $K_{i,j}$'s.

When the system exhibits large nonidealities in the liquid phase, the composition effects become as dominant as to the temperature. For an absorber where a highly nonideal liquid system is present, the performance of the IOM with the simple K-value model described in Equation (3.34) may be impaired in the absence of factors that can account for nonideality. To overcome the difficulties associated with nonideal multi-stage systems, i.e., the absorber in our study, we apply the model developed by Boston (1980) in which the K-values are partitioned further into three factors: $K_{b,j}$, $\alpha_{i,j}$ and $\gamma_{i,j}^*$, where $\gamma_{i,j}^*$ is a pseudo-activity coefficient for each component *i* on stage, *j*, i.e.,

$$K_{i,j} = K_{b,j} \alpha_{i,j} \gamma_{i,j}^*, \ i = 1, ..., NC, \ j = 1, ..., N.$$
 (3.35)

The pseudo-activity coefficient $\gamma_{i,j}^*$ is expressed as a function of additional parameters $a_{i,j}$ and $b_{i,j}$ and the resulting formulation is given as

$$\ln \gamma_{i,j}^* = a_{i,j} + b_{i,j} x_{i,j}, \ i = 1, ..., NC, \ j = 1, ..., N.$$
(3.36)

Similarly, an approximate enthalpy model replaces the enthalpy departure function with the simple linear functions, i.e.,

$$\Delta h_j^V = c_j - d_j \left(T_j - T_j^* \right),$$

$$\Delta h_j^L = e_j - f_j \left(T_j - T_j^* \right),$$
(3.37)

where T_j^* is a reference temperature. Δh_j^V is the vapour phase enthalpy departure for stage j, defined as $h_j^V - h_j^{V,o}$, where $h_j^{V,o}$ is the ideal-gas mixture enthalpy for stage j, and Δh_j^L is the liquid phase enthalpy departure for stage j, defined as $h_j^L - h_j^{V,o}$. The parameters d_j and f_j represent the mean residual heat capacities for the vapour and liquid phases, respectively, c_j represents the vapour enthalpy departure at T_j^* , and e_j accounts for the heat of vaporisation relative to that of the the ideal gas. The parameters c_j, d_j, e_j and f_j are evaluated at every outer-loop iteration. Note that we employ the approximate enthalpy model only when calculation with the rigorous thermodynamic model fail to achieve convergence. This is because the additional complexity involved in the use of two enthalpy models may not always be justified

(Jelinek, 1988).

Once all the parameters for the approximate thermodynamic model are specified in the outer-loop iteration, the original MESH equations can be reformulated with the following iteration (or independent) variables:

$$S_{b,j} = K_{b,j}V_j/L_j , j = 1, ..., N$$

$$R_j^L = 1 + U_j/L_j , j = 1, ..., N ,$$

$$R_i^V = 1 + W_j/V_j , j = 1, ..., N$$
(3.38)

where $S_{b,j}$ is a stripping factor for the base component, R_j^L and R_j^V are liquid-phase and vapour-phase withdrawal factors, respectively. In our study, there are no side streams resulting in the $R_j^L = R_j^V = 1$.

The calculation in the inside-loop is based on the vapour and liquid phase component flowrates rather than the mole fractions. Their relationships with the vapour and liquid phase compositions and the total molar flowrate are as follows:

$$y_{i,j} = v_{i,j}/V_j, \quad x_{i,j} = l_{i,j}/L_j, \quad z_{i,j} = f_{i,j}/F_j$$

$$V_j = \sum_{i=1}^{NC} v_{i,j}, \quad L_j = \sum_{i=1}^{NC} l_{i,j}, \quad F_j = \sum_{i=1}^{NC} f_{i,j}, \quad i = 1, ..., NC, \quad j = 1, ..., N$$
(3.39)

By incorporating the iteration variables and component flowrates, the MESH equations (Equation (3.1) to (3.4)) can be rewritten as:

$$l_{i,j-1} - \left(R_j^L + \alpha_{i,j}S_{b,j}R_j^V\right)l_{i,j} + \left(\alpha_{i,j+1}S_{b,j+1}\right)l_{i,j+1} - f_{i,j} = 0, \quad i = 1, ..., NC, \quad j = 1, ..., N$$
(3.40)

$$h_{j}^{L}R_{j}^{L}L_{j} + h_{j}^{V}R_{j}^{V}V_{j} - h_{j-1}^{L}L_{j-1} - h_{j+1}^{V}V_{j+1} - h_{j}^{F}F_{j} - Q_{j} = 0, \quad j = 1, ..., N$$
(3.41)

$$v_{i,j} = \alpha_{i,j} S_{b,j} l_{i,j}, \quad i = 1, ..., NC, \quad j = 1, ..., N$$
 (3.42)

3.3.3 Outer-loop property models

Given the set of primitive values for $v_{i,j}$, $l_{i,j}$, V_j , L_j and T_j obtained from the innerloop calculation, the parameters of the approximate thermodynamic model are updated using the rigorous thermodynamic model. All parameters in the approximate thermodynamic models are generated using the SAFT- γ Mie EOS (Papaioannou et al., 2014) model. To obtain values for A_j and B_j in Equation (3.30), two temperatures must be selected for each stage. Here, the estimated or current temperatures of the two adjacent stages, j - 1 and j + 1, are selected as T_1 and T_2 , respectively, in the following equations:

$$B_{j} = \frac{\partial \ln K_{b,j}}{\partial (1/T_{j})} = \frac{\ln (K_{b,T_{1}}/K_{b,T_{2}})}{(1/T_{1} - 1/T_{2})},$$

and
$$A_{j} = \ln K_{b,j} - B_{j} \left(\frac{1}{T_{j}} - \frac{1}{T_{j}^{*}}\right)$$
(3.43)

Note that $K_{b,j}$ is calculated based on Equations (3.31)-(3.33). Then, the relative volatilities are calculated based on the new $K_{b,j}$. Analogous to the $K_{b,j}$ calculation, the coefficients $a_{i,j}$ and $b_{i,j}$ for the nonideal system are updated by the evaluating of the activity coefficients for two compositions of $x_{i,j}$, separated by a difference δx , with the relative sizes of all other liquid-phase mole fractions kept constant:

$$a_{i,j} = \ln \gamma_{i,j} (T_j, P_j, \boldsymbol{x}_i) - b_{i,j} x_{i,j} \quad b_{i,j} = \frac{\ln \gamma_{i,j} (T_j, P_j, \boldsymbol{x}'_{\gamma}) - \ln \gamma_{i,j} (T_j, P_j, \boldsymbol{x}_{\gamma})}{\delta x}$$

where, $\boldsymbol{x}'_{\gamma} = (x'_{1,j}, \dots, x'_{i,j}, \dots, x'_{NC,j}),$
 $x'_{i,j} = x_{i,j} + \delta x, \quad x'_{i,k, \ k \neq i} = \frac{x_{k,j} (1 - x_{i,j} - \delta x)}{(1 - x_{i,j})}, \ i = 1, \dots NC, \ j = 1., ., N,$
(3.44)

where $\gamma_{i,j}$ is the liquid activity coefficient of component *i* for a given temperature T_j , pressure P_j and composition x_j , δx is an infinitesimal perturbation in the composition $x_{i,j}$. In practice, δx is chosen as 10^{-4} .

3.3.4 Implementation

All process models for the initialisation step are implemented in the gPROMS ModelBuilder 7.0.7 using a gSAFT Foreign Object interface. The convergence criterion used for the IOM is based on the relative change in of the relative volatility values between two successive iterations of the outer-loop (Jelinek, 1988):

$$\operatorname{error} = \sum_{j=1}^{N} \sum_{i=1}^{NC} \left| \alpha_{i,j}^{k+1} - \alpha_{i,j}^{k} \right| / \left(\alpha_{i,j}^{k} \right)^{2} \le \epsilon$$
(3.45)

where k is an iteration number, ϵ is a user-specified convergence tolerance. A tight tolerance of $\epsilon = 0.002 \times N$ was initially recommended by Russell (1983) and has been used in the literature (Jelinek, 1988; Wang et al., 2020). When a good quality of initial guesses is provided, fast convergence can be achieved with an equation-oriented (EO) process simulation framework in which a large set of algebraic equations is solved simultaneously without simplifying an thermodynamic model. One strategy to accelerate the of convergence of the calculations is therefore to make use of EO numerical solvers combined with the IOM. Owing to the robustness of the EO numerical solver embedded in the gPROMS, specifically "BDNLSOL" numerical solver, more practical and relaxed convergence tolerances of $\epsilon = 1$ for the absorber and $\epsilon = 5$ for desorber are used for the simulation. Once the convergence tolerance is reached, the solution procedure for the IOM is switched to "BDNLSOL" solver provided that the sufficiently good initial guess on V_j , L_j , x_j , y_j , and T_j is obtained from the last outer-loop calculation of the IOM.

When simulating the entire process, the IOM is used in a sequential manner: the absorber model is solved first for the initial lean solvent conditions using the IOM; Once the convergence achieved, the tighter convergence tolerance is achieved by solving the absorber model using the EO solver; then the absorber model is solved for the user-provided process specifications such as the purity of the clean gas and

the composition, temperature, pressure of the lean solvent; Having the properties of the liquid outlet stream conditions from the absorber model, the temperature of the rich solvent stream entering the desorber is estimated; Then, the solution on the desorber model is obtained in same manner. An overview of the algorithm is given in Figure 3.3.

3.3.5 Results

In order to investigate the proposed initialisation strategy and assess whether it can be used to provide a reliable way to achieve convergence for various molecules, we test its numerical behaviour for three chemically-different solvent structures: 30 wt% of 2-aminoethanol (MEA), 1,3-Diamino-2-propanol (DAP) and N'-methyl-2,2'-diaminodiethylamine (MDAEA). The process specifications, namely, the degree of CO₂ captured, lean solvent loading and desorber operating pressure, are varied within physically realistic ranges to analyse performance, as summarised in Table 3.5. The initial estimates of L_j , V_j , $x_{i,j}$, $y_{i,j}$ are given by solving flash calculations for the global composition z_j and T_j , P_j . The z_j for the absorber is are assumed to be the same for all stages and are initially estimated from the sum of the flue gas and lean solvent component molar flowrates. The temperature, T_j for the absorber is given

Table 3.5: Process specifications used for the evaluation of IOM. MEA, DAP, and MDAEA are shortened names of 2-aminoethanol, 1,3-Diamino-2-propanol, and N'-methyl-2,2'-diaminodiethylamine, respectively.

Design specification	Units	MEA	DAP	MDAEA
Degree of CO ₂ captured	%	85	90	90
Absorber operating pressure	MPa	0.101	0.101	0.101
No. of ideal stages in the absorber		10	10	10
Desorber operating pressure	MPa	0.200	0.108	0.102
No. of ideal stages in the desorber		10	10	10
Condenser temperature	К	333	333	333
Minimum temperature approach	К	10	10	10
Lean solvent circulation temperature	К	313	313	313
Lean loading	$mol mol^{-1}$	0.1	0.2	0.7



Figure 3.4: Column convergence profiles (error vs iteration number) for (a) absorber for MEA ($-\blacktriangle$ -), DAP ($-\bullet$ -), MDAEA ($-\times$ -) and (b) desorber with 30 wt% MEA ($-\blacktriangle$ -), 30 wt% DAP ($-\bullet$ -), 30 wt% MDAEA ($-\times$ -)



Figure 3.5: Column temperature profiles for the (a) absorber with 30 wt% MEA (- -), 30 wt% DAP (- -), 30 wt% MDAEA ($- \times -$) and (b) desorber with MEA (- -), DAP (- -), MDAEA ($- \times -$) at the convergence of IOM. The dashed lines represent the initial estimates of the equilibrium stage temperatures. In the desorber, the condenser stage is omitted since the temperature is fixed at 333 K and the stage 12 corresponds to the reboiler

as an average of the flue gas and lean solvent stream temperatures. The pressure P_j is fixed at the absorber operating pressure. In the case of the desorber, the initial global composition profile is set to be equal to the rich solvent composition coming in to desorber inlet. The temperatures of the top and bottom stages of the desorber are initially assigned via bubble point calculations at the expected composition and desorber pressure. Given the two temperature estimates, the temperature profile of the desorber is established as a linear temperature gradient.

In Figure 3.4, it can be seen that, when applied to the absorber, the IOM exhibits asymptotic convergence behaviour, successfully reaching to desired convergence tolerance of $\epsilon = 1$ within a few iterations for all cases. The IOM converges to the solution at a much slower rate when applied to the desorber with DAP and MDAEA. As can be seen in Figure 3.5, the initial estimates of the stage temperatures for the desorber with DAP and MDAEA are within a few degrees of the final values and are much closer than those of MEA. Nevertheless, the solution of the desorber column with DAP and MDAEA requires a large number of iterations. This is attributed to the large discrepancy between the initial estimates given for the liquid and vapour molar flowrates and the final solution, as reflected in the large initial error values, of magnitude of 10^4 (see Figure 3.4(b)). The slow convergence is also likely caused by a lack of parameters that take into account the compositional dependence in the K_b model. However, the use of the local compositional dependence model that is applied to the absorber introduces four additional parameters for each equilibrium stage and requires the calculation of activity coefficients for the $2NC \times N$ set of liquid compositions at every outer-loop iteration. Given that the desorber column operates at a higher temperature, where the compositional effects (or nonideality in the liquid phase) are expected to be less significant, the original K_b model may be significant as it can reduce the computational cost of the outer-loop.

It can also be seen that error in the desorber cases with DAP and MDEAE decreases rapidly in the few iterations but then progresses slowly towards the convergence tolerance. This suggests that applying an adaptive damping factor would be desirable to control the step size when updating the simple thermodynamic parameters, such that quicker convergence may be achieved by avoiding oscillations or overshoots in iteration variables. However, this additional complexity would not be in keeping with our objective to develop an initialisation procedure to support process optimisation. In summary, a sufficiently good overall convergence is achieved with the IOM, indicating that the proposed initialisation procedure can be applied prior to the process optimisation at different operating conditions, process specifications and solvent types.

3.4 Parametric study and process optimisation

In this section, a parametric study is carried out aiming at developing an optimisation formulation for the process by investigating the relative impact of selected process parameters on key performance indicators (KPIs).

3.4.1 Model input

The process model and cost model previously developed are applied to a 400 MWe combined CCGT power plant (Bailey & Feron, 2005) using 30 wt% MEA (mass of MEA/(mass of MEA + mass of H₂O)) as the solvent. The flue gas flowrate and composition taken from the power plant data and the process specifications defined as the base case are presented in Table 3.6. Note that the original data are modified so that the of oxygen mole fraction (10%) is lumped into the nitrogen mole fraction. The following process operating parameters are varied, starting from the baseline defined in Table 3.6: amount of CO₂ captured (%), lean solvent temperature T_0 (K) at the absorber inlet, desorber operating pressure P_{N_d} (MPa), lean loading θ_0 (mol mol⁻¹) and condenser temperature T_{cond} (K). The following criteria are employed as KPIs:

- Solvent circulation rate per ton of CO₂ removed (kg ton-CO₂⁻¹), which is indicative of equipment size and absorption/desorption efficiency of the solvent for given operating conditions. Note that the solvent circulation rate is defined as the total flowrate of the lean solvent stream recycling back to the top of the absorber.
- Four energy metrics in GJ ton-CO₂⁻¹: (i) the total thermal energy, (ii) the cooling duty in the lean amine cooler, (iii) the cooling duty in condenser, and (iv) the energy requirement in the reboiler per ton of CO₂ captured. These represent the energy efficiency of the CO₂ capture plant. The total thermal energy is calculated as the sum of the lean amine cooler, reboiler, and condenser duties.
- Three economic metrics in \$ millions year⁻¹: The total annualised cost, TAC, total cost of investment, TCI, and total operating expenditures, OPEX. Note that OPEX is calculated as the sum of VC and FOM/CF as can be seen in Equation (3.5).
- Solvent loss (or slippage) per ton of CO₂ removal (kg ton-CO₂⁻¹), which represents the potential risk of environmental impact associated with emissions of the amine solvent and its side products. The total solvent loss is calculated by summing the amount of MEA in the clean gas stream coming out from the top of the absorber and that in the CO₂ gas stream leaving the condenser.

3.4.2 Results and discussion

Effect of target CO₂ removal

The sensitivity of the KPIs is considered as a function of the amount of CO_2 removed from the flue gas while other parameters are fixed at the base case. The costs, energy requirements, solvent loss and solvent circulation rate are calculated, and the results are shown in Figure 3.6. As can be seen from Figure 3.6(a), there is a decrease in

Base line process specification	Units	Value
Lean solvent flow rate	$\mathrm{m}^3 \mathrm{h}^{-1}$	23
MEA concentration in lean solvent	wt %	30.4
Absorber inlet flue gas rate	$\mathrm{Nm}^3 \mathrm{h}^{-1}$	1,800,000
Absorber inlet flue gas CO ₂ molar composition	mol%	5
Absorber inlet flue gas H ₂ O molar composition	mol%	12
Absorber inlet flue gas N_2 molar composition	mol%	83
Absorber inlet flue gas temperature	Κ	323.15
Absorber operating pressure	MPa	0.101
Temperature approach in heat exchangers	Κ	10
Lean solvent temperature, T_0	Κ	313.15
Desorber operating pressure, P_{N_d}	MPa	0.181
Lean loading, θ_0	$mol mol^{-1}$	0.25
Condenser temperature, T_{cond}	Κ	333.15
Degree of CO ₂ captured	%	90

Table 3.6: Input values and baseline process specification of a CO_2 capture process model for a 400MW CCGT power plant (Bailey & Feron, 2005).

solvent circulation rate as the proportions of CO₂ removed is increased, although small scale of the axis should be noted. The solvent circulation rate decreases until it reaches a global minimum near 92% of CO₂ captured and starts to increase afterwards. This adverse effect of the target removal on the solvent circulation rate is due to the amount of CO₂ captured becoming a dominating factor at the lower CO₂ removal target, whereas the impact of the absolute solvent flowrates (in kg h^{-1}) in the system is predominant at the higher target values, yielding a higher solvent circulation rate for every ton of CO₂ removed. This is indeed in consistent with the trends in energy requirement as shown in Figure 3.6(b), making the changes in the specific thermal energy requirement marginal within a range between 46-82% of CO_2 removal. Although the energy requirements appear almost constant on first inspection, they increase slightly as the removal target increases (by 2.7% at 98% removal, relative to the base case) at the higher target range, whereas they decrease slightly at the lower target range. In Figure 3.6(c) the influence of the CO₂ removal target on the TAC and how it is distributed across TCI and OPEX can be seen. It is clear that the TAC, TCI and OPEX increase rapidly with increasing removal target.

Although not shown here, it is worth noting that the absolute solvent circulation rate (in kg h⁻¹) increases monotonically as the CO_2 capture target increases. This is therefore leads to larger sizes of the process units and higher operating costs. In Figure 3.6(d), it can be seen that there is a reduction in the specific amount of amine loss in the vapour phase as the CO_2 removal target increases. This can be explained by the higher amount of solvent circulation entering the absorber (i.e., more non-volatile solute is presents in the absorber) thus leading to a lower vapour pressure of the solvent in the liquid mixture.

Effect of solvent lean loading

The lean solvent loading of the MEA solution is varied between 0.05 and 0.42 mol- CO_2 mol-MEA⁻¹ for 80, 90 and 95% CO_2 removal and the results are displayed in Figure 3.7. As shown in Figure 3.7(a), the solvent circulation rate increases as the lean loading increases. As can be seen from the scale, the impact is much more pronounced than when varying the target CO_2 captured. At high values of the lean loading, the lower CO₂ cyclic capacity of the solvent, defined as the difference of the CO_2 loading in the rich solvent stream coming out of the bottom of the absorber and lean loading, leads to a higher solvent circulation rate in order to remove the target CO_2 amount. The variation of the lean loading is found to have a significant impact on the the thermal energy requirement and cost criteria as shown in Figure 3.7(b)and (c). The trend profiles have global optimal points near a lean amine loading of 0.33 for the total required energy and 0.34 for the TAC. At low lean loadings (0.05-0.30 mol mol⁻¹), the total required energy decreases with increasing lean loading despite the accompanying increase in the solvent circulation rates. This is because the energy requirement for the solvent regeneration dominates over the effect of increasing the solvent circulation rates. As a result, the greater ease in meeting solvent purity targets in the desorber leads to a net reduction in total energy consumption.



Figure 3.6: Results of the sensitivity analysis obtained by varying the degree of CO_2 captured from the flue gas using MEA: (a) The solvent circulation rate $(10^3 \text{ kg ton-}CO_2^{-1})$; (b) Energy requirement profiles in GJ ton- CO_2^{-1} , including the total required energy for the CO₂ absorption-desorption process (—-), a reboiler duty (—-), the condenser duty (—-) and the cooling duty(—-); (c) Cost profiles in \$million year⁻¹ including TAC (—-), the annualised OPEX (—), and the TCI (—); and (d) the solvent loss (kg ton- CO_2^{-1}).



Figure 3.7: Results of the sensitivity analysis obtained by varying the lean loading (moles of CO₂ dissolved in 1 mole of MEA of a lean amine solvent stream) at 90% of CO₂ removal using MEA: (a) The solvent circulation rate $(10^3 \text{ kg ton-CO}_2^{-1})$; (b) Energy requirement profiles in GJ ton-CO₂⁻¹, including the total required energy for the CO₂ absorption-desorption process (—), a reboiler duty (—), the condenser duty (—) and the cooling duty(—); (c) Cost profiles in \$million year⁻¹ including TAC (—), the annualised OPEX (—), and the TCI (—); (d) The effect of the lean loading on the TAC at different degrees of CO₂ removed (— : 85%, - - : 90%, and — : 95%); and (e) the solvent loss (kg ton-CO₂⁻¹).



Figure 3.8: Results of the sensitivity analysis obtained by varying the lean solvent temperature at 90% of CO_2 removal using MEA: (a) The solvent circulation rate (10^3 kg ton- CO_2^{-1}); (b) Energy requirement profiles in GJ ton- CO_2^{-1} , including the total required energy for the CO₂ absorption-desorption process (—-), a reboiler duty (—-), the condenser duty (—-) and the cooling duty(—-); (c) Cost profiles in \$million year⁻¹ including TAC (—-), the annualised OPEX (—-), and the TCI (—-); and (d) the solvent loss (kg ton- CO_2^{-1}).



Figure 3.9: Results of the sensitivity analysis obtained by varying the desorber operating pressure at 90% of CO₂ removal using MEA: (a) The solvent circulation rate (10^3 kg ton-CO₂⁻¹); (b) Energy requirement profiles in GJ ton-CO₂⁻¹, including the total required energy for the CO₂ absorption-desorption process (—), a reboiler duty (—), the condenser duty (—) and the cooling duty(—); (c) Cost profiles in \$million year⁻¹ including TAC (—), the annualised OPEX (—), and the TCI (—); and (d) the solvent loss (kg ton-CO₂⁻¹).



Figure 3.10: Results of the sensitivity analysis obtained by varying the condenser temperature at 90% of CO₂ removal using MEA: (a) The solvent circulation rate $(10^3 \text{ kg ton-CO}_2^{-1})$; (b) Energy requirement profiles in GJ ton-CO₂⁻¹, including the total required energy for the CO₂ absorption-desorption process (—-), a reboiler duty (—-), the condenser duty (—-) and the cooling duty(—-); (c) Cost profiles in \$million year⁻¹ including TAC (—), the annualised OPEX (—-), and the TCI (—-); and (d) the solvent loss (kg ton-CO₂⁻¹).

One other possible explanation for the decrease in reboiler and condenser duties at higher lean loading is the lower liquid traffic in the desorber, i.e., the lower reflux or boiling ratios required to achieve the solvent purity target; therefore, both the TAC and the total thermal energy requirement decrease as the value of lean loading increase. The higher partial pressure of CO_2 (i.e., higher CO_2 content) in the reboiler, which is linked to the heat of vaporisation, can also explain the low heat duty, as less steam generation is required to maintain the driving force. The decrease in TAC, OPEX, and TCI seen for lean loading of 0.05-0.30 mol mol⁻¹ (see Figure 3.7(c)) can be explained in the same manner.

A similar trend is observed for all degrees of CO_2 captured considered as shown in Figure 3.7(d). Note that the lean loading for the 95% removal target was varied up to 0.4 due to the limits on the minimum driving force for the CO_2 chemical absorption. The value of the optimal lean loading differs depending on the degree of CO_2 captured. The higher removal target results in a lower optimal lean loading at which a higher CO_2 absorption capacity is achieved and thus this effectively reduces the solvent circulation rate and the corresponding energy requirement for solvent regeneration. It should be noted that the differences in the optimal lean loading and the corresponding TAC value for each degree of CO_2 removal considered are insignificant.

It can also be seen from Figure 3.7(e) that the solvent loss decreases with increasing amine loading due to the increase in the solvent circulation rate, as also observed when varying the CO_2 removal target.

Effect of lean solvent temperature

In Figure 3.8 calculations for changes in the lean solvent temperature at the inlet of the absorber between 313K and 334K are shown. The impact of this variation on the KPIs is generally much smaller than that of varying the lean loading. As shown in

Figure 3.8(a), the solvent circulation rate decreases slightly as the lean solvent temperature increases within the ranges of interest, owing to the higher CO₂ solubility in the amine solution in the absorber, potentially induced by higher (average) CO_2 partial pressures. As can be observed from Figure 3.8(b), varying the lean solvent temperature at the absorber inlet has no significant effect on the reboiler and condenser duties; the duties are seen to increase slightly as the lean solvent temperature increases. This may be explained by the increases in the solvent concentration in the rich solvent stream caused by a higher loss of water in the absorber at higher lean solvent temperatures, leading to a higher reboiler temperature. Although not shown here, the reboiler operating temperature indeed increases as the lean solvent temperature increases. In contrast, the cooling duty of the lean cooler decreases by 31% when the lean solvent temperature is raised by 5K, resulting in a gradual decrease in the total thermal energy requirement. As shown in Figure 3.8(c) the TAC increases with higher lean solvent temperatures, while a large reduction in the overall heat duty is seen. Such trends are attributed to the absorber being at a higher operating temperature, at which more MEA evaporates at the top of the absorber. As a result, the solvent loss is found to increase (see Figure 3.8(d)) and thus there is a correspondingly higher demand for the solvent make-up. The potential discharge of the solvent can be reduced by adding a wash section in order to mitigate the environmental impact; however, this will require a higher utility cost for wash water.

Effect of stripper operating pressure

Figure 3.9 shows how the KPIs are influenced by the desorber operating pressure. As shown in Figure 3.9(a), the solvent circulation rates does not change over the ranges of desorber operating pressure considered since the pressure is not involved in the calculation of the solvent circulation rate required to achieve a specific CO_2 removal target. In Figure 3.9(b) it can be observed that the increase in pressure lead to a reduction in the reboiler duty and condenser duty, leading to a reduction in the total thermal energy consumption. This may be explained by the higher desorber temperature induced by the higher operating pressure. At the higher pressures considered, an increase in desorber operating temperature plays a dominant role in decreasing the CO₂ solubility and increasing relative volatility, making it possible to purify solvent at lower energy consumption. Interestingly the positive impact of having a higher temperature on the thermal performance of the process is reduced in the high operating pressure region. One of several possible explanations is that the increase in the total pressure of the desorber results in a rise of the CO₂ partial pressure making the gaseous CO_2 more soluble in the amine solution and competing with the effect of higher temperature. A similar trend is observed in Figure 3.9(c)in which TAC and OPEX decreases as the pressure decreases. This is attributed to the decreased energy requirement achieved. It can be seen that the changes in TCI are almost negligible, although it decreases slightly between 0.14-0.22 MPa. This is due to the fact that the purchased equipment cost is a function of operating temperature and pressure, in addition to size. As a result, the benefit of the cost reduction achieved by having smaller sizes of process units is counter-balanced due to the negative impact of increases in pressure and temperatures. As can be seen in Figure 3.9(d), it appears that operating the desorber at the highest pressure is preferable in order to improve the environmental aspects, as the lowest solvent loss is achieved.

Despite the benefits of higher pressures, it is not desirable to operate the desorber at higher than 393-403 K, which corresponds to the 0.175-0.24 MPa, because the corrosion and amine degradation rates can be accelerated at these elevated pressures and temperatures.

Effect of condenser temperature

The effects of varying the condenser operating temperature on the KPIs is shown in Figure 3.10. As can bee seen in Figure 3.10(a)-(c), the variation of the condenser operating temperature has no visible effect on the solvent circulation rate, energy consumption, and cost criteria, although there is a slight reduction in the condenser duty. As can bee seen in Figure 3.10(d), the amine loss increases as the condenser temperature increases due to the higher solvent content in the CO₂ gas stream leaving the condenser. The cost reduction associated with the energy penalty in the condenser is therefore balanced with the cost increase in the amine make-up, making the changes in the total cost and energy consumption insignificant.

3.4.3 Process optimisation for MEA and AMPD

Table 3.7: Process constraints used in the optimisation study

Parameters	Units	Bounds
Lean loading, θ_0	$mol mol^{-1}$	[0.02,1.5]
Desorber pressure, P_d	MPa	[0.102, 0.8]
Lean solvent temperature, T_0	Κ	[313, 333]
Lean solvent stream flow rate, $\dot{m}_{\rm sol}$	$mol \ s^{-1}$	$[10, 10^6]$

The parametric study showed that each key operating parameter has a different level of contribution on the cost and energy penalty criteria, meaning that an optimal design of CO_2 chemical absorption-desorption processes can be realised by selecting the appropriate combination of the process variables. Given the importance of choosing suitable operating conditions to achieve an optimal performance of the process, the mathematical model of the absorption-desorption process is used in formulating and solving an process optimisation problem. In view of the parametric study, the optimisation problem is formulated with degrees of freedom: the lean solvent loading (θ_0), the lean solvent temperature (T_0), and the desorber operating pressure (P_{N_d}), in order to identify the optimal combination of the process conditions that minimise the TAC. The target CO_2 removal, condenser temperature, and minimum approach temperature in the heat exchangers are fixed at the base case shown in Table 3.6. In Table 3.7 the bounds on the decision variables and constraints used in the optimisation problem are shown. In order to limit the negative environmental impact, the following operating conditions are constrained with suitable upper and lower bounds:

$$T_{\text{reboiler}} \le T_{\text{op}}^U,$$
 (3.46)

where T_{reboiler} is the reboiler operating temperature and T_{op}^U is the maximum allowable operating temperature introduced to avoid the thermal degradation of amine solvents. The T_{op}^U is set to 413 K for the optimisation.

Additional constraints to keep the size of the equipment reasonable are provided as:

$$D \le D_{\text{column}}^{U},$$

$$H \le H_{\text{column}}^{U},$$
(3.47)

where D_{column}^U and D_{column}^U is an upper bound of the column diameter and height, respectively. The same bounds are applied to both the absorber and desorber columns. The values are specified as $D_{\text{column}}^U = 25 \text{ m}$ and $H_{\text{column}}^U = 35 \text{ m}$.

The optimisation study is carried out for two solvents: MEA and 2-Amino-2methyl-1,3-propanediol (AMPD), to investigate the significance of choosing the sol-

Results	MEA		AMPD	
	Initial	Optimal	Initial	Optimal
TAC($\$$ million year ⁻¹)	33.77	29.81	28.45	25.73
TCI(\$ million year $^{-1}$	6.752	8.047	9.065	8.951
OPEX ($\$$ million year ⁻¹)	26.40	21.15	18.77	16.17
Total energy consumption (GJ ton- CO_2^{-1})	12.74	9.32	11.23	7.93
Reboiler temperature (K)	394.1	397.1	393.2	399.0
Amine cyclic capacity (mol mol $^{-1}$)	0.2272	0.1597	0.2251	0.2134
Lean amine loading, θ_0 (mol mol ⁻¹)	0.2500	0.3167	0.2500	0.2610
Lean solvent temperature, T_0 (K)	313.1	313.2	313.2	335.4
Desorber operating pressure, P_{N_d} (MPa)	0.180	0.206	0.180	0.216

 Table 3.8: Results of the optimisation of the process model for MEA and AMPD.

vent in conjunction with the optimal process conditions. The optimisation problem is solved by making use of the sequential quadratic programming algorithm embedded in gPROMS ModelBuilder 7.0.7 for multivariate nonlinear programming with the gSAFT Foreign Object interface for the SAFT- γ Mie calculations. The optimisation parameters used for gPROMS NLP solver are as follows: "InitialLineSearch-StepLength"= 0.1; "MaxLineSearchStepLength"= 0.4; "NoImprovementTolerance" = 10^{-15} ; "OptimisationTolerance" = 5^{-5} .

The results of the optimisation are shown in Table 3.8. For both MEA and AMPD, the TAC is reduced by 11.7% and 9.5%, respectively, compared to the performance of the process at the initial guess. The initial guess provided is same as the base case used for the parametric study. In the case of MEA, the reboiler duty associated with the solvent regeneration is reduced significantly by decreasing the purity requirement in the desorber (the lean loading is increased by 26.7%). The increase in the TCI caused by the higher solvent circulation rate is compensated by the significant reduction in the energy penalty. By contrast, the optimal performance is achieved at a slightly higher lean loading and increased lean solvent temperature for the case of AMPD, leading to decreases both in TCI and in OPEX. As can be seen in comparing of the results with the two solvents, the dominant factors that drive the optimal combination of process conditions clearly differ between the solvents, highlighting the important role played by the molecular properties within the process.

3.5 Conclusions

In this chapter, a techno-economic model for CO_2 absorption-desorption processes using an equilibrium-based approach has been developed with the aim of integrating it into a CAMPD framework in which a variety of operating conditions can be evaluated. A distinctive feature of the model presented here is that both vapourliquid equilibrium and reactions are treated with the SAFT- γ Mie (Papaioannou et al., 2014) thermodynamic framework, by which the performance of new solvents within the process can be assessed even when the available data is limited or non-existent. Simulation of the process model with MEA as a solvent has been shown to deliver quantitative agreement with the pilot-plant data of CASTOR (2004). Accurate predictions are obtained for the gas and liquid streams leaving of the absorber, with a moderate discrepancy (22.58%) in a reboiler duty.

In order to make the solution of the process model more robust, an initialisation strategy has been developed for the process simulations. The approach is derived from the inside-out algorithm in order to handle the numerical complexities inherent in the large number of mass- and heat-balance equations coupled with the complex thermodynamic model used here. The performance tests conducted for several solvents using the proposed initialisation strategy has shown it provides reliable convergence behaviour for a diverse set of process specifications without requiring good initial guesses.

Following the successful calculation of the process performance, a sensitivity study has been carried out to identify the contributions of the key operating parameters to the economic, environmental and thermal performance of the reactive CO₂ absorption-desorption process using an aqueous MEA solutions. The lean loading, lean solvent temperature and the desorber operating pressure are found to have the greatest impact on the total annual cost and the total energy consumption. A large reduction in the reboiler duty, which is the main contributor to the TAC, and in the total energy requirement, is observed by controlling the key operating parameters. The results of the parametric study has demonstrated that the process modelling approach developed can capture the trends of the overall process performance.

In order to balance the conflicting effects of the key operating parameters on process performance, an optimisation study has been carried out for two types of solvents, MEA and AMPD. The overall total annual cost in terms of capital investment and energy cost was minimised, while the degree of CO_2 captured and the condenser temperature were fixed at specified values. The results indicate that a reduced cost can be achieved by varying combinations of the optimal process conditions that are tailored to the type of solvent, highlighting the importance of accounting for the solvent performance within the context of the process as opposed to focusing solely on solvent properties.

CHAPTER 4

Computer-aided molecular and process design: optimal solvent design for CO_2 chemical absorption processes

Following the development of the CO_2 chemical absorption process model in the previous chapter, we present a robust CAMPD algorithm to solve the integrated design of optimal aqueous amine solvents and associated CO_2 chemical absorption processes. The focus is on improving an outer-approximation (OA)-based framework such that numerical difficulties caused by incompatible combinations of process and molecular variables are avoided. In order to achieve this, new feasibility tests are introduced as an extension of the approach proposed by Gopinath et al. (2016) in order to ensure its applicability to the more complex setting of CO_2 chemical absorption.

4.1 Introduction

Given the importance of computer-aided molecular and process design (CAMPD) techniques, a variety of solution methods have been developed to handle the complexities that arise from the large number of possible molecules and from the inherent non-linearity and non-convexity of structure-property relationships and process models. However, most algorithms are prone to failing in generating a feasible solution when the integrated solvent-process model entails a large-scale mixed-integer nonlinear formulation, and more importantly, when a significant portion of the search space is infeasible. Identifying feasible ranges of process variables that make it possible to avoid infeasibilities is difficult because it requires *a priori* knowledge of the properties of the solvents and their phase behaviour at process conditions.

In addition, it may be entirely infeasible to satisfy the separation requirements with particular solvent candidates. One class of methods suited for overcoming the infeasibilities aforementioned are decomposition-based approaches. In these, the process and molecular design are decoupled and treated as a series of separate subproblems. Each subproblem is often formulated with a different level of complexity and a reduced size of the design space in order to make the problem tractable.

Hostrup et al. (1999) proposed a hybrid method for the integrated design of solvents and environmentally-benign separation processes. In their method, they first used thermodynamic insights and knowledge of the system to eliminate less attractive solvents and process flowsheet options. The remaining candidate solvents and flowsheet structures were then optimised to find the best objectives. A similar CAMPD solution approach was adopted by Roughton et al. (2012) for the identification of new liquid entainers for extractive distillation processes to improve energy efficiency. Karunanithi et al. (2006) developed a decomposition-based CAMPD framework for the design of optimal solvents and solvent mixtures for the crystallisation of ibuprofen. The framework consists of several subproblems: the first subproblem was formulated as a computer-aided molecular design (CAMD) problem aiming to reduce the discrete solvent search space by evaluating molecular structural constraints, pure component properties, mixture properties and miscibility of compounds. Subsequently, a MINLP CAMPD problem was solved for the reduced search domain. Alternatively, the process optimisations were solved by enumerating all possible solvents if the number of remaining feasible molecular candidates

was very small. Papadopoulos & Linke (2006b,a) developed a CAMPD framework that decouples the original MINLP problem into two subproblems: a multi-objective optimisation (MOO) method was employed to screen Pareto-optimal solvents with respect to key molecular properties, without considering their interdependence with the relevant process; and a molecular clustering approach that integrates the process and molecular design was then applied to select solvents from the set of identified Pareto-optimal solvents. This method has been extended by Papadopoulos et al. (2010a, 2013) for the design of optimal working fluids and working fluid mixtures for Organic Rankine Cycle (ORC) processes. A more recent development in decomposition-based methods is outlined by Eden et al. (2004) and Eljack et al. (2007). In their studies, molecular properties were optimised to maximise process performance, such as an economic value of the process, without considering discrete decisions on molecular structures. Subsequently, molecular structures that can match the identified property targets were explored by solving a property-matching CAMD problem (Maranas, 1997). Bommareddy et al. (2010) incorporated a similar strategy using a group contribution method (Marrero & Gani, 2001) for the representation of molecular property operators. Within the family of property-targeting approaches, Bardow et al. (2010) and Oyarzún et al. (2011) proposed a two-stage method for integrated molecular and process design using the perturbed-chain statistical associating fluid theory (PC-SAFT) as the property model. In the first stage, continuous parameters characterising the molecules within the PC-SAFT equation of state were optimised together with process variables. The hypothetical optimal molecule obtained in the first step was then mapped onto an existing molecule in the second stage. The performance of the proposed method has been demonstrated for the design of solvents for pre-combustion CO_2 capture (Stavrou et al., 2014), and the design of solvents for the pre-combustion carbon capture in the work of Lampe et al. (2015).

While there have been encouraging advances in decomposition-based CAMPD

techniques that allow for the generation of optimal molecular candidates, some drawbacks of these methods have been discussed in Ng et al. (2015); Gopinath et al. (2016); Austin et al. (2016); Schilling et al. (2020). A major disadvantage of decomposition-based methods is that they can result in suboptimal solutions if the heuristic or expert judgement made in the initial step (introduced to reduce the search space) does not capture all process options. Therefore, the quality of the solutions is often highly dependent on the formulation of the subproblems. Unfortunately, it is not always straightforward to decompose the original problem into several steps. In order to overcome the limitations arising from solving the process and molecular design problem separately, direct solution approaches that aim to solve the full CAMPD problem have been receiving increasing attention.

Burger et al. (2015) proposed a hierarchical approach to address the numerical difficulties in the solution of direct CAMPD problems. Good initial guesses for an integrated solvent and CO₂ physical absorption process design problem were generated using an MOO technique applied to a simplified thermodynamic-based design problem. Once the Pareto-optimal set of solvent candidates has been generated based on the simplified process model, a MINLP problem with the full process model integrated was solved, taking the Pareto-optimal solvents as starting points. One difficulty in applying this method is that there is no guarantee that the Pareto-optimal solvents represent solutions that are near-optimal or even feasible in the full CAMPD model. Furthermore, simplified design problem that involve highly non-ideal phase behaviour and nonlinear structure-property model equations might be very challenging, implying that identifying each Pareto-optimal solution can become computationally very expensive.

Several attempts have been made to solve the full MINLPs directly. Zhou et al. (2017) adopted a direct solution approach for the MINLP arising from the formulation of the computer-aided solvent and process design problem. In their contribution, a hybrid stochastic-deterministic optimisation approach was proposed where a

genetic algorithm (GA) was applied to generate molecular candidates and a gradientbased nonlinear programming (NLP) algorithm was used to optimise the process for a given set of molecular candidates. The effectiveness of the method was tested on a CO₂ physical absorption process model. Although the results demonstrated the robustness of the algorithm, there were several difficulties when applying it to more complex systems. Firstly, the decisions made on the discrete variables which are handled by the GA are not the only concern when solving the CAMPD problem. In the optimisation of the process model, one needs to make sure that the molecules are feasible with respect to the specified process configurations such that the overall performance is correctly evaluated as a function of molecules. When generating a new set (population) of molecules with the GA, in the presence of strong nonlinear relationships between the molecule and process, the selection of feasible or high-performance molecules becomes very difficult if many of molecules violate the process constraints. Moreover, increases in the population size of the GA greatly increases the computational cost. Other authors have also focused on solving the full MINLP model directly. Schilling et al. (2017) extended the two-stage continuous molecular targeting (CoMT) to a 1-stage CoMT-CAMD approach (Bardow et al., 2010). The MINLP problem was solved using an outer approximation (OA) algorithm to identify optimal hypothetical working fluids, with the use of PC-SAFT, and associated ORC process conditions. The same approach was applied to the design of working fluid mixtures for the ORC process (Schilling et al., 2020). While the applicability of the method seems promising, the formulation of the problem was developed based on the reverse approach which requires the molecular mapping of the hypothetical molecular structure to a real molecule in a final step. The actual performance of the molecules found by reverse mapping deviated from the optimal value with the hypothetical working fluids as reported in Table 4 and 5 of the original paper (Schilling et al., 2017).

An alternative strategy for the simultaneous approach is outlined by Gopinath
(2017). Motivated by the work of Buxton et al. (1999), the authors developed a set of feasibility tests and incorporated them into the OA algorithm, with very promising results, as this approach provides excellent performance for complex CAMPD problems and it can capture the interactions between the full process model and molecular behaviour without the addition of great computational burden. The feasibility tests could served as precursors to the solution of the primal problem, through which infeasible molecules and process operating conditions could be eliminated from the search space before tackling the process optimisation problem. By automatically detecting the infeasibilities as a function of molecular structure, not only was convergence of the problem achieved regardless of user-provided initial guesses, but computational efficiency was also improved without making significant model simplifications or introducing any approximations of the process and molecular domains. The robustness of the algorithm was validated in the design of solvent and processes for the physical absorption of CO_2 from high pressure natural gas. The concept of physical reduction of the domain was also implemented in integrated working fluid and ORC process design (Bowskill et al., 2020).

The goal of the current study is to develop a robust optimisation framework for the integrated design of an optimal aqueous amine solvent and CO_2 chemical absorption process. The algorithm incorporates tailored feasibility tests into the OA algorithm (Duran & Grossmann, 1986) for the solution of CAMPD problems such that large molecular and process design spaces are explored simultaneously without difficulty. The design of the feasibility tests focuses on recognising the feasible domain based on: (1) the physicochemical properties of the pure solvent and aqueous solvent mixture; (2) an analysis of the phase behaviour of mixtures of the solvent, water and CO_2 carried out using the Helmholtz free Energy Lagrangian Dual (HELD) algorithm (Pereira et al., 2012), which provides reliable phase equilibrium calculation; (3) ability of the solvent mixture to meet a target degree of separation. The efficiency of the proposed algorithm is highlighted through case studies of CO_2 chemical ab-

sorption processes. An optimisation formulated is developed based on the process model introduced in Chapter 3 and the SAFT- γ Mie group contribution equation of state (EOS) (Papaioannou et al., 2014) is applied to facilitate the reliable prediction of the physical properties and phase behaviour of the water-solvent-CO₂ mixtures. For each case study, an economic criterion is used to evaluate the performance of the solvent/process and to identify optimal designs.

4.2 **Problem formulation**

4.2.1 Solvent design space

The molecular design space is constructed by selecting groups that are present in typical CO₂ capture solvents, taking into account the availability of group contribution parameters within the various group contribution methods used. The 13 functional groups are included: NH₂CH₂, NH₂CH, NH₂C, NHCH₃, NHCH₂, NHCH, NCH₃, NCH₂, CH₃, CH₂, CH, C, OH. The property prediction methods of Hukkerikar et al. (2012b) are used for the normal melting temperature $(T_{\rm mp})$, the auto-ignition temperature (T_{AIT}), the flash point (T_{fp}), and the LC50 toxicity of the solvents selected ($LC_{50,mgL}$). The method of Hsu et al. (2002) is used to predict surface tension (σ) and viscosity (μ). The SAFT- γ Mie group contribution EOS (Papaioannou et al., 2014; Khalit, 2019) is used to predict the fluid-phase behaviour of water, solvent and CO_2 mixtures. To make use of this thermodynamic model, the original functional groups are translated into the following SAFT- γ Mie groups: NH₂, NH, N, CH₂, CH, C, CH₂OH, CH₂OH_{Short}. The larger groups CH₂OH and CH₂OH_{Short} are introduced to provide improved accuracy relative to adopting simple groups such as CH₂ and OH (Haslam et al., 2020) by accounting for the polarisation of the CH_2 when close to a functional group. The CH_2OH_{Short} is introduced when the alkanolamine includes less than three carbon along the carbon backbone to account for proximity effects

between the amine and hydroxyl groups. For example, MEA, defined as $n_{\rm NH_2CH_2} = 1$, $n_{\rm CH_2} = 1$, $n_{\rm OH} = 1$, can be translated into an equivalent solvent structure for use in the SAFT- γ Mie EOS, i.e., $n_{S,\rm NH_2}=1$, $n_{S,\rm CH_2}=1$, $n_{S,\rm CH_2OH_{Short}}=1$, where the subscript S denotes the SAFT-based description of the molecule.

An equality constraint introduced to ensure molecular feasibility of the acyclic compounds (Odele & Macchietto, 1993) is defined as $\sum_{i=1}^{N} (2 - v_i)n_i - 2 = 0$, where v_i is the valence of group *i*. The total number of functional groups in the molecule is limited by an upper bound, n_t^U . The total number of groups with amine and hydroxyl functionality are constrained by lower and upper bounds $[n_{G_A}^L, n_{G_A}^U]$ and upper bound n_{OH}^U , respectively.

The use of the two sets of functional groups requires additional constraints to ensure the equivalence of the structures. The choice of groups means, for instance, that OH can only appear in the designed solvent when connected to CH₂. An additional constraint, $\sum_{j \in G_{CH_2}} n_{CH_2} \ge n_{OH}$, is imposed to enforce this. With GC-based approaches, the molecular structure is defined by the number of groups of each type appearing in the molecule without taking into account the connectivity, meaning that it is not possible to distinguish some isomers. As a result, it is assumed that molecular isomers represented by the same functional groups exhibit identical properties. With this mind, constraint that limits the total number of CH and C groups appearing in a solvent to an upper bound n_{iso}^U is introduced in order to reduce degeneracy as a consequence of having many isomers. The resulting formulation of the molecular feasibility constraints is as follows:

$$\sum_{i=1}^{N} (2 - v_i) n_i - 2 = 0,$$

$$n_{G_A}^L \le \sum_{j \in G_A} n_j \le n_{G_A}^U,$$

$$\sum_{i=1}^{N} n_i - n_t^U \le 0$$

$$\sum_{i=1}^{N} n_{OH} - \sum_{j \in G_{CH_2}} n_j \le 0$$

$$\sum_{j \in G_{iso}} n_j - n_{iso}^U \le 0$$

$$n_i \in \{n_{l,i}, n_{u,i}\}, \ i = 1, ..., q$$
(4.1)

where G_A is the set of amine groups given by $G_A = \{NH_2CH_2, NH_2CH, NH_2C, NHCH_3, NHCH_2, NHCH, NCH_3, NCH_2\}$, G_{CH_2} is the set of functional groups that include CH_2 given by $G_{CH_2} = \{NCH_2, NHCH_2, CH_2, CH_2, NH_2CH_2\}$, G_{iso} is a set of functional groups that include CH or C given by $G_{iso} = \{NHCH, NH_2CH, NH_2C, CH, C\}$.

4.2.2 Overall problem statement

For the formulation of the integrated design problem that encompasses solvent and chemical absorption process optimisation, we make use of the process and cost models that were developed and validated in Chapter 3, and the process configuration is shown in Figure 3.1. As for the process optimisation problem of Section 3.4.3, the total annualised cost (TAC) is selected as objective function to measure the overall economic performance and we consider three key process design variables: the temperature of the solvent entering the absorber (T_0), the lean solvent loading (θ_0) defined as moles of CO₂ absorbed in 1 mole of amine solvent, and the desorber pressure (P_{N_d}). The set of design variables is expanded to include the solvent structure as defined by *n*. This results in a MINLP problem (MINLP), as given in Section 2.2. The model input and process specification used in this study are listed in Table 3.6.

The main contribution of the presented CAMPD framework in this chapter is to solve the solvent and CO₂ chemical absorption process optimisation simultaneously without making significant model simplifications or introducing any approximations of the process and molecular domains. A key concept used in the proposed CAMPD approach is the introduction of feasibility tests within an OA framework (Duran & Grossmann, 1986; Fletcher & Leyffer, 1994) aiming to eliminate infeasible process conditions and solvent structures from the search space before solving the highly nonlinear process optimisation problems. In the original OA algorithm, the problem is decomposed into a nonlinear programming (NLP) subproblem, the primal problem, and a mixed-integer linear programming (MILP) subproblem, the master problem. The algorithm procedure begins by solving the first primal problem either for the fixed discrete variables, n or for relaxed NLP. The master problem is then solved for the approximated design space obtained by linearising objective functions and active constraints around the NLP solution. The solution of the master problem is used as input variables for the subsequent primal problem. The iterative procedure of NLP and MILP continues until the algorithm converges. In the proposed CAMPD framework, feasibility tests are used to determine if the current set of discrete variables can derive desired process behaviour without solving the full process optimisation problem. If the molecule is found to be infeasible, it is discarded from consideration in subsequent iterations, and the procedure is returned to the master problem to generate a new molecule. If tests are passed, the overall process performance of the molecule is evaluated by solving the primal problem. This process is repeated until the termination criteria have been satisfied. The overall procedure of the standard OA algorithm and with the feasibility tests are displayed in Figure 4.1 and elements of the proposed algorithm are discussed in more detail in the remainder of this chapter.



Figure 4.1: Schematic illustrating of (a) a standard outer-approximation algorithm and (b) the proposed outer approximation algorithm framework with feasibility tests. Red boxes represents feasibility tests introduced with modifications. This figure is an adaptation of Figure 2 in Bowskill et al. (2020)

4.3 Feasibility tests

In this section, we describe four feasibility tests that are applied to the solvent design formulation for the CO_2 chemical absorption processes. The aims of these tests are to determine whether a given solvent is infeasible, to eliminate process conditions that are incompatible with the chemical solvent, and to identify good starting points for NLP problem optimisation.

In order to adapt the feasibility tests proposed by Gopinath et al. (2016) to more complex setting of the CO_2 chemical absorption-desorption process, several significant modifications are made, such that the OA algorithm reinforced with new feasibility tests can reliably generate solutions. Key differences are at: the formulation of an optimisation problem to consider liquid immisibilities (Test 2); the reformulation of the separation feasibility test accounting for vapour-liquid-liquid equilibrium (VLLE) and chemical reactions (Test3 and 4); the application of feasibility tests to a quaternary system (Test3 and 4); and the derivation of new constraints to consider the desorber (Test 3 and 4). In addition, the performance of different flash calculation approaches for the solution of the tests are systematically compared to improve their convergence behaviour.

4.3.1 Test 1: Solvent property feasibility

Test 1 is employed to evaluate whether the properties of the pure candidate solvent or those of the aqueous solution are within suitable ranges. In Test 1, seven essential properties (Schilling et al., 2020; Harper et al., 1999); five pure solvent properties, namely the normal boiling temperature (T_{bp}), the normal melting point (T_{mp}), toxicity as measured by the lethal dose concentration ($LC_{50,mgL}$), the auto-ignition temperature (T_{AIT}) and the flash point (T_{fp}) and two mixture properties, namely the dew point temperature (T_{dew}), and the viscosity (μ). The thermodynamic property models used for the prediction of these properties and their sources are summarised in Table 4.1. The properties that are not specified in Table 4.1 are predicted using the SAFT- γ Mie EOS (Papaioannou et al., 2014).

For solvent handling to be feasible, the normal boiling point T_{bp} and the normal melting point T_{mp} of the solvent are constrained by the lower and upper bound on the solvent handling temperature i.e., T_{sh}^L and T_{sh}^U , respectively. This is to ensure the solvent is in the liquid state when it is transported or stored. The safety of the solvent is evaluated using $LC_{50,mgL}$, T_{fp} and T_{AIT} and each property is compared with desired ranges as defined in Table 4.1, where T_{op}^U is an upper bound on the operating temperature chosen to avoid solvent degradation. The viscosity of the aqueous solvent is limited by μ^U in order to make sure that the maximum permissible limit for a centrifugal pump is not exceeded. The viscosity is calculated at the minimum

Table 4.1: Property prediction methods and bounds on the properties used in Test 1, $(T_{sh}^L = 298.15\text{K}, T_{sh}^U = 308.15 \text{ K}, T_{op}^U = 413.15 \text{ K}, \mu^U = 0.1 \times 10^3 \text{ cP}$ (Gopinath et al., 2016) and $LC_{50,mgL}^U = 10$)

Physical property	Bounds	Reference
$T_{\rm mp}$ (K) at 1 atm	$[-10^{20}, T_{\rm sh}^L]$	Hukkerikar et al. (2012b)
$LC_{50,mgL}$ (mg/L)	$[-10^{20}, LC_{50}^U]$	Hukkerikar et al. (2012a)
$T_{\rm AIT}$ (K)	$[T_{op}^{U}, 10^{20}]$	Hukkerikar et al. (2012b)
<i>T</i> _{fp} (K)	$[T_{\rm sh}^{\hat{U}}, 10^{20}]$	Hukkerikar et al. (2012b)
μ (cP) at $T_{\rm sh}^L$ and 1 atm	$[0, \mu^U]$	Hsu et al. (2002)

solvent handling temperature T_{sh}^{L} . Finally, a lower bound on the process operating temperature T_{op}^{L} is imposed on the dew point temperature T_{dew} to ensure that the lean solvent is in the liquid phase at the absorber inlet. Here, we set T_{op}^{L} as to be equal to the cooling medium temperature. These low and upper bounds are listed in the caption of Table 4.1. The resulting formulation of Test1 is as follows:

$$T_{\rm sh}^{U} - T_{\rm bp}(P = 1 \operatorname{atm}, n) \le 0 \qquad T_{\rm mp}(P = 1 \operatorname{atm}, n) - T_{\rm sh}^{L} \le 0$$

$$LC_{50, \rm mgL}(n) - LC_{50, \rm mgL}^{U} \le 0 \quad \mu(T_{\rm sh}^{L}, P = 1 \operatorname{atm}, \boldsymbol{z}(n)) - \mu^{U} \le 0$$

$$T_{\rm sh}^{U} - T_{\rm fp}(P = 1 \operatorname{atm}, n) \le 0 \quad T_{\rm op}^{L} - T_{\rm dew}(P = 1 \operatorname{atm}, \boldsymbol{z}(n)) \le 0$$

$$T_{\rm op}^{U} - T_{\rm AIT}(P = 1 \operatorname{atm}, n) \le 0$$
(4.2)

where z(n) is the composition of the aqueous solvent mixture, which is fixed at 0.3 weight fraction of amine solvent. We denote the set of inequality constraints in Test 1 as $g_1(n)$.

It can be seen from the constraints that solvent candidate can be examined regardless of the process design since the properties in Test 1 are independent of the optimal process conditions. The property constraints expressed linearly with respect to n, specifically T_{mp} and T_{fp} , are included in the master problem to increase the likelihood of generating feasible solvent candidate and omitted from Test 1 after the first iteration.

4.3.2 Test 2: Separation feasibility

Test 2 is designed to examine whether there exist operating conditions in the absorber such that the solvent mixture remain in a homogeneous liquid phase. Many amine-water and amine-water- CO_2 mixtures exhibit partial miscibility and this has in fact enabled the consideration of biphasic solvents (also known as phase-change solvents), that are receiving increasing attention as alternatives to conventional solvents. They undergo liquid-liquid phase separation upon heating or CO_2 absorption, so that the solvent mixture split into an amine-rich phase with a high concentration of CO_2 and a water-rich phase with a low concentration of CO_2 . Because only the CO_2 -rich liquid phase is sent to the desorber for solvent regeneration, this reduces the energy requirements and equipment costs (Zhang et al., 2019). Nevertheless, it is necessary for the aqueous solvent to form a homogeneous liquid phase at the absorber operating conditions for successful operation.

Although the process configuration combined here does not allow for phase change solvents, Test 2 can be applied equally to standard and phase change solvents. It consist in determining whether the highest solvent mass fraction $W_{\text{solvent}}^*(\boldsymbol{z}(\boldsymbol{n}))$ at which only one liquid phase can form for the given absorber pressure, $P_{N_a} = 1$ atm is above a certain threshold. For a mixture of amine, water and CO₂, $W_{\text{solvent}}^*(\boldsymbol{z}(\boldsymbol{n}))$ can be calculated by maximising the solvent mass fraction at which an isobaric-isothermal flash (PT flash) calculation returns a single liquid and an vapour phase. The PT flash is carried out at P_{N_a} and any allowable absorber temperature. We make use of the general PT flash calculation framework embedded in the gPROMS ModelBuilder 7.0.7 software package. This is expressed as the following optimisation:

$$W_{\text{solvent}}^{*}(\boldsymbol{x}\boldsymbol{u}; P_{N_{a}}, \boldsymbol{n}) = \max_{\boldsymbol{x}\boldsymbol{u}} W_{\text{solvent}}$$
s.t. $\boldsymbol{fl}_{ext}(\boldsymbol{z}, T, \boldsymbol{y}, \boldsymbol{x}, \boldsymbol{x}\boldsymbol{b}, \alpha, \beta, \gamma; P_{N_{a}}, \boldsymbol{n}) = 0$
 $\alpha \leq \epsilon_{ph}$
 $\beta \geq \epsilon_{ph}$
 $\gamma \leq \epsilon_{ph}$
 $W_{\text{solvent}} = \frac{z_{\text{solvent}} m w_{\text{solvent}}}{z_{\text{H}_{2}\text{O}} m w_{\text{H}_{2}\text{O}} + z_{\text{solvent}} m w_{\text{solvent}}}$
 $0 \leq z_{i} \leq 1 \quad \forall i \in NC'$
 $\sum_{i=1}^{NC'} z_{i} = 1$
 $\max\left(T_{mp}\left(\boldsymbol{n}\right) + 10, T_{op}^{L}\right) \leq T \leq T_{op}^{U}$
(4.3)

where W_{solvent}^* is an optimal solvent concentration obtained for a fixed molecule \boldsymbol{n} and absorber pressure P_{N_a} , \boldsymbol{xu} is a vector of variables defined as $\boldsymbol{xu} = [\boldsymbol{z}, T, \boldsymbol{y}, \boldsymbol{x}, \boldsymbol{xb}, \alpha, \beta, \gamma, W_{\text{solvent}}]^{\top}$, \boldsymbol{z} is a global composition, $\boldsymbol{y}, \boldsymbol{x}$ and \boldsymbol{xb} are vapour, first liquid and second liquid mole fractions at equilibrium, respectively, α , β and γ are the phase fractions of the vapour, first liquid and second liquid at equilibrium state, NC'is the set of components considered in Test 2, i.e., $NC' \in \{H_2O, CO_2, \text{ solvent}\}$, and mw_{H_2O} and mw_{solvent} are molecular weights of H_2O and solvent, respectively. \boldsymbol{fl}_{ext} is an external function that computes the PT flash for a given global composition \boldsymbol{z} , temperature T, pressure, P_{N_a} and molecule \boldsymbol{n} . ϵ_{ph} is a small strictly positive scalar value introduced to ensure a homogeneous liquid phase is present. Specifically, the phase fraction of the first (most plentiful) liquid phase is set to be greater than ϵ_{ph} , while the phase fractions of the second liquid phase and vapour phase are set to be so small as to be negligible. A value of $\epsilon_{ph} = 10^{-3}$ is used typically.

If the optimal solvent mass fraction obtained is less than the upper bound of the solvent concentration, i.e.,

$$W_{\text{solvent}}^* \le W_{\text{solvent}}^U,$$
 (4.4)

the molecule is discarded from the search space. The upper bound of the solvent concentration in weight fraction is usually determined considering corrosion and foaming tendency. Here, the upper bound is set to 0.5 kg kg⁻¹.

4.3.3 Test 3: Absorption capacity

Test 3 is introduced to eliminate operating conditions or solvents that cannot achieve the required absorption capacity. In the design of a solvent for CO_2 removal, one of the most important properties is cyclic capacity, defined as the difference between CO_2 solubility in the rich solvent and that in the lean solvent. A cyclic capacity determines the solvent circulation rate in the process; a high cyclic capacity often leads to a smaller solvent circulation rate, consequently reducing the equipment size and heat requirement for regeneration. For a given solvent, the cyclic capacity is described as a function of the design variables, i.e., the lean loading, the temperature of the recycled solvent, and the absorber and desorber operating conditions. The optimal values of these variables can be determined by optimising for the entire process. However, the feasible ranges of these design variables change depending on the solvent structure, making it difficult to provide a good initial guess and even causing failure of the solver to converge. For example, MEA exhibits higher CO_2 solubility than MDEA for fixed CO₂ partial pressure, solvent concentration and temperature. As can be seen in Figure 4.2, if the initial guesses and bounds on the lean solvent conditions used for MEA are adopted for MDEA, this may lead to algorithmic failure during the optimisation search because the choice of some combinations of operating conditions violates the maximum solubility of the solvent. To avoid such unnecessary difficulties in the course of the optimisation, Test 3 is used to identify an upper bound on the lean solvent loading (θ_0) based on the thermodynamic feasibility in the bottom stage of the absorber and desorber.



Figure 4.2: Predicted solubility of CO₂, expressed as the partial vapour pressure of CO₂ (P_{CO_2}) as a function of the CO₂ loading, in aqueous solutions of MEA (blue solid line) and MDEA (red solid line) at 30 wt% and 323.15 K. The magenta marker (×) represents the initial guesses of the process conditions that corresponds to (a) $T_0 = 323.15$ K and $\theta_0 = 0.25$ mol mol⁻¹, at which the maximum solubility CO₂ for MDEA is violated and (b) $T_0 = 323.15$ K and $\theta_0 = 0.1$ mol mol⁻¹, at which both MEA and MDEA can achieve positive cyclic capacity. The black dashed line indicates the maximum possible CO₂ partial pressure of 5000 Pa, which corresponds to P_{CO_2} in the flue gas stream. The grey shaded area represents the region of the possible P_{CO_2} and CO₂ loading of liquid stream x_j in the absorber given based on the initial guess (θ_0). To have feasible cyclic capacity, the predicted solubility line must intersect the grey rectangular area.

Absorber

The first evaluation of Test 3 employs the formulation suggested by Gopinath (2017) in the context of physical gas absorption. The formulation of Gopinath (2017) was developed for ternary mixtures to determine whether target CO_2 removal can be achieved for a given solvent by maximising the absorber pressures with respect to the global composition, temperature and pressure on the last stage of the absorber. Here, it is adapted to take into account the quaternary mixture and their VLLE of N_2 , CO_2 , amine solvent, and water by assuming that the ratio of water to solvent remains unchanged, allowing the aqueous solvent mixture (water+solvent) to be lumped into one hypothetical component, CS.

The coexistence of a vapour phase and a homogeneous liquid phase on stage N_a of the absorber must be ensured to avoid any discontinuity caused by having either

only liquid or vapour phases during the process optimisation. This condition are expressed by following constraints:

$$\begin{aligned} \boldsymbol{fl}_{ext} \left(\boldsymbol{z}_{\boldsymbol{N}_{\boldsymbol{a}}}, T_{\boldsymbol{N}_{\boldsymbol{a}}}, \boldsymbol{y}_{\boldsymbol{N}_{\boldsymbol{a}}}, \boldsymbol{x}_{\boldsymbol{N}_{\boldsymbol{a}}}, \boldsymbol{x} \boldsymbol{b}_{\boldsymbol{N}_{\boldsymbol{a}}}, \boldsymbol{\alpha}, \boldsymbol{\beta}, \boldsymbol{\gamma}; P_{\boldsymbol{N}_{\boldsymbol{a}}}, \boldsymbol{n} \right) &= 0 \\ \alpha &\geq \epsilon_{ph} \\ \boldsymbol{\beta} &\geq \epsilon_{ph} \\ \boldsymbol{\gamma} &\leq \epsilon_{ph} \end{aligned}$$
(4.5)

where subscript N_a represents the last stage of the absorber.

In order to guides the separation in the desired direction, it is necessary to derive a constraint that can ensure the separation feasibility. Here, we expose the formulation in Gopinath (2017) in the context of CO_2 chemical absorption process. Let consider the compositions and flowrates entering and leaving the absorber envelope as described in Figure 4.3(a).

The assumptions used for the derivation are as follows:

- 1. The mole of solvent losses to the vapour stream over length of column is less than the mole of transferred from the gas stream to the liquid stream, i.e., $L_{N_a} > L_0$.
- 2. The concentrations of at least two of the components C1 and C2 in the vapour are greater than those in the lean solvent stream entering the top of the column. That is, $y_{N_a+1,C1} \ge x_{0,C1}$ and $y_{N_a+1,C2} \ge x_{0,C2}$ for $C1, C2 \ne CS$, where the index CS denotes the amine solvent.
- 3. Since the column operation aims at separating the impurity (CO₂) from the feed stream so that the treated clean gas stream leaving the top of the column must be enriched in one of the feed-components, i.e., $y_{1,C1} > y_{N_a+1,C1}$

A ternary diagram in Figure 4.3(b) shows the feasible regions for the separation. The region AED represents the target compositions y_1 , while region BEFG indicates all possible compositions x_{N_a} of the rich solvent. It can be observed that the separation is feasible when the vapour-liquid boundary (black dashed curve) at T_{N_a} , P_{N_a} intersects the region BEFG. Given the feed mixing line $\overline{[y_{N_a+1}, x_0]}$, the line segment $\overline{[y_1, x_{N_a}]}$ (blue dashed line) must intersect the mixing line to satisfy the overall material balance.

An analytical equation can be derived to represent this condition using the equations of the line segments $\overline{[y_{N_a+1}, x_0]}$ and $\overline{[y_1, x_{N_a}]}$ and their slopes, in addition to the overall and component material balances. The resulting constraint is given by:

$$x_{N_a,C2} - y_{N_a+1,C2} - \frac{(y_{N_a+1,C2} - x_{0,C2})}{(y_{N_a+1,C1} - x_{0,C1})} (x_{N_a,C1} - y_{N_a+1,C1}) \ge \epsilon_{sp},$$
(4.6)

where $x_{N_a,C1}$ and $x_{N_a,C2}$ are the liquid mole fractions of components C1 and C2 in the stream leaving the last (bottom) stage of the absorber, $x_{0,C1}$ and $x_{0,C2}$ are the liquid mole fractions of components C1 and C2 of the lean solvent stream entering the top of the absorber and $y_{N_a+1,C1}$ and $y_{N_a+1,C2}$ are the gas mole fractions of components C1 and C2 of the stream entering the bottom of absorber, i.e, the flue gas. For a comprehensive description of the derivation and assumptions used, the reader is referred to Gopinath (2017) and section 3.2.3.2 therein.

In addition, a feasible solvent must have a positive cyclic capacity, which restricts the allowable lean loading. A new upper bound on the cyclic capacity can then be formulated as:

$$\frac{x_{N_a,\text{CO}_2}}{x_{N_a,\text{solvent}}} - \theta'_0, \ge \epsilon_{\text{cyclic}}$$
(4.7)

where θ'_0 is the lean loading at the inlet of top of the absorber, $x_{N_a,\text{solvent}}$, and x_{N_a,CO_2} are liquid molar compositions of amine solvent and CO₂ in the rich solvent stream, and ϵ_{cyclic} is a strictly positive number need to ensure the positive cyclic capacity of the solvent is positive. The resulting optimisation problem is given as follows.

$$\theta_{0}^{U}(\boldsymbol{x}\boldsymbol{u}; P_{N_{a}}, \boldsymbol{n}) = \max_{\boldsymbol{x}\boldsymbol{u}} \theta_{0}'$$
s.t. $\boldsymbol{fl}_{ext}(\boldsymbol{z}_{N_{a}}, T_{N_{a}}, \boldsymbol{y}_{N_{a}}, \boldsymbol{x}_{N_{a}}, \boldsymbol{x}\boldsymbol{b}_{N_{a}}, \alpha, \beta, \gamma; P_{N_{a}}, \boldsymbol{n}) = 0$
 $\alpha \geq \epsilon_{ph}$
 $\beta \geq \epsilon_{ph}$
 $\gamma \leq \epsilon_{ph}$
 $\frac{\boldsymbol{x}_{N_{a},\text{CO}_{2}}}{\boldsymbol{x}_{N_{a},\text{solvent}}} - \theta_{0}' \geq \epsilon_{\text{cyclic}}$
 $\boldsymbol{x}_{N_{a},\text{cO}_{2}} - \boldsymbol{y}_{N_{a}+1,\text{CO}_{2}} - \frac{(\boldsymbol{y}_{N_{a}+1,\text{CO}_{2}} - \boldsymbol{x}_{0,\text{CO}_{2}})}{(\boldsymbol{y}_{N_{a}+1,N_{2}} - \boldsymbol{x}_{0,N_{2}})} (\boldsymbol{x}_{N_{a},N_{2}} - \boldsymbol{y}_{N_{a}+1,N_{2}}) \geq \epsilon_{sp}$
 $0 \leq \boldsymbol{z}_{N_{a},i} \leq 1 \quad \forall i \in NC$
 $\sum_{i=1}^{NC} \boldsymbol{z}_{N_{a},i} = 1$
 $\max \left(T_{mp}\left(\boldsymbol{n}\right) + 10, T_{op}^{L}\right) \leq T_{N_{a}} \leq T_{op}^{U}$
(4.8)

where $\boldsymbol{x}\boldsymbol{u}$ is a vector of variables defined as $\boldsymbol{x}\boldsymbol{u} = [\boldsymbol{z}_{N_a}, T_{N_a}, \theta'_0, \boldsymbol{y}_{N_a}, \boldsymbol{x}_{N_a}, \boldsymbol{x}\boldsymbol{b}_{N_a}, \alpha, \beta, \gamma]^\top$ and NC is a set of components in the system, i.e., $NC \in \{N_2, CO_2, H_2O, solvent\}$.

Desorber

Equivalently, a lower bound on the lean loading θ_0 is obtained by investigating the minimum loading achievable at the bottom stage of the desorber with respect to global composition z_{N_d} and temperature T_{N_d} at the minimum allowable operating pressure $P_{N_d}^L$. Since a lower content of solvent in the system leads to lower amount of CO₂ absorbed, the following constraint is used to prevent the search from converging to a trivial solution.

$$\frac{x_{N_d,\text{solvent}}}{x_{N_d,\text{solvent}} + x_{N_d,\text{H}_2\text{O}}} - \frac{x_{N_a,\text{solvent}}}{x_{N_a,\text{solvent}} + x_{N_a,\text{H}_2\text{O}}} \ge \epsilon_{\text{sol}},$$
(4.9)

where $x_{N_d,\text{solvent}}$, $x_{N_d,\text{H}_2\text{O}}$ are the liquid solvent and H₂O molar fractions of the lean solvent stream leaving the desorber, and ϵ_{sol} is a strictly positive number.

The resulting optimisation problem for the desorber is given as follows:

$$\begin{aligned} \theta_{0}^{L}(\boldsymbol{x}\boldsymbol{u};P_{N_{d}},\boldsymbol{n}) &= \min_{\boldsymbol{x}\boldsymbol{u}} \theta_{0} \\ \text{s.t. } \boldsymbol{fl}_{ext}\left(\boldsymbol{z}_{N_{d}},T_{N_{d}},\boldsymbol{y}_{N_{d}},\boldsymbol{x}_{N_{d}},\boldsymbol{x}\boldsymbol{b}_{N_{d}},\alpha,\beta,\gamma;P_{N_{d}},\boldsymbol{n}\right) &= 0 \\ \alpha &\geq \epsilon_{ph} \\ \beta &\geq \epsilon_{ph} \\ \theta_{0} &= \frac{x_{N_{d}},\text{cO}_{2}}{x_{N_{d}},\text{solvent}} \\ \frac{x_{N_{d}},\text{solvent}}{x_{N_{d}},\text{solvent}} - \frac{x_{N_{a}},\text{solvent}}{x_{N_{a}},\text{solvent} + x_{N_{a}},\text{H}_{2}\text{O}} \geq \epsilon_{\text{sol}} \end{aligned}$$
(4.10)
$$0 \leq z_{N_{d},i} \leq 1 \quad \forall i \in NC \\ \sum_{i=1}^{NC} z_{N_{d},i} &= 1 \\ \max\left(T_{mp}\left(\boldsymbol{n}\right) + 10, T_{op}^{L}\right) \leq T_{N_{d}} \leq T_{op}^{U} \end{aligned}$$

where $\boldsymbol{x}\boldsymbol{u}$ is a vector of variables $\boldsymbol{x}\boldsymbol{u} = [\boldsymbol{z}_{N_d}, T_{N_d}, \theta_0, \boldsymbol{y}, \boldsymbol{x}_{N_d}, \boldsymbol{x}\boldsymbol{b}_{N_d}, \alpha, \beta, \gamma]^\top$.

If the new lower bound on the lean loading is larger than the upper bound (i.e., $\theta_0^U < \theta_0^L$) or no feasible upper or lower bound is identified, it is clear that no process conditions will be feasible for CO₂ absorption, and the current solvent structure n is eliminated from the search space. If it is feasible, the solution of Test 3 is used to provide reduced feasible ranges for the loading $[\theta_0^L, \theta_0^U]$ for use in the primal problem.

4.3.4 Test 4: Desorber operating pressure range

Given the lean loading range $[\theta_0^L, \theta_0^U]$ generated from Test 3, Test 4 is designed to provide tighter bounds on the desorber pressure, P_{N_d} . This is done by finding the highest pressure at which: 1) a vapour-liquid phase split occurs in the bottom stage of the desorber, and 2) there exists a lean solvent composition that satisfies the target lean loading range. An additional constraint on the solvent weight fraction in the stream leaving the bottom stage of the absorber (W_{N_d}) is imposed in order to prevent the optimisation algorithm from converging to a trivial solution. Here, we assume that only trace amounts of N₂ can be present so that presence of N₂ can be neglected. The resulting formulation is as follows:

$$P_{N_d}^{U}(\boldsymbol{x}\boldsymbol{u};\boldsymbol{n}) = \max_{\boldsymbol{x}\boldsymbol{u}} P_{N_d}$$

s.t. $\boldsymbol{fl}_{ext}(\boldsymbol{z}_{N_d}, T_{N_d}, P_{N_d}, \boldsymbol{y}_{N_d}, \boldsymbol{x}_{N_d}, \boldsymbol{x}\boldsymbol{b}_{N_d}, \alpha, \beta, \gamma; \boldsymbol{n}) = 0$
 $\alpha \geq \epsilon_{ph}$
 $\beta \geq \epsilon_{ph}$
 $\gamma \leq \epsilon_{ph}$
 $\frac{x_{N_d,\text{solvent}}}{x_{N_d,\text{solvent}} + x_{N_d,\text{H}_2O}} - \frac{x_{N_a,\text{solvent}}}{x_{N_a,\text{solvent}} + x_{N_a,\text{H}_2O}} \geq \epsilon_{\text{sol}}$
 $\theta_0^L \leq \theta_0 \leq \theta_0^U$
 $\theta_0 = \frac{x_{N_d,\text{CO}_2}}{x_{N_d,\text{solvent}}}$
 $W_{N_d} \geq W_{\text{solvent}}$
 $W_{N_d} \equiv W_{\text{solvent}}$
 $W_{N_d} = \frac{x_{N_d,\text{solvent}} m w_{\text{solvent}}}{x_{N_d,\text{solvent}} m w_{\text{solvent}}}$
 $0 \leq z_{N_d,i} \leq 1 \quad \forall i \in NC$
 $\sum_{i=1}^{NC} z_{N_d,i} = 1$
 $\max\left(T_{mp}\left(\boldsymbol{n}\right) + 10, T_{N_d}^L\right) \leq T_{N_d} \leq T_{\text{op}}^U$
(4.11)

xu is a vector of variables defined as $xu = [z_{N_d}, T_{N_d}, \theta_0, y_{N_d}, x_{N_d}, xb_{N_d}, \alpha, \beta, \gamma]^\top$ and W_{solvent} is a pre-defined solvent concentration in the aqueous mixture of water and solvent.



Figure 4.3: Schematic of (a) the absorber envelope, (b) the last equilibrium stage of the absorber and (c) a ternary phase diagram of C1 (N₂), C2 (CO₂), and CS (aqueous solvent solution) at T_{N_a} , P_{N_a} . The region of a acceptable clean gas mole fractions y_1 is denoted by green shaded triangle EAD and the region of desirable rich solvent mole fractions x_{N_a} is denoted by blue shaded area BEFG. The solid line $\overline{[(y_{N_a+1}), x_0]}$ represents the mixing line of the feed streams on the ternary diagram. The thick dashed curve represents a vapour-liquid phase boundary.

4.3.5 Performance of the feasibility tests

CO₂ capture from an exhaust gas from a 400 MW CCGT power plant (Alhajaj et al., 2016a), described in section 3.4.1, is considered as a case study to assess the performance of the proposed feasibility tests. The key input parameters and the prespecified bounds on the design variables that are used throughout the study are provided in Table 4.2. An automated implementation of the sequence of tests and of the solution of the primal problem (process optimisation with fixed solvent structure) is developed in C++. Individual tests and the primal problem are implemented in gPROMS ModelBuilder 7.0.7 (Process Systems Engineering, 1997-2022) with the gSAFT Foreign Object interface for the SAFT- γ Mie calculations. The gO:RUN functionality of ModelBuilder is used to launch the solution of each test problem. The solution files of each tests are read and the required information extracted and transferred within the C++.

Parameter	Symbol	Value
Degree of CO ₂ captured (%)	-	90
Condenser temperature (K)	$T_{\mathrm{N_d}}^L$	333
Min. approach temperature (K)	$\Delta \ddot{T}_{min}$	10
Initial bounds on desorber pressure (MPa)	$[P_{\mathrm{N}_{\mathrm{d}}}^{L}, P_{\mathrm{N}_{\mathrm{d}}}^{U}]$	[0.1, 5]
Initial bounds on handling temperature (K)	$[T_{sh}^L, T_{sh}^U]$	[303, 333]
Initial bounds on lean solvent temperature (K)	$[T_0^L, T_0^U]$	[313, 353]
Initial bounds on lean loading (mol mol $^{-1}$)	$[heta_0^L, heta_0^U]$	[0.02, 2]
Minimum operating temperature (K)	$T^L_{\rm op}$	313
Phase fraction parameter	ϵ_{ph}	$1{ imes}10^{-3}$
Separation feasibility parameter	$\epsilon_{ m sp}$	$1{ imes}10^{-3}$
Minimum allowable cyclic capacity	$\epsilon_{\rm cyclic}$	1×10^{-1}
Minimum allowable solvent loss	$\epsilon_{ m sol}$	5×10^{-2}

Table 4.2: Key input parameters and specifications for the CO_2 capture case study

For testing purposes, the set of all possible combinations of solvent candidates is generated in accordance with the molecular feasibility constraints provided in Equation (4.1) with the bounds of $n_{\text{OH}}^U = 2$, $n_{G_A}^U = 2$, $n_{G_A}^L = 1$ and $n_{\text{iso}}^U = 5$. These give a molecular design space of 4,179 possible combinations of solvent structures. The investigation of the effectiveness of the feasibility tests is carried out by a bruteforce search on the entire design space.

The overall results of applying the feasibility tests to the specifications are summarised in Table 4.3. Within the 4,179 candidate molecules, only 1,449 solvents pass all feasibility tests. As can be seen in Table 4.3, the majority of the alkylamines are found to be infeasible in Test 1 and Test 2, mainly due to their low water miscibility as well as their low safety and environmental performance. For example, the maximum solvent mass fraction ($W^*_{solvent}$) of triethylamine (TEA) that can ensure a homogeneous liquid phase at absorber operating condition is identified as 0.019 in mass fraction (0.0015 in mole fraction). This indicates that the constraint $W^U_{solvent}(= 0.5) \leq W^*_{solvent}$ is violated and TEA should be eliminated from the molecular design space. The predicted regions of liquid-liquid immiscibility at 0.1 MPa for the aqueous solutions of TEA are shown in Figure 4.4 together with the available experimental data. At average absorber operating conditions (313 K-333 K), the system exhibits a large LLE region and a very small region of the homogeneous liquid



Figure 4.4: The temperature-mole fraction T- z_{TEA} fluid phase behaviour of a binary mixture of water and TEA at P=0.1 MPa. The continuous curves correspond to SAFT- γ Mie predictions and the symbols to experimental data. The liquid-liquid equilibrium region (L1+L2), vapour-liquid equilibrium regions (V+L1 or V+L2) are shown and phase boundaries are by continuous curve. The range of absorber temperatures is shown by the grey shaded area. This figure is an adaptation of Figure 11(b) in (Perdomo et al., 2021)

phase, at low TEA mole fractions. Such behaviour is not desirable for successful absorber operation. It is important to note that the starting point for the solution of Test 2 is at the lowest allowable temperature and nearly pure water. This is to start the optimisation algorithm from a feasible point, i.e., one liquid phase, setting up to the optimiser to remain in the one-liquid phase region until it reaches the boundary of the multi-phase envelope. This approach is particularly useful when the flash calculation fl_{ext} encounters discontinuities across the transition between the different regions of the phase diagram.

The performance of Tests 3 and 4 is examined for these solvents that pass Tests 1 and 2. Tests 3 and 4 lead to tighter bounds on the lean loading and desorber pressure, the percentage deviation, and the average values of the updated bounds are presented in the Table 4.3. The large deviation in the maximum lean loading and desorber pressure indicates that providing an initial guess that is feasible to all solvent molecular structures is very difficult. It is therefore important to provide

	Total	Mono A	mine	Dian	nine
	Iotal	Alkanol-	Alkyl-	Alkanol-	Alkyl-
Number of molecules tested	4179	765	416	1918	1080
Number of molecules eliminated by Test 1	793	64	292	31	406
Number of molecules eliminated by Test 2	889	292	124	371	102
Number of molecules eliminated by Test 3	1040	124	0	400	516
Number of molecules eliminated by Test 4	12	0	0	10	2
Number of feasible molecules	1445	285	0	1106	54
Percentage deviation of θ_0^L	1.12	1.17	-	1.08	0.12
Percentage deviation of θ_0^U	22.52	7.81	-	13.36	3.44
Percentage deviation of $P_{N_d}^U$	9.50	3.41	-	10.05	0.95
Average value of updated bound, θ_0^L (mol mol ⁻¹)	0.0401	0.0330	-	0.0391	0.0484
Average value of updated bound, θ_0^U (mol mol ⁻¹)	0.7302	0.3268	-	0.7973	0.9855
Average value of updated bound, $P_{N_d}^U$ (MPa)	0.3279	0.3601	-	0.2812	0.3424

a systematic way to recognise the feasible combinations of process conditions and solvents. As can be seen, there is a significant improvement in the average updated bounds, suggesting that many infeasible process conditions can be removed by the feasibility tests. For the case of MDEA, for example, the minimum requirement on lean solvent purity, $\theta_0^U = 0.237$, is calculated as a result of Test 3. This implies that if the initial guess on the lean loading were set to be greater than 0.237, the initialisation of the process model would lead to numerical failure, making it impossible to evaluate the performance of this solvent. It is worth mentioning that some convergence failures are encountered during the optimisation mainly due to the numerical complexities arising from the prediction of complex VLLE fluid phase behaviour for specific operating conditions and solvent types. For the case where the optimisation run for the tests is not successful, the associated solvent is treated as infeasible in the test failed.

To exemplify the impact of the feasibility tests and of the updated bounds on the solution of the primal problem, the specific case of MEA and 2-amino-2-methyl-1,3-propanediol (AMPD) are investigated. The solution of primal problem is run from five starting points randomly chosen from the initial bounds of the design variables in

order to investigate the impact of the choice of initial guesses and also to increase the likelihood of identifying a global solution. The five starting points are given in Table 4.4. The values of the starting points can be updated automatically if the feasibility tests identify these initial guesses to be infeasible for the specified solvent. Two algorithmic options, with feasibility and without feasibility tests, are considered for each solvent and the usefulness of the feasibility tests is assessed based on the ability to converge to a solution from each starting point and on the average computational time.

The results of the optimisation runs carried out are summarised in Table 4.5. The average computational cost is calculated only over the CPU time of the successful runs for the both algorithmic options thereby neglecting the cost of failed runs, which can often be large. It can be seen that all 10 runs with feasibility tests converge successfully, while only 5 of 10 runs converge in the absence of feasibility tests. For MEA, the average computational cost slightly higher (by 9%) for the runs with feasibility tests. The algorithm without feasibility tests fails to converge for runs S4 and S5 due to the infeasible lean loading conditions at the initial conditions for these run. The algorithm with the feasibility tests converges for all runs by updating the initial guesses on the lean loading through Test 3; while the original initial lean loading of 0.4 used in run S4 is only slightly outside the feasible region, but the solver fails to find a feasible point nonetheless, the new initial lean loading is given by 0.3995 for both S4 and S5.

The effectiveness of the introduction of the feasibility tests is further highlighted in the AMPD case. As reported in Table 4.5, equivalent solutions are obtained using

Table 4.4: Five starting points used for the solution of the primal problem MEA and AMPD. Each starting point is denoted as S1-S5

Optimisation variables	S1	S2	S3	S4	S5
Lean loading, θ_0 (mol mol ⁻¹)	0.10	0.20	0.30	0.40	0.50
Lean solvent temperature, T_0 (K)	313.15	333.15	323.15	323.15	313.15
Desorber pressure, P_{N_d} (MPa)	0.180	0.250	0.150	0.200	0.180

	N	IEA	AI	MPD
	no tests	with tests	no tests	with tests
Min. lean loading θ_0^L (mol mol ⁻¹)	0.02	0.02	0.02	0.0420
Max. lean loading θ_0^U (mol mol ⁻¹)	2.0	0.3995	2.0	0.3418
Max. desorber pressure $P_{N_d}^U$ (MPa)	0.80	0.305	0.80	0.340
TAC (\$million year ^{$-1$})	29.808	29.805	25.735	25.735
Total energy consumption (GJ ton- CO_2^{-1})	9.322	9.321	7.921	7.928
Reboiler temperature (K)	397.18	397.15	398.94	398.94
Cyclic capacity (mol mol^{-1})	0.1597	0.1595	0.2132	0.2134
Rich amine loading (mol mol ^{-1})	0.4764	0.4764	0.4744	0.4744
Lean amine loading, θ_0 (mol mol ⁻¹)	0.3168	0.3169	0.2611	0.2610
Lean solvent temperature, T_0 (K)	313.16	313.15	335.44	335.43
Desorber pressure, P_{N_d} (MPa)	0.206	0.206	0.216	0.216
No. of successful runs	3	5	2	5
Avg. CPU time (s)	251.76	273.91	328.56	294.31

Table 4.5: Outcome of the tests and of the solutions of the primal problems for MEA and AMPD over five runs. Only the run with the smallest objective function is presented as an optimal solution.

the algorithm with and without feasibility tests for AMPD. Importantly, we observe that the optimisations without the tests encounter numerical failures either during the course of the algorithm (S1) or at the start of the algorithm (S4 and S5). This demonstrates the importance of identifying feasible process conditions for a given solvents to avoid the algorithmic failure. In the context of solving MINLP CAMPD problems, one possible approach to resolve numerical failures that occur during the evaluation of process performance in the absence of the tests is to add an integer cut to the master problem in order to eliminate the solvent in question, so that the algorithm focuses the search on other solvent candidates. However, this is not only computationally expensive, but also it may lead to the unnecessary elimination of a promising solvent candidate (see the TAC for AMPD is lower than that of MEA) and the introduction of an integer cut does not guarantee that a feasible solution can be identified in a subsequent iteration. Indeed, successful convergence to an solution of the primal problem for AMPD is obtained with the introduction of feasibility tests, regardless of the initial guesses. The average computational time is slightly decreased (by 10%) potentially as a consequence of the reduction in the ranges of the design variables achieved in Test 3 and 4. The robustness achieved through the in-

4.4 Improving the robustness of feasibility tests

evaluation of the primal problems is computationally expensive.

As is apparent from Table 4.5, the implementation of the feasibility tests provides a more reliable way of solving the process optimisation problem by avoiding the numerical difficulties derived from infeasibilities of the process conditions. However, there are remaining challenges in the solutions of the tests; for some solvent candidates, convergence to a solution was not achieved for all tests. This is mainly because the constraints used to ensure the coexistence of vapour-liquid phases or the existence of a homogeneous liquid phase are subject to failure when the initial guesses for the degrees of freedom (or the number of phases) significantly differ from the solution of the solution of PT flash calculation. One widely used approach for the solution of the PT flash is based on a two-stage (Michelsen, 1982b) procedure alternating stability analysis and phase-split calculation for a fixed number of phases until a pre-defined stopping criterion is met (Liang, 2018). Within the procedure, the stability analysis is used for checking if the postulated equilibrium phases are stable, while the phase-split calculation determines the phase types, phase compositions, and phase fractions that correspond to the (local) minimum of the Gibbs free energy for a given number of phases. The phase-split calculation within the PT flash procedure employed, fl_{ext} , is therefore differentiable in the interior of multiphase or single-phase regions but not at the boundaries between these regions. The success of the feasibility tests critically depends on providing good initial guesses such that the flash calculation at the initial compositions, temperature, and pressure results in the desired number and types of phases. However, it is not always straightforward to provide such initial guesses, particularly when there are many

components involved in the mixture or when the mixture exhibits highly non-ideal behaviour. To address this, Gopinath (2017) initially modelled the phase equilibrium as equality of the chemical potentials of each species across all phases, taking advantage of the fact that this is continuous and differentiable across all phases, although additional constraints are required to avoid a trivial solution and one may converge to a local solution of the minimisation of the Gibbs free energy. Furthermore, even with this formulations, the solution of the phase equilibrium problem can be very challenging when the interactions between CO₂-water-solvent lead to complex phase behaviour such as vapour-liquid-liquid equilibrium (VLLE). In such cases, more sophisticated methods are needed to ensure that the results correspond to stable equilibria. Here, we aim to improve the feasibility tests by employing a robust approach for the flash calculation that is relatively less sensitive to the initial guesses and can reliably identify the equilibrium state. In the remainder of this section, we investigate several methods to establish a general strategy of solving the feasibility tests: two approaches to stability analysis, that is proposed by Michelsen (1993) and Castier (2014) and that of Nichita (2019), as well as a global solution approach to the minimisation of the Gibbs energy, hereafter referred to as Helmholtz free energy Lagrangian Dual (HELD) algorithm (Pereira et al., 2012).

we begin by briefly describing these methods.

4.4.1 HELD algorithm

Consider a system at constant temperature (T^0), pressure (P^0) and total mole numbers over all components (n^0). The total Gibbs free energy of the mixture (G^T) is defined as:

$$G^{T}(\boldsymbol{n^{0}}, P^{0}, T^{0}) = \sum_{j=1}^{NP} \sum_{i=1}^{NC} n_{i,j} \mu_{i,j} \left(\boldsymbol{n^{0}_{j}}, P^{0}, T^{0}\right), \qquad (4.12)$$

where NP is the number of phases present, NC is the number of components, n_j^0 is a matrix representing the number of moles of each component *i* in each phase *j* and $\mu_{i,j}(n_j^0, P^0, T^0)$ is the chemical potential of component *i* in phase *j* at the specified composition, pressure and temperature. The solution of the PT flash corresponds to the global minimum in the total Gibbs free energy function, G^T , over all phases at the specified conditions. Equivalently, problem (4.12) can be written in terms of the mole fraction vectors, $w_{j=1,...,NP}$, in which only NC - 1 independent mole fractions (variables) are considered, $w = [w_1, w_2, ..., w_{NC-1}]^{\top} \in [0, 1]^{NC-1}$. This is because one of the component mole fractions can be calculated from $w_{NC} = 1 - \sum_{i=1}^{NC-1} w_i$. The resulting phase equilibrium problem is as follows:

$$\begin{array}{ll}
\min_{\boldsymbol{w},NP} & G^{T}(\boldsymbol{w},P^{0},T^{0}) \\
\text{s.t.} & \sum_{j=1}^{NP} w_{i,j} - z_{i} = 0, \quad i = 1, \dots, NC - 1 \\
\text{where} & G^{T}(\boldsymbol{w},P^{0},T^{0}) \\
&= \left(\sum_{j=1}^{NP} \sum_{i=1}^{NC-1} w_{i,j} \mu_{i,j} \left(\boldsymbol{w}_{\boldsymbol{j}},P^{0},T^{0}\right)\right) \\
&+ \sum_{j=1}^{NP} \left(1 - \sum_{i=1}^{NC-1} w_{i,j}\right) \mu_{NC,j} \left(\boldsymbol{w}_{\boldsymbol{j}},P^{0},T^{0}\right)
\end{array}$$
(4.13)

where z_i is the overall composition of component *i*, *w* is a $(NC - 1) \times NP$ matrix representing the mole fractions of NC - 1 components in NP phase.

Three factors make the solution of Problem (4.13) challenging: first, the number of phases at equilibrium is unknown *a priori*; secondly the functions introduced are highly nonconvex; and finally the evaluation of the chemical potential at fixed P, Tand w with the SAFT- γ Mie EOS necessitates the solution of a nonlinear problem as the natural variables of the equation T, w and the molar volume V. To overcome these difficulties, Pereira et al. (2012) developed the HELD algorithm to facilitate the phase equilibrium calculations by reformulating the problem as a minimisation of the Helmholtz free energy in the volume-composition space and solving through the application of duality theory, building on ideas by Nagarajan et al. (1991); Mitsos & Barton (2007). This method is of particular interest since no user-supplied initial guesses are required for any aspect of the algorithm and the algorithm is applicable to the calculation of a variety of challenging phase behaviours such as azeotropy, liquid-liquid and vapour-liquid-liquid equilibria. The HELD algorithm consists of 1) a stability test and initialisation stage, where a tangent plane stability test is solved using a tunnelling algorithm (Nichita et al., 2002) aiming to locate a negative tangent plane distance as early as possible; 2) a stage to identifying candidate stable phases, where the algorithm iterates between inner and outer problems derived from a dual formulation of the Helmholtz free energy minimisation for a trial phase; 3) a stage for algorithm acceleration and convergence tests, where the free energy is minimised further for the given number of phases identified in the previous stage and the feasibility of the mass balance is tested.

To take advantage of the performance of the HELD algorithm in the context of the feasibility tests, the algorithm is implemented for Test 2, in which the PT flash calculation is solved for a given system state (z, T, and P). For this investigation, Test 2 is reduced by considering a binary mixture of water and amine solvent at a fixed temperature. Note that solvents that undergo CO₂-induced liquid-liquid demixing will be eliminated in Test 3, where a range of temperatures and molar compositions of the N₂-CO₂-aqueous amine mixture is explored. The modified formulation of Test 2 is as follows:

$$W_{\text{solvent}}^*\left(\boldsymbol{x}\boldsymbol{u};T_{N_a},P_{N_a},\boldsymbol{n}\right) = \max_{\boldsymbol{x}\boldsymbol{u}} W_{\text{solvent}}$$
(4.14a)

s.t.
$$\boldsymbol{fl}_{ext}\left(\boldsymbol{z}, \boldsymbol{y}, \boldsymbol{x}, \boldsymbol{xb}, \alpha, \beta, \gamma; T_{N_a}, P_{N_a}, \boldsymbol{n}\right) = 0$$
 (4.14b)

$$\beta \ge \epsilon_{ph}$$
 (4.14c)

$$\epsilon_{h} \leq \epsilon_{ph}$$
 (4.14d)

$$W_{\text{solvent}} = \frac{z_{\text{solvent}} m w_{\text{solvent}}}{z_{\text{H}_2\text{O}} m w_{\text{H}_2\text{O}} + z_{\text{solvent}} m w_{\text{solvent}}}$$
(4.14e)

$$0 \le z_i \le 1 \quad \forall i \in NC'' = \{\text{solvent, } H_2O\}$$
 (4.14f)

$$\sum_{i=1}^{NC''} z_i = 1 \tag{4.14g}$$

where xu is a variable vector defined as $xu = [z, y, x, xb, \alpha, \beta, \gamma, W_{solvent}]^{\top}$ and z is the total composition of the binary mixture of solvent and H₂O. The temperature and pressure for the test are fixed at the average operating conditions of the absorber, T=323K, P=1atm (Papadopoulos et al., 2019). The choice of this higher absorber operating temperature that $T_{op}^{L} = 313$ K would results in tighter on the feasible regions where a homogeneous liquid phase is present.

4.4.2 Stability analysis

In the original feasibility tests, the phase fractions obtained as solutions of the PT flash calculation are constrained to ensure either a single liquid phase or vapourliquid phase equilibrium. As an alternative treatment of such constraints, it is useful to adopt the phase stability analysis to decide whether the phase at given z, T^0, P^0 is thermodynamically stable or if a phase-split occurs. The most widely-used general concept in phase stability analysis to date is based on the analysis of the tangent plane to the Gibbs free energy surface and the surface itself (Baker et al., 1982; Michelsen, 1982a). For a given total composition z, temperature T^0 and pressure P^0 , the tangent plane distance (TPD) criterion is given by the following problem:

TPD
$$(\boldsymbol{w}, P^0, T^0; \boldsymbol{z}) = G(\boldsymbol{w}, P^0, T^0) - G(\boldsymbol{z}, P^0, T^0) + \sum_{i=1}^{NC-1} g_i^0(z_i - w_i) \ge 0, \ \forall \boldsymbol{w} \in [0, 1]^{NC-1},$$

(4.15)

where w is a trial phase composition, z is the vector of the total molar composition, and $g_i^0 = (\partial G/\partial z_i)_{z_{k\neq i,k=1,\dots,NC-1},P^0,T^0}$, the gradient of the Gibbs free energy with respect to mole fraction at the specified conditions.

In the volume-composition space, the TPD function can be written as (Castier, 2014; Nichita, 2019):

TPD
$$(\boldsymbol{w}, P^0, T^0; \boldsymbol{z}) = A(\boldsymbol{w}, V(P^0), T^0) + P^0 V + \sum_{i=1}^{NC-1} g_i^0(z_i - w_i),$$
 (4.16)



Figure 4.5: Schematic of a reduced Gibbs free energy surface of a water-hexylamine mixture, as a function of water mole fraction of a trial phase composition (w_{H_2O}), predicted using the SAFT- γ Mie EOS at T=323 K, P=1 atm (black dashed curve) and a tangent plane on the free energy surface at w_{H_2O} =0.34 (black solid line).

where V is the molar volume of the system and A is the Helmholtz free energy at constant temperature T^0 .

Geometrically speaking, the TPD function represents the vertical distance from the Gibbs free energy surface to the supporting hyperplane tangential to the surface at the trial composition w, as shown in Figure 4.5. The necessary and sufficient condition for the stability of the mixture z at the specified condition P^0 , T^0 is that the TPD is non-negative for any trial phase composition w. In practice, the TPD criterion is often formulated as an optimisation problem given by:

$$TPD^{*}(\boldsymbol{z}, P^{0}) = \min_{\boldsymbol{w} \in W, V \in [\underline{V}, \overline{V}]} TPD^{V}(\boldsymbol{w}, V, T^{0}; \boldsymbol{z}, P^{0})$$

$$= A(\boldsymbol{w}, V, T^{0}) + P^{0}V + \sum_{i=1}^{NC-1} g_{i}^{0}(z_{i} - w_{i}), \qquad (4.17)$$

where \underline{V} and \overline{V} are lower and upper bounds on molar volume, respectively. The problem is parametric in P^0 and \boldsymbol{z} and where the function TPD^V has been used with independent variables \boldsymbol{w}, V, T^0 and parameters P^0 and \boldsymbol{z} . It can be shown that at the solution of the minimisation of (4.17), $V^* = V(P^0)$ (Pereira et al., 2012). If the

global solution w^* of problem (4.17) is found to be identical to the total composition z, one can guarantee that the postulated phase is stable. We denote the optimal objective function value by TPD^{*}. A negative value of TPD^{*} implies that formation of a small amount of new phase of this composition w^* leads to a reduction in the total Gibbs free energy, therefore, a phase-split occurs. Under these conditions constraints (4.14b)-(4.14d) in problem (4.14) can be replaced by TPD^{*} ≥ 0 . Given the TPD criterion, Test 2 is rewritten as:

$$W_{\text{solvent}}^* = \max W_{\text{solvent}}$$
 (4.18a)

s.t.
$$\operatorname{TPD}^{*}(\boldsymbol{z}, P^{0}) = \min_{\boldsymbol{w} \in W, V \in [\underline{V}, \overline{V}]} \operatorname{TPD}^{V}(\boldsymbol{w}, V, T^{0}; \boldsymbol{z}, P^{0}) \ge 0$$
 (4.18b)

$$\beta \ge \epsilon_{ph}$$
 (4.18c)

$$\gamma \le \epsilon_{ph} \tag{4.18d}$$

$$W_{\text{solvent}} = \frac{z_{\text{solvent}} m w_{\text{solvent}}}{z_{\text{H}_2\text{O}} m w_{\text{H}_2\text{O}} + z_{\text{solvent}} m w_{\text{solvent}}}$$
(4.18e)

$$0 \le z_i \le 1 \quad \forall i \in NC'' = \{\text{solvent, } H_2O\}$$
(4.18f)

$$\sum_{i=1}^{NC^*} z_i = 1 \tag{4.18g}$$

A multi-start approach is employed to solve the nonconvex problem (4.17) to increase the likelihood of converging to a global solution, using different initial guesses for (w, V). The starting points are randomly generated from a uniformly distributed function. We also consider an alternative formulation (Michelsen, 1982a) derived based on the first-order optimality conditions of problem (4.17) to improve computational efficiency in terms of molar composition and fugacity coefficients. Here, the reformulation of an Gibbs energy to Helmholtz energy is not considered, meaning that the correct volume root is calculated explicitly at the constant pressure. The alternative formulation is given as:

$$TPD(\boldsymbol{w}, P^{0}, T^{0}; \boldsymbol{z}) = \sum_{i=1}^{NC} w_{i} \left(\ln w_{i} + \ln \varphi_{i}(\boldsymbol{w}, P^{0}, T^{0}) - \ln z_{i} - \ln \varphi_{i}(\boldsymbol{z}, P^{0}, T^{0}) \right)$$

$$\sum_{i=1}^{NC} w_{i} = 1$$
(4.19)

where φ_i is the fugacity coefficient of component *i* at P^0, T^0 . All stationary points, w^{SP} of problem (4.19) must satisfy the following conditions:

$$\nabla_{w_i} \mathcal{L} = \ln w_i + \ln \varphi_i(\boldsymbol{w}^{SP}) - \ln z_i - \ln \varphi_i(\boldsymbol{z}) + 1 - \lambda = 0,$$

for $i = 1, \dots, NC$, (4.20)
$$\nabla_{\lambda} \mathcal{L} = -\sum_{i=1}^{NC} w_i^{SP} + 1 = 0$$

where \mathcal{L} is the Lagrangian function corresponding to Equation (4.19) and λ is the Lagrangian multiplier of the mass balance equality constraint $\sum_{i=1}^{NC} w_i^{SP} = 1$. By solving the equations above, we can obtain the value of the TPD function at a stationary point:

$$TPD^{SP}(\boldsymbol{w}^{SP}, P^{0}, T^{0}; \boldsymbol{z}) = \sum_{i=1}^{NC} w_{i}^{SP} \left(\ln w_{i}^{SP} + \ln \varphi_{i}(\boldsymbol{w}^{SP}, P^{0}, T^{0}) - \ln z_{i} - \ln \varphi_{i}(\boldsymbol{z}), P^{0}, T^{0} \right)$$
$$= \lambda - 1,$$
(4.21)

Therefore, Test 2 with the use of the first-order approach can be formulated as follows:

$$W_{\text{solvent}}^* = \max_{z} W_{\text{solvent}} \tag{4.22a}$$

s.t.
$$\text{TPD}^{\text{SP}}(\boldsymbol{w}^{SP}, P^0, T^0; \boldsymbol{z}) = \lambda - 1 \ge 0$$
 (4.22b)

$$\beta \ge \epsilon_{ph}$$
 (4.22c)

$$\gamma \le \epsilon_{ph}$$
 (4.22d)

$$W_{\text{solvent}} = \frac{z_{\text{solvent}} m w_{\text{solvent}}}{z_{\text{H}_2\text{O}} m w_{\text{H}_2\text{O}} + z_{\text{solvent}} m w_{\text{solvent}}}$$
(4.22e)

$$0 \le z_i \le 1 \quad \forall i \in NC'' = \{\text{solvent, H}_2O\}$$
 (4.22f)

$$\sum_{i=1}^{NC''} z_i = 1$$
(4.22g)

where λ is calculated from Equation (4.20) for a specified $(\boldsymbol{z}, T^0, P^0)$.

4.4.3 Results and discussion

To evaluate the performance of the proposed approaches using the HELD algorithm, TPD analysis and TPD analysis with the use of the first-order optimality condition, each method is applied to Test 2 for a number of solvent candidates: N-methylpentyl-1-amine (MP1A) and pentyl-1-amine (P1A), and N-Methyldiethanolamine (MDEA). The optimisation algorithm is initialised with two types of initial compositions z, one for which the system exhibits either liquid-liquid phase equilibrium and one for single-liquid phase. This is to investigate how the algorithm can overcome potential difficulties near the phase boundaries and accurately predict the phase behaviour regardless of the initial guesses. All runs are performed on a single Intel(R) Xeon(R) Gold 5122 CPU @ 3.60GHz processor with 384 GB of RAM. Tests with the formulation (4.14) and (4.18) are implemented in FORTRAN and we make use of the Numerical Algorithms Group (NAG) NAG E04UFF algorithm, which is a sequential quadratic programming method (SQP). Problem (4.22) is implemented in gPROMS ModelBuilder 7.0.7 and the internal SQP solver is used to perform the optimisation of the problem. We will use the notation T2O, T2HELD, T2TPD and T2KKT to refer to each formulation (4.14) solved with the original PT flash, (4.14) solved with the HELD algorithm, (4.18) and (4.22) solved with TPD-based methods, respectively.

The results obtained using a homogeneous liquid state as a starting point for aqueous mixtures of MP1A, P1A, and MDEA are detailed in Table 4.6. In Figure 4.6, we display the reduced free energy surface with respect to the mole fraction of water and its convex hull for visual inspection. The Gibbs free energy of the aqueous solution of amine is modelled using the SAFT- γ Mie EOS.

It can be seen that T2O, T2HELD and T2TPD converge to the same mole fraction of the water, $z^*_{\rm H_2O}$ (0.9606 for M1PA, 0.9670 for P1A, 0.8687 for MDEA), corresponding to the highest possible solvent weight concentration that ensures a homogeneous liquid phase in the system. In the case of T2KKT, the optimal solvent concentration in weight fraction is found to be higher in all three cases. In this method, the solution of the TPD function is based on the first-order optimality conditions and this results in the inaccurate prediction of stability as a consequence of converging to a local or trivial solution. Despite fewer iterations being required for T2TPD, the computational cost of the optimisation is approximately equivalent to that of T2O or slightly higher across the test cases. A potential source of this higher computational cost is that the quasi-Newton optimisation, in which the calculation of first-order and second-order derivatives is required, is solved for multiple starting points to increase the likelihood of obtaining the global solution. Implementing the HELD algorithm reduces the computational time required to find the optimal solution of Test 2. It should note that, in the HELD algorithm, a stability test is conducted prior to solving the phase-split calculation. However, this only focuses on locating a negative TPD value using a derivative-free method, rather than obtaining a local optimal solution.

In Table 4.7, the results generated from each formulation using an initial guess in the liquid-liquid region are summarised. The result for MDEA is not described here since this amine solvent exhibits full miscibility with water. The results show similar trends in terms of the ability to obtain an accurate solution of Test 2. Interestingly the solution with T2KKT converges to a globally minimum point at $z^*_{H_2O}$ =0.9606 for M1PA and 0.9670 for P1A. This is due to the inclusion of the initial trial composition located in the unstable regions of the Gibbs surface, which prevents the TPD minimisation from converging to the trivial solution. Although there are possible strategies (Michelsen & Mollerup, 2004; Qiu et al., 2014; Li & Firoozabadi, 2012) for gener-



Figure 4.6: Schematic of the Gibbs free energy surface as a function of water mole fractions for binary mixtures of (a) water-MP1A, (b) water-P1A, and (3) water-MDEA, obtained using the SAFT- γ Mie EOS at T=313 K, P=1 atm (black dashed curve). The convex hull of the free energy surface in nonconvex is shown by a continuous blue line. Blue markers (\circ) represent the solvent-rich and water-rich liquid phase compositions at equilibrium. The solid blue lines thus represent the compositions at which the mixture exhibits liquid-liquid immiscibility. The red and amber straight lines represent the initial guesses for the total composition of water, i.e., $z_{\rm H_2O}^{\rm initial} = 0.95$ and 0.98, respectively.

ating initial estimates of the trial phase composition, these cannot guarantee global optimality and such strategies may not be efficient when the system involves many components or a high degree of non-ideality. As can be seen in Figure 4.6(a) and (b) the results for M1PA and P1A are in agreement with the global solution, but the solutions are obtained at higher computational cost for T2TPD. Overall, the use of the HELD algorithm (T2HELD) shows more reliable optimisation results without a significant increase in the CPU time.

From the analysis of the results of Test 2 obtained with a variety of PT flash approaches, it appears that the HELD algorithm is particularly useful for the analysis of systems with complex phase behaviour; the algorithm is found to be robust and reliable in the identification of the best-known solution within a practical computational time. Another advantage of employing the HELD algorithm is that it identifies all stable phases, amounts and phase compositions. Therefore, the results of the phase equilibrium for Test 3 and 4 can be used to calculate other constraints that needs the vapour and liquid compositions at equilibrium (see Equation 4.6), allowing one to eliminate the requirement of the explicit PT flash function. In contrast, if the feasibility test is formulated with the TPD function, an external procedure for the phase equilibrium calculation is required, which may result in inconsistencies in the calculations and increases in computational cost.

One potential improvement that could be made in the TPD analysis is to use a stochastic methods, such as using a tunnelling algorithm (Nichita et al., 2002) combined with a deterministic optimisation method, in the exploration of the minimum TPD value with the aim of reducing the computational burden. In addition, the results from the stability test could be used as initial estimates in the flash calculation to improve performance, although this is beyond the objectives of the current study. Here, the final formulations of the feasibility tests are based on the introduction of the HELD algorithm for the calculation of the PT flash. This means that the same mathematical formulations (4.8), (4.10), (4.11) are used for Test 3 and 4. The prob-

Table 4.6: Performance	of T2O, T2K	IKT, T2'	TPD and	T2HELD i	in the so.	ution of	Test 2 fo	r aqueous	solvents	M1PA, P1	lA, and M	IDEA. The
initial guess for the total	compositio	n of wa	ter, $z_{\rm H_20}$	¹ , corresp(onds to a	single li	quid pina	ise of the s	ystem.			
		EM	PA			Ъ.	IA			IW	DEA	
	T20 T.	2KKT	T2TPD	T2HELD	T20	T2KKT	T2TPD	T2HELD	T20	T2KKT	T2TPD	T2HELD
$z_{\rm H,O}$	0.98 0.	98	0.98 (0.98	0.98	0.98	0.98	0.98	0.98	0.98 (0.98	0.98
2.**2 ZH3O	0.9606 0.	9010	0.9606	0.9606	0.9670	0.9318	0.9670	0.9670	0.8687	0.9423	0.8687	0.8687
W_{solvent}^{z} (kg kg ⁻¹)	0.1817 0.	3817	0.1817 (0.1871	0.1417	0.2614	0.1417	0.1417	0.5	0.2883	0.5	0.5
No. of iterations taken	137 59	6	185 (2	152	67	с С	വ	51	ъ Г	170	41
CPU time (s)	112.31 2	1.37	224.68	29.91	11.89	16.73	18.43	35.35	9.74	1.33	1333.07	32.96

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		Μ	1PA			Р	1A	
	T2O	T2KKT	T2TPD	T2HELD	T2O	T2KKT	T2TPD	T2HELD
$z_{\rm H_2O}^{\rm initial}$	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95
$z_{\rm H_2O}^{*2}$	0.9606	0.9606	0.9606	0.9606	0.9670	0.9670	0.9670	0.9670
W_{solvent}^* (kg kg ⁻¹)	0.1817	0.1817	0.1817	0.1871	0.1417	0.1417	0.1417	0.1417
No. of iterations taken	137	59	185	6	139	32	34	4
CPU time (s)	32.82	7.51	41.16	19.93	52.76	7.75	58.05	23.41

lem of Test 2 is reduced to evaluating separation feasibility at the specified average absorber temperature and pressure as expressed in Problem (4.14).

4.5 Proposed CAMPD algorithm

4.5.1 Primal and master problem

As discussed in Section 4.2.2, the proposed CAMPD algorithm is based on the outer approximation (OA) algorithm (Duran & Grossmann, 1986), in which an alternating finite sequence of NLP subproblems and MINLP subproblems are solved. In presenting the formulation of primal and master problem in conjunction with feasibility tests, we adopt the same notation introduced in the work of Gopinath et al. (2016) and Bowskill et al. (2020). Given the feasible domain defined with tightened bounds on the operating conditions from Test 3 and 4, the primal problem (P) of the OA algorithm is formulated as a nonlinear process optimisation problem over continuous variables with fixed solvent structure $n^{(k)}$ where k is an iteration counter. Since we solve the NLP in gPROMS, we recognise explicitly that a feasible path approach is used, so that the set of continuous variables x^d with $x = (u, x^d)$. The set of dependent variables x^d is calculated using process and physical property models, as represented by the equalities. Note that n_S is included in x^d as it is fully specified once n is given. A set of inequality constraints $g \leq 0$ in problem (MINLP) is reduced to $g_p \leq 0$, where $g_p \subset g$, by removing the constraints used in Test 1. The resulting formulation of the primal problem is given by:

$$f^{(k)} = \min_{\boldsymbol{u}} f(\boldsymbol{u}, \boldsymbol{n}^{(k)})$$

s.t. $\boldsymbol{g}_{p}(\boldsymbol{u}, \boldsymbol{x}^{d}(\boldsymbol{u}, \boldsymbol{n}^{(k)}), \boldsymbol{n}^{(k)}) \leq 0$
 $\boldsymbol{x}^{d,L(k)} \leq \boldsymbol{x}^{d}(\boldsymbol{u}, \boldsymbol{n}^{(k)}) \leq \boldsymbol{x}^{d,U(k)}$, (P)
 $\boldsymbol{u}^{L(k)} \leq \boldsymbol{u} \leq \boldsymbol{u}^{U(k)}$

where $f^{(k)}$ is the optimal objective value at iteration k, and superscripts L and U denote lower and upper bounds, respectively. The variable bounds at each iteration may be specified by the user or derived from the tests. The solution of the primal problem yields an upper bound, on the objective function to be minimised.

The master problem is formulated by deriving a set of the linearised constraints and objective functions (hyperplanes) from the solution of each primal problem, such that the original problem domain is approximated via a polyhedral representation. As iterations proceed, the approximation is improved by accumulating the linearised equations and tightening the outer bounds on the solution region of the given problem. The final form of the master problem differs depending on the outcome of the feasibility tests and the primal problem. In a formulation, we define several sets in order to distinguish the equations generated from different outcomes such as failing or passing the feasibility tests, or the convergence of the primal problems. The set $F^{(k)}$ contains the index l of all previous major iterations, i.e., $l \in \{1, ..., k\}$ where the primal problem is feasible. For each index $l \in F^{(k)}$, the set $A^{(k)}$ is used to store the pairs of indices (l, m), where m is the index of an active constraints, $g_m \in g_p$ in g_p at the solution of the primal problem. If the evaluation of a molecule in Test 1 violates at least one constraint, the indices of all violated constraints are stored in set $A1^{(k)}$. The set $A1^{(k)}$ contains indices (l, j), where j denotes the index of active or violated constraints $g_i \in g_1$. Finally, set $IC^{(k)}$ is used to store the indices of all molecules for which an integer cut is introduced in the master problem to remove infeasible molecules from the design space. A molecule is deemed infeasible when the molecule fails to pass the feasibility tests, when the primal problem is infeasible $(l \leq k)$, or when the solution to the master problem $n^{(l+1)}$ yields a repetition of a previously generated combination. The integer cuts employed are based on the "big-M" approach suggested by Samudra & Sahinidis (2013) as follows:

$$M^{L}(1-y_{l}) + \varepsilon_{ic} \leq \sum_{i=1}^{N_{G}} (\ln(p_{i})(n_{i} - n_{i}^{(l)})) \leq M^{U}y_{l} - \varepsilon_{ic},$$
(4.23)

where p_i is a prime number, N_G is the number of infeasible molecules identified, n with elements n_i denotes the solvent being sought in the master problem, M^L and M^U are large negative and positive numbers, respectively, ϵ_{ic} is a small positive number, and y_l is a binary variable introduced for iteration l to ensure the central term is strictly positive or negative, but not equal to zero.

Within the algorithm, the linearisation of the constraints and objective function to formulate the master problem requires a convexity assumption to provide valid bounds of the problem. However, in many cases, problem (MINLP) is nonconvex and thus the linearisations can cut off the candidate integer points from feasible region, which may result in convergence to suboptimal solutions. To overcome this, the augmented penalty version of the outer approximation (OA/AP), which is a modification of OA proposed by Viswanathan & Grossmann (1990), is implemented in our study. The OA/AP algorithm makes use of a relaxation of the linearisations in the master problem, in that the feasible region is expanded with slack variables by allowing some violation of the constraints. The violations of the linearisation are penalised via a weighted-sum in the objective function. The resulting formulation of the master problem is as follows:

$$\begin{split} \min_{\boldsymbol{u},\boldsymbol{n},\eta} & \eta + 1000(e_{1} + e_{2}) \\ \text{s.t.} & f(\boldsymbol{u}^{(l)},\boldsymbol{n}^{(l)}) + \nabla_{\boldsymbol{n}}^{T} f(\boldsymbol{u}^{(l)},\boldsymbol{n}^{(l)}) \left[\boldsymbol{n} - \boldsymbol{n}^{(l)}\right] \\ & + \nabla_{\boldsymbol{u}}^{T} f(\boldsymbol{u}^{(l)},\boldsymbol{n}^{(l)}) \left[\boldsymbol{u} - \boldsymbol{u}^{(l)}\right] \leq \eta + e_{1}, \quad \forall l \in F^{(k)} \\ g_{p,m}(\boldsymbol{u}^{(l)},\boldsymbol{n}^{(l)}) + \nabla_{\boldsymbol{n}}^{T} g_{p,m}(\boldsymbol{u}^{(l)},\boldsymbol{n}^{(l)}) \left[\boldsymbol{n} - \boldsymbol{n}^{(l)}\right] \\ & + \nabla_{\boldsymbol{u}}^{T} g_{p,m}(\boldsymbol{u}^{(l)},\boldsymbol{n}^{(l)}) \left[\boldsymbol{u} - \boldsymbol{u}^{(l)}\right] \leq e_{2}, \quad \forall (l,m) \in A^{(k)} \\ g_{1,j}(\boldsymbol{u}^{(l)},\boldsymbol{n}^{(l)}) + \nabla_{\boldsymbol{n}}^{T} g_{1,j}(\boldsymbol{u}^{(l)},\boldsymbol{n}^{(l)}) \left[\boldsymbol{n} - \boldsymbol{n}^{(l)}\right] \leq e_{2}, \quad \forall (l,j) \in A1^{(k)} \\ M^{L}(1 - y^{u}) + \varepsilon_{ic} \leq \sum_{i=1}^{N_{G}} (\ln(p_{i})(n_{i} - n_{i}^{(l)})) \leq M^{U}y_{l} - \varepsilon_{ic}, \quad \forall l \in IC^{(k)} \\ y^{u} \in \{0,1\}, \quad \forall l \in IC^{(k)} \\ \boldsymbol{u}^{L} \leq \boldsymbol{u} \leq \boldsymbol{u}^{U} \\ \boldsymbol{Cn} \leq \boldsymbol{d} \\ \eta \leq f^{U} \end{split}$$

where y^u is the best own upper bound on the solution of (MINLP), given by $y^u = \max_{l \in F^{(k)}} = \{y^{(l)}\}$. The parameter value of ϵ_{ic} is given as 10^{-2} in our study.

4.5.2 Algorithm overview and implementation

An automated implementation of the proposed CAMPD algorithm is developed in C++ in Visual Studio 2019, with an interface to gPROMS ModelBuilder 7.0.7 using gO:RUN functionality and an interface to Gurobi 8.1 MILP solver. The feasibility tests are implemented in FORTRAN and gPROMS ModelBuilder, and the results, such as the updated bounds and infeasibility of the molecule, are transferred to the primal problem via the gO:RUN interface. The default continuous nonlinear optimiser in gPROMS, which makes use of a sequential quadratic programming (SQP) method, is applied to solve the primal problems. The gradients of the objective function and active inequality constraints are calculated using first-order forward finite differences with respect to integer variables and central differences for the continuous variables.



An overview of the algorithm is provided in Figure 4.7.

Figure 4.7: An overview of the proposed CAMPD algorithm

When using the OA/AP framework to overcome the nonconvexities of the problem, care must be taken in choosing a termination criterion to prevent the algorithm from converging to a solution prematurely. For a convex MINLP, the master problem produces a valid lower bound on the objective function of the primal problem and this lower bound increases monotonically as iterations proceed, while updates of the upper bound on the problem are generated through the primal problem. Hence, it can guarantee that the best NLP solution found is global optimal when the lower bound exceeds or is close to the upper bound for the convex MINLP. However, using such a criterion as a stopping rule for nonconvex MINLP problems may result in premature convergence, particularly when the set of linear approximations leads to part of the feasible region being cut off, possibly eliminating a global solution (Floudas, 1995). It therefore becomes necessary to employ heuristics to improve the quality of the solutions. Generally good convergence behaviour has been observed using the stopping criteria presented in Bowskill et al. (2020). Hence, we resort to termination based on the same heuristics by which the algorithm is stopped when: 1) the number of iterations at which the augmented penalty term becomes nonzero exceeds a pre-defined limit, $N_{max,slack}$, 2) the number of unique molecules that has been evaluated either in the feasibility tests or the primal problem exceeds a pre-defined limit $N_{max,unq}$, and 3) when the MILP master problem becomes infeasible.

4.6 Results of the CAMPD problem

The proposed algorithm is applied to three design cases to identify the best-performing solvents. Each design case (DS) is different in that the maximum allowed number of amine groups is specified as $n_{G_A}^U = 1$, 2 or 3 in an attempt to consider different amine functionalities in the solvent molecule. The information on the molecular design space, process parameters and bounds on process variables, and algorithmic parameters is given in Tables 4.2 and 4.8.

Given the nonconvex nature of the problem, the CAMPD algorithm is run from ten starting points for each case study to explore more diverse search directions thus increasing the likelihood of obtaining globally optimal solvents. The starting points are chosen from the studies of Bernhardsen & Knuutila (2017) and Papadopoulos et al. (2016) which yield chemically feasible molecular structures and also pass the feasibility tests. The list of starting points is given in Table A.1 in the appendix, where the groups are given in the following order: NH₂CH₂, NH₂CH, NH₂C, NHCH₃, NHCH₂, NHCH, NCH₃, NCH₂, CH₃, CH₂, C, and OH. Following the termination of

 Table 4.8: Molecular design space defined for each design case.

 DS denotes a design case.

Parameter	n_t^U	$n_{G_A}^U$	$n_{G_A}^L$	$n_{\rm OH}^U$	$n_{\rm iso}^U$	$N_{max,slack}$	N _{max,unq}
DS1	12	1	1	3	2	5	50
DS2	12	2	1	3	4	8	100
DS2	12	3	1	3	4	8	100

the algorithm from all starting points, the solvent that presents the lowest TAC value is reported as an optimal solution. Although multiple initial guesses are used, this does not guarantee the global optimality of the solution. Furthermore, the solution generated is specific to the process specifications and modelling assumptions, and thus it is desirable to generate a list of candidate solvents by which high-performing solvents can be evaluated further by means of other simulation settings or experiments. Once the best-known solvent is obtained by solving the problem from ten starting points, the solvent structure is added to an integer cut in the master problem and then restart the algorithm to generate the next-best solvent from the multiple starting points.

4.6.1 Overall performance

The computational performance of the proposed algorithm is reported in Table 4.9 and the detailed results are summarised in Tables 4.10-4.13. Throughout the discussion, the performance for each DS is calculated as an average over 50 simulations corresponding to the five top-ranked solvents generated from the ten starting points (molecules). All 150 runs converge successfully to locally optimal solutions regardless of the starting points. From Table 4.9, it can be seen that different tests are active in each of the DSs. It is evident that the introduction of feasibility tests successfully eliminates infeasible molecules and process conditions from the design space, making it possible to evaluate feasible molecules in the primal problem without encountering numerical difficulties. The infeasibilities are more prominent for

	DS1	DS2	DS3
Average number of molecules failing in the tests	2.56	1.50	0.30
Percentage of molecules failing in Test 1 (%)	12.63	2.42	0.20
Percentage of of molecules failing in Test 2 (%)	9.47	9.68	0.00
Percentage of of molecules failing in Test 3 (%)	0.00	0.00	0.00
Percentage of of molecules failing in Test 4 (%)	2.11	0.00	0.10
Average number of iterations	16.67	20.90	20.10
Average CPU time (s)	3186.6	6628.9	5846.3

Table 4.9: Computational performance of the algorithm with feasibility tests for all three design cases, averaged over 50 runs for each design case.

DS1 and DS2, as some of molecules such as mono-alkylamines are found to undergo an undesirable liquid-liquid phase split at the absorber operating conditions.

It is clear from Table 4.9 that the computational cost is high even for the smaller design space (3186 s for DS1, 6628 s for DS2, and 5846 s and for DS3), suggesting that the computational cost would be significantly increased if many infeasible combinations of molecular structures and process conditions were explored in the absence of feasibility tests. User-provided initial guesses are found to be infeasible for some molecular candidates – for example, the initial value of lean loading for MDEA is automatically updated to 0.05 mol mol⁻¹ from 0.15 mol mol⁻¹ by the algorithm, allowing the algorithm to assess the overall process performance though the solution of the primal problem. Without the feasibility tests, the initialisation of the process model may fail and incorrectly result in being considered an infeasible molecule. The overall statistics indicate that the feasibility tests prior to the primal problem are particularly important when the solution of the process optimisation incurs a high computational cost and that providing a feasible combination of process conditions is critical to the convergence of the problem. This reliable convergence achieved the whole CAMPD algorithm in the exploration of a large set of solvent structures and associated process performance highlights the effectiveness of each step of the algorithm developed and discussed in Section 3.3.5, 4.3.5 and 4.4.3.

4.6.2 Optimal solvents identified using the proposed approach

The top five solvents identified and their corresponding performance indicators are summarised in Tables 4.10-4.12. Detailed information including optimal solvents and process conditions are presented in Table 4.13.

Design case 1

In DS1, DEA is identified as the best solvent with a TAC of 17.577 \$million year⁻¹, while other top-ranked solvent candidates exhibit relatively higher TAC values (31-46 % higher than that of DEA). The heat requirement and the total cost with DEA are decreased by 41.03 % and 46.70 %, respectively, when compared to those with MEA. Such reduction in cost is achieved through higher cyclic capacity and lower reboiler duty in the desorber, thereby decreasing the total energy requirement of the system significantly. It is noteworthy that a high cyclic capacity is obtained with DEA in spite of the low solubility of CO_2 in aqueous mixtures of DEA. In Figure 4.8, the CO_2 partial pressures is predicted as a function of CO_2 loading at two different temperatures (313 K and 383 K) using the SAFT- γ Mie EOS. At a fixed partial pressure of CO_2 , it can be seen that DEA exhibits very low CO_2 loading at 313K. However, a high purity of the regenerated solvent, i.e., a low lean loading, is attainable with a low reboiler duty, resulting in a high cyclic capacity (0.321 mol mol⁻¹ for DEA and 0.160 mol mol⁻¹ for MEA at the optimal process conditions, see Table 4.13). As a result, the solvent circulation rate, equipment size, and total energy consumption are decreased. As reported in Ramachandran et al. (2006), the process with MEA is indeed known to use a large amount of energy for solvent regeneration due to the formation of a highly stable carbamate in the absorber. Interestingly, no tertiary amine is identified in the list of the optimal solvents although low regeneration energy and high theoretical absorption capacity are usually expected for these molecules (Chowdhury et al., 2013). This is likely due to the higher molecular weight associated with the bulky alkylgroup, CH₃, attached to the nitrogen atom resulting in a lower molar

Table 4.10: The candidate list of top five molecular structures for DS1 identified by minimising the total annualised cost using the proposed CAMPD approach with integercuts. The total annualised cost (TAC), total cost of investment (TCI) and operating cost (OPEX) are in units of US million dollar per year (\$million year⁻¹). The total energy consumption of the process (Q_{total}) is presented in units of GJ ton- CO_2^{-1} . MEA is added in the last row as a benchmark solvent.

Rank	Solvent name or molecular code (short code)	TAC	TCI	OPEX	$Q_{\rm total}$
1	2-(2-hydroxyethylamino)ethanol (DEA)	17.577	5.818	11.144	4.969
2	2-aminopropane-1,3-diol (2APD)	23.108	7.735	14.758	7.261
3	3-(3-hydroxypropylamino)propan-1-ol (3HPAP)	24.799	9.000	15.183	8.160
4	2-(aminomethyl)propane-1,3-diol (2AMPD)	24.996	8.541	15.840	7.800
5	2-amino-2-methyl-1,3-propanediol (AMPD)	25.735	8.952	16.167	7.926
Ref.	2-aminoethanol (MEA)	29.806	8.047	21.144	9.323

concentration of the tertiary amine in the mixture. The absence of tertiary amines from the list of top five solvent may also be explained by the fact that the absorption capacity of these solvents is greatly influenced by the CO₂ partial pressure. For example, the CO₂ solubility of MDEA at low partial pressures ($P \le 10$ kPa) is similar or significantly less than that of MEA and DEA. It is worth mentioning that the highest achievable CO₂ partial pressure in the absorber for given process specifications is approximately 5 kPa, which is estimated by multiplying the absorber operating pressure and the mole fraction in CO₂ of the flue gas stream. Similar discussions can be found in the study of Bernhardsen & Knuutila (2017) in which absorption capacity, cyclic capacity and basicity (pKa) of 132 aqueous amine solvents available in the literature were compared. The authors reported that the cyclic capacity of the best primary and secondary amines is higher than that of any tertiary amines.

Design case 2

In DS2, solvent molecules can contain upto two amine groups, so that the design space of DS1 is a subset of that for DS2. With the exception of DEA, all highly-ranked solvents are diamines, which comprise two amino groups that participate in the CO_2 removal reactions and thus enable higher CO_2 loadings to be achieved. According to the work of Choi et al. (2014), where the performance of aqueous blends of MDEA and multiamine (alkyl-) solvents with primary and secondary amino groups was in-



Figure 4.8: Predicted partial pressure of CO_2 as a function of CO_2 loading for a 30 wt% (mass) aqueous solution of MEA (dark grey), DEA (yellow) and MDEA (green). The solid line and dotted lines are the predictions of the SAFT- γ Mie EOS for 313 K and 383 K, respectively.

vestigated, the stability of the carbamate ions decreases in the following order: primary carbamate > primary-primary dicarbamate > primary-secondary dicarbamate. This means that the heat required to break the bonds of a dicarbamate is lower than that required for a carbamate. This is one possible explanation as to why a lower heat of regeneration is observed with diamine solvents. The higher cyclic capacity at the optimal process conditions shown in Table 4.13 corresponds to a lower solvent circulation rate, allowing one to reduce the equipment and operating costs.

The molecular weights of all high-performing solvents are within a range of 104-118 g mol⁻¹, i.e., the molecular size is kept as small as possible, while including two amino groups. This trend may be due to the use of a fixed weight concentration of solvent in the problem formulation and to the large impact of the circulation rates on both the cost and energy consumption. As a result, the algorithm moves towards smaller molecular structures in order to decrease the amount of solvent, while maximising the number of amino groups. The use of large molecules can lead to an increase in the reboiler operating temperature and also manifest as a larger solvent viscosity, resulting in the relatively large process units and a greater risk of thermal

degradation. It is also noticeable that no alkylamine is included in the list of Table 4.11. Many of the alkylamines are found to be immiscible with water at the absorber operating conditions (see Table 4.3) and hence they are removed from consideration in the feasibility tests. Although not shown here, the feasible dialkylamines that are explored in the course of the algorithm lead to a slightly higher TAC at the optimal solution of the problem, whilst their cyclic capacity and energy consumption are similar to or less than those of some of the highly-ranked solvents. The increase in TAC with alkylamines is caused by the larger amine losses to the atmosphere at the top of the absorber and desorber, which increase the operating costs for amine makeup. For example, the TCI and total energy consumption for 1,3-propanediamine (CAS registry number: 109-76-2), which is one of the solvents evaluated during the search, are reduced by 4.9 and 7.0%, respectively, when compared to 1,3-diamino-2-propanol (CAS registry number: 616-29-5). However, the cost for amine make-up increases by 98.7%, which outweighs the reduction in the TCI and required energy. This is because the addition of hydroxyl groups in the amine facilitates the formation of hydrogen bonds with water, making the amine more soluble in water and less volatile. Care must be taken, however, when considering the introduction of hydroxyl groups in the molecular structure, as the increase in the number of hydroxyl groups has an adverse effect on the heat duty for regeneration and CO₂ solubility, as demonstrated in the experimental study of Muchan et al. (2017).

Design case 3

In DS3, the larger molecular design space of molecules with up to three amine groups is explored. As can be seen in Table 4.12, only triamines that have multiple reaction sites and can form various species of carbamate or bicarbonate with CO_2 appear in the list of high-performance solvents. Molecules with a higher number of amine groups lead to a high CO_2 loading in the rich solvent and low regeneration energy is attained, leading two lower steam costs for regeneration, which constitute a major component of the TAC with a share of 40-45%. A significant reduction in **Table 4.11:** The candidate list of top five molecular structures for DS2 identified by minimising the total annualised cost using the proposed CAMPD approach with integercuts. The total annualised cost (TAC), total cost of investment (TCI) and operating cost (OPEX) are in units of US million dollar per year (\$million year⁻¹). The total energy consumption of the process (Q_{total}) is presented in units of GJ ton- CO_2^{-1} . MEA is added in the last row as a benchmark solvent.

Rank	Solvent name or molecular code (short code)	TAC	TCI	OPEX	Q_{total}
1	[0-0-1-0-1-0-0-0-2-0-0-0-1] (SOL01)	17.144	5.327	11.202	4.785
2	2-(2-hydroxyethylamino)ethanol (DEA)	17.577	5.818	11.144	4.969
3	2-(2-Aminoethylamino)ethanol (AEEA)	17.991	5.544	11.832	5.356
4	[2-0-0-0-0-0-0-0-0-1-2] (SOL02)	19.599	6.186	12.799	6.390
5	1,3-Diamino-2-propanol (DAP)	19.754	6.091	13.048	6.645
Ref.	2-aminoethanol (MEA)	29.806	8.047	21.144	9.323

the TAC of the top-ranked solvents is achieved due to the increased cyclic capacity. The TAC with SOL03 is decreased by 50.1% compared to MEA and 13.2% compared to the top ranked solvent (SOL01) in DS2. The cyclic capacity with SOL03 at the optimal process operating conditions is increased by 333.7% compared to MEA and 37.5% compared to SOL01. As discussed for DS2, the formation of dicarbamates entails a lower heat of reaction than that of the carbamate formed from MEA. In addition, the combined effect of the higher prevalence of weak binding between CO_2 and amino groups and the high cyclic capacity results in a relatively low regeneration energy. It can be observed that the solvent structures in the list comprise primary and secondary amines, which may be explained by the fact that the effect of cyclic capacity on the cost dominates compared to the low heat of regeneration that can be derived from the introduction of a tertiary amine group in the molecule.

4.6.3 Comparison between CAMPD and CAMD formulations

Having developed a robust CAMPD algorithm, we now discuss the significance of evaluating the molecular properties within the process context. In Figure 4.9, we compare the key molecular properties of the top-ranked optimal solvents identified from each DS, in addition to MEA. The properties are selected based on the studies of Papadopoulos et al. (2016) and Lee et al. (2020), where the CAMD was formu-

Table 4.12: The candidate list of top five molecular structures for DS3 identified by minimising the total annualised cost using the proposed CAMPD approach with integercuts. The total annualised cost (TAC), total cost of investment (TCI) and operating cost (OPEX) are in units of US million dollar per year (\$million year⁻¹). The total energy consumption of the process (Q_{total}) is presented in units of GJ ton- CO_2^{-1} . MEA is added in the last row as a benchmark solvent

Rank	Solvent name or molecular code (short name)	TAC	TCI	OPEX	$\boldsymbol{Q}_{\rm total}$
1	[2-0-0-0-1-0-0-0-1-0-2] (SOL03)	14.872	4.509	9.748	4.492
2	[2-0-0-0-1-0-0-0-0-0-1] (SOL04)	15.041	4.597	9.829	4.571
3	propane-1,2,3-triamine (PTA)	15.148	4.875	9.658	4.458
4	N'-(aminomethyl)-N'-methylmethanediamine (NAMDA)	15.278	4.859	9.804	4.569
5	[2-0-0-0-1-0-0-0-0-0-1-2] (SOL05)	15.288	4.720	9.953	4.577
Ref.	2-aminoethanol (MEA)	29.806	8.047	21.144	9.323

lated as a multi-objective optimisation (MOO) problem to identify the trade-offs (a set of Pareto-optimal solvents) between the desired properties; these are: saturated vapour pressure (P_{vap}) , liquid density (ρ) , heat capacity (C_p) and relative energy difference (RED) of a pure solvent. Each property is normalised based on its minimum and maximum values so that the values are rescaled to lie in the a range of 0 to 1. The liquid density is scaled based on $-\rho$ so that smaller values of these objective functions are indicative of better performing solvents in terms of each property criterion. Additionally, the heat of absorption (- ΔH_{abs}), which is an indicator of the heat requirement for regeneration, and the CO₂ loading, which is an important parameter associated with the absorption capacity of the solvents, are presented for the optimal solvents identified. The heat of absorption is calculated based the simulation approach proposed by Graham (2020) who aimed to mimic the experimental setting of Arcis et al. (2012), rather than applying the Gibbs-Helmholtz equation. As can be seen in Figure 4.9, it is not possible to correlate the performance of the solvents in terms of property targets with their overall performance when evaluated within the relevant process. SOL03, identified as the most cost effective solvent in the solution of the CAMPD problem, appears as the best solvent only with respect to density and CO_2 loading. SOL03 is also the third best molecule in terms of energy efficiency when assessed through the heat of absorption within the range of 0-1 mol

CHAPTER 4.	CAMPD: OPTIMAL	. SOLVENT	DESIGN	FOR CO_2	CHEMICAL
ABSORPTION	I PROCESSES				

are presented in	the orde	r of hig	h to low	rank wi	th their	short na	me.								
			DS1					DS2					DS3		
Optimal Value	MEA (ref.)) DEA	3PAP1	2AMPD	AMPD	SOL01	DEA	AEEA	SOL02	DAP	SOL3	SOL4	PTA	NAEMDA	SOL05
TAC ($\$$ million year ⁻¹)	29.806	17.577	24.799	24.996	25.735	17.144	17.577	17.991	19.599	19.754	14.872	15.041	15.148	15.278	15.288
CAPEX (\$million year ⁻¹)	8.048	5.818	9.000	8.541	8.952	5.327	5.818	5.544	6.186	6.091	4.509	4.597	4.875	4.859	4.720
OPEX ($\$$ million year ⁻¹)	21.144	11.144	15.183	15.840	16.167	11.202	11.144	11.832	12.799	13.048	9.748	9.829	9.658	9.804	9.953
Q_{total} (GJ ton-CO ₂ ⁻¹)	9.323	4.969	8.160	7.800	7.926	4.785	4.969	5.356	6.390	6.645	4.492	4.571	4.458	4.569	4.577
Sol circ. rate (kg h^{-1})	0.3731	0.2992	0.4816	0.4658	0.4637	0.1990	0.2992	0.2272	0.3299	0.3055	0.1902	0.1759	0.1698	0.1547	0.1937
Reboiler temperature (K)	397.18	386.95	385.87	398.81	398.98	400.99	386.95	402.15	398.69	398.60	401.12	401.64	401.81	401.28	401.12
Cyclic capacity (mol mol ⁻¹)	0.160	0.321	0.254	0.212	0.213	0.503	0.321	0.446	0.316	0.294	0.692	0.600	0.538	0.571	0.681
Rich loading (mol mol^{-1})	0.476	0.341	0.345	0.475	0.474	0.936	0.341	0.979	0.929	0.932	1.394	1.410	1.378	1.154	1.402
Lean loading, θ_0 (mol mol ⁻¹	0.317	0.020	0.090	0.262	0.261	0.432	0.020	0.533	0.613	0.638	0.702	0.810	0.839	0.583	0.721
Lean temperature, T ₀ (K)	313.15	334.54	316.86	335.07	335.43	333.76	334.54	333.67	335.84	335.33	334.98	335.12	338.66	337.95	334.85
P _{Nd} (MPa)	0.206	0.153	0.166	0.218	0.216	0.246	0.153	0.253	0.211	0.216	0.235	0.241	0.221	0.215	0.236
Q _{reb} (MJ)	209.332	168.348	194.078	231.462	234.193	163.522	168.348	180.248	191.296	194.422	152.380	152.164	145.071	146.623	154.624
Q _{cond} (MJ)	-99.585	-49.603	-52.745	-110.698	-113.509	-46.344	-49.603	-54.675	-89.000	-97.081	-44.668	-48.330	-50.455	-53.808	-46.154
Solvent loss (kg ton CO_2^{-1})	3.10	6.92×10^{-1}	² 2.37×10	24.00×10^{-1}	³ 6.78×10 ⁻³	³ 3.70E×10 ⁻	⁻¹ 6.92×10 ⁻	21.75×10^{-1}	7.86×10^{6}	1.61×10^{-2}	2.32×10^{-7}	6.31×10^{-4}	3.67×10^{-3}	2.52×10^{-2}	2.74×10^{-7}

are presented in the order of high to low rank with their short name.	Table 4.13: Results of the solution of the integrated solvent and chemical absorption process design for each case study. The molecules

mol⁻¹ of CO₂ loading. However, the results of the CAMPD formulation uncover that the SOL3 leads to the most energy efficient process (lowest value of Q_{total}).

Another aspect of interest in the design of the solvent is the value of the vapour pressure of the solvent, P_{vap} , at 323 K which can be used as an indicator of solvent losses and which should be as low as possible to minimise the environmental impact. Clearly, DEA exhibits the lowest vapour pressure in Figure 4.9(a). However, the solvent losses which are calculated as the sum of the amount of the solvent in kg ton- CO_2^{-1} in the clean gas and in the CO_2 gas stream at the optimal process conditions, suggests that SOL03 leads to the lowest value (3.10 for MEA, 6.92×10^{-2} for DEA, 3.70×10^{-1} for SOL1 and 2.32×10^{-7} for SOL3 in units of kg ton- CO_2^{-1}). The discrepancies in the CAMD and CAMPD approaches demonstrate that the best overall performance of the processing materials can only be realised when the molecular properties are evaluated within integrated molecular-process models. As has been shown, the proposed CAMPD algorithm provides a systematic way of identifying promising solvents in a process that is economically or environmentally favourable, allowing one to quantify the performance of the solvent in the process domain and to embed the trade-offs between properties in the decision-making.

4.6.4 Comparison between direct and decomposition-based solution approaches

An important aspect of the proposed CAMPD algorithm is that it considers the process and molecular-level decisions simultaneously. As discussed, alternatives to the direct solution approach that can avoid the numerical difficulties of solving a large MINLP process-molecular model are decomposition-based approaches, also known as two-stage approaches, in which a set of feasible molecular candidates is generated and selected first and subsequently, the candidate molecules are further investigated using a detailed process model. In order to compare the performance of the two ap-



Figure 4.9: A comparison of the molecular properties of DEA (amber), SOL01 (blue) and SOL03 (red) which are identified as the top solvents in each design case. The properties of MEA (dark grey) are provided as a reference. In (a), normalised value of properties, P_{vap} , ρ , C_p and *RED* are shown. (b) the heat of absorption (- Δ H_{abs}) at 323 K, as a function of CO₂ loading and (c) partial pressure of CO₂ (P_{CO2}) at 313 K, as a function of CO₂ loading predicted using the SAFT- γ Mie EOS for 30 wt% (mass) of amine in the aqueous mixture.

proaches, the list of potential solvents candidates from the study of Lee et al. (2020), presented here in Chapter 5, in which 40 optimal solvents are generated by solving the multi-objective CAMD problem using the sandwich algorithm (Rennen et al., 2011), are considered. The total CPU time taken to generate the set of 40 optimal amine solvents and the average CPU time taken to generate one optimal solution were reported as 353 s and 8.38 s, respectively, in Table 12 of Lee et al. (2020). Among the 40 optimal solvents, the 19 solvents that satisfy the molecular structure constraints of problem (P) for DS3 are further evaluated in the primal problem, i.e., process optimisation. The set of structurally feasible molecules and the result of the application of in the feasibility tests to these molecules are given in Table A.2 of Appendix. As can be seen in Table A.2, many of the solvents are found to be infeasible for the given process specifications, mainly due to high melting points, high flash points, and immiscibility with water. The best solvent among the evaluated solvent candidates is identified as M26, with a corresponding TAC of 16.0 \$million year⁻¹ (See Table 4.14). It is interesting to note that of the optimal TAC value with M26 is higher than that of the top five solvents from DS3. This suggests that the use of the decomposition-based approach can lead to sub-optimal solutions by forcing the exploration toward limited or biased molecular domains. Nevertheless the TAC value for M26 is larger than any of DS2/DS1 solutions, indicating that the CAMD

methodology identifies good solvents. Decomposition may also give rise to high computational cost, as a large number of molecules needs to be enumerated to identify optimal or near optimal solutions. The CPU time taken to evaluate the feasibility tests and primal problem for the 19 solvents is 3422 s, which is less than that of DS3. However, this saving results in part from the presence of infeasible molecules that fail to pass the feasibility tests in the course of the algorithm. It also does not account for the cost of generating the set of Pareto-optimal solvents. In summary, there is clear evidence that the proposed algorithm offers a more reliable way to identify promising solvents with the desired overall performance. **Table 4.14:** Optimal solvent identified by enumerating the list of 19 molecules generated by solving MOO CAMD problem (Lee et al., 2020) that satisfy the molecular feasibility constraints in problem (MINLP).

Parameters	Value
Optimal solvent	M26
Molecular code of M26	[0-0-0-0-0-1-1-1-3-0-0-0-1]
TAC (\$million year ⁻¹)	16.007
TCI (\$million year ⁻¹)	4.851
OPEX (\$million year ⁻¹)	10.541
$Q_{ m total}$ (GJ ton-CO $_2^{-1}$	4.676
Solvent circ. rate (kg h^{-1})	0.166
Cyclic capacity (mol mol ^{-1})	0.806
lean loading, θ_0 (mol mol ⁻¹)	0.204
Lean solvent temperature, T_0 (K)	333.59
Desorber pressure, P_{N_d} (MPa)	0.234
Total CPU time (s)	3422

4.6.5 Conflicting nature of key performance indicators

In Figure 4.10, the top solvents identified are plotted on two-dimensional projection of the space of KPIs, including TCI vs. total energy consumption per ton of CO₂ removed and TAC vs. total energy consumption per ton of CO₂ removed. As can be gleaned from the figure for each design case, the ranking of the five amine solvents determined based on the TAC is not in the same order as when the overall performance is measured using one of the other two KPIs metric. For instance, the top solvent based on the minimisation of TAC for DS3 (SOL03) ranks second in terms of the total energy requirement. This suggests that there exist trade-offs between the performance criteria, and it may be useful to deploy a MOO technique to explore the set of optimal solvents that capture the multiple conflicting criteria.

4.7 Conclusions

In this work, a robust CAMPD framework has been proposed for the simultaneous design of optimal aqueous solvents and CO_2 chemical absorption processes. The focus of the development has been to overcome the numerical challenges that arise due to the complex nonlinear interactions between process models and molecule-structure



Figure 4.10: Plots of the TAC and TCI values vs. to total energy consumption for the top 5 solvents for DS1 (•), DS2 (•) and DS3 (•)

property models. New feasibility tests have been combined with the primal problem of the OA algorithm to provide a reliable way to converge to an optimal solution by removing infeasible process conditions and molecular structures from the search space before attempting to solve the process optimisation problem. The efficiency and robustness of the proposed algorithm has been demonstrated on a CO₂ chemical absorption process for a 400 MW combined CCGT power plant (Bailey & Feron, 2005) where solvent molecular structure and process operating conditions have been simultaneously optimised to maximise the overall economic performance of the process. A systematic investigation of the performance of the proposed CAMPD algorithm over 150 runs has shown that the feasibility tests combined with the improved initialisation strategy of Chapter 3 enhance robustness and increase the likelihood of identifying high performance solutions. By identifying infeasible regions within molecular and process domains, numerical errors are prevented over the course of the exploration, which leads to a reduction in the computational cost.

Furthermore, we have also shown how the proposed algorithm is an improvement over the traditional decomposition-based approaches used in the determination of the best performing solvents. The comparison of the results obtained with two versions of the algorithm exemplifies that despite the complexities of solving a large nonconvex MINLP problem, the simultaneous consideration of molecular and process-level decisions provides a useful way of generating better solution without resorting to problem decomposition or over-simplification of the models.

Future work involves the investigation of the effect of various choices of process specifications, such as high or low concentration of CO_2 in the flue gas. Given the high predictive capabilities of the SAFT- γ Mie EOS, it would be useful to extend the molecular search domain to a more diverse set of functional groups, for example, cyclic amines, which have been applied widely as rate promoting additives.

Finally, the comparison of other key performance criteria for the optimal solvents, such as TCI and total energy consumption for the optimal solvents, has exemplified molecular design, we focus on the development of MOO algorithms in the remainder of the thesis.

CHAPTER 5

A Comparative Study of Multi-objective Optimisation Methodologies for Molecular and Process Design

Following the development of the CAMPD framework in the previous chapter, it was found that it is beneficial in many cases to consider multiple conflicting objectives in molecular design – for example, property targets, sustainability targets, societal impact, and economic performance – that cannot easily be combined together in a single metric. Multi-objective Optimisation (MOO) is thus receiving increasing attention in the area of CAM(P)D. In principle, for a problem with continuous decision variables, the presence of conflicting objectives results in an infinite number of optimal solutions, commonly known as Pareto-frontier solutions. Usually, it is not possible to derive an analytical description of the Pareto frontier (Deb, 2001). Hence, in practical applications, the Pareto frontier is approximated by a finite number of Pareto-optimal solutions (Marler & Arora, 2004). As has been discussed, the CAM(P)D problems are usually formulated as mixed-integer nonlinear problems (MINLPs) and present a significant challenge for MOO algorithm. In view of these challenges, there is a need to gain a better understanding of the the suitability of different multi-objective optimisation (MOO) algorithm for the solution of such design problems. In this chapter, we present a systematic comparison of the performance of a variety of mixed-integer non-linear programming (MINLP) multi-objective optimisation algorithms on the selection of computer-aided molecular design (CAMD) and computer-aided molecular and process design (CAMPD) problems.

Please note that this chapter is an edited version of a paper (Lee et al., 2020), previously published.

5.1 Introduction

In a nutshell, the main idea in the development of MOO algorithms is to (1) find non-dominated points that can represent the Pareto-frontier in reasonable computational time; and (2) generate these points so that they are distributed evenly along the Pareto front. The main MOO methods that have been used in molecular design include scalarisation methods (e.g. weighted-sum method, sandwich algorithm), ϵ -constraint methods, and metaheuristic methods. Papadopoulos & Linke (2006b) proposed a multi-objective molecular design technique linked with a process synthesis framework by using the weighted-sum method, extending it to the design of binary working fluid mixtures in Organic Rankine Cycles (ORC) (Papadopoulos et al., 2010a) and to the design of solvents for CO_2 capture (Papadopoulos et al., 2016, 2020). The authors adopted the simulated annealing (SA) algorithm proposed by Marcoulaki & Kokossis (2000) to explore the design space directly. Burger et al. (2015) utilised the sandwich algorithm (Bortz et al., 2014) within their MINLP solution strategy to design a solvent for a CO_2 physical absorption process, avoiding the difficulty in assigning weight vectors. The solutions generated by MOO were used as starting points for the solution of the CAMPD MINLP. In this last step, a single (economic) objective was used. Zhou et al. (2019) also introduced the sandwich algorithm to identify a list of solvent candidates in their MOO CAMD formulation, which were further optimised using rigorous thermodynamic analysis. In their CAMD problem, selectivity and capacity of the solvents were optimised simultaneously to consider their efficiency within extractive distillation process. Buxton et al. (1999) and Hugo et al. (2004) considered both process economics and environmental impact simultaneously in the formulation of a CAMPD MINLP and proposed the use of the ϵ -constraint method (Haimes et al., 1971) for its solution. The environmental impact metrics were treated as constraints in their formulation, while the economic performance was set as the objective function. Kim & Diwekar (2002) proposed a novel MOO framework based on the ϵ -constraint method to solve the integrated design of solvent recycling process and environmentally benign solvents for acetic acid removal from water. In their study, four-objective problem was transformed to SOO problems and the minimisation of the problem is solved by efficient sampling of the number of SOO problems using the Hammersley stochastic annealing algorithm. Schilling et al. (2017) solved an integrated working fluid and ORC process design problem with the ϵ -constraint method to identify the trade-off between net power output and total capital investment. The CAMPD problem was formulated as MINLP and one-stage continuous-molecular targeting (CoMT) approach was applied. Ng et al. (2014) introduced a metaheuristic method, fuzzy optimisation (Liang, 2008), in developing a MOO CAMPD approach to the design of optimal chemical products, by considering both the optimality of product properties and the accuracy of the property prediction models. Venkatasubramanian et al. (1994) employed a genetic algorithm (GA) in the design of a optimal structure of the polymer and refrigerant. They introduced a string representation of the molecular structures as an encoding strategy and used the molecular genetic operators (single-point crossover, chainmutation, insertion, deletion, and blending) to SOO MINLP problems. Dörgő & Abonyi (2016, 2019) extended the GA approaches to the design of refrigerants for ORC processes. The authors solved the MOO MINLP problems using Non-dominated sorting genetic algorithm II (NSGA-II) (Deb, 2001) to investigate trade-off between several properties of molecules. Xu & Diwekar (2007) developed a Multi-objective

efficient genetic algorithm (MOEGA) in the integrated design of solvents and solvent recycling process of acetic acid and water mixture. The authors considered up to six objectives including acetic acid recovery, process flexibility, two environmental impacts based on LC_{50} , an environmental factor based on bioconcentration factor and reboiler energy consumption.

While several MOO methods have been applied to CAM(P)D, CAM(P)D presents challenges due to the nonconvexity of the the search space that arise from the continuous functions and the presence of integer variables. The Pareto front can be discontinuous and nonconvex, so that the efficient identification of a well-distributed set of points on or near the Pareto front is non-trivial. In particular, weighted-sum approaches are highly dependent on the choice of weight vectors. An even distribution of the weights among objective functions does not always leads to an even distribution of solutions on the Pareto front (Das & Dennis, 1997). Therefore, the use of the WS is often time-consuming as a large number of SOO problems need to be solved. Although this drawback has been addressed in the SD algorithm, in which the weight vectors are selected systematically, the WS and SD approaches can only identify convex regions of the Pareto front (Marler & Arora, 2004). This is in fact a limitation of all weighted-sum based methods (Bortz et al., 2014). This limitation can be overcome with ϵ -constraint methods, but a challenge is to choose appropriate values of epsilon, ϵ that can maximise the improvement in the quality of the Pareto front at each iteration in the absence of the relationship between the approximation accuracy of the Pareto front and ϵ value. This is significant especially when the problem entails more than two objectives (Mavrotas, 2009) and the Pareto fronts consists of many disjointed parts. Moreover, the constraints added to the original problem increase the complexity of solving each SOO problem. It may be difficult to find new Pareto point at each iteration with the weighted sum and convergence to dominated solution is common, while it can be mitigated by using the ϵ -constraint method. This is apparent when single objective optimisation problems are solved repeatedly and the mixed-integer and nonconvex nature of most molecular design problems means the solver may converge to a local (dominated) solution rather than a Pareto point. In fuzzy methods and genetic algorithms a set of solutions that is close to the Pareto front may be identified, but there can be no guarantee that the points found are Pareto-optimal (Deb, 2001). The application of these methods may result in a large number of unsuccessful computations due to the highly constrained nature of such MINLPs. Despite the many challenges faced in applying MOO to MINLPs, there has been no systematic analysis to compare the performance of various algorithms for CAM(P)D applications.

In this work, we present a comparative analysis of the performance of three classes of MINLP MOO approaches, the weighted-sum (WS), the sandwich algorithm (SD) (Rennen et al., 2011), and the non-dominated sorting algorithm-II (NSGA-II) (Deb et al., 2000b). The WS method and SD are chosen over the ϵ -constraint method with particular interest in their simplicity in the formulation of the subproblem, i.e., no additional constrains are involved. The solution of each scalarised problem with WS and SD can be challenging in the presence of nonlinearities. To increase the likelihood of identifying the globally-optimal Pareto front, we introduce the simulated annealing (SA) (Marcoulaki & Kokossis, 2000) and multi-level single linkage (MLSL) (Kucherenko & Sytsko, 2005) as global search methods. We first make use of a SA version of the WS (WSSA) and a MLSL version of the WS (WSML). These two algorithms are compared with the WS to investigate the effectiveness of global search methods. Based on findings, we also put forward two variants of the algorithms: MLSL with the WS (WSML) and the SD (SDML), and the comparison between WSML, SDML and NSGA-II is undertaken. The resulting set of algorithms is applied to three case studies: the design of solvents for the chemical absorption of CO₂, the design of working fluids for ORC based on property metrics, and the integrated design of working fluids and ORCs processes. The performance of the different algorithms is compared based on reliability and efficiency criteria.

The main contributions of this work include: 1) the introduction of different global search methods to solve single objective MINLPs within MOO secularisation methods; 2) a systematic comparative study of the performance of different classes of MOO algorithms on solving several literature MOO CAM(P)D problems. In addition, several modifications of the SA, MLSL and NSGA-II approaches are introduced to adapt these algorithms to CAM(P)D problems.

5.2 Multi-objective optimisation methodologies

In this chapter, a brief of each MOO methodology and the problem formulation is provided focusing on the molecular design problems which are often posed as MINLP problems. Note that more general description of the MOO problem and the details of sandwich algorithm for general cases will be provided in Chapter 6 in which the development of a new MOO approach based on the sandwich algorithm will be discussed.

5.2.1 Problem formulation

The generic mathematical formulation of the MINLP MOO problem is:

$$\begin{split} \min_{{m{x}},{m{y}},{m{n}}} & f_1^o({m{x}},{m{y}},{m{n}}), \ f_2^o({m{x}},{m{y}},{m{n}}), \dots, f_m^o({m{x}},{m{y}},{m{n}}) \\ \text{s.t.} & {m{g}}({m{x}},{m{y}},{m{n}}) \leq {m{0}} \\ & {m{h}}({m{x}},{m{y}},{m{n}}) = {m{0}} \\ & {m{x}} \in \mathbb{R}^{n_1}, \ {m{y}} \in \{0,1\}^{n_2'}, \ {m{n}} \in {m{N}} \subset \mathbb{Z}^{n_2} \end{split}$$
 (MOP2)

where *m* is the number of objectives, *x* is a n_1 -dimensional vector of continuous variables, *y* is a n'_2 -dimensional vector of binary variables, *n* is a n_2 -dimensional vector of integer variables, g(x, y, n) is a vector of inequality constraints that define design constraints and feasibility constraints, h(x, y, n) is a vector of equality constraints

that include structure-property models, process models and chemical feasibility constraints such as the octet rule (Odele & Macchietto, 1993).

5.2.2 Scalarisation-based methods

weighted-sum method

The weighted-sum method is one of the most widely used scalarisation-based algorithms in MOO. Multiple objective functions f_i^o , $j=1,\cdots,m$ are aggregated into a single objective function using weight coefficients, represented by the normalised vector, \boldsymbol{w} . Thus, the scalar objective function is given by $\sum_{i=1}^{m} w_i f_i^o(\boldsymbol{x}, \boldsymbol{y}, \boldsymbol{n})$, where $\sum_{i=1}^{m} w_i = 1$. The WS method is easy to implement and the problem is of same degree of difficulty as the original MOO problem since there are no additional constraints involved and the feasible region remains unchanged. However, the weights have to be determined a priori and an even distribution of weights does not always yield an even distribution of Pareto solutions. The Pareto points generated are strongly dependent on the weight vectors used and a poor choice might lead to points that are clustered. Alternatively, weight vectors can be randomly generated to try and obtain a sufficient coverage of the Pareto front and to overcome these deficiencies; this is the approach taken in our study. However, the use of randomly generated of the weight vectors might also be time-consuming as a large number of such vectors may be required to achieve good coverage of the Pareto front. Before formulating the scalarised problem, each objective function is normalised (f_i) with respect to the limits of the objective space to avoid generating search directions that are biased towards specific (larger) objectives.

$$f_i(\boldsymbol{x}, \boldsymbol{y}, \boldsymbol{n}) = \frac{f_i^o(\boldsymbol{x}, \boldsymbol{y}, \boldsymbol{n}) - f_i^{\mathrm{nd}}(\boldsymbol{x}, \boldsymbol{y}, \boldsymbol{n})}{f_i^{\mathrm{id}}(\boldsymbol{x}, \boldsymbol{y}, \boldsymbol{n}) - f_i^{\mathrm{nd}}(\boldsymbol{x}, \boldsymbol{y}, \boldsymbol{n})}, \ i=1, \cdots, m$$
(5.1)

where $f_i^o(\boldsymbol{x}, \boldsymbol{y}, \boldsymbol{n})$ is the *i*-th original objective function, $f_i(\boldsymbol{x}, \boldsymbol{y}, \boldsymbol{n})$ is the *i*-th normalised objective function, and $f_i^{\text{id}}(\boldsymbol{x}, \boldsymbol{y}, \boldsymbol{n})$ and $f_i^{\text{nd}}(\boldsymbol{x}, \boldsymbol{y}, \boldsymbol{n})$ are the ideal and nadir points of *i*-th objective functions.

The mathematical formulation of the scalarised problem is as follows:

$$\begin{split} \min_{\boldsymbol{x},\boldsymbol{y},\boldsymbol{n}} \quad \boldsymbol{w}^{\top} \boldsymbol{f} &= \sum_{i=1}^{m} w_i f_i(\boldsymbol{x},\boldsymbol{y},\boldsymbol{n}) \\ \text{s.t.} \quad \boldsymbol{g}(\boldsymbol{x},\boldsymbol{y},\boldsymbol{n}) &\leq \boldsymbol{0} \\ \quad \boldsymbol{h}(\boldsymbol{x},\boldsymbol{y},\boldsymbol{n}) &= \boldsymbol{0} \\ \quad \boldsymbol{x} \in \mathbb{R}^{n_1}, \ \boldsymbol{y} \in \{0,1\}^{n_2'}, \ \boldsymbol{n} \in \boldsymbol{N} \subset \mathbb{Z}^{n_2} \end{split}$$
(5.2)

The general scheme of the weighted-sum algorithm is outlined in Algorithm 1.

Algorithm 1 weighted-sum method for CAM(P)D
1: procedure WEIGHTED-SUM ALGORITHM
2: $W = \emptyset$; iteration, $k = 1$, where W is a set of weight vectors
3: while Stopping criterion is satisfied (i.e. $k \le N_{iter}$) do
4: Generate a random vector v from uniform distribution
$\boldsymbol{v} = \{v_{i,k} \mid i=1,,m\}$
5: Calculate a weight vector $\boldsymbol{w}_{\boldsymbol{k}} = \{w_{i,k} \mid i = 1,, m\}$,
$w_{i,k} = v_{i,k} / \sum v_{i,k}$
6: if $w_k \not\subseteq W$ then
7: Solve problem (5.2)
8: end if
9: $k = k + 1, W = W \cup \boldsymbol{w}_{\boldsymbol{k}}$
10: end while
11: end procedure

Sandwich algorithm

The sandwich algorithm (Solanki et al., 1993; Rennen et al., 2011) has been proposed as a scalarisation method with the aim to approximate the (convex) Pareto front with as few optimisation runs as possible (Rennen et al., 2011). Within the algorithm, a convex hull (inner approximation, *IPS*) and outer approximation (*OPS*) of the Pareto front are constructed sequentially based on the incumbent Pareto points

until the approximation error falls below some given tolerance, $\epsilon \ge 0$. The approximation error d_{max} is defined as the maximum distance between the inner and outer approximations. In our study, we follow the approach of Rennen et al. (2011) of considering dummy points and ϵ -dominance in the calculation of the approximation error, $d_{error,p}$ where $p = 1, ..., N_F$ and N_F is the number of facets generated by the inner approximation, between the inner and outer approximations, whereby the maximum error, $d_{max} = \max_{p=1,...,N_F} d_{error,p}$, is determined by solving the following linear programming problem for each facet of IPS, F_S^p . The $d_{error,p}$ is defined as:

$$d_{error,p} = \max_{\boldsymbol{z}} \; \frac{\boldsymbol{w}_{\boldsymbol{p}}^{\top}(\boldsymbol{z}^{vertex} - \boldsymbol{z})}{\boldsymbol{w}_{\boldsymbol{p}}^{\top}\boldsymbol{\epsilon}_{\boldsymbol{d}}}, \; p = 1, ..., N_{F}$$
s.t. $\boldsymbol{z} \in OPS$
(5.3)

where w_p is a normal vector of the pth facet F_S^p , z^{vertex} is one of extreme points of the facet F_S^p and ϵ_d is a user defined vector that represents ϵ -dominance. Note that the facet which is defined by a negative normal vector, i.e., outer normal vector or only dummy points are eliminated from consideration in the calculation of the error. The weight vectors are chosen systematically from the set of normal vectors to the facets constructed by inner approximation. The basic scheme of SD algorithm is outlined in Algorithm 2. A graphical illustration of the procedure is shown in Figure 5.1. The error tolerance is selected for each case study depending on the size of the problem. The general description of SD is further detailed in Section 6.3.1.

Global phases

A challenge in applying the weighted-sum and sandwich algorithms to MOO problems is ensuring that the global solution of each scalarised problem is identified, as local solutions are dominated solutions of the MOO problem rather than Paretooptimal solutions. To increase the likelihood of finding global solutions, two global optimisation algorithms are used to solve scalarised problems at step 7 of Algo-



Figure 5.1: Schematic illustrating the procedure of the sandwich algorithm in objective space for two objectives f_1 and f_2 . The dotted blue curve represents the true Pareto front, the black circles are the Pareto points identified. The red lines represent the outer approximation and the black lines represent the inner approximation. In (a), the algorithm begins with the construction of the convex hull based on anchor points z^{A1} and z^{A2} (black diamonds) and the first Pareto point z^1 (black circle). This gives two facets, that are used to define the first outer and inner approximations. (b) The approximation error (the distance between the inner and outer approximations) is computed for each facet. The second Pareto point z^2 is obtained by solving problem (5.2) for the facet (inner approximation) that has the largest approximation error. In this case, this is the facet (z^1, z^{A1}) . The weight vector w is defined by the normal vector of this facet. (c) The third Pareto point z^3 is obtained in the same manner as described in (b) after calculating the approximation error between inner and outer approximations based on z^A , z^1 and z^2 , with largest error occurring on facet (z^{A2}, z^1) . This figure is an adaptation of Figure 1 in Lee et al. (2020).

Algorithm 2 Sandwich algorithm for CAM(P)D

1: procedure SANDWICH ALGORITHM $Z_E = \emptyset$; $d_{max} = \infty$; k = 1, where Z_E is a set of Pareto optimal solutions. 2: Find all anchor points $Z^A = \{ z^{Ai} \mid i = 1, ..., m \}.$ 3: Choose an initial weight vector, $\boldsymbol{w} = [1/m \stackrel{\times m}{\cdots}]$ and solve problem (5.2) to 4: obtain the initial outer approximation for z^1 . while $d_{max} \ge \epsilon$ do 5: Initialise a set of inner approximation, *IPS* 6: where IPS is obtained by constructing convexhull based on the set Z_E , $IPS = \text{convexhull}(\mathbf{Z}_{E}),$ $Z_E = \{z^{A1}, ..., z^{Am}, z^1, ..., z^k\}.$ Calculate the error, $d_{error,p}$, for each facet of IPS, i.e., $p = 1, ..., N_F$. 7: Select the facet, FS*, that has largest error, $d_{max} = \max_{p=1,\dots,N_F} d_{error,p}$ 8: where $p = \operatorname{argmax}(d_{error,p})$ and $FS^* = FS^p$. Select weight w to be normal to the FS* Let H(w, b) be a supporting hyper plane at FS^{*} then, $H(\boldsymbol{w}, \boldsymbol{b}) : \boldsymbol{w}^{\top} \boldsymbol{z} = \boldsymbol{b}$ Determine z^* by solving problem (5.2) with w9: if $(w^{\top}z^* = b)$ then 10: Set the error of the FS* to zero and return to Step 8 11: end if 12: Update outer approximation by adding the inequality $w^{\top} z^* > b$ 13: Update Z_E by replacing it with $Z_E = \{Z_E, z^*\}$ 14: Set k = k + 115: end while 16: 17: end procedure

rithm 1 and step 4 and 9 of Algorithm 2. Multi-Level Single Linkage (MLSL), a deterministic incomplete global optimisation method (Neumaier, 2004), and Simulated Annealing (SA) (Marcoulaki & Kokossis, 2000), a stochastic incomplete global optimisation method, are applied in our study. These are briefly described in the remainder of this section.

Multi-Level Single Linkage (MLSL)

The Multi-level Single Linkage (MLSL) method is derived from the multi-start method, which aims to find local minima by performing multiple local minimisation procedures from a set of starting points distributed in an appropriate way (e.g., sampled from a uniform distribution) over the decision space (Rinnooy Kan, 1987). A major difference between the multi-start and MLSL methods is that the local search in MLSL is invoked from a reduced set of sample points, N_r , chosen such that there is no other sample point within some critical distance, $r_{k'}$, that has a lower objective function value. The reduced set is obtained by taking $N_r = \gamma k' N_s$ points from the cumulated sample points that have the lowest function values, where $\gamma \in (0, 1)$ is a control parameter, k' is the number of iteration and N_s is a total number of sample points. Starting points that do not satisfy this conditions are clustered into one of the regions of attraction, C_l , $l=1,..., W_{min}$, where W_{min} is the number of distinct local minima that have been found up to the current iteration of the algorithm. Here, we denote the cardinality of the set C_l as $|C_l|$. The main algorithmic options for this class of approaches are the choice of an appropriate acceptance/rejection criterion for local search, of the sampling methodology and of a stopping criterion for the overall algorithm. In our study, we modify the algorithm Kucherenko & Sytsko (2005) to account for the mixed-integer nature of problem (5.2). We adopt a Sobol' sequence (Sobol' et al., 2011) to generate starting points. Sample points are generated in the space of continuous variables \tilde{y} and \tilde{n} , where \tilde{y} and \tilde{n} are obtained by relaxing the integrality of y and n, with the k-th point denoted by $(\tilde{y}^{(k)}, \tilde{n}^{(k)})$. To enable evaluation of the objective function and subsequent clustering at each sample point, it is imperative to ensure that the point is feasible. For this purpose, a pure integer problem is solved to find the closest point $(y^{(k)}, n^{(k)})$ to $(\tilde{y}^{(k)}, \tilde{n}^{(k)})$, as measured by Euclidean distance, that satisfies the integer constraints. The formulation of this problem at iteration k is given by

$$\min_{\boldsymbol{y}^{(k)},\boldsymbol{n}^{(k)}} \left\| \left(\boldsymbol{y}^{(k)}, \boldsymbol{n}^{(k)} \right) - \left(\tilde{\boldsymbol{y}}^{(k)}, \tilde{\boldsymbol{n}}^{(k)} \right) \right\|_{2} \\$$
s.t. $\boldsymbol{h}(\boldsymbol{y}^{(k)}, \boldsymbol{n}^{(k)}) = 0$

$$\boldsymbol{y} \in \{0, 1\}^{n'_{2}}, \ \boldsymbol{n} \in \boldsymbol{N} \subset \mathbb{Z}^{n_{2}}, \ n_{k,j} \in \{n_{l,j}, n_{u,i}\}, \ j = 1, ..., n_{2}$$
(5.4)

where $||\cdot||_2$ is euclidean norm and $n_{l,j}$ and $n_{u,j}$ is lower and upper bounds on each integer variable.

In CAMD problems where the degrees of freedom are fully specified once the binary and integer variables are fixed, the continuous variables at sample point $(y^{(k)}, n^{(k)})$ are obtained by solving the model equations $h(x^{(k)}, y^{(k)}, n^{(k)}) = 0$. The objective function of problem (5.2) can then be evaluated to determine whether a local (MINLP) optimisation should be run from this starting point. In CAMPD problems, there are usually the degrees of freedom for continuous variables and the generation of starting points is applied to both integer and continuous variables. Such variables can be generated using a Sobol' sequence restricted to the feasible region based on the method as described in Section 5.4.3. In our study, we focus on generating a set of starting points only for integer and binary variables, since the outer approximation (OA) algorithm (Viswanathan & Grossmann, 1990) is used as a local search method to solve Problem (5.2). Within this algorithm only integer and binary variables are specified as the starting points and the continuous variables are specified by solving Primal problems within the OA algorithm.

The stopping rule is given by $W_{exp} \leq W_{min,k}$, where W_{exp} is the number of local minima calculated based on a Bayesian stopping rule (Pál, 2013). The maximum

number of generated starting point, N_{max} , is also used as the stopping criteria and set to $N_{max} = 10 \times N_s$. The pseudo-code for the MLSL algorithm is shown as Algorithm 3.

Simulated Annealing (SA)

Simulated Annealing algorithms originate from the analogy of the heating and slow cooling of liquid metal so that crystallisation into a structure that corresponds to a minimum free energy can be achieved (Metropolis et al., 1953). Markov processes and probability theory are combined in order to move from one state to another based on transition probabilities. The essential algorithmic feature of SA is that it encourages extensive exploration of the search space by accepting "worse-performing" random moves, thereby increasing the likelihood of convergence to a global solution. The choice of algorithmic parameters is a critical aspect of any implementation of SA (Papadopoulos & Linke, 2006b; Marcoulaki & Kokossis, 2000). Relevant parameters include: the length of the Markov chain (N_{mc}) , the cooling schedule, cooling parameter (δ), stopping criterion, initial temperature (T_i), stopping temperature (T_{stop}), and the method used for the generation of perturbation moves. In our study, we employ the method described in Papadopoulos & Linke (2006b) to determine appropriate parameter settings. The Markov chain length is selected by examining the standard deviation in the value of the optimal objective. Specifically, ten SA simulations are executed with different seeds and starting points and the smallest chain length is selected by which the standard deviation is below 0.2 % is selected as the value of N_{mc} . The cooling parameters and cooling schedule are set according to Marcoulaki & Kokossis (2000) and Aarts & Laarhoven (1985), respectively. All other heuristic parameters used in the case studies are listed in Table 5.1.

The difficulty in applying the SA to CAM(P)D is in ensuring the random moves satisfy the structural feasibility constraints. Note that the random moves should not be biased, so an optimisation problem is formulated and solved to find the nearest
Algorithm 3 MLSL algorithm for CAM(P)D
1: procedure Multi-level Single Linkage
2: Initialise $C_l = \emptyset$; $k' = 1$; $W_{exp} = 0$; $W_{min} = 0$, Set N_s and γ .
3: Set list of objective functions and corresponding sample points, $L = \emptyset$.
4: while $W_{exp} \leq W_{min}$ or $k'N_s \leq N_{max}$ do
5: for $k = (k' - 1)N_s + 1$ to $k'N_s$ do
6: Generate k-th Sobol' point, $(\tilde{\boldsymbol{y}}^{(k)}, \tilde{\boldsymbol{n}}^{(k)}) \in [0, 1]^r \times [\boldsymbol{n_l}, \boldsymbol{n_u}].$
7: Solve Problem (5.4) to find $(y^{(k)}, n^{(k)})$.
8: Generate $x^{(k)}$ from $(y^{(k)}, n^{(k)})$.
9: Evaluate objective function
$f^{(k)} = \sum_{j=1}^{m} w_j f_j(m{x^{(k)}},m{y^{(k)}},m{n^{(k)}}).$
10: Add $((\boldsymbol{x^{(k)}}, \boldsymbol{y^{(k)}}, \boldsymbol{n^{(k)}}), f^{(k)})$ to L , so that L is sorted in ascending order
of objective functions.
11: end for
12: Set $N_r = \gamma k' N_s$; N_r sample points are selected from <i>L</i> .
13: for $i = 1$ to N_r do
14: if $W_{min} > 0$ and there exist <i>j</i> , <i>l</i> such that
$f(m{x^{(j)}},m{y^{(j)}},m{n^{(j)}}) \geq f(m{x^{(i)}},m{y^{(i)}},m{n^{(i)}})$ and
$\left \left (m{x^{(j)}},m{y^{(j)}},m{n^{(j)}}) - (m{x^{(i)}},m{y^{(i)}},m{n^{(i)}}) \right ight _2 < r_{k'},$
where $j \in \{1,, C_l \}$ and $l \in \{1,, W_{min}\}$ then
15: Assign the point $(x^{(i)}, y^{(i)}, n^{(i)})$ to C_l .
16: else
17: Solve Problem (5.2) starting from $(x^{(i)}, y^{(i)}, n^{(i)})$ using a local
search method.
18: if feasible and solution $(x^*, y^*, n^*) \notin C_l$ then
19: Assign (x^*, y^*, n^*) to $C_{W_{min}+1}$; $W_{min} = W_{min} + 1$.
20: end if
21: end if
22: end for
23: Set $k' = k' + 1$, Calculate W_{exp}
24: end while
25: end procedure

point $(\mathbf{y'}_k, \mathbf{n'}_k)$ to the newly generated points $(\mathbf{y}_k, \mathbf{n}_k)$, which satisfies all structurerelated constraints. The formulation of this problem at iteration k is given by

$$\min_{\boldsymbol{y'}_k, \boldsymbol{n'}_k} ||(\boldsymbol{y}_k, \boldsymbol{n}_k) - (\boldsymbol{y'}_k, \boldsymbol{n'}_k)||_2$$
s.t. $\boldsymbol{h}(\boldsymbol{y'}_k, \boldsymbol{n'}_k) = 0$
 $\boldsymbol{y'} \in \{0, 1\}^r, \ \boldsymbol{n'} \in \boldsymbol{N} \subset \mathbb{Z}^s, \ n'_{k,j} \in \{n_{l,j}, n_{u,j}\}, \ j = 1, ..., s$

$$(5.5)$$

Due to the difficulty of handling design constraints in simulated annealing, these are handled via a penalty function (Marcoulaki & Kokossis, 2000), $F_k(x_k, y'_k, n'_k; M)$. Note that the molecular feasibility constraints are not included in the penalty function F_k , since only the structurally feasible molecules are generated within the algorithm. The penalty function used to combine the objective function and the constraints is as follows:

$$F_{k}(\boldsymbol{x}_{k}, \boldsymbol{y'}_{k}, \boldsymbol{n'}_{k}; M) = \sum_{i=1}^{m} w_{i} f_{i}(\boldsymbol{x}_{k}, \boldsymbol{y'}_{k}, \boldsymbol{n'}_{k}) + M \left(\sum_{j=1}^{m_{g}} \left[\max\left(0, g_{j}(\boldsymbol{x}_{k}, \boldsymbol{y'}_{k}, \boldsymbol{n'}_{k})\right) \right] + \sum_{j=1}^{m_{h}} \left| h_{j}(\boldsymbol{x}_{k}, \boldsymbol{y'}_{k}, \boldsymbol{n'}_{k}) \right| \right)$$
(5.6)

where M is a penalty weight imposed on inequality and equality constraints, and m_g and m_h are the number of inequality and equality constraints, respectively.

The SA algorithm applied to CAM(P)D is outlined in Algorithm 4.

5.2.3 Non-dominated Sorting Genetic Algorithm-II (NSGA-II)

The NSGA-II algorithm (Deb et al., 2000b) is a particular form of genetic algorithm (GA) and is one of the most prominent methods for evolutionary-based stochastic search. The NSGA-II is directly applicable to MOO as it uses an explicit diversity-preserving mechanism based on a crowding distance metric to generate uniformly

Algorithm 4 SA algorithm for CAM(P)D

1:	procedure Simulated Annealing
2:	Initialisation $\boldsymbol{y}_0, \boldsymbol{n}_0, \boldsymbol{x}_0 \leftarrow \text{initial guesses; } T = T_i; \text{Set} M.$
3:	Calculate initial objective function value, $F_0(\boldsymbol{x}_0, \boldsymbol{y'}_0, \boldsymbol{n'}_0; M)$.
4:	while $T \leq T_{stop}$ do
5:	for $k = 1$ to N_{mc} do
6:	Generate random vector $\Delta oldsymbol{y}_k, \Delta oldsymbol{n}_k$ and corresponding move
7:	$oldsymbol{y}_k = oldsymbol{y'}_{k-1} + \Delta oldsymbol{y}_k, oldsymbol{n}_k = oldsymbol{n'}_{k-1} + \Delta oldsymbol{n}_k$ Solve Problem (5.5) to find $oldsymbol{y'}_k, oldsymbol{n'}_k$; $oldsymbol{x}_k = oldsymbol{x} \left(oldsymbol{y'}_k, oldsymbol{n'}_k ight)$
8:	$\Delta F_k = F_k(\boldsymbol{x}_k, \boldsymbol{y'}_k, \boldsymbol{n'}_k; M) - F_{k-1}(\boldsymbol{x}_{k-1}, \boldsymbol{y'}_{k-1}, \boldsymbol{n'}_{k-1}; M).$
9:	if $\Delta F_k \ge 0$ then
10:	Sample random number, $P_{r,k}$ from uniform distribution function
	and calculate probability of accepting the random move, P_{accept} ,
	where $P_{accept} = \exp(-\Delta F_k/T)$.
11:	if $P_{accept} \leq P_{r,k}$ then
12:	Discard the value of n'_k and F_k and assign the values from the
	iteration $k - 1$; $F_k = F_{k-1}$ and $x_k = x_{k-1} y'_k = y'_{k-1}$, $n'_k = n'_{k-1}$
13:	end if
14:	else
15:	Accept the next move $(\boldsymbol{x}_k, \boldsymbol{y'}_k, \boldsymbol{n'}_k)$.
16:	end if
17:	end for
18:	Set $k = k + 1$
19:	Reduce the Temperature T based on cooling schedule.
20:	end while
21:	end procedure

distributed Pareto points. Furthermore, it makes use of elite-preserving operators to give "elite genes" an opportunity to survive in the next generation. In order to adapt the NSGA-II for CAM(P)D problems, one needs to encode molecular structure in an operable and interpretable form, and to specify a suitable set of heuristic parameters. In this work, the dynamic tree structure proposed by Zhou et al. (2017) is implemented to represent molecules. The construction of the tree-like structure guarantees the generation of structurally feasible molecules and allows the application of the crossover and mutation operators over molecules to be more tractable. For CAM(P)D problems, a penalty-based (Zhou et al., 2017) fitness vector ($F_{fit,k}$) is assigned to an individual solution, $f_{i,k}$ to measure their relative merit: $F_{fit,i,k} =$ $f_{i,k}(\boldsymbol{x_k}, \boldsymbol{y_k}, \boldsymbol{n_k}) \times P_k$. The fitness function is chosen to be proportional to the magnitude of an aggregate constraint violation, P_k : $P_k = 1000 \times (\sum_{j=1}^{m_g} \max [0, g_j(\boldsymbol{x_k}, \boldsymbol{y_k}, \boldsymbol{n_k})] +$ $\sum_{i=1}^{m_h} |h_i(x_k, y_k, n_k)|$). The tournament selection technique is employed as a selection strategy to choose parents for the next generation, since it can avoid premature convergence and stagnation (Deb et al., 2000b). In tournament selection, four population members are randomly chosen to compete each other and the best one out of the pool of the members is selected to be a parent. All other parameters used in the case studies are specified in Table 5.1.

5.2.4 Algorithmic combinations

The combination of global phase and MOO methods results in four scalarisation algorithms: weighted-sum with multi-level single linkage (WSML), weighted-sum with simulated annealing (WSSA), sandwich algorithm with multi-level single linkage (SDML), sandwich algorithm with simulated annealing (SDSA). This set of four combinations is augmented with the weighted-sum without global phase (SWS) and non-dominating sorting genetic algorithm II (NSGA-II), which is not based on scalarisation. These approaches are summarised in Table 5.2. Convergence to the global

Method	Parameter	CS1	CS2	CS3
	Number of Sobol' points, N_s	128	256	128
MLSL	Fraction to define reduced set, γ	0.25	0.25	0.5
	Control parameter, σ	3	3	2
	Initial temperature, T_i	10^{5}	10^{5}	10^{5}
S٨	Final temperature, T_{stop}	10^{-3}	10^{-3}	10^{-3}
SA	Markov chain length, N_{mc}	70	120	80
	Cooling parameter, δ	0.8	0.5	0.2
SD	Error tolerance, ϵ	9.5×10^{-3}	1.5×10^{-2}	5.0×10^{-4}
	Crossover fraction	0.2	0.2	0.2
NCCA II	Mutation fraction	0.8	0.8	0.8
NSGA-II	Elite gene preservation Fraction	0.05	0.1	0.05
	Population size	100	150	50

Table 5.1: Algorithmic parameters used in the case studies, where CS denotes case study

Table 5.2: Algorithmic used in this work

Algorithm nar	ne Pseudo code
SWS	Algorithm 1 + local MINLP solver for Step 7
WSML	Algorithm $1 + $ Algorithm 3 for Step 7
WSSA	Algorithm 1 + Algorithm 4 for Step 7
SDML	Algorithm $2 + $ Algorithm 3 for Step 9
NSGA-II	-

optimal solution of the single objective optimisation problem, Problem MOP2, is especially critical in the sandwich algorithm since the algorithm uses the incumbent solution set to generate the convex hulls and weight vectors. On the basis of this observation, the comparison of the performance of the algorithms is divided into two stages: a comparative study of the performance of two global search methods with the weighted-sum approach is first carried out; in the second stage, only the global search method that gives better performance is used in further comparisons. The methods compared in the first stage include the SWS, WSML, and WSSA. As will be shown, MLSL gives the best performance for this investigation so that WSML, SDML and NSGA-II are compared in the second stage.

5.3 Quality measures for multi-objective optimisation

Since no single metric can represent the performance of the algorithms, a series of appropriate metrics is used to assess performance in the specific domain of molecular design. In particular, in developing the metrics, we take into account the fact that some of the case studies involve only discrete decision variables, in which case a full enumeration of the solution is possible and provides further insights. Other case studies include both discrete and continuous variables and such an enumeration is not possible. Thus, we define the following two quantities:

- 1. The exact number of Pareto points (N_{true}): For some CAMD problems, the exact set of Pareto points, P_T , can be obtained by complete enumeration of all possible combinations of the functional groups. This set contains N_{true} Pareto points, i.e. $N_{true} = |P_T|$ where |A| denotes the cardinality of set A.
- 2. The number of best-known Pareto points (N_{BP}) : For some CAMD and CAMPD problems, the best-known Pareto front, P_{BP} , contains a set of non-dominated points (i.e. $N_{BP} = |P_{BP}|$) obtained by evaluating dominance across all points generated from several runs for a given problem. It is an approximation of the true Pareto front, which may contain some points that are not Pareto-optimal and/or may be missing Pareto points.

The following quantitative metrics are used to measure the quality of the solution set obtained following a MOO run:

- 1. The number of unique non-dominated solutions (N_{unq}): The set P_U contains all the unique non-dominated solutions obtained in a given run with $N_{unq} = |P_U|$. This number captures the diversity of the solution set.
- 2. The number of non-dominated points (N_{PF}): The set P_{PF} contains the N_{PF} non-dominated points generated in a given run that lie on the true Pareto front

(or the best-known Pareto front), i.e. $P_{PF} = P_U \cap P_T$ (or $P_{PF} = P_U \cap P_{BP}$). N_{PF} is a measure of the extent of convergence to the Pareto front.

- 3. The number of supporting non-dominated points (N_{SPF}) : The P_{SPF} contains the non-dominated points that have been identified during a SOO in which the weight vector supports the Pareto front, i.e. $P_{SPF} \subseteq P_{PF}$. Specifically, if a point is in P_{SPF} , this indicates that the point was identified following termination of the SOO algorithm at a global solution rather than at a local solution. If a point in P_{PF} is not in P_{SPF} , this point was identified following convergence of the SOO algorithm to a local solution, indicating a fortunate outcome to what is essentially a failure of the global SOO solver.
- 4. Hypervolume (HV): The hypervolume (Zitzler et al., 2003) of a set P_{PF} of non-dominated solutions is the volume of the *m*-dimensional region in the objective space enclosed by the non-dominated solutions obtained and a reference point, f_{ref,i}: f_{ref,i}=1, i=1, ..., p. The larger HV, the better P_{PF} in terms of convergence to the true Pareto front and/or in terms of diversity of the solutions.
- 5. CPU time: Fast convergence to the Pareto frontier is a critical aspect for computationally expensive MOO problems. Both the average CPU time to generate a true (or best known) solution ($t_{cpu,a}$) and the total CPU time to generate all solutions ($t_{cpu,t}$) are reported.

5.4 Case Studies

The optimisation methodologies presented are applied to three case studies to assess their performance and to examine the applicability of each method. The case studies are selected so that different levels of complexity are explored in terms of problem size and the numerical difficulty.

5.4.1 Case study 1: Solvent design for chemical absorption of carbon dioxide (CAMD)

A CAMD application focused on the design of solvents for the chemical absorption of CO_2 is chosen as a first example. The formulation is based on the first of the recent approach of Papadopoulos et al. (2016) who considered an extensive list of property criteria for the design of solvents for the CO₂ capture. Four of the solvent properties are selected as objective functions in this case study, namely, liquid density (ρ), heat capacity (C_p), saturated vapour pressure (P_{vap}), and relative energy difference (RED). With four objectives and only discrete decision variables, this case study provides an opportunity to enumerate the entire search and gain insights into some of the key features of CAMD MOO problems. Several other performance criteria are considered as constraints: a) the normal melting point (T_m) , to ensure that the solvent is in the liquid phase at the lowest process operating temperature, b) the normal boiling point (T_b) to avoid excessive evaporation at absorber operating conditions, c) the viscosity (μ) to ensure ease of transport and d) the surface tension (σ), to promote mass transfer performance. The property targets and performance criteria are summarised in Table 5.3. Note that several authors include other properties, such as reactivity (Papadopoulos et al., 2016) and synthesisability(Zhang et al., 2015) in their final design. Here, we focus on the first subproblem in the methodology of Papadopoulos et al. (2016) as it provides a useful test for MOO algorithms. The SAFT- γ Mie group contribution equation of state Papaioannou et al. (2014) is used to predict ρ , C_p , P_{vap} , and T_b . The property prediction method of Hukkerikar et al. (2012b) is used for T_m , Hsu et al. (2002) is used to predict σ , RED and μ . A set of 13 functional groups (N = 13), occurring n_i (i=1,...,N) times in the molecule including 8 amine groups is selected as building blocks based on the applicability of the property prediction methods. The set is shown in Table 5.4 and includes eight amine groups. The total number of functional groups in the molecule and the to
 Table 5.3: Property constraints for CS1

 Table 5.4:
 Solvent design space for CS1

Physical properties, $g(n)$	Bounds	Functional groups	Bounds
ρ (g/cm ³) at 25°C and 1 atm	[0.6,1.5]	CH ₂ N ,CH ₃ N,	
RED	$[10^{-5}, 6.5]$	CHNH, CH_2NH	
T_b (K) at 1 atm	[393, 550]	CH_3NH , CNH_2 ,	$n_{tot} = 13$
T_m (K) at 1 atm	[273,313]	$CHNH_2$, CH_2NH_2 ,	$n_{tot,A} = 5$
σ (dyn/cm) at 25°C	[25, 60]	CH_3 , CH_2 ,	
μ (cP) at 40°C	$[10^{-5},\!60]$	CH, C, and OH	

tal number of groups with amine functionality are constrained by bounds n_{tot} and $n_{tot,A}$, respectively. The set of amine group is given by $G_A = \{CH_2N, CH_3N, CHNH, CH_2NH, CH_3NH, CNH_2, CH_2NH_2\}$. In this case study, only acyclic molecules are considered. The resulting mathematical formulation is as follows:

$$\min_{n} C_{p}, P_{vap}, RED$$

$$\max_{n} \rho$$
s.t. $g(n) \leq 0$

$$\sum_{i=1}^{N} (2 - v_{i})n_{i} - 2 = 0,$$

$$\sum_{i \in G_{A}} n_{j} - n_{tot,A} \leq 0,$$

$$\sum_{i=1}^{N} n_{i} - n_{tot} \leq 0$$

$$n_{i} \in \{n_{l,i}, n_{u,i}\}, i = 1, ..., n_{2}$$
(5.7)

where g(n) is a vector of inequality constraints on the physical properties (cf. Table 5.3, and v_i is the valence of group *i*.

5.4.2 Case study 2: Working fluid design for ORC (CAMD)

In the second case study, we consider the design a working fluid for an ORC following the CAMD formulation of Papadopoulos et al. (2010a) and Palma-Flores et al. (2015). The Pareto front generated by solving such a problem is useful in iden**Table 5.5:** Property constraints for case study 2, ($T_{max,op}$ = 353.15K, $T_{min,op}$ = 308.15K, T_{op} = 330K, T_b is normal boiling point of a working fluid)

Physical property	Bounds	Reference
$\overline{\rho_L}$ (g/cm ³) at T_{op} and 1 atm	[0.2, 1.86]	Poling et al. (2001)
H_V (kJ/mol) at T_b	[0.2, 2.5]	Constantinou & Gani (1994)
λ_L (W/m-K) at T_{op}	[0.06, 1]	Sastri & Rao (1999)
$Cp_{,L}$ (J/mol K) at T_{op}	[110, 500]	Sahinidis & Tawarmalani (2000)
μ (cP) at 30°C and 1 atm	$[10^{-5}, 10]$	Hsu et al. (2002)
T_m (K) at 1 atm	[273 , <i>T</i> _{min,op}]	Constantinou & Gani (1994)
T_c (K)	$[T_{max,op}, 313]$	Joback & Reid (1987)

Table 5.6: Solvent design space for CS2

Functional groups	Bounds
CH_3 , CH_2 , CH_2 = CH , CH = CH ,	
CH_3O , CH_2O , FCH_2O , CF_3 , CF_2 ,	~ — 6
CH ₂ NH ₂ , CHNH ₂ , CH ₃ NH, CH ₂ NH, CH ₃ N,	$n_{tot} = 0$
CH_3COO , CH_2COO , COO , $COOH$,	$n_{tot,E} = 2$
$\rm CH_3CO,\rm CH_2CO,\rm CHO,\rm HCOO$, and OH	

tifying high-performance ORC fluids as part of a two-stage CAMPD methodology (Papadopoulos et al., 2010a). The purpose of this case study is to investigate the performance of each algorithm for a higher problem dimension. The objective functions for working fluid design are expressed as five thermodynamic properties: liquid density (ρ_L), which is indicative of the size of process equipment and should be maximised, latent heat of vaporisation (H_V), which is a measure of how much heat can be added to the ORC system, thermal conductivity (λ_L), for which a higher value is desirable to obtain a larger heat transfer coefficient in the heat exchangers, liquid heat capacity ($Cp_{,L}$), and viscosity (μ) to increase the heat transfer coefficient and achieve reduced energy consumption.

In addition to the properties aforementioned, the melting temperature (T_m) and critical temperature (T_c) are also considered as property constraints in order to make sure that the working fluid is in the two-phase region across the range of operating conditions of the ORC. The predictive thermodynamic models used for each property and the relevant bounds are listed in Table 5.5. The molecular design space is generated from 24 functional groups, including hydrocarbon, ether, fluoro, amine, formate, aldehyde, and hydroxyl groups (Table 5.6). The design space of possible working fluids consists of compounds generated by linear combination of functional groups containing up to 6 functional groups. The resulting optimisation problem is as follows:

$$\begin{split} \max_{\boldsymbol{n}} & \rho_{L}, \ H_{V}, \ \lambda_{L} \\ \min_{\boldsymbol{n}} & C_{p,L}, \ \mu \\ \text{s.t.} & T_{m}(\boldsymbol{n}) \leq T_{min,op}, \ T_{max,op} \leq T_{c}(\boldsymbol{n}) \\ & \sum_{i=1}^{N} (2 - v_{i})n_{i} - 2 = 0, \\ & \sum_{i \in G_{E}} n_{j} - n_{tot,E} \leq 0, \\ & \sum_{i \in I}^{N} n_{i} - n_{tot} \leq 0 \\ & n_{i} \in \{n_{l,i}, n_{u,i}\}, \ i = 1, ..., n_{2} \end{split}$$
(5.8)

where $T_{min,op}$, $T_{max,op}$ are the minimum and maximum operating temperature of the ORC system, respectively, n_{tot} is the maximum allowable number of groups in a molecule, $n_{tot,E}$ is the maximum allowable number of end groups to ensure the molecule is a linear combination of the functional groups and $G_E = \{CH_3, CH_2 = CH, CH_3O, FCH_2O, CF_3, CH_2NH_2, CH_3NH, CH_3COO, COOH, CH_3O, CH_3O, CHO, HCOO,$ $OH \}. Note that once a molecular structure has been specified, all continuous vari$ ables are fully determined.

5.4.3 Case study 3: Integrated working fluid and ORC process design (CAMPD)

In this case study, we consider the integrated design of working fluid and ORC process. The aim of the optimisation is to determine the optimal molecular structure of the working fluid as well as the process operating conditions that maximise the net power output (P_{net}) extracted from the ORC and to minimise the total cost of investment (TCI), for a specified heat source and heat sink (Schilling et al., 2017). The ORC system is defined as a single-stage, sub-critical, non-recuperated cycle and comprises a turbine, a condenser, a pump, and an evaporator. A schematic of this process configuration is shown in Figure 5.2. As a basis for the selection of the working fluid, the following nine function groups are selected: CH_3 , CH_2 , CH_2 =, CH=, eO (end group oxygen), cO (central oxygen), and OH. eO represents an oxygen atom connected to one CH₃ and one CH₂ group, and cO describes an oxygen atom bonded to two CH₂ groups. Alongside the functional groups, four ORC process variables (m_{WF} : mass flow of working fluid, $P_{in,pump}$, $P_{out,pump}$: pump inlet, outlet pressure, $\Delta T_{superheat}$: extent of superheating) can also be optimised. The optimisation variables and their upper and lower bounds are listed in Table 5.7. In solving the CAM(P)D problem, the feasible range of process variables is found to vary depending on the molecule used in the process; thus it becomes challenging to provide reasonable starting points and bounds for the process variables, especially as many of the relevant bounds are typically expressed as implicit constraints (e.g., a two-phase system is expected in the evaporator and condenser) (Gopinath et al., 2016). As a result, these assumptions are readily violated when a new ORC fluid is selected and this usually leads to numerical failure in the calculation of phase behaviour. To avoid these failures, Bowskill et al. (2020) extended the modified outer-approximation algorithm of Gopinath et al. (2016) and introduced feasibility tests to recognise the feasible domain for a specific choice of molecule. Here, we

Table 5.7: Property constraints, g(x, n) for CS3. The bounds of pump inlet and outlet pressure (P_{min} , P_{max}) are determined by feasibility tests.

Physical properties, $g(x,n)$	Bounds
Mass flowrate of working fluid, m_{WF} (kg/s)	[0, 1000]
Extent of superheating, $\Delta T_{superheat}$ (K)	[0, 500]
Pump inlet pressure, $P_{in,pump}$ (Pa)	$[P_{min}, P_{max}]$
Pump outlet pressure, $P_{out,pump}$ (Pa)	$[P_{in,pump},P_{max}]$
Minimum approach temperature, ΔT_{min} (K)	$[10, 10^5]$

adopt the same optimisation framework and modelling assumptions. For a detailed description of the optimisation strategy and assumptions used, see Bowskill et al. (2020) and case study 2 (Table 1) therein. The generic formulation of case study 3 is as follows:

$$\min_{\boldsymbol{x},\boldsymbol{n}} P_{net},$$

$$\max_{\boldsymbol{x},\boldsymbol{n}} TCI$$

$$\text{s.t. } \boldsymbol{g}(\boldsymbol{x},\boldsymbol{n}) \leq 0,$$

$$\boldsymbol{h}(\boldsymbol{x},\boldsymbol{n}) = 0,$$

$$(5.9)$$



Figure 5.2: Schematic of the organic Rankine cycle used in Case Study 3

where g(x, n) is a vector of inequality constraints (see Table 5.7), h(x, n) is a vector of equality constraints. The detailed equations for g and h are described in the supplementary information of (Bowskill et al., 2020)

Remarks on the application of SA and NSGA-II to case study 3

For the application of the SA and NSGA-II algorithm to the solution of a single objective CAMPD problem, both integer variables and continuous variables need to be sampled. However, the feasible domain is not defined unless the molecular structure is selected. Here, we combine NSGA-II, to optimise integer (molecular) variables, with a gradient-based deterministic algorithm, to optimise the continuous nonlinear variables at the given molecular structure proposed by NSGA-II. For the application of SA, we divide the generation of random moves of SA approach in two parts: (1) the generation of a new molecule that can pass the feasibility tests of Bowskill et al. (2020); (2) the generation of continuous variables based on the feasible region derived for the new molecule.

5.5 Results and Discussion

In this section, we compare the relative performance of all algorithms. Table 5.8 summarise the comparison of the problem size for the model defined in each case study. Note that the feasibility tests are not considered in the problem size of case study 3. All MOO methods are implemented with common subfunctions using the same programming language in Matlab 2018a and all runs are performed on single Intel(R) Xeon(R) Gold 5122 CPU @ 3.60GHz processor with 384 GB of RAM. For the local solution of MINLPs, the single-objective optimisation problem is solved using an in-house implementation of the outer approximation algorithm with augmented penalty (Viswanathan & Grossmann, 1990) that interfaces with gPROMS Model-Builder 5.1.1 (process model and NLP solver) and Gurobi 8.1 MILP solver to solve

	CS1	CS2	CS3
Number of objectives	4	5	2
Number of total model variables	98	105	275
Number of discrete variables	13	24	9
Number of continuous design variables	85	81	266
Number of constraints	93	96	282

Table 5.8: Problem size of the model for each case study, where CS denotes case study

Table 5.9: Enumeration of all solutions for all possible combinations of functional groups in each case study. $N_{structure}$: the number of molecules that satisfy structural feasibility, $N_{feasible}$: the number of molecules that satisfy all constraints, N_{true} : the number of exact Pareto Points, N_{BP} : the number of best-known Pareto Points, HV: hypervolume, $t_{cpu,t}$: total CPU time to enumerate the space in seconds. The value in (.) of N_{true} of case study 3 is the number of different molecular structures within true points.

	Case Study 1	Case Study 2	Case Study 3
N _{structure}	284,964	5,196,075	3,175
$N_{feasible}$	6,200	905,168	267
N_{true}	283	2,748	-
N_{BP}	-	-	203 (12)
HV	0.4054	0.1435	0.9160
$t_{cpu,t}$ (s)	$3.18{ imes}10^4$	$1.03 { imes} 10^{6}$	$1.06{ imes}10^4$

the primal and master problems iteratively. The SAFT- γ Mie calculations are carried out using gSAFT via a Foreign Object interface. We carry out two types of runs: fixed number of iterations and fixed CPU time. For the scalarisation-based methods (WS and SD), the number of iterations is defined as the number of weight vectors that are explored. For NSGA-II, the number of iterations is defined as the number of generations. Where a limit is imposed on CPU time, this is selected based on the time taken for SDML to reach a pre-defined error tolerance for each case study.

5.5.1 True Pareto fronts

For all case studies, the true Pareto front is generated using exhaustive enumeration of a finite set of molecular structures in order to provide a benchmark for the quality of the solutions produced by each algorithm. For case study 3, it is impossible to construct a complete set of Pareto points as there is an infinite number of solutions



Figure 5.3: Parallel coordinate plots of the set of true Pareto points on the (a) fourobjective space of case study 1; and (b) five-objective space of case study 2, obtained by the enumeration of all possible combinations of molecules



Figure 5.4: Best-Known Pareto front (blue marker, \times) and feasible points (gray marker, \circ) of the normalised net power output, $-P_{net}$ (f_1) versus the normalised total capital investment, TCI (f_2) resulting from the enumeration of all possible working fluids in case study 3

due to the presence of continuous variables. As an alternative, 23 NLP optimisations corresponding to different weight vectors are conducted for each of the 267 feasible working fluids, resulting in 6141 NLPs. The resulting set of the solution is combined with the solutions obtained with each method across all runs during all computational studies carried out in Section 5.5.2 and 5.5.3 with the different algorithms. The results of these extensive calculations can be used as a reasonable approximation of the true Pareto front for graphical comparison. Information on the true/best-known Pareto frontier obtained for each case study is shown in Table 5.9. A graphical representation of the Pareto points in the domain of the objective function is given in Figures 5.3 and 5.4. Within the 66 Pareto points identified in Case Study 3, there are only 7 distinct molecular structures, but a range of values of the continuous variables.

5.5.2 Comparisons between global search methods

We begin by comparing the effectiveness of MLSL and SA in identifying global solutions using the same scalarisation method (WS). To compare SWS, WSML, and WSSA, an identical set of randomly generated weight vectors is used for all algorithms. We note that in all cases the number of iterations used falls far below the number of true or best known Pareto points. Thus these runs can only provide a partial view of the Pareto front and we therefore assess the efficiency with which Pareto points are generated. As can be seen in Table 5.10, 5.11 and Figure 5.5, WSSA can generate more diverse solutions (larger N_{una}) for case studies 1 and 2 compared to MLSL. However, only 55-65% of solutions produced by SA are found to be true Pareto optimal points, and the solutions identified as true Pareto optimal are not necessarily supported by the corresponding weight vector, and are thus obtained as a fortuitous result of the convergence of the SA algorithm to a local solution. For example, 38 of the solutions that are identified by WSSA as true Pareto points in case study 1 are sub-optimal solutions; hence, only four solutions lie on the convex Pareto fronts. Therefore, an algorithm with SA might mislead a priori articulation of preferences (weight vectors) of a decision-maker, since some solutions solved from specified weight vectors are correspond to different weight vectors as a results of premature convergence to the Pareto front. This trend becomes more evident in case study 3. As shown in Figure 5.6, many of the points identified by WSSA are not on the true Pareto front, and are therefore dominated by other solutions, resulting in the lowest value of N_{PF} for this case study. In addition, a comparison of the average CPU times in Table 5.12 and Table 5.13 for WSML and WSSA shows that the lowest value is obtained systematically with WSML, indicating that the use of MLSL for SOO is more efficient. Furthermore, in all cases, we find that for WSML, $N_{PF}=N_{SPF}$, indicating that the MLSL algorithm always converges to the global (or best-known) solution of Problem (5.2).

For the problems considered here, the SWS algorithm performs nearly as well as WSML. While the number of non-dominated solutions found is similar for both approaches, some of the points identified by SWS are local solutions ($N_{SPF} \leq N_{PF}$). However, the fact that similar values of HV are obtained for SWS and WSML indicates that these local solutions are close to the Pareto front. This is also evident from Figures 5.5 and 5.6. The greater confidence in the quality of the solutions afforded by WSML comes at a computational cost, as is always the case when global optimisation is used.

Overall, since MLSL is found to show much better performance than WSSA in the experiments across all case studies, only MLSL is be used as the global search method with WS and SD in the subsequent simulations.

Table 5.10: Performance metrics for case study 2 and 3 using a fixed number of iterations and the weighted-sum approach with three SOO approaches (SWS, MLSL and SA)

	Case Study 1			Case Study 2		
	SWS	WSML	WSSA	SWS	WSML	WSSA
N_{iter}	100	100	100	150	150	150
N_{unq}	14	12	58	30	35	69
N_{PF}	14	12	38	28	35	40
N_{SPF}	12	12	4	20	26	23
HV	0.3584	0.3592	0.3865	0.0745	0.1081	0.1003
$t_{cpu,a}$ (s)	1.41	20.26	800.07	2.74	16.68	304.11
$t_{cpu,t}$ (s)	$1.98{ imes}10^1$	$2.47{ imes}10^2$	$3.04{ imes}10^4$	$7.67{ imes}10^1$	$5.84{ imes}10^2$	$1.22{ imes}10^4$

Table 5.11: Performance metrics for case study 3 a fixed number of iterations and the weighted-sum approach with three SOO approaches (SWS, MLSL and SA)

	Case Study 3				
	SWS	WSML	WSSA		
N_{iter}	100	100	100		
N_{unq}	98	100	100		
N_{PF}	83	95	7		
N_{SPF}	52	95	1		
HV	0.9084	0.9103	0.8872		
$t_{cpu,a}$ (s)	1.76	88.93	4268.89		
$t_{cpu,t}$ (s)	$1.50{ imes}10^2$	$7.38{ imes}10^3$	$3.24{ imes}10^4$		



Figure 5.5: Parallel coordinate plots of true Pareto fronts (P_{PF}) generated by SWS (— —), WSML (—A—), and WSSA (——) for (a) case study 1 and (b) case study 2, and true Pareto fronts (P_T) (---). The unique Pareto fronts (P_U) that do not intersect the P_{PF} , i.e. $P_U - (P_{PF} \cap P_U)$, are described as dash-dotted lines $(- \cdot - \cdot -)$ and empty makers in each plot.



Figure 5.6: Best-known Pareto fronts (P_{BP}) for case study 3 generated by (a) SWS (•), (b) WSML (\blacktriangle), and (c) WSSA (\blacklozenge). Gray markers (*) indicate best-known Pareto points (P_B) obtained by full enumeration. The empty markers in each case study indicate the unique Pareto fronts (P_U) that do not intersect the best-known Pareto fronts, i.e., $P_U - (P_U \cap P_{BF})$.

5.5.3 Comparison between MOO methods

Having selected the MLSL algorithm to solve single objective optimisation problems to global optimality, we now focus on comparing the performance of weighted-sum (MLSL), the sandwich algorithm (SDML) and the NSGA-II algorithm. The results of the three case studies with these algorithms for a fixed number of iterations are summarised in Table 5.12, 5.13, Figure 5.7 and Figure 5.8. The results for a fixed CPU time are reported in Table 5.14, 5.15, Figure 5.9 and Figure 5.10.

In case studies 1 and 2, each point in the feasible region corresponds to a distinct molecular structure. As a result, the Pareto set and set of dominated solutions are entirely disjoint in terms of the molecular structures they represent. In case study 3, it is possible for some molecular structures to appear both on the Pareto front and in the set of dominated solutions, as these may differ in terms of the continuous variables alone. However, in our experience, the dominated solutions generated by the NSGA-II algorithm correspond to different molecules from those on the "true" Pareto front. The set of optimal solutions (P_T , P_U , P_{PF}) is given in full in the Supporting Information (See the data statement).

Focusing first on the fixed number of iterations, we consider the values of HV and N_{PF} obtained with each approach and shown in Table 5.12 and Table 5.13. The highest values of HV and N_{PF} for all cases are obtained when using SDML. These HVs (0.3917 for case study 1, 0.1186 for case study 2, and 0.9138 for case study 3) are the closest value to the HVs of the true Pareto fronts (0.4054 for case study 1, 0.1435 for case study 2, and 0.9160 for case study 3, see Table 5.9). From visual inspection of Figure 5.7 and 5.8, it can be observed that SDML performs best in generating a diverse set of solutions close to the true Pareto front.

The performance of WSML is similar to that of SDML in terms of HV, but fewer points are identified in the Pareto front, indicating a less diverse set of solutions. The similar trends can be seen for the case of fixed CPU time. The highest HV and N_{PF}

	Case Study 1			Case Study 2		
	WSML	SDML	NSGA-II	WSML	SDML	NSGA-II
N_{iter}	100	100	100	150	150	150
N_{ung}	12	40	24	35	83	11
N_{PF}	12	40	6	35	83	5
HV	0.3529	0.3917	0.2558	0.1081	0.1186	0.0353
$t_{cpu,a}$ (s)	20.60	8.83	43.98	37.49	7.58	546.45
$t_{cpu,t}$ (s)	2.47×10^{2}	$3.53{ imes}10^2$	2.64×10^{2}	$5.84{ imes}10^{1}$	6.29×10^{2}	1.64×10^{3}

Table 5.12: Performance metrics for case study 1 and 2 using WSML, SDML and NSGA-II for a fixed number of iterations

Table 5.13: Performance metrics for case study 3 using WSML, SDML and NSGA-II for a fixed number of iterations

	Case Study 3				
	WSML	SDML	NSGA-II		
N _{iter}	40	40	40		
N_{ung}	40	40	37		
N_{PF}	39	40	3		
HV	0.8617	0.9138	0.8261		
$t_{cpu,a}$ (s)	50.47	55.32	325.03		
$t_{cpu,t}$ (s)	$1.97{ imes}10^{3}$	$2.31{ imes}10^{3}$	9.75×10^{2}		

Table 5.14: Performance metrics for case study 1 and 2 using WSML, SDML and NSGA-II for a fixed CPU time

	Case Study 1			Case Study 2		
	WSML	SDML	NSGA-II	WSML	SDML	NSGA-II
$t_{cpu,t}$ (s)	380	380	380	1000	1000	1000
N_{iter}	150	177	140	266	225	128
N_{unq}	13	46	28	51	108	22
N_{PF}	13	46	6	51	108	12
HV	0.3673	0.3928	0.3232	0.1121	0.1239	0.0798

Table 5.15: Performance metrics for case study 3 using WSML, SDML and NSGA-II for a fixed CPU time

	Case Study 3				
	WSML	SDML	NSGA-II		
$t_{cpu,t}$ (s)	1800	1800	1800		
$\dot{N_{iter}}$	35	31	135		
N_{ung}	35	31	38		
N_{PF}	34	31	2		
HV	0.9038	0.9132	0.8888		

values for case study 1 and 2 are achieved with SDML for a given time as described in Table 5.14, showing 6 - 55 % higher values of the hypervolume and 2.1 - 7.7 times higher values of N_{PF} , respectively. Although the highest N_{PF} can be obtained by WSML in the case study 3, the highest HV and similar N_{PF} are achieved with SDML as can be seen in Table 5.15. This is because the direction of the weight vector in the SDML approach is updated deterministically in a sequence of iterations that increase the likelihood of finding Pareto points that are evenly distributed. The results confirm that diverse molecular structures and properties are found in the Pareto-optimal set generated by SDML.

In contrast, only a small number of chemical structures is identified with WSML in case study 1 and case study 2. This indicates that randomly generated weight vectors do not always lead to different solutions. One may wonder why some of the solutions generated by SDML are non-unique for the pure-integer problem (i.e. case study 1 and 2). This is mainly due to the fact that the mapping of the weights onto objective space assumes that the feasible region is convex. As a result, the assigned weights may converge to one of the Pareto points previously identified if there are no supported solutions in the integer domain.

In Table 5.12 - 5.15, it appears that the NSGA-II exhibits a lower HV than other methods although a larger number of unique points (N_{unq}) are generated for both stopping criteria. This suggests that the reliability of the Pareto front generated is not satisfactory when using NSGA-II with the parameters in Table 5.1. It can be observed that the use of the mutation and crossover operators make it challenging for the algorithm to generate feasible offspring when constraints are involved. Accordingly, this forces premature convergence to a sub-optimal front. This issue is likely to be especially acute in molecular design problems where many combinations of the integer variables are infeasible.



Figure 5.7: Parallel coordinate plots of the exact true Pareto front (P_T) (----) and true Pareto fronts (P_{BF}) generated by WSML (_____), SDML (_____), and NSGA-II (_____) for (a) case study 1 and (b) case study 2 for a fixed number of iterations. The unique Pareto fronts (P_U) that do not intersect the P_{PF} , i.e. $P_U - (P_{PF} \cap P_U)$, are described as dash-dotted lines $(- \cdot - \cdot -)$ and empty makers in each plot.



Figure 5.8: Best-known Pareto fronts (P_{BP}) generated by WSML (\blacktriangle), SDML (\blacklozenge), and NSGA-II (\bullet) for case study 3 for a fixed number of iterations. The empty markers in each case study indicate the unique Pareto fronts (P_U) that do not intersect the best-known Pareto fronts, i.e. $P_U - (P_U \cap P_{BF})$



Figure 5.9: Parallel coordinate plots of the exact true Pareto front (P_T) (----) and true Pareto fronts (P_{BF}) generated by WSML (----), SDML (----), and NSGA-II (----) for (a) case study 1 and (b) case study 2 for a fixed CPU time. The unique Pareto fronts (P_U) that do not intersect the P_{PF} , i.e. $P_U - (P_{PF} \cap P_U)$, are described as dash-dotted lines $(- \cdot - \cdot -)$ and empty makers in each plot.



Figure 5.10: Best-known Pareto fronts (P_{BP}) generated by WSML (\blacktriangle), SDML (\diamondsuit), and NSGA-II (\bullet) for case study 3 for a fixed CPU time. The empty markers in each case study indicate the unique Pareto fronts (P_U) that are not mutual to the best-known Pareto fronts, i.e. $P_U - (P_U \cap P_{BF})$

5.6 Conclusions

In this chapter, we have compared several MOO algorithms by assessing their performance on molecular design applications. The algorithms include two types of scalarisation-based methods and one evolutionary algorithm. In order to avoid premature convergence to a suboptimal front, two global search algorithms were combined with one of the scalarisation methods (weighted-sum) and tested for reliability and efficiency. Two CAMD case studies and one CAMPD case study, each with a different size of design space and numerical complexity, were employed to evaluate the performance of the algorithms.

For the global search phase, comparative results highlighted the robustness of the MLSL algorithm in terms of computational efficiency and success in reaching a global solution. Furthermore, the findings from the case studies have provided clear evidence of the effectiveness of the SDML to solve CAM(P)D problems, relative to WSML and NSGA-II. SDML can be used to generate well-distributed Pareto fronts in comparatively few solves, requiring low computational effort. Although stochastic approaches have been successfully implemented in many practical problems, SA and NSGA-II have been found to encounter difficulties in converging to the Pareto optimal front for the case studies investigated. This is mainly attributed to the fact that the gene operators in NSGA-II and the random moves in SA cannot guarantee the generation of molecules that satisfy property constraints. Based on the results of this work, SDML offers a very promising route to solve CAMD and CAMPD problems formulated as MOO and its performance should be investigated on additional case studies. The Pareto-solutions generated by SDML lie on convex portions of the Pareto front. Further work could be directed at testing the MOO algorithms on more case studies to derive general conclusions of their performance on the CAM(P)D problems. It is useful to investigate different types of scalarised subproblems e.g., hyper-boxing algorithm suggested by Bortz et al. (2014) and normal boundary section method suggested by Das & Dennis (1998) by which the weighted-sum subproblem of SDML is replaced, making it possible to explore nonconvex regions of the Pareto front.

CHAPTER 6

The SDNBI Algorithm: A deterministic optimisation approach for nonconvex and combinatorial bi-objective programming

In Chapter 5, the performance of MOO techniques commonly used in the molecular design domain was studied. While the performance of the sandwich algorithm have shown the best performance for a given set of CAM(P)D problems, the approach face specific challenges when seeking to produce optimal solutions reliably along the nonconvex or non-continuous regions of a Pareto front. The mathematical formulations of many practical multiobjective optimisation (MOO) problems indeed include discrete decision variables and nonlinear model equations, which often results in a smooth nonconvex or disconnected Pareto surface. In this chapter, motivated by the well-known normal boundary intersection (NBI) method and the sandwich algorithm, we present the SDNBI algorithm, a robust algorithm for general bi-objective optimisation (BOO) designed to address the theoretical and numerical challenges associated with the solution of general nonconvex and discrete BOO problems.

6.1 Introduction

Many real-world problems in operational research, engineering, biology and chemistry, are often characterised as multi-objective optimisation (MOO), due to the presence of multiple objective functions that cannot be easily merged into a single metric. The objective functions are typically conflicting, so that MOO problems do not have a single solution that is optimal for all objectives simultaneously. Instead, a set of points that each correspond to a trade-off between the objectives, commonly known as Pareto-optimal solutions (or Pareto points, or nondominated points), are sought, such that an improvement in one objective can only be achieved through a sacrifice in another (Miettinen, 1998). In most practical applications, it is not possible to derive an analytical expression that describes the loci of these points, i.e., the Pareto frontier (Deb, 2001). As a result, the development of MOO algorithms that can be used to construct an approximation of the Pareto frontier efficiently is of special interest.

Among the several classes of MOO solution approaches, such as stochastic methods (Zimmermann, 1978; Serafini, 1994; Huang et al., 2006), evolutionary algorithms (Deb et al., 2000a; Deb & Jain, 2013; Li et al., 2019) and exact solution strategies (Belotti et al., 2013; Przybylski & Gandibleux, 2017), one of most widely used class of approaches is based on the concept of scalarisation, in which the multiple objective functions are combined into a single objective function through parameters and/or additional constraints, making it possible to identify solutions of the MOO problem by solving a series of single objective optimisation (SOO) problems using standard optimisation methods. A popular scalarisation method is the weighted-sum method (Marler & Arora, 2004), in which a set of Pareto-optimal solutions is generated by varying the weights assigned to the multiple objective functions. The weighted-sum method is easy to implement and the problem is of same degree of computational complexity as the original MOO problem since there are no

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additional constraints involved. However, this approach suffers from the theoretical limitations that it is not possible to capture any Pareto optimal solutions on nonconvex regions of the Pareto frontier (Miettinen, 1998) and that an even distribution of the weights does not guarantee an even distribution of solutions on the Pareto front. The ϵ -constraint method, on the other hand, does not require any convexity assumptions on the Pareto frontier. In this method, one of the objective functions is selected to be optimised while the others are transformed into additional constraints and the solution of the scalarised problem is proven to always be weakly Pareto optimal. However, it has the drawback of being sensitive to the ϵ values taken by the objective functions in the feasible region, possibly resulting in infeasible or repeated Pareto-optimal solutions (Ehrgott, 2005b). The choice of ϵ values that can maximise the accuracy of the approximation of the Pareto front might not be straightforward particularly when many objective functions are considered (Laumanns et al., 2006). The ϵ values can be chosen to be equidistant aiming to produce evenly distributed the nondominated points. The enumeration of such ϵ values, however, does not always yield the well-distributed Pareto approximation especially when the Pareto front comprises many disconnected parts. To determine the ϵ value systematically, Laumanns et al. (2006) proposed the adaptive ϵ -constraint method in which the ϵ is determined using the incumbent set of the Pareto points.

To deal with these shortcomings, several scalarisation methods have been proposed with a special focus on the development of a systematic way to determine scalarisation parameters and to capture Pareto points from nonconvex regions of the Pareto surfaces. Kim & De Weck (2005) proposed the adaptive weighted-sum algorithm (AWS). To derive a rough representation of the Pareto frontier, the algorithm starts by generating some solution points using the weighted-sum method with a (large) uniform step size in the weighting coefficients. Thereafter, the algorithm continues to solve the weighted-sum scalarisation with additional upper bounds on the objective functions for the regions that need further refinement. These regions

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are determined by computing the distance between neighbouring solutions, in order to control the distribution and uniformity of the Pareto points. With this method, it is possible to investigate nonconvex regions of the Pareto front. Furthermore the approach provides a systematic way of obtaining more uniformly distributed Pareto points. However, the algorithm can generate some dominated solutions (i.e., feasible points that are not on the Pareto frontier and hence are suboptimal) and it cannot be guaranteed to cover the entire set of nondominated points.

Das & Dennis (1998) introduced the normal boundary intersection (NBI) method for identifying the solutions of nonconvex MOO problems. The method generates a well-spaced set of points on the boundary of the space of objective function values by iteratively solving a scalarised subproblem with respect to reference points placed on the convex hull of the individual minima (CHIM) of the objectives. In contrast to weighted-sum methods where problem size is preserved in the subproblems, a new vector of equality constraints is introduced, resulting in a size increase. The performance of the method was tested for large-scale and highly-constrained optimisation problems in the area of optimal control (Logist et al., 2010). While the method was found to produce evenly-distributed solutions, its focus is on identifying the boundary of the feasible objective space, which may include some points dominated by others. Furthermore, it may difficult to achieve convergence when there is no feasible solution that satisfies the equality constraints for the given choice of scalarisation parameter values. Following similar concepts, Ismail-Yahaya & Messac (2002) proposed the normal constraint (NC) method as an alternative to the NBI method to avoid getting dominated solution or improve convergence behaviour. Instead of introducing equality constraints in the subproblems, as in the NBI method, a set of inequality constraints is used to reduce the size of the feasible region. Messac et al. (2003) further modified the NC method by incorporating a so-called Pareto filter, which is used to eliminate non-Pareto optimal solutions. However, these normal constraint methods share the same drawbacks as the NBI method because they rely on the CHIM as a reference plane. Further adjustments were made by Messac & Mattson (2004) and Shao & Ehrgott (2007), with the aim of reducing the likelihood of missing regions of the nondominated set. Messac & Mattson (2004) used an extension of the reference plane defined by the CHIM, so that the entire Pareto set can be enclosed by a hypercube. These studies indicate that the non-connectivity of the Pareto surface and the presence of isolated Pareto optimal points can cause severe problems for the NBI method, whereas the WS and NC methods are less likely to be affected by the disconnected nature of the Pareto set. In further work on the NBI method, Shao & Ehrgott (2016) suggested an extension of an approach initially designed for the solution of multi-objective linear programming (MOLP) problems Shao & Ehrgott (2007), in which they combined the global shooting method (Benson & Sayin, 1997) with the NBI method to guarantee coverage of the Pareto frontier as well as an even distribution of the Pareto points.

While the methods discussed so far are designed to identify evenly distributed points on the Pareto frontier, the development of Benson's outer approximation algorithm (Benson, 1998) has motivated the emergence of another class of algorithms designed to generate outer and/or inner approximations of the Pareto frontier. The majority of such methods have been focused on obtaining polyhedral approximations to ensure an even spread of points over the Pareto surface. Shao & Ehrgott (2008); Ehrgott et al. (2011) presented improvements to Benson's algorithm for the solution of MOLP problems by introducing the sandwich (SD) algorithm so that the Pareto frontier is located between the inner and outer approximation. The SD algorithm and its variants have several useful properties. As the real Pareto surface is sandwiched between the inner and outer approximation, an upper bound on the approximation error can be calculated; it provides valuable information on the accuracy of the Pareto-optimal solutions generated during the course of the algorithm. Furthermore, the approximation quality can be improved efficiently by adding more solutions in the region where the error bound is at the largest. However, the method

is limited to MOLP problems and it cannot easily be applied to general nonlinear MOO problems. Modified versions of the SD algorithm were proposed by Solanki et al. (1993); Craft et al. (2006); Rennen et al. (2011); Klamroth et al. (2003); Bokrantz & Forsgren (2013) to address general convex MOO problems. Solanki et al. (1993) extended the SD algorithm to make it applicable for higher dimensions of the MOLP problems (i.e., with more than two objective functions). At each iteration, a weighted-sum subproblem is solved for the facet that exhibits the largest distance to a point constrained to the outer approximation. Within the algorithm, the accuracy of the Pareto front approximation is improved by recursively constructing inner and outer approximations through the generation of a convex hull and the identification of supporting hyperplanes. Although this method is directed towards the solution of MOLP problems, it can also be applied to general convex MOO problems. Klamroth et al. (2003) used two separate algorithms for generating the inner and outer approximations of the Pareto set and combined them by alternatively solving one iteration of each algorithm. A major feature of their algorithm is the use of vertices as reference points to construct an inner approximation with maximal combination of the vertices of each facet or a solution closer to any vertex in the outer approximation, instead of relying on the weighted-sum method. Other authors have proposed further developments of this approach, refining the method for calculating the error between inner and outer approximations Craft et al. (2006) or modifying the way in which parameters are chosen Rennen et al. (2011). In Craft et al. (2006), the error is calculated by considering the hyperplanes of the outer approximation that pass through the corner points of a facet rather than by solving a linear programming problem. The next weight vector is taken from the linear combination of the weight vectors used to obtain the corner points of the facet. Rennen et al. (2011) further improved the algorithm by incorporating dummy points to ensure that all facet have a non-negative normal, which is crucial for the weighted-sum method. To reduce the computational expense, which increases exponentially with the num-
ber of objectives, Bokrantz & Forsgren (2013) have suggested employing a vertex enumeration method rather than the facet enumerative algorithm of Rennen et al. (2011). While sandwich-type algorithms have provided a promising route to solving MOO problems, their applicability is often limited to convex MOO problems as they rely on weighted-sum subproblems. Accordingly, SD algorithms cannot achieve entire coverage of the regions of the Pareto frontier that are nonconvex, disconnected or consist of discrete points.

In this study, we propose to address these limitations by introducing a new scalarisation technique and a corresponding solution algorithm, the SDNBI algorithm, for the accurate approximation of nonconvex and combinatorial Pareto fronts in bi-objective optimisation (BOO) problems. Such problems may contain nonconvex functions and involve a mixed set of continuous and integer decision variables. Given the similarity in terms of the use of convex hulls, the development of the approach is focused on the interplay between the SD algorithm and NBI method, exploiting the strengths of both. The properties of the modified NBI method (mNBI) subproblem is studied to make use of the is We present three main modifications, in particular making use of the modified NBI (mNBI) method suggested by Shukla (2007), and we investigate their theoretical properties: 1) the validity of the inner and outer approximations derived from the solution of the scalarised subproblem and convex hull generation, 2) the completeness of decomposing of an objective search space based on the convexity of the Pareto front and 3) the effectiveness of modifying the subproblem in avoiding unnecessary search steps for the disconnected or isolated portion of the Pareto front. To assess the performance of the proposed SDNBI algorithm, a numerical tests are conducted for five bi-objective benchmark problems (MOP1, SCH2, TNK, ZDT3, and ZDT5) and compared with the results produced by the original SD algorithm and mNBI method. The performance of the different algorithms is compared based on reliability and efficiency criteria.

The remainder of this chapter is organised as follows. In section 6.2, all relevant

preliminaries including the notation, definitions and the formulation of the problems are introduced. In section 6.3, we describe the NBI, mNBI and SD algorithm and their properties. In section 6.4, we propose the new algorithm and highlight its characteristics. We perform numerical experiments in Section 6.5 and 6.6 to investigate algorithmic efficiency. Finally, we state the main conclusions, also including future perspectives for this research in Section 6.7.

6.2 Preliminaries

Following the basic notations and definition provided in Chapter 2.3, we repeat the mathematical formulation of the MOO problem (MOP) for convenience. The generic mathematical formulation of the MOO problem is defined as:

$$\begin{array}{ll} \min & \left(f_1(\boldsymbol{x}),\ldots,f_m(\boldsymbol{x})\right)^\top \\ \text{subject to} & \boldsymbol{x}\in X:=\{\boldsymbol{x}\in\mathbb{R}^{n_1}\times\mathbb{N}^{n_2}\mid \boldsymbol{g}(\boldsymbol{x})\leq\boldsymbol{0},\boldsymbol{h}(\boldsymbol{x})=\boldsymbol{0}\}, \end{array}$$
 (MOP)

We consider problems for which a constraint qualification holds so that the Karush-Kuhn-Tucker (KKT) optimality conditions apply when the problem is specified only for continuous variables, i.e., nonlinear programming (NLP) problem.

6.3 Background and Motivation

In this section, we start with a short recapitulation of the two MOO algorithms that motivate the new algorithm proposed in this paper.

6.3.1 Sandwich Algorithm

The SD algorithm proposed by Solanki et al. (1993) is a scalarisation method developed with the aim of approximating a (convex) Pareto front while solving as few optimisation subproblems as possible. While there are variations of the approach, SD algorithms are based on the successive solution of weighted-sum subproblems in which the multiple objective functions are aggregated into a single objective function using a weight vector, w, as follows:

$$\min_{\boldsymbol{x} \in X} \quad \boldsymbol{w}^{\top} \boldsymbol{f}(\boldsymbol{x}) = \sum_{i=1}^{m} w_i f_i(\boldsymbol{x}). \tag{WSP}w$$

We set out the key concepts necessary to describe a SD algorithm following the definitions and notation of Rennen et al. (2011).

Definition 8. Anchor point – Anchor point z^{Ai} is a point in objective space equal to the optimal objective function vector obtained by solving problem (WSPw) with weight vector w^i such that $w_i^i = 1 - \delta$ and $w_j^i = \delta$, j = 1, ..., m, $j \neq i$, where δ is a small positive infinitesimal scalar value. Thus $z^{Ai} = f(x^*)$, where $x^* = \underset{m \in V}{\operatorname{argmin}} f_i(x)$.

Definition 9. Hyperplane – A hyperplane in the objective space is given by $H(w, b) = \{z \in Z \mid w^{\top} z = b\}$ with $w \in \mathbb{R}^m \setminus \{0\}$ and $b \in \mathbb{R}$.

Remark. The vector w is a normal of the hyperplane. In this study, the vector w is always taken to be a unit normal vector, such that |w| = 1.

Next we define half-spaces and inner and outer normals.

Definition 10. Half-space – The set $HS(\boldsymbol{w}, b) = \{\boldsymbol{z} \in \mathbb{R}^m \mid \boldsymbol{w}^\top \boldsymbol{z} \ge b\}$ is the half-space given by $\boldsymbol{w} \in \mathbb{R}^m \setminus \{0\}$ and $b \in \mathbb{R}$.

Remark. The vector w, |w| = 1, is an *inner unit normal* of the half-space.

Definition 11. Supporting hyperplane of a convex set – Suppose C is a convex set and z_0 is a point lies on the boundary of C, bd C, i.e., $z_0 \in bd C$. If $w \neq 0$ satisfies $w^{\top} z \leq w^{\top} z_0$ for all $z \in C$, then a hyperplane H(w, b) defined by $w^{\top} z = b$, where $b = w^{\top} z_0$, is called a supporting hyperplane to C at point z_0 . This is equivalent to saying that a hyperplane H(w, b) supports C at z_0 .

Definition 12. *k-face, facets and extreme points* – A set of points *F* of dimensionality k is a *k*-face of *C* if there exists a hyperplane H(w, b) that supports *C* at F_S and for which it holds that $H(w, b) \cap C = F$. If $C \subseteq \mathbb{R}^m$, its (m - 1)-faces are facets F_S and its 0-faces are the extreme points (vertices).

For m = 2, we denote a *p*-th facet which is defined with two extreme points z^{p1} and z^{p2} as $F_S^p(z^{p1}, z^{p2})$, where it holds $z_1^{p1} < z_1^{p2}$. In Figure 6.1, we provide a visual interpretation of the supporting hyperplane, (m - 1)-face and 0-face in two dimensional space.



Figure 6.1: Schematic of (a) a supporting hyperplane H(w, b) to a convex set C at its boundary point z_0 (black circle), (b) a facet defined as H(w, b), where $\forall z \in C$ and $b = w^{\top} z$ (red solid line) and a extreme point (blue circle) in two dimensional space.

Definition 13. *Inner and outer approximations* – A set $IPS \subseteq Z$ is an inner approximation of Ψ^* if it satisfies:

$$\forall \boldsymbol{z'} \in IPS, \exists \boldsymbol{z} \in \boldsymbol{X_E} : \boldsymbol{z'} \geq \boldsymbol{z},$$

where the inequality is understood component-wise. Similarly, a set $OPS \subseteq \mathbb{R}^m$ is an outer approximation of Ψ^* if it satisfies:

$$\forall \boldsymbol{z'} \in OPS, \exists \boldsymbol{z} \in \boldsymbol{X_E} : \boldsymbol{z'} \leq \boldsymbol{z}.$$

The SD algorithm is based on iteratively constructing a convex hull (inner approximation) and adding an hyperplane and its positive half-space at a nondominated point (outer approximation) between which the Pareto front is sandwiched. At each iteration, these piecewise approximations are improved by solving subproblem (WSPw). Specifically, the outer approximation constructed by the successive solutions of weighted-sum subproblems (WSPw) can be re-defined with multiple Pareto points and their associated weight coefficients as below.

$$OPS = \{ \boldsymbol{z} \mid \boldsymbol{W}^{\top} \boldsymbol{z} \ge \boldsymbol{B} \}$$
(6.1)

where W is a matrix with each column corresponding to a particular weight vector w^k and B is a column vector where the k-th element is obtained by the vector product between the transpose of the k-th column of W and corresponding nondominated solution $z^k \in Z_E$, i.e., $B = W^{\top}Z_E$. The recursive procedure of the approximations continues until the approximation error, a measure of the distance between IPS and OPS satisfies a given tolerance, $\epsilon > 0$. In our study, we follow the approach of Rennen et al. (2011) of considering dummy points in the calculation of the approximation error, $d_{error,p}$, $p = 1, ..., N_F$ where N_F is the number of facets generated by the inner approximation, between the inner and outer approximations, whereby the maximum error, $d_{max} = \max_{p=1,...,N_F} d_{error,p}$, is determined by solving the following linear programming problem for each facet of IPS, F_S^p .

$$d_{error,p} = \max_{z} \frac{\boldsymbol{w}_{p}^{\top}(\boldsymbol{z}^{vertex} - \boldsymbol{z})}{\boldsymbol{w}_{p}^{\top}\boldsymbol{\epsilon}_{d}}$$
s.t. $\boldsymbol{z} \in OPS$
(6.2)

where w_p is a normal vector of the pth facet F_S^p , z^{vertex} is one of extreme points of the facet F_S^p and ϵ_d is a user defined vector that represents ϵ -dominance. Note that the facet which is defined by a negative normal vector, i,e., outer normal vector or only dummy points are eliminated from consideration in the calculation of the error. The basic scheme of the algorithm is stated in Algorithm 5, and a schematic illustration of the procedure for a bi-objective problem is shown in Figure 5.1.

The major advantage of this method is that the weight vectors are systematically chosen to be normal to the facets generated by the inner approximations and the accuracy of the approximation is measured during the course of the algorithm, providing a natural stopping criterion.

Alge	orithm 5 Sandwich algorithm for MOO
1:	procedure Sandwich Algorithm
2:	$Z_E = OPS = IPS = \emptyset; d_{max} = \infty; k = 1$, where Z_E is a set of non-
	dominated solutions. Specify error tolerance ϵ and initial weight coefficients
	w^1
3:	Find all anchor points $oldsymbol{Z^A} = ig\{oldsymbol{z^{Ai}} \mid i=1,,mig\}.$
4:	Update the set $oldsymbol{Z_E}$: $oldsymbol{Z_E} = ig\{oldsymbol{z^{A1}},,oldsymbol{z^{Am}},oldsymbol{z^1}ig\}$
5:	Solve problem (WSP w) with initial w^1 to obtain the initial outer approxima-
	tion z^1 .
6:	while $d_{max} \ge \epsilon \ \mathbf{do}$
7:	Set $k = k + 1$.
8:	Generate the inner approximation set IPS with N_F facets:
	$IPS = \text{convexhull}(\mathbf{Z}_{E})$
9:	Calculate the error, $d_{error,p}$, for each facet F_S^p of IPS .
10:	Select the facet, $F_S^{p^k}$, that has largest error, $d_{max} = d_{error,p^k}$
	where $p^k = \underset{p=1,,N_F}{\operatorname{argmax}} (d_{error,p}).$
11:	Set $oldsymbol{w}^k$ to be the unit inner normal to $F_S^{p^k}$
12:	Determine \boldsymbol{z}^k by solving problem (WSPw) with \boldsymbol{w}^k .
13:	Compute $b^k = \boldsymbol{w}^{k \top} \boldsymbol{z}^k$ and define $H(\boldsymbol{w}^k, b^k)$
14:	Compute $b_{i'} = \boldsymbol{w}^{k op} \boldsymbol{z}_{i'}$ for all $\boldsymbol{z}_{i'} \in \boldsymbol{Z}_{\boldsymbol{E}}.$
15:	if $\exists i'$ such that $b_{i'} = b^k$ then
16:	Set the error $d_{error,p^k} = 0$ and return to Step 9.
17:	end if
18:	Update outer approximation: $OPS = OPS \cup \{ \boldsymbol{w}^{k\top} \boldsymbol{z}^k \ge b^k \}.$
19:	Update $oldsymbol{Z}_{oldsymbol{E}}\colon oldsymbol{Z}_{oldsymbol{E}}=oldsymbol{Z}_{oldsymbol{E}}\cup\{oldsymbol{z}^k\}.$
20:	end while
21:	end procedure

6.3.2 Normal Boundary Intersection

The NBI method was proposed by Das & Dennis (1998) to construct uniformly spread nondominated solutions for a general nonlinear multi-objective optimisation problem. In the NBI method, the individual minima or anchor points are found as a first step. The convex hull of individual minima (CHIM) is then generated as the set of all convex combinations of these individual minima. The CHIM can be expressed as $\{\Phi\beta : \beta \in \mathbb{R}^m_+, \sum_{j=1}^m \beta_j = 1\}$ where $\Phi \in \mathbb{R}^{m \times m}$ is a matrix with *i*th column $z^{Ai} - f^{id}$. The NBI subproblem (NBI β) is formulated to search for the maximum distance *t* along the normal vector $\bar{\mathbf{n}}$ to the CHIM at a point defined by a specific choice of β .

$$\max_{\boldsymbol{x} \in X, t} t$$
s.t. $\boldsymbol{\Phi}\boldsymbol{\beta} + t\bar{\boldsymbol{n}} = \boldsymbol{f}(\boldsymbol{x}) - \boldsymbol{f}^{id}$
 $t \in \mathbb{R}, \ \bar{\boldsymbol{n}} \in \mathbb{R}^m$
(NBI β)

where \bar{n} is the outer normal direction at some points on CHIM pointing toward the ideal point. The solution of the above problem (x^*, t^*) gives to the maximum value of t at which the normal vector and the boundary of the feasible region intersect, which corresponds to a boundary point, $(x^*, f(x^*))$.

During the course of the algorithm, the NBI subproblem (NBI β) is solved for a set of β values that give reference points $\Phi\beta$ evenly distributed over the CHIM.

A drawback of the original formulation of the NBI subproblem is that the method aims at getting boundary points and some of these points may not be Pareto-optimal points. To overcome this issue, Shukla (2007) modified the formulation with the use of the goal-attainment approach such that Pareto-optimality of solution is guaranteed. The modified NBI method is denoted as mNBI and the resulting subproblem is CHAPTER 6. THE SDNBI ALGORITHM: A DETERMINISTIC APPROACH FOR NONCONVEX AND COMBINATORIAL BOO



Figure 6.2: Schematic illustrating the mNBI method for two objectives f_1 and f_2 . The blue solid curve represents the parts of the boundary of the feasible region where no Pareto points exist. In (a), at the start of the algorithm the CHIM (black dashed line) is constructed based on the anchor points z^{A1} , z^{A2} . Pareto point z^1 is then obtained by solving (mNBI β) for $\Phi\beta^1$. In (b), (mNBI β) is solved with $\Phi\beta^2$ and the resulting new Pareto point is z^2 . If (NBI β) was solved instead with $\Phi\beta^2$, point *b* (blue diamond) would be obtained, which is dominated by z^2 .

described as:

$$\begin{array}{l} \max_{\boldsymbol{x}\in X,t} t \\ \text{s.t. } \boldsymbol{\Phi}\boldsymbol{\beta} + t\bar{\boldsymbol{n}} \geq \boldsymbol{f}(\boldsymbol{x}) - \boldsymbol{f}^{\boldsymbol{id}} \\ t \in \mathbb{R}, \ \bar{\boldsymbol{n}} \in \mathbb{R}^{m} \end{array} \tag{mNBI}\beta)$$

The advantage of the mNBI algorithm is that it allows one not only to avoid any dominated boundary points but also to screen out some non-efficient regions in the objective space. The generic mNBI algorithm is outlined in Algorithm 6 and a geometric illustration of the optimisation is shown in Figure 6.2

6.3.3 Discussion

The performance of the SD algorithm has been proven in several practical applications such as the intensity-modulated radiation therapy optimisation problem (Craft et al., 2006; Rennen et al., 2011), the design of distillation processes for separating a binary mixture of chloroform and acetone (Bortz et al., 2014), integrated solvent and process design problem (Burger et al., 2015), the design of a plate-fin heat-sink

Algorithm 6 mNBI for MOO
1: procedure Modified NBI method
2: $\boldsymbol{Z}_{\boldsymbol{E}} = \emptyset; \ k = 1$
3: Find all anchor points $Z^A = \{ z^{Ai} \mid i = 1,, m \}.$
4: Generate equidistant reference points for a pre-defined number of iterations
$N_eta, C^{ref} = \left\{ oldsymbol{\Phi} oldsymbol{eta}^k, k = 1,, N_eta ight\}$
5: Define vector \bar{n} to be normal to CHIM.
6: while $k \leq N_{\beta}$ do
7: Solve problem (mNBI β) with $\Phi \beta^k$ and obtain solution (t^*, x^*) .
Compute $z^* = f(x^*)$. 8: Update the set of Pareto points Z_E with $Z_E = \{Z_E, z^*\}$
9: Set $k = k + 1$
10: end while
11: end procedure

to improve economic and thermal performance (Andersson et al., 2018) and the solution of parameter estimation problems in the development of the equation of state model (Graham, 2020), yet there are remaining difficulties to overcome. Since the SD algorithm is closely related to weighted-sum methods, unsupported solutions that lie in the nonconvex regions of the objective space cannot be attained. Thus, there is no weight vector w suitable for finding an efficient solution x^* in such a region. On the other hand, the mNBI method can yield solutions that lie on the nonconvex (concave) parts of the Pareto front as well as points on the convex regions. These nondominated points can be generated with the appropriate choice of β . The efficiency of the NBI method and its variants has been investigated in the context of the optimal design of methylethyl ketone production process by carrying out bi-objective optimisation of an economic value and potential environmental impact (Lim et al., 2001), the development of optimal bidding strategies for the participants of oligopolistic energy markets (Vahidinasab & Jadid, 2010), the design of an optimal heat exchanger that maximises the amount of heat transfer and minimises tube length (Siddiqui et al., 2012), and the solution of a scheduling problem for pumped-hydro-thermal power in which a cost function and an emission metric are considered as bi-objective criteria (Simab et al., 2018). However, unlike the SD algorithm, the mNBI method neither provides information on approximation accuracy nor on the maximum achievable approximation quality level in the presence of disconnected regions, thus making it difficult to determine when to stop the algorithm and how to choose the iteration number N_{β} . These drawbacks also preclude the user from choosing the set of reference points $\Phi \beta^k \in C^{ref}$ systematically. Given the advantages derived from each algorithm and their similarity in terms of the use of convex hulls, an extension of the SD algorithm through its combination with the mNBI method is discussed in the following sections.

6.4 Proposed Algorithm

In this section, we present the SDNBI algorithm, a novel adaptive MOO approach for the solution of BOO problems. It is more general than the SD algorithm in that it is applicable to nonconvex problems, in particular to those with a disconnected Pareto front and feasible region. A new feature is the use of the mNBI subproblem, such that the mNBI parameters are systematically determined by the SD algorithm, in an adaptive fashion. Although the SD algorithm and the mNBI method are applicable to higher-dimensional MOO cases (m > 2) (Bokrantz & Forsgren, 2013), we focus here on the solution of two-dimensional (BOO) problems and adapt the terminology appropriately, as described in the following definition.

Definition 14. Line, half-plane, tangent – A line $H_2(w, b)$ and half-plane $HS_2(w, b)$ are a special case of the hyperplane H(w, b) and half-space HS(w, b) defined for the two-dimensional objective space, i.e., when m = 2. If a line is tangential to a curve in the bi-objective space at the point z_0 , it is called a *tangent* at z_0 .

The main aspects of the proposed methodology are explained in the remainder of this section.

6.4.1 Setting the parameters of the mNBI subproblem

The main idea behind the proposed algorithm is to replace the weighted-sum subproblem that appears in the SD algorithm with the mNBI subproblem so as to obtain solutions on the nonconvex part(s) of the Pareto front. Consider a facet $F_S^{p^k}(z^{p1}, z^{p2})$ connecting two nondominated points z^{p1} and z^{p2} at some iteration k. The normal vector of the facet can be used as the normal vector \bar{n}^k in the mNBI subproblem. Then, Φ^k is defined by the two extreme points of the facet, with its i^{th} column given by $z^{pi} - z^o$, i = 1, 2 where $z^o = [\min(z_1^{p1}, z_1^{p2}), \min(z_2^{p1}, z_2^{p2})]^{\top} = [z_1^{p1}, z_2^{p2}]^{\top}$. Subsequently, the reference point $\Phi^k \beta^k$ on the facet can be determined by choosing an appropriate β^k . In this study, β^k is chosen such that the reference point $\Phi^k \beta^k$ is located at the midpoint of the facet, in order to generate a Pareto point that may be evenly placed between z^{p1} and z^{p2} . Note that β^k could be also chosen by projecting the solution of Equation (6.2) onto the facet in order to minimise the error between the inner and outer approximations.

6.4.2 Constructing valid inner and outer approximations

The solution of the mNBI subproblem with the proposed parameter values results in point z^k that may be used to update the approximations of the Pareto front. This requires some careful analysis due to the potential nonconvexity of the efficient frontier. In the original SD algorithm, the outer approximation OPS is improved at iteration k by adding a line tangential to the recently-identified nondominated point z^k , $H_2(w^k, b^k)$, and its half-plane $HS_2(w^k, b^k)$ where $b^k = w^{k\top} z^k$, for m = 2. The weight vector w^k is that used in the weighted-sum scalarisation problem as described in Section 6.3.1. The inner approximation IPS of the Pareto front is obtained as a polyhedral approximation of the set of points $z \in Z_E \subseteq \Psi^*$. This polyhedral approximation is defined as the set of all convex combinations of points in Z_E in the objective space and it is denoted by convexhull(Z_E).



Figure 6.3: Representation of a line at the nondominated point z^1 generated by the solution of (mNBI β) with the normal vector \bar{n}^1 (blue dashed line) and the reference point $\Phi^1\beta^1$. The grey curve represents the boundary of the feasible region in bi-objective space and the black dashed line is a facet obtained by generating a convex hull using z^{A1} and z^{A2} . If the next upper bounds, i.e., inner approximations are obtained by constructing the convex hull based on the updated set of the Pareto points, $Z_E = \{z^{A2}, z^1, z^{A1}\}$, the solid black lines are obtained, cutting off part of the Pareto front.

Thus, in the original SD algorithm, the Pareto front must be convex to ensure that valid upper and lower bounds are obtained that do not cut off any part of the front. Furthermore, the line $H_2(\bar{\mathbf{n}}^k, b^k)$ generated as a solution of problem (mNBI β) does not necessarily support the Pareto front at point \mathbf{z}^k . A simple example where the use of the mNBI subproblem to generate a new Pareto point leads to erroneous inner and outer approximations is shown in Figure 6.3. It is clear that the Pareto frontier is not supported by the line $H_2(\bar{\mathbf{n}}^1, b^1)$, where $b^1 = \bar{\mathbf{n}}^{1\top} \mathbf{z}^1$, at nondominated point \mathbf{z}^1 . The inner approximation generated by facets $F_S^{p^k}(\mathbf{z}^{A2}, \mathbf{z}^1)$ and $F_S^{p^k}(\mathbf{z}^1, \mathbf{z}^{A1})$ is valid only for Pareto points $\mathbf{z}^{\top} = (z_1, z_2)$ in objective space such that $z_1 \leq z_1^1$. We address these issues in the remainder of this subsection.

Tangent at the solution of mNBI

To analyse further the properties of the mNBI subproblem, it is useful to partition the vector of variables into a binary variable vector, denoted as $\boldsymbol{y} \in Y = \{0, 1\}^{n_2}$, and a continuous variable vector $\boldsymbol{x} \in \mathbb{R}^{n_1}$. Without loss of generality, any function

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q(x, y) in the MOO problem, where q can refer to the objective function, an equality or an inequality constraint, can be written as

$$q(\boldsymbol{x}, \boldsymbol{y}) = c_q^\top \boldsymbol{y} + q_x(\boldsymbol{x})$$
(6.3)

Then the mNBI subproblem is given by

$$\max_{\boldsymbol{x} \in X, \boldsymbol{y} \in Y, t} t$$

s.t. $\boldsymbol{\Phi}\boldsymbol{\beta} + t\bar{\boldsymbol{n}} \geq \boldsymbol{f}_x(\boldsymbol{x} + \boldsymbol{c}_f^T \boldsymbol{y}) - \boldsymbol{f}^{id}$
 $t \in \mathbb{R}, \ \bar{\boldsymbol{n}} \in \mathbb{R}^m$ (6.4)

At the solution (\hat{x}, \hat{y}, t^*) of the MINLP problem, one can obtain Lagrange multipliers at fixed values of $y = \hat{y}$, provided that the corresponding NLP meets an appropriate constraint satisfaction.

Therefore, given an efficient solution (\hat{x}, \hat{y}) obtained by solving an mNBI subproblem and at which $t = t^*$, there exist μ^* and ν^* such that the KKT optimality conditions for optimisation problem (6.4) at fixed y are satisfied and therefore:

$$\nabla_{\boldsymbol{x}} \mathcal{L} = \boldsymbol{\mu}^{*\top} \nabla_{\boldsymbol{x}} \boldsymbol{f}_{x} \left(\hat{\boldsymbol{x}} \right) + \boldsymbol{\nu}^{*\top} \nabla_{\boldsymbol{x}} \hat{\boldsymbol{h}}_{x} \left(\hat{\boldsymbol{x}} \right) = \boldsymbol{0}$$
(6.5)

$$\nabla_t \mathcal{L} = -1 + \boldsymbol{\mu^*}^\top \bar{\boldsymbol{n}} = 0 \tag{6.6}$$

where $\mathcal{L}(\boldsymbol{x}, t, \boldsymbol{\mu}, \boldsymbol{\nu}; \hat{\boldsymbol{y}}) = -t + \boldsymbol{\mu}^{\top} \left(\boldsymbol{f}_{\boldsymbol{x}}(\boldsymbol{x}) + \boldsymbol{c}_{f}^{\top} \hat{\boldsymbol{y}} - \boldsymbol{f}^{id} - \boldsymbol{\Phi}\boldsymbol{\beta} - t\bar{\boldsymbol{n}} \right) + \boldsymbol{\nu}^{\top} (\hat{\boldsymbol{h}}_{\boldsymbol{x}}(\boldsymbol{x}) + \boldsymbol{c}_{h}^{\top} \hat{\boldsymbol{y}}), \boldsymbol{\mu} \in \mathbb{R}^{m}$ represents the vector of Lagrange multipliers corresponding to the augmented objective constraints $\boldsymbol{f}_{\boldsymbol{x}}(\boldsymbol{x}) + \boldsymbol{c}_{f}^{\top} \hat{\boldsymbol{y}} - \boldsymbol{f}^{id} - \boldsymbol{\Phi}\boldsymbol{\beta} - t\bar{\boldsymbol{n}} \leq \boldsymbol{0}, \text{ and } \boldsymbol{\nu} \in \mathbb{R}^{s}$ is the vector of Lagrange multipliers for the *s* active constraints in the set { $\boldsymbol{g}_{\boldsymbol{x}}(\boldsymbol{x}) + \boldsymbol{c}_{g}^{\top} \hat{\boldsymbol{y}} \leq \boldsymbol{0}, \boldsymbol{h}_{\boldsymbol{x}}(\boldsymbol{x}) + \boldsymbol{c}_{h}^{\top} \hat{\boldsymbol{y}} = \boldsymbol{0}$ }, represented by the vector $\hat{\boldsymbol{h}}_{\boldsymbol{x}}(\boldsymbol{x}) \in \mathbb{R}^{s}, q \leq s \leq p + q$. Furthermore, at the KKT point, the following complementary condition must hold:

$$\boldsymbol{\mu}^{*\top} \left(\boldsymbol{f}_{\boldsymbol{x}}(\hat{\boldsymbol{x}}) + \boldsymbol{c}_{\boldsymbol{f}}^{\top} \hat{\boldsymbol{y}} - \boldsymbol{f}^{id} - \boldsymbol{\Phi}\boldsymbol{\beta} - t^* \bar{\boldsymbol{n}} \right) = 0$$
(6.7)

From equation (6.6), it can be deduced that at least one of the augmented objective constraints must be active. This can be shown by contradiction. Let us assume that all constraints of the augmented objective constraints are inactive, i.e., $f_x(x) + c_f^{\top} \hat{y} - f^{id} - \Phi\beta - t\bar{n} < 0$ and $\mu^* = 0$. Then, equation (6.6) is reduced to $\nabla_t \mathcal{L} = -1 \neq 0$, which is the violation of the KKT necessary conditions. Therefore, if we solve problem (mNBI β) for any choice of parameters (\bar{n}, β), there exists a corresponding normal vector $w' \geq 0$, where the inequality is understood componentwise, that defines a tangent to the Pareto front at the nondominated solution, z, and is given by:

$$w' = \frac{1}{\sum_{i=1}^{m} \mu_i^*} \mu^*, \ \sum_{i=1}^{m} w_i' = 1.$$
(6.8)

As Das & Dennis (1998) and Shukla (2007) have shown, an even stronger relationship between the NBI/mNBI and weighted-sum subproblems exists when the solution of the NBI/mNBI subproblem is located on a convex part of the Pareto front. Consider problem (WSPw). If (x^*, y^*) is an efficient solution of this problem, then there exists a unique vector λ^* at fixed $y = y^*$ such that

$$\nabla_{\boldsymbol{x}} \mathcal{L}^{w} = \boldsymbol{w}^{\top} \nabla_{\boldsymbol{x}} \boldsymbol{f}_{\boldsymbol{x}} \left(\boldsymbol{x}^{*} \right) + \boldsymbol{\lambda}^{*\top} \nabla_{\boldsymbol{x}} \hat{\boldsymbol{h}}_{\boldsymbol{x}} \left(\boldsymbol{x}^{*} \right) = \boldsymbol{0}$$
(6.9)

where $\mathcal{L}^{w}(\boldsymbol{x}, \boldsymbol{\lambda}; \boldsymbol{y}^{*}) = \boldsymbol{w}^{\top}(\boldsymbol{f}_{\boldsymbol{x}}(\boldsymbol{x}) + \boldsymbol{c}_{f}^{\top}\boldsymbol{y}^{*}) + \boldsymbol{\lambda}^{\top}(\hat{\boldsymbol{h}}_{\boldsymbol{x}}(\boldsymbol{x}) + \boldsymbol{c}_{h}^{\top}\boldsymbol{y}^{*}), \hat{\boldsymbol{h}} \in \mathbb{R}^{s}, q \leq s \leq p + q$ is the vector of active constraints and $\boldsymbol{\lambda}$ is the vector of Lagrange multipliers for the active constraints.

The following lemma is then derived from the claims in (Das & Dennis, 1998; Shukla, 2007) and establishes the relationship between problems (mNBI β) and (WSPw).

Lemma 1. Let $(\hat{x}, \hat{y}, t^*, \mu^*, \nu^*)$ be a solution of problem (mNBI β), with $\sum_{i=1}^{m} \mu_i^* \neq 0$ and normal vector: $w' = \frac{1}{\sum_{i=1}^{m} \mu_i^*} \mu^*$. Then, if (\hat{x}, \hat{y}) is a supported efficient solution, the solution of problem (WSPw) with weight vector w = w' is

$$\left(\boldsymbol{x}^{*}, \boldsymbol{y}^{*}, \boldsymbol{\lambda}^{*} = \frac{1}{\sum_{i=1}^{m} \mu_{i}^{*}} \boldsymbol{\nu}^{*}\right), \qquad (6.10)$$

where $x^* = \hat{x}$ and $y^* = \hat{y}$.

Proof. Divide equation (6.5) by the nonzero scalar $\sum_{i=1}^{m} \mu_i^*$:

$$\frac{\boldsymbol{\mu}^{*\top}}{\sum_{i=1}^{m}\mu_{i}^{*}}\nabla_{\boldsymbol{x}}\boldsymbol{f}_{\boldsymbol{x}}\left(\hat{\boldsymbol{x}}\right) + \frac{\boldsymbol{\nu}^{*\top}}{\sum_{i=1}^{m}\mu_{i}^{*}}\nabla_{\boldsymbol{x}}\hat{\boldsymbol{h}}_{\boldsymbol{x}}\left(\hat{\boldsymbol{x}}\right) = \boldsymbol{0}.$$
(6.11)

If (\hat{x}, \hat{y}) is a supported efficient solution, then there must exist a weight vector such that (\hat{x}, \hat{y}) is the solution of a (WSPw) subproblem. By comparing equation (6.11) and equation (6.9), it can be observed that if (\hat{x}, \hat{y}) is the solution of a weighted-sum problem, the following must hold:

$$\boldsymbol{w} = \frac{1}{\sum_{i=1}^{m} \mu_i^*} \boldsymbol{\mu}^*, \ \sum_{i=1}^{m} w_i = 1,$$
 (6.12)

with
$$x^* = \hat{x}$$
 and $y^* = \hat{y}$.

Note that the solution (\hat{x}, \hat{y}) of the mNBI problem differs from (x^*, y^*) at the solution of the weighted-sum problem in Lemma 1 if the objective vector $f_x(\hat{x}) + c_f^{\top} \hat{y}$ is on the nonconvex part of the Pareto front, i.e., it cannot be generated by means of weighted-sum scalarisation.

According to Lemma 1, if we solve problem (WSPw) for any choice of weight coefficients, w, there exist corresponding mNBI parameters (\bar{n}, β) such that problem (mNBI β) and problem (WSPw) have the same solution. Moreover, the weight vector w defines a supporting line tangential to the Pareto front at the nondominated solution, z. Interestingly, w = w', as evident when comparing equations (6.8) and (6.12). It is worth mentioning that the vector w' in the mNBI method consists of non-negative elements since the augmented objective functions are inequality constraints, in contrast to to the original NBI method in which non-negative or positive elements of the multiplier $\mu^* \in \mathbb{R}^m$ may be generated. This can also be understood graphically from Figure 6.4. For specified parameters ($\Phi^2\beta^2, \bar{n}^2$), one can see that the solution of problem (NBI β) produces a tangent at $z^{2,e}$ with its normal vector w' that contains a negative element, while the elements of the normal vector from (mNBI β) are all positive. This is because the original NBI method aims to obtain the boundary of the feasible domain in objective space, rather than Pareto points only. This results in the identification of dominated point $z^{2,e}$.



Figure 6.4: Representation of the solutions $z^{2,e}$ (•) and z^2 (•) obtained by solving subproblem (NBI β) and (mNBI β), respectively, for the specified parameter ($\Phi^2\beta^2, \bar{n}^2$). The magenta dashed line and blue solid line denote line calculated from equation (6.8) and (6.12) at each solution, respectively. The grey curve represents the boundary of the feasible regions in bi-objective space and the black solid lines are facets obtained by constructing a convex hull based on the current Pareto points z^{A1} and z^{A2} (•).

Decomposition of the search space

Given the line $H_2(w'^1, b^1)$ tangential to the Pareto front at z^1 , the next step is to construct the outer and inner approximations. However, one can observe from Figure 6.5 is that the tangent at z^1 intersects the nonconvex part of the Pareto front and cannot be used to generate a valid outer approximation. Similarly, the facet (z^1, z^{A1})



Figure 6.5: Representation of the line $H_2(w'^1, b^1)$ passing through z^1 with normal vector w'^1 (red solid line), calculated based on equation (6.8). The grey curve represents the boundary of the feasible region in bi-objective space and the black solid lines are the facets obtained by constructing a convex hull based on the current Pareto points z^{A1} , z^{A2} and z^1 . Facet (z^1, z^{A1}) and line $H_2(w'^1, b^1)$ cannot be used to construct approximations of the Pareto front due to nonconvexity.

is below the Pareto front and cannot be used as an inner approximation. To provide valid inner and outer approximations of the Pareto front, we introduce a systematic decomposition of a search region based on the convexity of the Pareto front at the Pareto points identified, such that each Pareto optimal point z^k is supported by a line $H_2(w'^k, b^k)$ in a given space and the collection of supporting lines represents the upper or lower bounds of the Pareto front.

The idea underlying the decomposition of the search space is to divide the objective space into a number of sub-regions whenever there exist Pareto points that are exterior to the outer approximation as defined in the SD algorithm, i.e., the polyhedral set given by the supporting lines that have been derived so far.

Definition 15. Subspace – A l^{th} subspace $C^{l}(\boldsymbol{z^{i}}, \boldsymbol{z^{j}})$ is a subset of bi-objective space defined by the two nondominated points $\boldsymbol{z^{i}}$ and $\boldsymbol{z^{j}}$, where $z_{1}^{i} < z_{1}^{j}$, without loss of generality. It consists of the rectangle whose diagonal is the line segment $[\boldsymbol{z^{i}}, \boldsymbol{z^{j}}]$ such that all Pareto points in the interior of the search space satisfy $z_{1}^{i} \leq z_{1} \leq z_{1}^{j}$ and $z_{2}^{j} \leq z_{2} \leq z_{2}^{i}$, where z_{1} and z_{2} are elements of $\boldsymbol{z} \in \Psi^{*}$.

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Definition 16. Extreme points of a subspace – Points z^i and z^j in subspace $C^l(z^i, z^j)$ are referred to as extreme points of the subspace.

Let $C^0(z^{A2}, z^{A1})$ denote an initial search space defined by the anchor points z^{A1} and z^{A2} , as can be seen in Figure 6.6. The initial set of Pareto points is $Z_E = \{z^{A1}, z^{A2}\}$. It is initially assumed that the Pareto front in C^0 is convex. By solving subproblem (mNBI β), a new nondominated point z^1 is obtained that enables one to define the corresponding supporting line $H_2(w'^1, b^1)$ and its half-plane $HS_2(w'^1, b^1)$. Note that in Figure 6.6, z^1 is located on the concave (or nonconvex) part of the Pareto front. The current objective space is then investigated to determine if the convexity assumption can be justified based on the current set of Pareto points. For this purpose, we make use of the supporting hyperplane theorem described in Theorem 6.4.1, a proof of which can be found in Luenberger (1997).

Theorem 6.4.1. Supporting hyperplane theorem – Suppose $C \subseteq \mathbb{R}^m$ is a nonempty convex set and z_0 is a point on its boundary bd(C), i.e., $z_0 \in bd(C)$. Then, there exists a hyperplane $\{ \boldsymbol{z} \mid \boldsymbol{w'}^\top \boldsymbol{z} = \boldsymbol{w'}^\top \boldsymbol{z}_0 \}$ such that $\boldsymbol{w'}^\top \boldsymbol{z} \geq \boldsymbol{w'}^\top \boldsymbol{z}_0$ for all $\boldsymbol{z} \in C$, $\boldsymbol{z} \neq 0$.

Corollary 6.4.1.1. Suppose convex set $V \subseteq C \subseteq \mathbb{R}^m$, where m = 2, is a polyhedron defined by a finite number of half-planes and lines $V = \{ \boldsymbol{z} \mid \boldsymbol{w'^k}^\top \boldsymbol{z} \ge \boldsymbol{w'^k}^\top \boldsymbol{z^k}, \ k = 1, ..., n \}$. If each point $\boldsymbol{z^k}$ is supported by line $H_2(\boldsymbol{w'^k}, b^k)$ where $b^k = \boldsymbol{w'^k}^\top \boldsymbol{z^k}$, then every point $\boldsymbol{z} \in V$ must satisfy $\boldsymbol{w'^k}^\top \boldsymbol{z} \ge b^k$ for all k = 1, ..., n.

It can be observed in Figure 6.6(a) that the nondominated point z^{A1} does not satisfy $w^{1^{\top}}z^{A1} \ge b^1$, implying that z^{A1} is located on a nonconvex part of the Pareto front in the subspace of C^0 . On the other hand, the nondominated point z^{A2} satisfies $w^{1^{\top}}z^{A2} \ge b^1$ so that the hyperplane can be assumed to be supporting in the subspace $C^1(z^{A2}, z^1)$. Subsequently, the search region is decomposed, as shown in Figure 6.6(b), into $C^1(z^{A2}, z^1)$, with a convexity assumption on the Pareto front in



Figure 6.6: Schematic illustrating the procedure for the decomposition of the biobjective space: (a) An initial objective space is characterised by subspace $C^0(z^{A2}, z^{A1})$ (black rectangular box), assumed to contain a convex Pareto front. An new nondominated point z^1 is found by solving problem (mNBI β) for $\Phi^1\beta^1$; (b) the initial objective space is decomposed into subspaces $C^1(z^{A2}, z^1)$ and $C^2(z^1, z^{A1})$ that are assumed to contain convex and nonconvex Pareto fronts, respectively. The inner approximation of the Pareto front in C^1 is the facet (z^{A2}, z^1) (black dashed line) and the outer approximation is given by the segment (red solid line) connecting z^1 to the $f_1 = 0$ line and by the $f_1 = 0$ line. For subspace C^2 , the inner approximation is given by the segment (red solid line) the form $f_1 = 1$ line while the outer approximation is given by the facet (z^1, z^{A1}) ; (c) the approximation of the Pareto front is improved by adding z^2 and the subspace C^2 is not decomposed since $w'^{2T}z \leq b^2$ holds for all $z \in Z_E^{C^2}$

this subspace, and $C^2(z^1, z^{A1})$, with a nonconvexity assumption. For any subspaces that fall under a convexity assumption, the inner approximation and outer approximation are obtained as described in Section 6.3.1, following the SD algorithm. By contrast, for subspaces that fall under a nonconvexity assumption, the inner approximation is constructed using the supporting lines of the nondominated points in the subspace, $IPS = \{z \mid W'^{\top}z \geq B'\}$, where W' is a matrix with each column corresponding to a particular normal vector w'^k and B' is a column vector where the k-th element is obtained by the vector product between the transpose of the k-th column of W' and corresponding nondominated solution z^k . The outer approximation is constructed as the convex hull of the nondominated points in the subspace. The impact of adding a further Pareto point in subspace C^2 is shown in Figure 6.6(c) and does not require further decomposition of this subspace.

The decomposition strategy can be generalised as follows:

- Consider a search subspace C^l(zⁱ, z^j) in which the Pareto front is assumed to be convex, an associated set of known nondominated points, Z_E^{C^l}, and a newly identified nondominated point z^{*} within the subspace, with the corresponding line H₂(w'^{*}, b^{*}), where b^{*} = w'^{*⊤}z^{*}. If w'^{*⊤}z ≥ b^{*} holds for all z ∈ Z_E^{C^l}, add z^{*} to Z_E^{C^l} and retain the convexity assumption on subspace C^l.
- Consider a search subspace C^l(zⁱ, z^j) in which the Pareto front is assumed to be nonconvex, an associated set of known nondominated points, Z_E^{C^l}, and a newly identified nondominated point z^{*} within the subspace, with corresponding line H₂(w'^{*}, b^{*}), where b^{*} = w'^{*⊤}z^{*}. If w'^{*⊤}z ≤ b^{*} holds for all z ∈ Z_E^{C^l}, add z^{*} to Z_E^{C^l} and retain the nonconvexity assumption on subspace C^l.
- 3. If the conditions in 1 and 2 are violated, then partition subspace C^l into two or more subspaces by investigating all nondominated points, z ∈ Z_E^{C^l} ∪ {z*}. N^l new subspaces are created based on the supporting hyperplane theorem, such that ⋃_{dc=1}^{N^l} C^{l,dc} = Z_E^{C^l} ∪ {z*} and for each dc = 1,..., N^l, C^{l,dc} must be such that:

$$\hat{\boldsymbol{w}}^{\top} \boldsymbol{z} \geq \hat{\boldsymbol{w}}^{\top} \hat{\boldsymbol{z}} \text{ for all } \boldsymbol{z}, \hat{\boldsymbol{z}} \in C^{l,dc},$$
 (6.13)

or

$$\hat{\boldsymbol{w}}^{\top} \boldsymbol{z} \leq \hat{\boldsymbol{w}}^{\top} \hat{\boldsymbol{z}} \text{ for all } \boldsymbol{z}, \hat{\boldsymbol{z}} \in C^{l,dc}.$$
 (6.14)

where \hat{w} is the vector associated with nondominated point \hat{z} .

The number of subspaces is chosen to be as small as possible while meeting the supporting hyperplane criteria. A convexity (resp. nonconvexity) assumption is made on the Pareto front in a subspace $C^{l,dc}$ if equation (6.13) (resp. equation (6.14)) holds.

6.4.3 Identification of disconnected regions of a Pareto front

One important aspect of the use of the mNBI method combined with the SD algorithm is that the likelihood of finding new Pareto points can be increased by preventing the algorithm converging to a boundary point. However, the mNBI method may not be efficient when a Pareto front consists of many disconnected regions or for the extreme case when a Pareto front consists a finite set of points, i.e., for a purely integer problem. This is because the portion of the objective space that can be explored by the mNBI method is limited by the choice of parameters (\bar{n}, β) . If the search direction defined by these parameters does not lead to any region where as-yet-unknown nondominated points exist, the algorithm will converge to a previously-identified nondominated solution, making it difficult to determine a new search direction. As a result, the algorithm may not identify Pareto points efficiently for some problems, leading to a higher computational cost. For example, a case involving the repeated computation of the same nondominated point is shown in Figure 6.7. For a given subspace defined by $C^3(z^4, z^5)$, the solution of subproblem (mNBI β) for facet normal \bar{n}^6 with reference point $\Phi^6\beta^6$ returns the already-known nondominated point z^4 . As a result, it is possible to discard the reference points belonging to the line segment defined by $\theta z^4 + (1 - \theta) \Phi^6 \beta^6$, $\theta \in [0, 1]$. However, it is not possible to ensure that subsequent explorations will result in the identification of new nondominated points in the absence of a clear criterion for the selection of appropriate mNBI parameters. In fact, as can be seen in Figure 6.8(b), any choice of β such that the reference point lies on the line segment defined by $\theta \Phi^6 \beta^6 + (1-\theta) \Phi^6 \beta'^6$, where $0 < \theta \leq 1$ returns the z^4 . Note that z^6 is obtained by solving an modified mNBI subproblem (mNBI $\bar{n}(a)$), which we will discuss in the remaining part of this section and β'^6 is calculated by using the objective constraints of the NBI subproblem (NBI β) for a given parameter \bar{n}^6 and objective function value, $f = z^6$.

To address this, two subproblems are introduced to fathom regions where no



Figure 6.7: A geometrical illustration of the solution of $(\mathbf{mNBI}\beta)$ subproblem for a disconnected Pareto front. We begin by considering subspace $C^3(z^4, z^5)$ (black rectangular box). The solution of the $(\mathbf{mNBI}\beta)$ subproblem for facet $F_S(z^4, z^5)$ and β^6 lies at z^4 . The blue shaded region represents the area where $\Phi^6\beta^6 + t^*\bar{n}^6 \ge z^4 - f^{id}$.



Figure 6.8: A geometrical illustration of the SDNBI procedure for a disconnected Pareto front when using an alternative subproblem $(\mathbf{mNBI}\bar{n}(a))$. (a) A new Pareto point z^6 is generated as a solution of $\mathbf{mNBI}\bar{n}(a)$. The red shaded region represents the area where $\Phi^6\beta^6 + t'^*\bar{n}^6 \ge z^6 - f^{id} \cap z_1^6 \ge z_1^4 + \epsilon_z$. The solid red line at z^6 represents an supporting line at the solution. The facet $F_S(z^4, z^6)$ generated by an inner approximation is discarded from the search space in the following iterations. In (b), it illustrates the case that any choice of the reference point between the line segment defined by $\theta z^4 + (1 - \theta) \Phi^6 \beta'^6$ where $0 < \theta \le 1$ produces the same solution z^4 .

Pareto-optimal solutions exist. These are modifications of the original mNBI subproblem. For an arbitrary *p*-th facet denoted by $F_S^p(z^{p1}, z^{p2})$ where $z_1^{p1} < z_1^{p2}$, if the solution of subproblem (mNBI β) for given parameters ($\bar{n}^k, \Phi^k \beta^k$) lies at z^{p1} , then the following subproblem is solved:

$$\begin{array}{l} \max_{\boldsymbol{x}\in X,t} t \\ \text{s.t. } \boldsymbol{\Phi}^{\boldsymbol{k}}\boldsymbol{\beta}^{\boldsymbol{k}} + t\bar{\boldsymbol{n}}^{\boldsymbol{k}} \geq \boldsymbol{f}(\boldsymbol{x}) - \boldsymbol{f}^{\boldsymbol{id}} \\ f_1(\boldsymbol{x}) \geq z_1^{p1} + \epsilon_z \\ \boldsymbol{x}\in \mathbb{R}^n, \ t\in \mathbb{R}, \ \bar{\boldsymbol{n}}^{\boldsymbol{k}}\in \mathbb{R}^m \end{array}$$
(mNBI $\bar{n}(a)$)

where $z^{p1}, z^{p2} \in Z_E$ are nondominated points obtained in previous iterations, \bar{n}^k is an unit normal vector to F_S^p and ϵ_z is a small positive number.

Similarly, for the case when the solution of subproblem (mNBI β) lies at extreme point z^{p2} , the following subproblem is solved:

$$\begin{array}{l} \max_{\boldsymbol{x}\in X,t} t \\ \text{s.t. } \boldsymbol{\Phi}^{\boldsymbol{k}}\boldsymbol{\beta}^{\boldsymbol{k}} + t\bar{\boldsymbol{n}}^{\boldsymbol{k}} \geq \boldsymbol{f}(\boldsymbol{x}) - \boldsymbol{f}^{\boldsymbol{id}} \\ f_1(\boldsymbol{x}) \leq z_1^{p2} - \epsilon_z \\ \boldsymbol{x} \in \mathbb{R}^n, \ t \in \mathbb{R}, \ \bar{\boldsymbol{n}}^{\boldsymbol{k}} \in \mathbb{R}^m \end{array}$$
(mNBI $\bar{n}(b)$)

Theorem 6.4.2. Given two Pareto points z^{p_1} and z^{p_2} , such that $z_1^{p_1} < z_1^{p_2}$, and the facet $F_S^p = (z^{p_1}, z^{p_2})$ with normal vector \bar{n}^k , if (x^*, z^*, t^*) is a solution of subproblem (mNBI $\bar{n}(a)$) and z^* is a nondominated point, then there is no nondominated point $z = (z_1, z_2)^{\top}$ such that $z_1^{p_1} + \epsilon_z < z_1 < z_1^*$. If (x^*, z^*, t^*) is a solution of a subproblem mNBI $\bar{n}(b)$ and z^* is a nondominated point, then there is no nondominated point $z = (z_1, z_2)^{\top}$ such that $z_1^{p_1} + \epsilon_z < z_1 < z_1^*$. If (x^*, z^*, t^*) is a solution of a subproblem $z = (z_1, z_2)^{\top}$ such that $z_1^{p_1} - \epsilon_z$.

Proof. Let z^* be a nondominated point obtained at the solution (x^*, z^*, t^*) of subproblem (mNBI $\bar{n}(a)$) for facet $F_S^p = (z^{p1}, z^{p2})$ as defined in Theorem 6.4.2, with parameters $\beta^k = [\beta_1^k, 1 - \beta_1^k]$, Φ^k and \bar{n}^k . Suppose there exists a nondominated point z' such that $z_1^{p1} < z_1' < z_1^*$. Because z' is nondominated, there must exist a point (x', z', t') that is feasible for subproblem (mNBI β). Then the first inequality of subproblem (mNBI $\bar{n}(a)$) must hold for both (x^*, z^*, t^*) and (x', z', t'):

$$\Phi^k \beta^k + t^* \bar{\boldsymbol{n}}^k \geq \boldsymbol{z}^* - \boldsymbol{f}^{id}$$
(6.15)

$$\Phi^k \beta^k + t' \bar{n}^k \geq z' - f^{id}$$
(6.16)

Furthermore, there must exist β^* and β' with $\beta'_1 > \beta^*_1$ such that the following equalities hold:

$$\Phi^{k}\beta^{*} + t^{*}\bar{\boldsymbol{n}}^{k} = \boldsymbol{z}^{*} - \boldsymbol{f}^{id}$$
(6.17)

$$\Phi^{k}\beta' + t'\bar{n}^{k} = z' - f^{id}$$
(6.18)

By subtracting equation (6.18) from equation (6.17) and rearranging, we find

$$\Phi^{k}(\beta^{*} - \beta') + (t^{*} - t')\bar{n}^{k} = z^{*} - z'$$
(6.19)

where Φ^k is a $m \times m$ matrix given by:

$$\boldsymbol{\Phi}^{\boldsymbol{k}} = \begin{bmatrix} 0 & z_1^{p2} - z_1^{p1} \\ z_2^{p1} - z_2^{p2} & 0 \end{bmatrix}$$
(6.20)

 $ar{m{n}}^{m{k}}$ is the outer-facing normal vector of the facet F_S^p and can be written as:

$$\bar{\boldsymbol{n}}^{\boldsymbol{k}} = -\boldsymbol{\Phi}^{\boldsymbol{k}}\boldsymbol{e} = -\begin{bmatrix} 0 & z_1^{p^2} - z_1^{p^1} \\ z_2^{p^1} - z_2^{p^2} & 0 \end{bmatrix} \begin{bmatrix} 1 \\ 1 \end{bmatrix} = -\begin{bmatrix} z_1^{p^2} - z_1^{p^1} \\ z_2^{p^1} - z_2^{p^2} \end{bmatrix}$$
(6.21)

Therefore, \bar{n}^k is always negative and the non-principal elements of Φ^k are positive. Note that the principal diagonal elements are always zero. The first term of equation (6.19) is expressed as component-wise:

$$\begin{split} \boldsymbol{\Phi}^{\boldsymbol{k}}(\boldsymbol{\beta}^{*}-\boldsymbol{\beta}^{\boldsymbol{\prime}}) &= \begin{bmatrix} 0 & z_{1}^{p2}-z_{1}^{p1} \\ z_{2}^{p1}-z_{2}^{p2} & 0 \end{bmatrix} \begin{bmatrix} \beta_{1}^{*}-\beta_{1}^{\prime} \\ (1-\beta_{1}^{*})-(1-\beta_{1}^{\prime}) \end{bmatrix} \\ &= \begin{bmatrix} (z_{1}^{p2}-z_{1}^{p1})(\beta_{1}^{*}-\beta_{1}^{\prime}) \\ (z_{2}^{p1}-z_{2}^{p2})(\beta_{1}^{\prime}-\beta_{1}^{*}) \end{bmatrix} \end{split}$$
(6.22)

where $\beta_1^* - \beta_1'$ is strictly negative and $\beta_1' - \beta_1^*$ is strictly positive.

Since t^* is a maximum value obtained as a solution of the problem (mNBI $\bar{n}(a)$), the strict inequality relation $t^* > t$ holds for all other feasible t. This means $(t^* - t')\bar{n}^k$ is always negative, while the first row of $\Phi^k(\beta^* - \beta')$ is strictly negative and the second element is strictly positive. Apparent from the first row of the resulting matrix in equation (6.19), where the element in LHS is always negative value, the first element of RHS must be negative value, meaning that it holds $z_1^* < z_1'$. However, this contradicts the assumption that $z_1' < z_1^*$. Therefore z' cannot be a nondominated point and there exist no Pareto point z such that $z_1^{p1} < z_1 < z_1^*$.

Given a Pareto front, whenever the solution of subproblem (mNBI β) for the current facet $F_S^p = [z^{p1}, z^{p2}]$ generates a previously-identified nondominated point, the facet is further explored by solving (mNBI $\bar{n}(a)$) or (mNBI $\bar{n}(b)$), so that the empty part of the subspace can be excluded from the search space. If the solution of (mNBI $\bar{n}(a)$) or (mNBI $\bar{n}(b)$) lies at one of the Pareto points obtained in a previous iteration, the entire facet represented by $F_S^p = [z^{p1}, z^{p2}]$ is discarded from the search space in a subsequent iteration.

6.4.4 Outline of the methodology

In this section, we provide the pseudocode for the proposed SDNBI algorithm for the solution of BOO problems in Algorithm 7. The algorithm is built on the theory developed in previous sections. The user specifies a convergence tolerance, ϵ , as input to the algorithm. In Step 3, key quantities are initialised: the set of known Pareto points Z_E and the inner and outer approximations, IPS and OPS, respectively, are all empty. The approximation error d_{max} , the iteration counter k and the subspace counter l are also initialised. The two anchor points, z^{A1} and z^{A2} with $z_1^{A2} < z_1^{A1}$, are also identified. This enables the definition of the first subspace $C^0 = (z^{A2}, z^{A1})$, which is assumed to be convex as indicated by setting the Boolean function $Is_Convex(C^0)$ to TRUE, and of the first facet $F_S^0 = [z^{A2}, z^{A1}]$. There may be Pareto points in the subspace defined by this facet (i.e., C^0) so this facet is considered to be "open" and the Boolean function Is_Open is set to TRUE. The set of subspaces C and the set of facets F are initialised.

The main loop then begins at Step 4. For the first loop the facet is set to F_S^p , i.e., $p^k = 0$. For $k \ge 2$, the next facet and corresponding subspace determined from Steps 25-31, the parameters of subproblem (mNBI β) at iteration k is specified in Step 6. Subproblem (mNBI β) is then solved in Step 7, yielding (\boldsymbol{z}^*, t^*) . In Steps 8 to 14, the fathoming of facet $F_S^{p^k}$ is considered as described in Section 6.4.3. Specifically, if \boldsymbol{z}^* is a member of \boldsymbol{Z}_E , i.e., a previously-determined Pareto point, subproblem (mNBI $\bar{n}(a)$) or (mNBI $\bar{n}(b)$) is solved for a new (\boldsymbol{z}^*, t^*) . If the resulting vector \boldsymbol{z}^* is once more a known Pareto point, the entire facet is discarded, i.e., $Is_-Open(F_S^{p^k})$ is set to FALSE.

If a new Pareto point has been found, the convexity property of the Pareto front in the current subspace C^{l^k} is examined in Steps 16-23 and new subspaces are created as required, based on Section 6.4.2. Specifically, if all the Pareto points in the subspace, $z \in Z_E^{C^{l^k}}$, are found lie on the half-plane consistent with the convexity / nonconvexity assumption on C^{l^k} , then z^* can simply be added to the subspace and the set of facets updated to take this new point into account. The convexity / nonconvexity of C^{l^k} is unchanged. If on the contrary, there exists at least one point in the other half-plane, the set of Pareto points $Z_E^{C^{l^k}}$ by z^* and the set of Pareto is partitioned to create subspaces that only contain Pareto points that lie in the same half-space. The number of subspaces is updated as is the set of facets.

The iteration counter is then increased. The approximations IPS and OPS are updated in Step 26 and if there are no remain facets to explore, the algorithm terminates regardless the stopping tolerance has been satisfied. The next facet $F_S^{p^k} = [z^{p_2^k}, z^{p_1^k}]$ to be explored is identified in Steps 27 and 31 as the open facet at which the largest approximation error is observed. The corresponding subspace is also identified, defined as the subspace $C^{l^k} \in C$ such that $z^{p_2^k}, z^{p_1^k} \in C^{l^k}$. and the algorithm terminates when the maximum approximation error is less than ϵ .

Alg	orithm 7 SDNBI Algorithm for bi-objective optimisation
1:	procedure SDNBI ALGORITHM
2:	Inputs:
	Set a quality threshold, ϵ .
3:	Initialize:
	$\mathbf{Z}_{E} = IPS = OPS = \emptyset; d_{max} \leftarrow \infty, \ k \leftarrow 1, dc \leftarrow 0, N_{F} \leftarrow 1$
	Find anchor points $\boldsymbol{z^{A1}}$ and $\boldsymbol{z^{A2}}$ with $z_1^{A2} < z_1^{A1}$
	Define an initial search region, $C^0(\boldsymbol{z^{A2}}, \boldsymbol{z^{A1}})$, set
	$Is_Convex(C^0) = \texttt{TRUE} \text{ and } \mathcal{C} = \{C^0\}$
	Define facet $F_S^0 = [\mathbf{z}^{A2}, \mathbf{z}^{A1}]$, set $Is_Open(F_S^0) = TRUE$ and
	$\mathcal{F} = \{F_S^0\}$
4:	Set $Z_E = \{ z^{A1}, z^{A2} \}$, set $p^k = 0$.
5:	while $d_{max} \ge \epsilon \ \mathbf{do}$
6:	Set the next normal $ar{m{n}}^{m{k}}$ to be the outer normal to $F_S^{p^k}$ and set the reference
	point $\Phi^{k} \beta^{k}$ by choosing β^{k} to be the midpoint of $F_{S}^{p^{k}}$.
7:	Determine $(\boldsymbol{z^*}, t^*)$ by solving (mNBI β) with $\Phi^{\boldsymbol{k}} \beta^{\boldsymbol{k}}$ and $\bar{\boldsymbol{n}}^{\boldsymbol{k}}$.
8:	if $(oldsymbol{z}^k\in oldsymbol{Z}_E)$ then
9:	Obtain new (z^*, t^*) by solving (mNBI $\overline{n}(a)$) or (mNBI $\overline{n}(b)$)
	with parameters $\Phi^k eta^k$ and $ar{n}^k$.
10:	if ($\boldsymbol{z^*} \in Z_E$) then
11:	Fathom facet $F_S^{p^k}$ by setting $Is_Open(F_S^{p^k}) = FALSE$.
12:	Set $k = k + 1$ and return to step 6.
13:	end if
14:	else
15:	Define the supporting line $H_2(\boldsymbol{w'^k}, b^k) : b^k = \boldsymbol{w'^{k \top} z^*}$ using Equation (6.8)

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16:	$\text{if } (Is_Convex(\boldsymbol{Z_E^{C^{l^k}}}) == \texttt{TRUE} \text{ and } \boldsymbol{w'^k}^\top \boldsymbol{z} \geq b^k \text{ for all } \boldsymbol{z} \in \boldsymbol{Z_E^{C^{l^k}}})$
	or $(Is_Convex(oldsymbol{Z_E^{Cl^k}}) ==$ FALSE and $oldsymbol{w'^k}^{ op}oldsymbol{z} \leq b^k$ for all $oldsymbol{z} \in oldsymbol{Z_E^{Cl^k}}$) then
17:	Add $m{z}^*$ to $m{Z}_{m{E}}^{C^{l^k}}$ and replace $F_S^{p^k}\in \mathcal{F}$ by two new facets $F_S^{p_1^k}$ and $F_S^{p_2^k}$ in
	which z^* is an extreme point. Set $Is_Open(F_S^{p_1^k}) = Is_Open(F_S^{p_2^k}) = TRUE$.
18:	else
19:	Update $oldsymbol{Z}_E^{C^l} = oldsymbol{Z}_E^{{C^l}^\kappa} \cup \{oldsymbol{z}^*\}$
20:	Decompose current subspace C^{l^k} into two or more subspaces by
	investigating all nondominated points, $oldsymbol{z} \in oldsymbol{Z}_{oldsymbol{E}}^{{Cl}^k}$ and set
	corresponding <i>Is_Convex</i> .
21:	Update facets for the subspaces that contain z^*
22:	Set $dc = dc + N^l$, where N^l is the number of new subspaces created.
23:	end if
24:	end if
25:	Set $k = k + 1$
26:	For all subspaces $C^l \in \mathcal{C}$, $l = 1,, dc$, construct IPS and OPS .
27:	if $(Is_OpenF_S^p = \text{FLASE}, \forall p)$ then
28:	Break
29:	end if
30:	Compute the approximation error $d_{error,p}$ between <i>IPS</i> and <i>OPS</i>
	for each facet F_S^p such that $Is_Open(F_S^p) = \text{TRUE}, p = 1, \dots, N_F$.
31:	Select the facet $F_{S}^{p^{k}}$ that presents the largest error, i.e.,
	$p^k = \operatorname{argmax}(d_{error,p})$, and the corresponding subspace C^{l^k} .
	$p=1,,N_F$
~~	Set $d_{max} = d_{error,p^k}$.
32:	ena while
33:	ena proceaure

6.5 Performance of the algorithm

In this section, the numerical experiments undertaken to evaluate the performance of the proposed algorithm are discussed and the behaviour of the algorithm on test cases is compared with the SD algorithm and mNBI method.

6.5.1 Test functions

To assess the performance of the three algorithms studied, five well-known problems are selected from the MOP1 (Van Veldhuizen & Lamont, 1999), ZDT (Zitzler et al., 2000), SCH (Schaffer, 1984), and TNK (Tanaka et al., 1995) test suites developed for testing evolutionary MOO algorithms. The test problems are chosen to vary in complexity in terms of problem size and numerical difficulty with convex, nonconvex and disconnected Pareto fronts. The test problems are summarised in Table 6.1 where the number of decision variables n, their bounds, and the nature of the Pareto-optimal front are specified. Problem ZDT5 is a mixed-integer problem and the integer variables are denoted by the vector $\boldsymbol{y} \subseteq \mathbb{N}^{n_2}$, to distinguish them from the continuous variable vector, denoted by variables v_i , $i = 1, \ldots, 11$ and g in this problem.

Before formulating the scalarised problems (WSPw) and (mNBI β), each objective function is normalised with respect to the limits of objective space, i.e., the ideal and nadir point, to avoid generating any biased search directions towards particular objectives. Note that the mNBI method has been proven to be independent of the relative scales of the objective functions (Das & Dennis, 1998), but the normalisation is applied to all method in order to make a fair comparison. The m-dimensional objective vector of normalised functions is denoted by \hat{f} and each component is defined as follows:

$$\hat{f}_{i}(\boldsymbol{x}) = \frac{f_{i}(\boldsymbol{x}) - f_{i}^{\text{nd}}(\boldsymbol{x})}{f_{i}^{\text{id}}(\boldsymbol{x}) - f_{i}^{\text{nd}}(\boldsymbol{x})}, \ i=1,\cdots,m$$
(6.23)

6.5.2 Performance metrics

The main goal when solving MOO problems is to generate, in the minimum time possible, a diverse set of nondominated points that are evenly distributed along the Pareto front. For nonconvex problems, there is the added challenge of ensuring that the points found are as close as possible to the true Pareto front. Based on these considerations, we use following performance metrics for evaluating the quality of the solution set obtained by each algorithm.

- 1. The number of unique non-dominated solutions (N_{unq}): N_{unq} denotes cardinality of the set of unique Pareto points obtained in a given run. This performance indicator is a measure of the diversity of the solution set.
- 2. Distribution metric (DM): The distribution metric was suggested by (Zheng et al., 2017) to capture the spread of the solution set over the Pareto front approximation and the extent of the true Pareto front covered by the nondom-inated points. This metric addresses some of the deficiencies of the metrics of Schott (1995) and Wu & Azarm (2001). Smaller values of the DM indicate better distributed solution sets. The DM is given by:

$$DM(\mathbf{Z}_{E}) = \frac{1}{|\mathbf{Z}_{E}|} \sum_{i=1}^{m} \left(\frac{\sigma_{i}}{\tau_{i}}\right) \left(\frac{\left|f_{i}^{id} - f_{i}^{nd}\right|}{R_{i}}\right)$$
$$\sigma_{i} = \frac{1}{|\mathbf{Z}_{E}| - 2} \sum_{e=1}^{|\mathbf{Z}_{E}| - 1} \left(d_{e}^{i} - \overline{d^{i}}\right)^{2}, \ \tau_{i} = \frac{1}{|\mathbf{Z}_{E}| - 1} \sum_{e=1}^{|\mathbf{Z}_{E}| - 1} d_{e}^{i}, \ i = 1, \dots, m,$$
$$R_{i} = \max_{\mathbf{x} \in \mathbf{X}_{E}} f_{i}(\mathbf{x}) - \min_{\mathbf{x} \in \mathbf{X}_{E}} f_{i}(\mathbf{x}), \ i = 1, \dots, m,$$
(6.24)

ZDT5	ZDT3	TNK	SCH2	MOP1	Name
$ \min_{\boldsymbol{y}} f_1(\boldsymbol{y}) = 1 + y_1 $ $ \min_{\boldsymbol{y}} f_2(\boldsymbol{y}) = g \cdot h $ s.t. $g = \sum_{i=2}^{11} v(y_i), h = \frac{1}{1+y_1} $ $ v_i = \begin{cases} 2 + y_i & \text{if } y_i < 5 \\ 1 & \text{if } y_i < 5 \\ 1 & \text{if } y_i \in \end{cases}, i = 2, \dots, 11 $ $ y_1 \in \{0, 30\}, y_i \in \{0, 5\}, i = 2, \dots, 11. $	$\min_{x} f_{1}(x) = x_{1}$ $\min_{x} f_{2}(x) = g \cdot h$ s.t. $g = 1 + \frac{9}{n-1} \sum_{i=2}^{11} x_{i}$ $h = 1 - \sqrt{x_{1}/g} - (x_{1}/g) \sin(10\pi x_{1})$ $0 \le x_{i} \le 1, \ i = 1, \dots, 30$	$\min_{\mathbf{x}} f_1(\mathbf{x}) = x_1$ $\min_{\mathbf{x}} f_2(\mathbf{x}) = x_2$ s.t. $x_1^2 + x_2^2 - 1 - 0.1 \cos\left(16 \arctan \frac{x_1}{x_2}\right) \ge 0$ $(x_1 - 0.5)^2 + (x_2 - 0.5)^2 \le 0.5$ $0 \le x_1 \le \pi, \ 0 \le x_2 \le \pi$	$\min_{\boldsymbol{x}} f_1(\boldsymbol{x}) = (x_1 + x_2 - 7.5)^2 + \frac{(x_2 - x_1 + 3)^2}{4}$ $\min_{\boldsymbol{x}} f_2(\boldsymbol{x}) = \frac{(x_1 - 1)^2}{4} + \frac{(x_2 - 4)^2}{2}$ s.t $\frac{(x_1 - 2)^3}{x_1 + x_2} + \frac{x_2 - 2.5 \le 0}{8(x_2 - x_1 + 0.65)^2 - 3.85 \le 0}$ $0 \le x_1 \le 5, \ 0 \le x_2 \le 3$	$ \min_{\boldsymbol{x}} f_1(\boldsymbol{x}) = \frac{x_1^2 + x_2^2 + 1}{x_1^2 + x_2^2 + 1} \\ \min_{\boldsymbol{x}} f_2(\boldsymbol{x}) = x_1^2 + 3x_2^2 + 4 \\ \text{s.t} -3 \le x_1 \le 3, \ -3 \le x_2 \le 3 $	Formulation
24	32	Ν	Ν	2	Number of variables, n
Integer; convex when integrality is relaxed	Nonconvex, disconnected	Nonconvex, continuous	Nonconvex, disconnected	Convex, continuous	Type of Pareto front
Zitzler et al. (2000)	Zitzler et al. (2000)	Tanaka et al. (1995)	Schaffer (1984)	Van Veldhuizen & Lamont (1999)	Reference

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Table 6.1: Two-objective test problems from the literature used in this work

where $|\mathbf{Z}_{E}|$ is the number of nondominated points, d_{e}^{i} is the absolute difference between the values of the i^{th} objective at two adjacent nondominated points in objective space, $\overline{d^{i}}$ is an average value of d_{e}^{i} over e, \mathbf{z}^{e} and \mathbf{z}^{e+1} , σ_{i} and ν_{i} are the standard deviation and mean of d_{e}^{i} over all $e = 1, \ldots, |\mathbf{Z}_{E}|$ for the i^{th} objective, σ_{i}/τ_{i} is the coefficient of variance for the i^{th} objective, R_{i} is the difference between the maximum and minimum values of the i^{th} objectives over all points in \mathbf{Z}_{E} and \mathbf{X}_{E} is the set of all Pareto solutions that have been identified.

- 3. Hypervolume (HV): The hypervolume (Zitzler et al., 2003) of a set of nondominated solutions is the volume of the *m*-dimensional region in objective space enclosed by the nondominated solutions obtained and a reference point, $f_{ref}, i = 1, ..., m$. The larger HV, the better the solution set in terms of convergence to the true Pareto front and/or in terms of diversity of the solutions. In the evaluation of the hypervolume in this work, the reference point is chosen by selecting the worst (largest) value of each objective across all nondominated solutions generated by the three algorithms considered.
- 4. CPU time: The computational time required to obtain the approximation of the Pareto frontier is a critical aspect for computationally-expensive MOO problems. Both the total CPU time to generate all solutions ($t_{cpu,t}$) and the average CPU time taken to generate one nondominated point ($t_{cpu,a}$), defined as $t_{cpu,t}/N_{ung}$ are reported.

6.5.3 Implementation overview

All algorithms are implemented in Matlab 2018a using the same common subfunctions. Each subproblem derived from the scalarisation method is solved through the GAMS modelling environment interfaced with CONOPT (Drud, 1994) for nonlinear programs and DICOPT (Grossmann et al., 2002) for the mixed-integer program. Both are local solvers. All runs are performed on single Intel(R) Xeon(R) Gold 5122 CPU @ 3.60GHz processor with 384 GB of RAM.

To increase the likelihood of identifying globally optimal Pareto points, an multistart approach (Pál, 2013) is adopted in the solution of the subproblems. The multiple starting points (N_{sobol}) are generated via a Sobol' sequence (Sobol' et al., 2011) to ensure their diversity in the space of design variables x. For the SD algorithm and mNBI method, the stopping criterion is defined as a fixed number of iterations $N_{iter,fix}$, selected based on the number of iterations taken for SDNBI to reach a predefined error tolerance for each test problem. This is because, although the SD algorithm benefits from a stopping criterion based on a convergence tolerance, it tends to terminate early as it cannot explore nonconvex regions of the Pareto front. Furthermore the only stopping criterion for the mNBI algorithm is related to the computational effort – it is not possible to estimate the quality of the approximation of the Pareto front generated.

The initial set, C^{ref} , of N_{β} reference points for the mNBI method is chosen such that consecutive reference points $\Phi \beta^k$ and $\Phi \beta^{k+1}$ are equally spaced, with a spacing δ . This is expressed as:

$$\beta_2^k = k \times \delta, \ \beta_1^k = \beta_2^k, \ \text{for } k = 1, ..., N_\beta, \delta = 1/(N_\beta + 1).$$
 (6.25)

Once the parameters in the initial set have been enumerated by the algorithm, the next β to be chosen, i.e., $\beta_1^{N_{\beta}+1}$ is determined by taking the midpoint between two adjacent β vectors used in previous iterations of the algorithm. As previously mentioned, the values of the parameter β for the SDNBI algorithm are chosen as facet midpoints, i.e., $\beta^{k} = [0.5, 0.5]^{\top}$. All other parameters used in the numerical tests are specified in Table 6.2.

Parameter	MOP1	SCH2	TNK	ZDT3	ZDT5
N _{sobol}	20	20	20	50	30
ϵ in SDNBI	0.001	0.001	0.0015	0.005	0.005
$N_{iter,fix}$	33	27	59	36	40
N_{eta}	10	10	15	10	10
f^{id}	[7.251, 0.5]	[7.251, 0.5]	[0.0416, 0.0416]	[0, -0.7733]	[0, 0.3226]
f^{nd}	[18.5, 3.045]	[18.5, 3.045]	[1.0384, 1.0384]	[0.8518, 1]	[31, 10]

 Table 6.2:
 Algorithmic parameters used in the test problems

Table 6.3: Values of the relevant performance metrics for the best-known Pareto fronts of the test problems

Quality Metrics	MOP1	SCH2	TNK	ZDT3	ZDT5
N _{finite}	100	200	301	100	100
N_{unq}	100	153	200	67	31
HV (10^{-2})	92.96	63.78	30.82	51.46	89.57
DM	0.0157	0.0389	0.0238	0.0455	0.0944

6.6 Results and discussion

In this section, we present the relative performance of all algorithms: SD, mNBI and SDNBI. The "true" Pareto front and the boundary of the feasible region are generated by solving (NBI β) for MOP1, SCH2, TNK, and ZDT3 and (mNBI β) for ZDT5 using exhaustive enumeration of a finite set (N_{finite}) of reference points $\Phi\beta$ in order to provide a benchmark for the quality of the solutions produced by each algorithm. The results of these calculations are denoted as the best-known approximations of the true Pareto fronts and used for graphical comparison. The values of relevant metrics for the best-known Pareto front obtained for each test problem are shown in Table 6.3. Graphical representations of the Pareto fronts and boundary points in bi-objective space are given in Figure 6.9.

6.6.1 Test problem MOP1

The results generated by applying the SD, mNBI, and SDNBI algorithms and the relative performance of the algorithms are summarised in Tables 6.4-6.8. The algorithms are run for 33 iterations, corresponding to the convergence of the SDNBI

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Figure 6.9: Best-known Pareto front (black symbols •) and boundary points (grey symbols •) of the feasible region in bi-objective space for the test functions: (a) MOP1, (b) SCH2, (c) TNK, (d) ZDT3, and (e) ZDT5 obtained by solving problem (NBI β) for many reference points $\Phi\beta$.

algorithm with the chosen value of ϵ . For test problem MOP1, all three algorithms show a similar performance in terms of HV and N_{unq} , as can be seen in Table 6.4. This is attributed to the convexity of the Pareto front that allows the three algorithms to generate a new nondominated point at every iteration, resulting in an equal number of Pareto points at termination. While the SD algorithm is marginally better in terms of HV, the SDNBI algorithm yields the lowest DM, indicating better-distributed solutions along the Pareto front. This can be observed in Figure 6.10, in which the approximate Pareto front at the $33^{\rm rd}$ iteration is shown. This better performance in DM is mainly due to the fact that in the SDNBI algorithm, the next search direction is chosen by taking into account both a spacing and an approximation error: the spacing between two adjacent Pareto points is used to set the parameter β as the midpoint of a facet and the facet itself is chosen based on the distance between the inner and outer approximation, which in turn determines the value of the parameters \bar{n} and Φ , in order to minimize the error. By contrast, in the mNBI and SD

Table 6.4:	Performance	metrics	for test	problem	MOP1	using	the SD,	mNBI	and	SDNBI
algorithms	. The fixed nu	umber of	iteratio	ons is N_{ite}	$e_{r,fix} =$	33.				

Quality Metrics	SD	mNBI	SDNBI
N _{unq}	33	33	33
HV (10^{-2})	92.57	92.54	92.45
DM	0.0586	0.0534	0.0478
$t_{cpu,a}$ (s)	15.05	13.78	15.12
$t_{cpu,t}$ (s)	$4.96{ imes}10^2$	$4.54{ imes}10^2$	$4.94{ imes}10^2$

algorithms, either spacing or error is considered, but not both.

Although the mNBI algorithm outperforms the SDNBI in terms of HV, it is important to note that the accuracy of the mNBI-generated approximation depends highly on the initial set of β values chosen. Yet, the number of β values required in the initial set and the number of additional values required to achieve a particular quality of solution set is unknown and there is no systematic method for determining an appropriate number. This is reflected in Figure 6.11(a) and (b) where the HV and DM values for the mNBI method exhibit the lowest initial performance. The SD and SDNBI algorithm, on the other hand, achieve high HV and low DM values that are close to the reference values (92.69 for HV and 0.0157 for DM) in few iterations, most likely because the scalarisation parameters are chosen to maximise the accuracy of the approximation.

The computational cost of generating Pareto points comes at a relatively higher price for SD and SDNBI (9.2% and 9.7% higher $t_{cpu,t}$ value, cf Table 6.4 and Figure 6.11(d) and (e)). The higher computational time is mainly associated with the time taken for convex hull generation and linear optimisation runs for the calculation of the error between the inner and outer approximations of each facet.

6.6.2 Test problem SCH2

Test problem SCH2 is much more challenging than MOP1 because the Pareto-optimal set consists of two disconnected regions, as shown in Figure 6.12. The first consists


Figure 6.10: Pareto points generated by (a) SD (\times), (b) mNBI (\triangle), and (c) SDNBI (\circ) for test problem MOP1. The best-known Pareto front is shown in grey.



Figure 6.11: Performance metrics as a function of iteration number for the application of the SD algorithm ($-\times$ -), mNBI algorithm ($-\infty$ -), and SDNBI algorithm ($-\infty$ -) to MOP1 for 33 iterations (a) Scaled hypervolume, HV, (b) Scaled distribution metric, DM, (c) Number of unique Pareto points, N_{unq} , (d) CPU time spent per iteration in seconds, $t_{cpu,a}$, (e) overall CPU time in seconds, $t_{cpu,t}$

of a single point and the second is a large continuous, nonconvex region. There is a large gap between these two regions.

The desired approximation quality is achieved with the SDNBI algorithm in 27 iterations. As shown in Table 6.5, the highest value of HV and the lowest value of DM are achieved when using SDNBI, indicating that the nondominated points generated by SDNBI are the closest approximation to the best-known Pareto front and offer a better distribution. This can also be observed by comparing the three panels in Figure 6.12. It can further be seen in the figure that the points identified by SD algorithm lie only on the convex part of the true Pareto front, as is expected, resulting in the lowest value of N_{unq} , HV and the highest value of DM metrics. In view of this, subsequent discussion is focused on comparing the mNBI and SDNBI algorithms.

The overall performance of the mNBI algorithm is similar to that of SDNBI in terms of HV and DM, although the mNBI algorithm trails SDNBI in early iterations (see Figure 6.13(a) and (b)).

The better overall quality of the solution set obtained with SDNBI arises in part as a result of recognising the presence of a discontinuity in the Pareto front. Once the corresponding facet has been fathomed, this makes it possible to generate a new Pareto point at every subsequent iteration. For example, the disconnected region of the Pareto front between $0 \le \hat{f}_1 \le 0.07$ (see Figure 6.12) is removed from the search space at the 8th iteration by solving an alternative SDNBI subproblem (mNBI $\bar{n}(b)$). This event is also observed as a kink in the plot of N_{unq} as a function of iteration number for the SDNBI algorithm (Figure 6.13(c)). Fewer points are identified by the mNBI algorithm within the fixed number of iterations. This is mainly because at several iterations, the solution of the mNBI subproblem fails to results in new Pareto points as searching takes place along the large disconnected region. In fact, this region is repeatedly explored during the mNBI search procedure as iterations proceed. This algorithmic behaviour is illustrated in Figure 6.13(c), where a lower

Table 6.5:	Performance	metrics	for test	problem	SCH2	using	the SD	, mNBI	and	SDNBI
algorithms.	The fixed nu	umber of	iteratio	ons is N_{ite}	$e_{r.fix} =$	27.				

Quality Metrics	SD	mNBI	SDNBI
N _{unq}	26	25	26
HV (10^{-2})	53.09	62.70	62.94
DM	0.2512	0.0998	0.0910
$t_{cpu,a}$ (s)	9.35	9.46	9.41
$t_{cpu,t}$ (s)	2.43×10^{2}	2.36×10^2	2.44×10^{2}

value of N_{unq} is observed with the mNBI algorithm than with the SDNBI algorithm after the 20th iteration.

Finally, all three algorithms exhibit a similar performance in terms of CPU time per iteration and overall, as seen in Table 6.5 and in Figure 6.13(d) and (e).

6.6.3 Test problems TNK and ZDT3

Similar trends are observed for problems TNK and ZDT3 in which the nondominated sets comprise two disconnected regions for TNK and four for ZDT3, as shown in Figure 6.9(c) and (d).

A key challenge in solving these two problems is to identify a set of parameter values so that the Pareto points identified are evenly distributed and, more importantly, so that the solution of optimisation subproblem that result in convergence to an already known Pareto point are avoided.

The results are shown in Tables 6.6 and 6.7, and Figures 6.14-6.17. Note that results with the SD algorithm are not presented in Table 6.6 nor in Figure 6.15 for problem TNK, since there are no convex parts on the Pareto front and solutions other than the anchor points cannot be identified, as can be seen in Figure 6.14(a).

From an examination of the tabulated and graphical results, we can conclude that the SDNBI algorithm outperforms the SD algorithm and the mNBI method in all metrics except for $t_{cpu,t}$ and $t_{cpu,a}$. The higher total computational cost of SDNBI may be explained by the additional calculation procedures required for: the generation



Figure 6.12: Pareto points generated by (a) the SD algorithm (\times), (b) the mNBI algorithm (\triangle), and (c) the SDNBI algorithm (\circ) for test problem SCH2. The best-known Pareto front is shown in grey.



Figure 6.13: Performance metrics as a function of iteration number for the application of the SD ($-\times-$), mNBI ($-\infty-$), and SDNBI ($-\infty-$) algorithms to SCH2 for 27 iterations: (a) Scaled hypervolume, HV, (b) Scaled distribution metric, DM, (c) Number of unique Pareto points, N_{unq} , (d) CPU time spent per iteration in seconds, $t_{cpu,a}$, (e) overall CPU time in seconds, $t_{cpu,t}$

Table 6.6: Performance metrics for test problem TNK using the SD, mNBI and SDNBI algorithms. The fixed number of iterations is $N_{iter,fix} = 59$.

Quality Metrics	mNBI	SDNBI	
N _{unq}	56	59	
HV (10^{-2})	30.34	30.46	
DM	0.0674	0.0629	
$t_{cpu,a}$ (s)	15.88	16.27	
$t_{cpu,t}$ (s)	$8.89{ imes}10^2$	$9.60 imes 10^{2}$	

of inner and outer approximations of the Pareto front; the removal of subspaces that do not contain Pareto points, and the addition of objective constraints inherent in the mNBI subproblem. The SDNBI algorithm, all disconnected regions of the Pareto front are detected and screened out from consideration, with confidence that no Pareto points exist in these areas. By solving the $(mNBI\bar{n}(a))(a)$ subproblems invoked, not only two empty parts are discarded, but new Pareto points are identified. As a result, the SDNBI algorithm succeeds in improving the Pareto approximation efficiently at each iteration, whilst the performance of the mNBI is limited when it encounters a large disconnected region. These aspects are illustrated in Figures 6.15 and 6.17, where the progress of each quality measure can be compared. As can be seen in Figure 6.15(d) the differences $t_{cpu,a}$ between the algorithms is decreasing despite the rapid increase in $t_{cpu,t}$ with SDNBI (see Figure 6.15(e)), since a larger number of Pareto points (N_{unq}) are identified with SDNBI as iterations proceed. In Figure 6.17(d), the lower values in $t_{cpu,a}$ are observed with SDNBI after 25th when it compared to that of mNBI as a result of identifying more Pareto points, suggesting that the SDNBI algorithm may be more computationally efficient when many disconnected regions are involved in a Pareto front.

6.6.4 Test problem ZDT5

The results for test problem ZDT5 obtained with SD, mNBI and SDNBI for 40 iterations are summarised in Table 6.8 and Figures 6.18 and 6.19. For this test problem,



Figure 6.14: Pareto points generated by (a) the SD algorithm (\times), (b) the mNBI method (\triangle), and (c) the SDNBI algorithm (\circ) for test problem TNK. The best-known Pareto front is shown in grey.

Table 6.7: Performance metrics for test problem ZDT3 using the SD, mNBI and SDNBI algorithms. The fixed number of iterations is $N_{iter,fix} = 36$.

Quality Metrics	SD	mNBI	SDNBI
N _{unq}	36	35	36
HV (10^{-2})	48.85	51.12	51.21
DM	0.1356	0.0776	0.0667
$t_{cpu,a}$ (s)	45.06	47.38	46.10
$t_{cpu,t}$ (s)	16.22×10^{2}	16.58×10^{2}	16.59×10^2



Figure 6.15: Performance metrics as a function of iteration number for the application of the mNBI (\rightarrow) and SDNBI (\rightarrow) algorithms to problem TNK for 59 iterations: (a) Scaled hypervolume, HV, (b) Scaled distribution metric, DM, (c) Number of unique Pareto points, N_{unq} , (d) CPU time spent per iteration in seconds, $t_{cpu,a}$, (e) overall CPU time in seconds, $t_{cpu,t}$



Figure 6.16: Pareto points generated by (a) SD algorithm (\times), (b) mNBI (\triangle), and (c) SDNBI (\circ) for the test problem ZDT3



Figure 6.17: Performance metrics as a function of iteration number for the application of the SD algorithm ($-\times$ -), mNBI method ($-\diamond$ -), and SDNBI algorithm ($-\circ$ -) to ZDT3 for 36 iterations: (a) Scaled hypervolume, HV, (b) Scaled distribution metric, DM, (c) Number of unique Pareto points, N_{unq} , (d) CPU time spent per iteration in seconds, $t_{cpu,a}$, (e) overall CPU time in seconds, $t_{cpu,t}$

the true Pareto front is represented as a set of 31 integer Pareto points and the SDNBI identifies the complete set of solutions for a given tolerance, while the mNBI method and the SD algorithm appear to be relatively ineffective in achieving high performance in DM and N_{unq} with the given number of iterations. These results demonstrate the effectiveness of the SDNBI algorithm at finding a diverse and accurate set of Pareto points over the discrete bi-objective domain. As can be observed in Figure 6.19(d), the performance of the SDNBI algorithm in terms of $t_{cpu,a}$ improves as iterations proceed with the lowest computational cost is obtained at iteration 40, i.e., the iteration at which convergence is reached.

In order to investigate how the SDNBI algorithm works after identify the complete Pareto set, the convergence tolerance, ϵ is reduced to 10^{-3} such that each algorithm further iterates the search procedure. As can bee seen in Figure 6.19(d), the $t_{cpu,a}$ values increase rapidly with the SDNBI algorithm. This follows the identification of the complete set of Pareto points (at 40^{th}) and is associated with the solution of the subproblems (mNBI $\bar{n}(a)$) and (mNBI $\bar{n}(b)$) through which facets are removed, but no additional Pareto points are identified. It is notable that all regions where Pareto points do not exist are removed from the search space after 61 iterations (see Figure 6.19), and this allows the SDNBI algorithm to terminate although the pre-defined error tolerance, ϵ is not satisfied. Although not shown here, the SD algorithm iterates the search procedure until there are no remaining facets to be investigated (terminated at 66^{th} iteration).

As can be observed from Figure 6.19(c), by iteration 56, all 31 Pareto points have been identified with the mNBI method. However, β values are enumerated until the 87th iteration at which the possible choice of reference points, $\Phi\beta$ become almost empty. This suggests that the mNBI method can fail to recognise that all Pareto points have been found when a highly disconnected or discrete Pareto front is involved, due to the in the lack of a problem-specific termination criterion.

Quality Metrics	SD	mNBI	SDNBI
N _{unq}	23	23	31
HV (10^{-2})	89.46	89.48	89.57
DM	0.1377	0.1230	0.0944
$t_{cpu,a}$ (s)	73.40	52.86	51.92
$t_{cpu,t}$ (s)	1688.20	1215.88	1609.64

Table 6.8: Performance metrics for test problem ZDT5 using the SD, mNBI and SDNBI algorithms. The fixed number of iterations is $N_{iter, fix} = 40$.



Figure 6.18: Pareto points (*z*) generated by the (a) SD algorithm (×), (b) the mNBI method (\triangle), and (c) the SDNBI algorithm (•) for test problem ZDT5 with $N_{iter,fix} = 40$. The grey points represent the set all Pareto points.



Figure 6.19: Performance metrics as a function of iteration number for the application of the SD ($-\times$ -), mNBI (->-), and SDNBI algorithms (->-) to ZDT5 for up to 64 iterations. The white area corresponds to the 40 iterations consistent with the SDNBI stopping criterion, while the grey shaded area corresponds to additional iterations needed for eliminating all empty area and so terminating the algorithm before reaching the stopping tolerance.

6.7 Conclusions

In this study, we have proposed a novel algorithm, SDNBI, that combines features of the SD and NBI methods with the aim of generating accurate approximations of nonconvex and combinatorial Pareto fronts in bi-objective space. The main improvements in the algorithm are focused on the exploration of nonconvex regions of the Pareto front and on the identification of regions where no further nondominated solutions exists, indicating that parts of the Pareto front are disconnected. Key aspects of the SDNBI algorithm include: 1) the characterisation of inner and outer approximations such that the accuracy of the incumbent set of Pareto points can be assessed during the course of the algorithm, 2) a systematic way of setting scalarisation parameters of the mNBI subproblem, 3) a decomposition of an objective space based on the convexity and nonconvexity of parts of the Pareto front, and 4) the refinement of the scalarised subproblem to avoid unnecessary iterations over disconnected or empty regions of the objective space.

To access the performance of the proposed algorithm, numerical tests were conducted for five bi-objective benchmark problems (MOP1, SCH2, TNK, ZDT3, and ZDT5). The performance of the algorithm in terms of accuracy of the approximation of the Pareto front constructed in disconnected nonconvex objective domains is compared to two MOO approaches: a SD algorithm and the mNBI method. The comparative results have provided clear evidence of the effectiveness of the SDNBI algorithm in terms of generating a more diverse and better-distributed set of Pareto points over disconnected and/or nonconvex Pareto fronts compared to the approximations generated with the mNBI method and the SD algorithm. The solution of test problem ZDT5, in which the true Pareto front comprises 31 discrete points, has highlighted the robustness of the SDNBI algorithm: the whole set of Pareto points was generated with relatively few iterations, leading to high computational efficiency.

Further work will be directed at testing the MOO algorithms on more additional

literature and engineering problems to derive general conclusions of the performance. The implementation of the proposed solution approach in an algorithm involving three or more objective functions also should also be considered in future work.

CHAPTER 7

Application of the SDNBI algorithm to CAM(P)D problem

In Chapter 6, we discussed the development of a robust algorithm (SDNBI) for a class of solving a mixed-integer nonlinear bi-objective optimisation (BOO) problems. We assessed the efficiency of the proposed algorithm through the solution of five benchmark problems. In this chapter, the effectiveness of the proposed algorithm is investigated through CAM(P)D problems in an attempt to assess its applicability and reliability in the context of practical mixed-integer nonlinear problems (MINLPs). We first focus on reformulating into BOO of two MOO CAM(P)D case studies that were introduced in Section 5.4. The resulting formulations are further modified so that they can be adapted to the subproblems of the SDNBI, and then the performance of the algorithm is compared to that of two different methods: the sandwich (SD) algorithm and the modified normal boundary intersection (mNBI) method.

7.1 Problem statement

We first begin by briefly restating the original formulation of the CAM(P)D problems of case study 1 and case study 3 introduced in Chapter 5, modifying the problem statement as appropriate.

7.1.1 Case study 4: Solvent design for chemical absorption of CO₂

A CAMD application for the design of optimal solvents for the chemical absorption of CO_2 is chosen as a first test problem. The formulation is modified based on problem (5.7) such that the number of objective functions and the molecular design space are reduced for BOO. In the design of optimal solvents for CO_2 capture, some of the most important properties are the total heat required to regenerate the solvent and the CO_2 loading capacity. The total heat demand for solvent regeneration can be expressed as the sum of 1) the heat of absorption, which is the enthalpy change when 1 mole of CO_2 is absorbed in the solvent, 2) the sensible heat required to raise the temperature of the CO₂-rich solvent for regeneration, whose value is proportional to the specific heat (or heat capacity), and 3) the stripping heat, which is approximately equal to the heat of vaporisation of water. The CO_2 loading capacity, i.e., the ability to dissolve gaseous CO₂, is also an important consideration. A higher loading capacity is desirable to reduce the solvent circulation rate in a process. As a result, the two objective functions selected are the heat capacity (C_P) , which correlates with the sensible heat requirement and hence to the heat demand for regeneration and relative energy difference (*RED*), which correlates inversely with the amount of CO_2 dissolved in the liquid solvent. Although the heat of absorption and the CO_2 loading could be computed using the SAFT- γ Mie equation of state, as discussed in Chapter 5, we choose the objective functions for the BOO problem from the original objective functions used in Case Study 1 of Chapter 5 as analysis of the Pareto front (5.5.1) has shown it is highly nonconvex in the space of these two objectives. This makes it an ideal problem to test the performance of the SDNBI algorithm, which is the primary objective in this chapter. As in Case Study 1, upper and lower bounds are imposed on the liquid density (ρ) at standard conditions, the normal melting point (T_m) , the normal boiling point (T_b) , the viscosity (μ) and the surface tension

(σ), as shown in Table 5.3. The resulting optimisation problem is as follows:

where $n \in N \subseteq \mathbb{N}^{n_2}$ is a n_2 -dimensional vector of non-negative integer variables that make up the molecular design space, g(n) is a vector of inequality constraints on the physical properties (cf. Table 5.3), h(n) is a vector of equality constraints that include structure-property models that link the structure of the solvent to its thermophysical properties, and $Cn \leq d$ is a set of linear constraints that represent molecular feasibility constraints so that only chemically feasible molecules are considered in the optimisation.

The same set of functional groups as in Case Study 1 in Chapter 4 is used here for property prediction techniques other than the SAFT- γ Mie equation of state (Gani et al., 1991; Hsu et al., 2002; Hukkerikar et al., 2012b). These are: NH₂CH₂, NH₂CH, NH₂C, NHCH₃, NHCH₂, NHCH, NCH₃, NCH₂, CH₃, CH₂, CH, C, and OH. We also further reduce the molecular design space by limiting the maximum number of CH and C groups present in a molecule to avoid the structural complexity caused by the inclusion of many isomers, i.e., $n_{iso}^U = 4$. Finally, from the brute-force evaluation for all feasible combinations of solvent structures, we find that most of the molecules with more than five amine groups or more than 12 functional groups are infeasible with respect to the properties. Therefore, the maximum allowable number of amine groups are reduced to $n_{GA}^U = 4$ and $n_t^U = 12$, respectively, to reduce the computational burden arising from infeasibilities.

7.1.2 Case study 5: Integrated working fluid and ORC process design (CAMPD)

In the second test, we consider the simultaneous design of pure-component working fluids and Organic Rankine Cycle (ORC) processes. The net power output (P_{net}) and the total cost of investment (TCI) are considered as the two objective functions in order to investigate trade-offs between the efficiency of the working fluid in extracting the power from the ORC process for a specified heat source and heat sink, and the overall economic performance of the combined working fluid-ORC process model. The formulation of this test is identical to case study 3 described in Section 5.4. For the sake of brevity, the reader is directed to the comprehensive description of Bowskill et al. (2020) and Lee et al. (2020) for further details on the problem formulation. For convenience, we repeat the formulation in order to describe the properties of the mNBI/SDNBI scalarised subproblems in the subsequent sections.

$$\begin{split} \min_{\boldsymbol{x},\boldsymbol{n}} & P_{net}, \\ \max_{\boldsymbol{x},\boldsymbol{n}} & TCI \\ \text{s.t.} & \boldsymbol{g}(\boldsymbol{x},\boldsymbol{n}) \leq \boldsymbol{0}, \\ & \boldsymbol{h}(\boldsymbol{x},\boldsymbol{n}) = \boldsymbol{0}, \\ & C\boldsymbol{n} \leq \boldsymbol{d} \end{split}$$

where x is a n_1 -dimensional vector of continuous variables that represent process conditions, g(x, n) is a vector of inequality constraints (see Table 5.7), h(x, n) is a vector of equality constraints including heat and mass balance equations, thermodynamic relations, and other structural-property relationship models. (cf. Supplementary Information of Bowskill et al. (2020) for an exact formulation of h(x, n) and $Cn \leq d$).

As a basis for the molecular design space of the working fluid, the following nine

functional groups are selected: CH₃, CH₂, CH₂=, CH=, eO (end group oxygen), cO (central oxygen), COOH, COO and OH. eO represents an oxygen atom connected to one CH₃ and one CH₂ group, and cO describes an oxygen atom bonded to two CH₂ groups. For the evaluation of the overall performance of the ORC process as a function of working fluid structures, the following four process conditions are selected as optimisation variables: the mass flow of working fluid (m_{WF}), the pump inlet pressure ($P_{in,pump}$), the pump outlet pressure ($P_{out,pump}$), and the extent of superheating in an evaporator ($\Delta T_{superheat}$). The optimisation variables and their upper and lower bounds are listed in Table 5.7.

7.2 Scalarisation of the MOO problems

The original MOO problems (7.1) and (7.2) can be converted to a (scalarised) single objective optimisation (SOO) either by assigning weights to the objective functions or by introducing an additional free variable, t and objective constraints.

7.2.1 Weighted-sum subproblem

The weighted-sum subproblem (5.2) for case study 4 (CS4) can be written as:

$$egin{aligned} \min_{m{n}} w_1 f_1(m{n}) + w_2 f_2(m{n}) \ & \ ext{s.t.} \ m{g}(m{n}) \leq m{0} \ & \ m{h}(m{n}) = m{0} \ & \ ext{CN} \leq m{d} \ & \ m{w} \in \mathbb{R}^2, m{n} \in m{N} \subseteq \mathbb{N}^{n_2} \end{aligned}$$

where w is a two-dimensional and vector of weighting factors that is determined by the inner approximation of the SD algorithm, $f(n) \in \{0,1\}^2$ is a vector of the normalised objective functions of C_P and RED. Throughout the study, each objective function value is normalised between 0 to 1 using the limits of the objective space to make a fair comparison between the methods, as was the case in Chapters 5 and 6. The normalisation of the original objective function values, f^o , is described by:

$$f_i = \frac{f_i^o - f_i^{\rm nd}}{f_i^{\rm id} - f_i^{\rm nd}}, \ i = 1, 2,$$
(7.3)

where f_i^{id} is the lowest possible Pareto-optimal value of *i*-th objective function and can be obtained by minimising a single objective function, subject to the constraints. f_i^{nd} is the highest possible Pareto-optimal value of the *i*-th objective function and can be obtained by maximising a single objective function, subject to the constraints. All nadir and utopia points that are used for the normalisation is shown in Table 7.1.

For case study 5 (CS5), the weighted-sum subproblem is given by:

where $f(x, n) \in [0, 1]^2$ is a vector of normalised functions of each objective functions, P_{net} and TCI.

Table 7.1: Nadir and utopia point used for the normalisation of the objective functionsin CS4 and CS5

	C_p	RED	P_{net}	TCI
ı	$(kJ mol-K^{-1})$	(-)	(MW)	$(10^6 \text{ US}\$)$
f_i^{nd}	0.434	4.181	5.01×10^{-8}	7.50
f_i^{id}	0.139	0.226	31.62	6.00×10^{-2}

7.2.2 Modified normal boundary intersection/SDNBI subproblem

In a similar manner, the subproblem with the mNBI/SDNBI parameters for CS4 is defined as:

$$egin{aligned} & \max_{m{n},t} t \ & ext{s.t.} \ m{\Phi}m{eta} + tar{m{n}} \geq m{f}(m{n}) - m{f}^{m{id}} \ & & \ & m{g}(m{n}) \leq m{0} \ & & \ & m{h}(m{n}) = m{0} \ & & \ & m{C}m{n} \leq m{d} \ & & \ & m{t} \in \mathbb{R}, \ ar{m{n}} \in \mathbb{R}^2, \ m{n} \in m{N} \subseteq \mathbb{N}^{n_2} \end{aligned}$$

where t is a continuous scalar variable to be maximised, \bar{n} is the outer normal direction pointing towards the ideal point $f^{id} = [f_1^{id} f_2^{id}]^{\top}$ at the reference point $\Phi\beta$. For CS5, it is given by:

$$egin{aligned} &\max_{oldsymbol{x},oldsymbol{n},t}t\ & ext{s.t.} \; oldsymbol{\Phi}eta+toldsymbol{ar{n}} \geq oldsymbol{f}(oldsymbol{x},oldsymbol{n}) - oldsymbol{f}^{id}\ &oldsymbol{g}(oldsymbol{x},oldsymbol{n}) \leq oldsymbol{0}\ &oldsymbol{h}(oldsymbol{x},oldsymbol{n}) = oldsymbol{0}\ &oldsymbol{h}(oldsymbol{x},oldsymbol{n}) = oldsymbol{0}\ &oldsymbol{C}n \leq oldsymbol{d}\ &\in \mathbb{R}, \; ar{oldsymbol{n}} \in \mathbb{R}^m \; oldsymbol{x} \in \mathbb{R}^{n_1}, \; oldsymbol{n} \in oldsymbol{N} \subseteq \mathbb{N}^{n_2} \end{aligned}$$

In problem (CS4w) and (CS4 β), the integer variables are the only degree of freedom so once a molecular structure has been specified, all continuous variables are fully specified.

7.3 Solution strategy for SOO subproblems

t

Now that we have the scalarised BOO problems, a set of non-dominated points for each problem (7.1) and (7.2) can be obtained by solving the SOO subproblems with

chosen parameters. There are several numerical difficulties that arise in the solution of the CAM(P)D problems.

Each MINLP SOO subproblem is solved using the outer approximation (OA) algorithm, in which the problem is decomposed into a nonlinear programming (NLP) subproblem, the primal problem, and a mixed-integer linear programming (MILP) subproblem, the master problem. As has been discussed in Chapter 4, care needs to be taken when employing the OA algorithm for the solution of large-scale nonconvex MINLP models that present many infeasibilities in the search space. For example, an optimal solution of the MILP subproblem in which a feasible space is approximated by a collection of hyperplanes, i.e., a polyhedral relaxation of the objective function and constraints, may not be feasible in the next NLP search step. The failure of the NLP step may be avoidable by either solving an infeasible primal problem (Fletcher & Leyffer, 1994) or adding integer cuts. However, it is not only computationally expensive, but also it does not guarantee that a feasible solution can be identified in a subsequent iteration. An solvent obtained as a solution of the MILP master problem (CS4 β) that violate nonlinear property constraints, for instance, makes the NLP primal problem infeasible because increasing or decreasing the continuous decision variable *t* cannot reduces the violation of any constraint in $\{g(n) \leq 0, h(n) = 0\}$. If infeasible NLPs appear repeatedly in the course of the solution, the algorithm either terminate prematurely or fail to produce an optimal solution. This is a particular problem when applying the OA algorithm to MINLPs with nonconvexities in the continuous variables as the constraints generated during the solution of repeated variable or infeasible primal problem may cut of the optimal solution. Similarly, in CS5, the primal problem is infeasible for all values of the operating conditions xin the ORC process when 1) the working fluid is not at sub-critical conditions for any operating ranges, 2) the melting point of the working fluid is greater than the minimum operating temperature, 3) a vapour-liquid phase transition of the working fluid cannot occur within the ORC process for a given heating and cooling source. To

mediate such difficulties, we incorporate an extension of the OA method proposed by Buxton et al. (1999), Gopinath et al. (2016), and Bowskill et al. (2020) as used in Chapter 4, in which tailored feasibility tests are introduced to recognise infeasible molecules and process conditions. The overall procedure employed is shown in Figure 7.1 and elements are discussed in more detail in the remainder of this section.

7.3.1 Case study 4: CAMD

In the study of Lee et al. (2020) and as discussed in Chapter 5, it was observed that solving the weighted-sum subproblem (CS4w) with a standard OA algorithm with equality relaxation and augmented penalty (OA/ER/AP) (Viswanathan & Grossmann, 1990) using the default MINLP optimiser in gPROMS (Process Systems Engineering, 1997-2022) is a suitable approach to generate optimal solutions reliably, provided good initial guesses are given. This is because once the integer variables are fixed, the model equations are fully defined and the objective function and constraints can be evaluated without taking an NLP optimisation step. Furthermore, any solvent encountered in the evaluation of the properties is excluded from further consideration by introducing an integer cut in the master problem. One possible modification that can be made when encountering the infeasible solvents is to add the linearisations of the violated constraints to the master problem in order to increase the likelihood of generating a feasible solvent candidate. This approach is similar to the extended cutting plane method proposed by Westerlund & Pettersson (1995) and Westerlund & Lundqvist (2001). The linearisation of the constraints, however, potentially increases the computational cost as the first derivatives of the properties with respect to the molecular variables, *n*, need to be calculated explicitly, and the addition of constraints in the master problem may lead to further computational expense. In view of this, the weighted-sum subproblem (CS4w) is solved with the a standard OA/ER/AP solver embedded in gPROMS, without linearisation.



Figure 7.1: An overview of the algorithmic procedure employed in the solution of subproblems (CS5w), ($CS4\beta$), and ($CS5\beta$). The red shaded box (Test 0 and Test 2) are only applied for case study 5.

Solving the mNBI/SDNBI subproblem (CS4 β) reliably, on the other hand, necessitates the application of one feasibility test designed to examine whether the properties of the solvent candidate are within the desired ranges. The formulation of the test is as follows:

$$T_b^L \le T_b(P = 1 \operatorname{atm}, \boldsymbol{n}) \le T_b^U,$$

$$\rho^L \le \rho(T = 313K, P = 1 \operatorname{atm}, \boldsymbol{n}) \le \rho^U$$

$$\mu^L \le \mu(T = 313K, \boldsymbol{n}) \le \mu^U$$
(7.4)

where superscripts L and U denote upper and lower bounds, respectively. Note that the properties expressed as linear combinations of the number of occurrences of the functional groups, n, such as the surface tension, σ , and the melting point, T_m , are employed in the master problem to generate more feasible molecules and therefore do not need to be included in the feasibility test. We denote the set of the inequality constraints in the feasibility test by $g_1(n)$ and "Test 1". Accordingly, g_p is defined as the subset of inequality constraints obtained by excluding the constraints used in Test 1 ($g_1 \leq 0$) from g. A molecule that passes the feasibility test is subsequently evaluated by solving the NLP primal problem with respect to the continuous variable t. Should a molecule fail the test, the violated constraints are linearised and used in the master problem to guide the search towards new feasible molecules.

The formulation of the master problem follows the original formulation (Duran & Grossmann, 1986; Fletcher & Leyffer, 1994) with modifications applied specifically to aid in CO₂ solvent design. The master problem includes an augmented penalty (AP) framework with slack variables e_1 and e_2 (Viswanathan & Grossmann, 1990), so that the convexity assumption can be relaxed. In order to keep track of the outcome of the feasibility test, primal problem, and of the linearised constraints, we use several sets defined in Section 4.5.1, thereby providing consistency in the formulation. The resulting formulation of the master problem at iteration l is summarised

by problem (M4 β):

$$\begin{split} \min_{\boldsymbol{n},t} & -t + 1000(e_{1} + e_{2}) \\ \text{s.t.} & f_{1}(\boldsymbol{n}^{(l)}) + \nabla_{\boldsymbol{n}}^{\top} f_{1}(\boldsymbol{n}^{(l)}) \left[\boldsymbol{n} - \boldsymbol{n}^{(l)}\right] - \bar{n}_{1} \left[t - t^{(l)}\right] \leq e_{1}, \quad \forall l \in F^{(k)} \\ & f_{2}(\boldsymbol{n}^{(l)}) + \nabla_{\boldsymbol{n}}^{\top} f_{2}(\boldsymbol{n}^{(l)}) \left[\boldsymbol{n} - \boldsymbol{n}^{(l)}\right] - \bar{n}_{2} \left[t - t^{(l)}\right] \leq e_{1}, \quad \forall l \in F^{(k)} \\ & g_{p,m}(\boldsymbol{n}^{(l)}) + \nabla_{\boldsymbol{n}}^{\top} g_{p,m}(\boldsymbol{n}^{(l)}) \left[\boldsymbol{n} - \boldsymbol{n}^{(l)}\right] \leq e_{2}, \quad \forall (l,m) \in A^{(k)} \\ & g_{1,j}(\boldsymbol{n}^{(l)}) + \nabla_{\boldsymbol{n}}^{\top} g_{1,j}(\boldsymbol{n}^{(l)}) \left[\boldsymbol{n} - \boldsymbol{n}^{(l)}\right] \leq e_{2}, \quad \forall (l,j) \in A1^{(k)} \\ & M^{L}(1 - y_{l}) + \varepsilon_{ic} \leq \sum_{i=1}^{n_{2}} (\ln(p_{i})(n_{i} - n_{i}^{(l)})) \leq M^{U}y_{l} - \varepsilon_{ic}, \quad \forall l \in IC^{(k)} \\ & y_{l} \in \{0,1\}, \quad \forall l \in IC^{(k)} \\ & \boldsymbol{u}^{L} \leq \boldsymbol{u} \leq \boldsymbol{u}^{U} \\ & \boldsymbol{Cn} \leq \boldsymbol{d} \\ & -t \leq f^{U} \end{split} \end{split}$$

where the set $F^{(k)}$ is the set of major iteration numbers, l, such that the primal problem is feasible with $l \in \{1, ..., k\}$. For each index $l \in F^{(k)}$, the set $A^{(k)}$ is used to save the pair of indices (l, m), where m is the index of an active constraint in g_p at the solution of the primal problem. If the evaluation of a molecule in Test 1 violates one or more constraints, all violated constraints are stored in a set $A1^{(k)}$. The set $A1^{(k)}$ contains pairs of indices (l, j), where j denotes the index of an active or violated constraint of g_1 . Finally, a set $IC^{(k)}$ is used to store the structure of all molecules that are to be excluded via an integer cut (Samudra & Sahinidis, 2013) introduced to remove infeasible molecules from the design space. Infeasibility of a molecule arises when the molecule fails to pass the feasibility test, and the primal problem becomes infeasible $(l \le k)$, or the solution of the master problem $n^{(l+1)}$ is a repeat of a previously generated structures. p_i is a prime number, the vector n with elements n_i denotes the solvent being sought in the master problem, M^L and M^U is a large negative and positive number, respectively, ϵ_{ic} is a small positive number, and y_l is a binary variable introduced for iteration l to ensure the central term is strictly positive or negative, but not to equal to zero.

7.3.2 Case study 5: CAMPD

In solving (CS5w) and (CS5 β), we employ the same optimisation strategy as Bowskill et al. (2020), in which a set of optimal working fluids were identified reliably from a large space of over 50,000 molecules at a low computational cost. The robustness of the algorithm was achieved through the implementation of three feasibility tests: 1) **test 0**: to derive reasonable bounds on the operating pressure and temperature to ensure that process operation is within the sub-critical region and above the melting point of the current fluid, 2) test 1: to examine whether the transition from vapour to liquid phase in the condenser , and vice versa in the evaporator, can occur within the ranges of the operating conditions defined in **test 0**, 3) **test 2**: to tighten the pressure bounds based on the feasible domain of the working fluid. The reader is referred to the original paper for a more detailed discussion on the development of the robust algorithm and the full formulation of the tests, primal and master problem. Note that, compared to Bowskill et al. (2020), only changes in the formulation of (CS5w) is in the objective function as there are no additional variables and constraints involved. In the case of $(CS5\beta)$, two additional constraints are introduced, and so we summarise the full formulation of the master problem herein. The set of continuous variables x is partitioned into a set of independent variables u and a set of dependent variables x^d so that $x = (u, x^d)$. The a set of dependent variables x^d is calculated using process and physical property models, as represented by the equalities. The set of inequality constraints $g \leq 0$ is reduced to $g_{p2} \leq 0$, where $g_{p2} \subset g$ is obtained by removing the constraints ($g_{t1} \leq 0$) used in test 1. The resulting formulation of the master problem

$$\begin{split} \min_{\boldsymbol{x},n,t} & -t + 1000(e_{1} + e_{2}) \\ \text{s.t.} & f_{1}(\boldsymbol{x}^{(l)},\boldsymbol{n}^{(l)}) + \nabla_{n}^{\top}f_{1}(\boldsymbol{x}^{(l)},\boldsymbol{n}^{(l)}) \left[\boldsymbol{n} - \boldsymbol{n}^{(l)}\right] \\ & + \nabla_{\boldsymbol{x}}^{\top}f_{1}(\boldsymbol{x}^{(l)},\boldsymbol{n}^{(l)}) \left[\boldsymbol{x} - \boldsymbol{x}^{(l)}\right] - \bar{n}_{1}\left[t - t^{(l)}\right] \leq e_{1}, \quad \forall l \in F^{(k)} \\ f_{2}(\boldsymbol{x}^{(l)},\boldsymbol{n}^{(l)}) + \nabla_{n}^{\top}f_{2}(\boldsymbol{x}^{(l)},\boldsymbol{n}^{(l)}) \left[\boldsymbol{n} - \boldsymbol{n}^{(l)}\right] \\ & + \nabla_{\boldsymbol{x}}^{\top}f_{p2}(\boldsymbol{x}^{(l)},\boldsymbol{n}^{(l)}) \left[\boldsymbol{x} - \boldsymbol{x}^{(l)}\right] - \bar{n}_{2}\left[t - t^{(l)}\right] \leq e_{1}, \quad \forall l \in F^{(k)} \\ g_{p2,m}(\boldsymbol{u}^{(l)},\boldsymbol{n}^{(l)}) + \nabla_{n}^{\top}g_{p2,m}(\boldsymbol{u}^{(l)},\boldsymbol{n}^{(l)}) \left[\boldsymbol{n} - \boldsymbol{n}^{(l)}\right] \\ & + \nabla_{\boldsymbol{u}}^{T}g_{p2,m}(\boldsymbol{u}^{(l)},\boldsymbol{n}^{(l)}) \left[\boldsymbol{n} - \boldsymbol{n}^{(l)}\right] \\ g_{l1,j}(\boldsymbol{u}^{(l)},\boldsymbol{n}^{(l)}) + \nabla_{n}^{\top}g_{f1,j}(\boldsymbol{u}^{(l)},\boldsymbol{n}^{(l)}) \left[\boldsymbol{n} - \boldsymbol{n}^{(l)}\right] \leq e_{2}, \quad \forall (l, j) \in A^{(k)} \\ M^{L}(1 - y_{l}) + \varepsilon_{ic} \leq \sum_{i}^{n_{2}}(\ln(p_{i})(n_{i} - n_{i}^{(l)})) \leq M^{U}y_{l} - \varepsilon_{ic}, \quad \forall l \in IC^{(k)} \\ y_{l} \in \{0, 1\}, \quad \forall l \in IC^{(k)} \\ \boldsymbol{u}^{L} \leq \boldsymbol{u} \leq \boldsymbol{u}^{U} \\ \boldsymbol{Cn} \leq \boldsymbol{d} \\ -t \leq f^{U} \end{split}$$
(M2 β)

7.3.3 Remarks on the application of the OA-based framework

Despite the robustness of the optimisation procedure employed, finding a globally optimal solution can be challenging when the problem exhibit many local optima due to the highly nonlinear and nonconvex nature, of the model equations. For MOO approaches that make use of the incumbent set of the Pareto optimal solutions for choosing a suitable set of scalarisation parameters, the performance of the algorithm is strongly dependent on the quality of these solutions. It is therefore of interest to carry out a global search to obtain an accurate representation of the true Pareto front. Furthermore, the choice of initial guesses for the decision variables impacts the convergence behaviour of the MINLP algorithms in solving the nonconvex SOO subproblems. A specific example where a poor choice of initial guesses results in



Figure 7.2: An example of the nonlinear relaxation (shaded red) of the mixed-integer nonlinear feasible set for a problem with two integer variable n_1 and n_2 . The black dots represent the integer domain. The blue solid lines represent the hyperplanes produced by linearising the objective function and active constraints at the solution. Assume that all linearisations are obtained from the first NLP step. The blue arrows show the feasible direction of the hyperplanes and indicate all feasible points have eliminated.

algorithmic failure is shown in Figure 7.2. We assume that the first NLP step where the molecular variables are fixed at the initial guesses successfully converges to a (local) optimal solution. By visual inspection of the search domain, it is clear that the MILP master problem cannot generate any feasible solutions in the region resulting from linearising the objective function and active constraints and thus the algorithm may get trapped at the initial molecular structure.

To overcome this behaviour, we use a modified Multi-Level Single Linkage (MLSL) method (Kucherenko & Sytsko, 2005; Lee et al., 2020) derived from a multi-start approach whereby the local search procedure is invoked for a selected set of starting points, as is consistent with the work presented in Chapter 5. Once the SOO subproblem is defined by assigning parameter values, starting points are sampled within the hyperrectangle defined by the variable bounds based on a Sobol' sequence (Sobol' et al., 2011). We choose to a power of 2 for the number of Sobol' points (N_{sobol}) based on the study of Morokoff & Caflisch (1994) who investigated the error in uniformity and discrepancy for various quasi-random sampling sequences. The al-

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7.4 Implementation overview

All three MOO methods are implemented with common subfunctions using the same programming language in Matlab 2018a, whilst the implementation of the CAM(P)D algorithms presented in Figure 7.1 has been carried out in C++, with an interface to gPROMS ModelBuilder 7.0.7 for the solution of the primal problems and the Gurobi 9.0 MILP solver to solve the master problems. Each feasibility test is modelled as a separate gPROMS entity and the gradients of the objective function and inequality constraints with respect to the decision variables are calculated using first-order forward finite differences. The bounds on the variables, the optimal solutions and the gradients obtained at each stage of the calculations are reported through a C++interface. The CAM(P)D algorithm iterates until the user-provided termination criteria is satisfied. The space-decomposition scheme within the SDNBI algorithm is suited to parallelisation to increase computational efficiency. Specifically, the inner and outer approximation of the Pareto front can be generated for each subset of the objective search space independently and thus the solution of the mNBI subproblem can be obtained for each subset. For ease of comparison, all computations were run on single Intel(R) Xeon(R) Gold 5122 CPU @ 3.60GHz processor with 384 GB of RAM.

As discussed in Chapter 4, when using the OA/ER/AP framework to overcome nonconvexities of the problem, care must be taken in choosing termination criteria to prevent the algorithm from stopping too early and generating suboptimal solutions. Provided that good convergence behaviour has been observed using the stopping criteria presented in Bowskill et al. (2020) and in Chapter 4, the same termination criteria introduced in in Chapter 4 are used. Specifically, the iterative procedure of the algorithm is terminated when: 1) the number of iterations at which the augmented penalty term becomes nonzero exceeds a pre-defined limit, $N_{max,slack}$, 2) the number of unique molecules that has been evaluated either in the feasibility tests or the primal problem exceeds a pre-defined limit $N_{max,unq}$, and 3) when the MILP master problem becomes infeasible.

In their study, Viswanathan & Grossmann (1990) suggested that the starting algorithm by solving the relaxed NLP problem, in which all integer variables are relaxed between their bounds and optimised with continuous variables, is in practice desirable. Following extensive computational studies, the authors found that the solution of the relaxed NLP can yield good initial guesses on the continuous variables and, hence, the resulting linear approximation to the problem is often of good quality. However, in our case studies, it has been observed that the relaxed NLP problem often fails to converge or is computationally very expensive for a specific combination of the MOO parameters and initial guesses, compared to the NLP primal problem with the fixed integer variables. This is explained by the highly nonlinear nature of the molecular structure-property relationships and the strong inter-dependency between molecular properties and process models that lead to changes in the feasible domain of the process with each choice of molecular structure. Given that good starting points for molecular candidates are provided as a part of the global search phase, the first NLP problem is solved with all integer variables fixed to the values specified by the Sobol' sequence.

The convergence criteria of the SDNBI algorithm are based on the maximum admissible error, ϵ between the inner and outer approximations and the maximum admissible spacing, sp_{max} . The spacing is additionally introduced as a measure of how well the Pareto points are distributed and it is calculated with a distance measure between consecutive solutions in the obtained Pareto points. The quantity of sp_{max} is calculated by computing the perimeter of the rectangle formed by

	SOO Phase			MOO Phase			
Parameter	N_{sobol}	$N_{max,slack}$	$N_{max,unq}$	ϵ	sp_{max}	N_{β}	$N_{iter,fix}$
CS4	64	10	50	5.0×10^{-3}	10^{-3}	10	27
CS5	128	4	20	5.0×10^{-3}	4.0×10^{-2}	10	61

 Table 7.2: Algorithmic parameters used in the tests

two extreme (Pareto) points of each facet, sp_p , $p = 1, ..., N_F$, where N_F is the number of facets at a current iteration and by taking the maximum value, i.e., $sp_{max} = \max_{p=1,...,N_p} (sp_1, ..., sp_p).$

For comparison purpose, the stopping criteria used for the SD and mNBI algorithm are based on a fixed number of iterations $N_{iter,fix}$ which is set as the number of iterations taken for the convergence of the SDNBI algorithm. The value of $N_{iter,fix}$ corresponds to the number of weight vectors for the SD algorithm and the number of β vectors for the mNBI method. Note that the SD algorithm may not proceed for the user-specified number of iterations, as there may be no more facet to be investigated. In this case, the performance criteria are calculated based on the obtained approximation at the last iteration number. The initial set, C^{ref} , of N_{β} reference points for the mNBI method is chosen such that consecutive reference points $\Phi\beta^k$ and $\Phi\beta^{k+1}$ are equally spaced, with a spacing δ . This is expressed as:

$$\beta_2^k = k \times \delta, \ \beta_1^k = \beta_2^k, \ \text{ for } k = 1, ..., N_\beta, \delta = 1/(N_\beta + 1).$$
 (7.5)

Once the parameters in the initial set have been enumerated by the algorithm, the next β to be chosen, i.e., $\beta_1^{N_{\beta}+1}$ is determined by taking the midpoint between two adjacent β vectors used in previous iterations of the algorithm. As previously mentioned, the values of the parameter β for the SDNBI algorithm are chosen as facet midpoints, i.e., $\beta^{k} = [0.5, 0.5]^{\top}$. All parameters and stopping tolerances used in the comparative study is specified in Table 7.2.

7.5 Results and discussion

7.5.1 True/Best-known Pareto fronts

Providing a reference for the true Pareto front of each problem is necessary in order to verify the quality of the approximate Pareto fronts produced by each algorithm. In CS4, the true Pareto front can be obtained by enumerating all possible combinations of molecular structures, whereas it is very difficult to generate a complete set of Pareto points for CS5 due to the presence of continuous variables. For CS5, as an alternative, the 123 optimisation runs corresponding to different beta vectors β are carried out based on the mNBI method to construct a initial approximation to the true Pareto front. A different β is used for each run. The resulting set of the solutions is combined with the solutions generated by all runs of the SD algorithm, the mNBI method and the SDNBI algorithm. We also make use of the solutions obtained in our previous study (Lee et al., 2020) where the number of solutions were produced using exhaustive enumeration of the MOO parameters (weight vectors) for each of the 267 feasible working fluids. Putting this all together, an approximate Pareto front consisting of 326 points is obtained and denoted as best-known Pareto front. A graphical representation of the true/best-known Pareto front for each case study is shown in Figure 7.3, in the space of objective functions. Information on the true/best-known Pareto front obtained for each test is provided in Table 7.3. As can be seen in Figure 7.3(a), each point in the feasible region corresponds to a distinct solvent structure, meaning that the Pareto front for CS4 is entirely disjoint. In the case of CS5, one can observe two disconnected parts, corresponding to points where one of the objective constraints of the mNBI method become inactive, implying that there be two disconnected regions. The list of Pareto-optimal molecules for each case study is given in Tables A.3 and A.4 in the Appendix. It should be noted that each Pareto-optimal working fluid in CS5 typically appears in more than two Pareto



Figure 7.3: True/best-Known Pareto front (blue marker, \times) and feasible points (grey marker, \circ) of (a) the normalised heat capacity, C_p (f_1) versus the normalised relative energy difference, RED (f_2) of CS4; and (b) the normalised net power output, $-P_{net}$ (f_1) versus the normalised total capital investment, TCI (f_2) of CS5, resulting from the enumeration of all possible combination of molecules

Table 7.3: Enumeration of all solutions for all possible combinations of functional groups in each test. $N_{structure}$: the number of molecules that satisfy structural feasibility, $N_{feasible}$: the number of molecules that satisfy all constraints, N_{true} : the number of exact Pareto Points, N_{BP} : the number of best-known Pareto Points, HV: hypervolume, DM: distribution metric. The value in (.) of N_{BP} of CS5 is the number of different molecular structures contained within this set.

	CS4	CS5
N _{structure}	67,664	3,175
$N_{feasible}$	3,160	267
N_{true}	15	-
N_{BP}	-	326 (6)
HV	79.12×10^{-2}	91.62×10^{-2}
DM	0.1366	0.0144

points, characterised by different optimal process conditions. Therefore, we only present the distinct molecular structures in Table A.4 and omit objective function values.

7.5.2 Results for CS4

The results of CS4 with each MOO algorithm for a fixed number of iterations are summarised in Table 7.4 and Figure 7.4. From Figure 7.4, it can be seen that both the SDNBI and mNBI methods generate well-distributed and globally Pareto-optimal
solutions, whereas the SD algorithm fails to produce an accurate representation of the Pareto front. This is because the weighted-sum subproblem over the large nonconvex part of the Pareto front, converges to the previously identified optimal solution forcing the algorithm to premature termination. The resulting values of HV and DM for the SD algorithm show a large discrepancy compared to the benchmark quantities. Interestingly, none of the algorithms achieves convergence based on the maximum allowable error criteria as the Pareto front is entirely disjoint, and Pareto point are separated by large gaps. This indicates that it is essential to recognise the subspaces where no Pareto points exist so as to curtail the search for lower approximation error and avoid a significant increase in (unnecessary) computational effort. Consequently, the SDNBI algorithm outperforms the mNBI method and SD algorithm resulting in the lowest DM and the highest HV. The effectiveness of the SDNBI method for the CAMD domain is also highlighted at the 27th iteration, where the SDNBI algorithm terminates by carrying out the objective space-fathoming steps. The higher computational cost of SDNBI is partly attributed to the solution of additional subproblems (mNBI $\bar{n}(a)$) or (mNBI $\bar{n}(b)$). It should be noted that a total of 14 optimisation runs for the solution of the subproblems (mNBI $\bar{n}(a)$) or (mNBI $\bar{n}(b)$) have been conducted. The increase in computational cost can also be explained by the fact that the SDNBI subproblem includes additional constraints, making it difficult to find feasible regions that satisfy all the constraints. Consequently, the solution of the subproblems may entail an increased computational burden to identifying a feasible point during the course of the optimisation and more SOO optimisation runs may be invoked in the global search phase as some local runs fail to converge successfully as a result of having infeasible starting points.

Despite the higher computational cost, one main advantage of using the SDNBI method over mNBI and SD is that the empty parts of are effectively discarded from the consideration and that it provides a richer description of the Pareto front through the identification of empty subspaces. In the case of the mNBI method, the algorithm

iterates until the set of β becomes empty when other stopping criteria such as the progression metric (Van Veldhuizen & Lamont, 1999), which measures the progression of the Pareto front approximation, are not employed. In order to investigate such algorithmic behaviour in the mNBI method, we consider a set of additional β . In Figure 7.5 as a function of iteration number, the progress of total CPU time and the number of Pareto points are displayed for each algorithm. At the 30th iteration, all 15 Pareto-optimal solvents are identified by the mNBI method. However, a higher total CPU time is observed with mNBI as the iteration proceeds because the objective search regions that do not include any new Pareto points are only partially eliminated by mNBI and thus the algorithm iterates over the remaining search domain in an attempt to achieve the pre-defined approximation quality tolerance. This demonstrates that the iterative search using the mNBI method may not be computationally efficient and an improvement in the quality of Pareto approximation is not always achieved when the Pareto front comprises many disconnected parts.

	CS4			CS5		
	SD	mNBI	SDNBI	SD	mNBI	SDNBI
N _{iter}	11	27	27	61	61	61
N_{unq}	9	14	15	61	60	60
N_{PF}	9	14	15	59(3)	58(4)	60(4)
$HV(10^{-2})$	76.430	79.048	79.119	91.230	91.473	91.442
DM	0.2323	0.1521	0.1366	0.1130	0.0472	0.0388
$t_{cpu,a}$ (s)	34.55	28.31	43.77	30.97	144.99	115.78
$t_{cmu,t}$ (s)	$3.11{ imes}10^2$	$3.96 imes 10^2$	6.58×10^{2}	1.68×10^{3}	8.41×10^{3}	6.95×10^{3}

 Table 7.4: Performance metrics for CS4 and CS5 using the SD, mNBI and SDNBI algorithms

7.5.3 Results of CS5

In Figure 7.6, we show the Pareto points generated by each algorithm with the bestknown Pareto front. The quality measures calculated based on the fixed number of iterations are summarised in Table 7.4. It is clear from Figure 7.3 that most parts of the Pareto front are characterised as convex, allowing the SD algorithm to access



Figure 7.4: Pareto points in a bi-objective space generated by the (a) SD algorithm (\times), (b) mNBI method (\diamond), and (c) SDNBI algorithm (\triangle) for CS4. Grey markers (\bigcirc) indicate true Pareto points



Figure 7.5: Progress of the total CPU time, $t_{cpu,t}$ and the number of Pareto points identified, N_{PF} with respect to the number of iterations for the SD (-×-), mNBI (- \diamond -), and SDNBI (- Δ -) algorithms.

a diverse set of Pareto-optimal solutions along the Pareto surface. The differences in HVs (91.230×10⁻² for SD, 91.473×10⁻² for mNBI, and 91.442×10⁻² for SD) are indeed very small and all values are close to the reference value (91.62 \times 10⁻²). Similar values of N_{PF} are achieved with each algorithm. This is also explained in the same manner, although the SDNBI algorithm is marginally better at identifying more diverse combinations of working fluids and thermal-economic performance. In Table 7.4, it appears that the mNBI and SDNBI algorithm exhibit higher computational cost than the SD algorithm. As discussed in the case of CS4, such increases are likely due to the increased numerical complexity inherent in the mNBI/SDNBI subproblem in which two objective constraints are added to the original MINLP formulation. The increase in computational time is significantly higher in CS5 than in CS4. This is mainly due to the fact that the evaluation of the ORC process models, where complex mass- and heat-balance equations are involved, is computationally expensive and hence the performance of the OA-based framework highly relies on the use of a feasible combination of continuous and discrete optimisation variables for the primal problem. Therefore, the algorithm requires more iterations in search for a feasible domain or becomes prone to failing when many of the molecular structures are found to be infeasible with respect to the added objective constraints. In addition, it is worth noting that starting points are sampled in the space of the molecular structures, meaning that the continuous variables are specified by solving the primal problem for a fixed molecule. This may further increase the computational complexity when using infeasible starting points in the global search phase, requiring more sampling points to be evaluated or higher computational time to obtain convergence of the NLP primal problem.

The highest value of DM is obtained when using SDNBI, indicating that it performs best in generating well-distributed Pareto points close to the best-known Pareto front. This is also evident in Figure 7.6, where the Pareto points obtained with SDNBI can be seen to be the better distributed. By comparing the best-known Pareto front with the one approximated with SD in Figure7.3(a), it can be seen that there are relatively large empty parts of the Pareto front in the region of $0.48 \le f_1 \le 0.6$ and $0.59 \le f_2 \le 0.7$. This indicates that there exist disconnected or nonconvex regions of the Pareto front. A key advantage of the SDNBI algorithm is the capability of recognising disconnected parts or nonconvex parts of a Pareto front, and therefore the shape of the Pareto front can be confirmed by investigating the results generated with SDNBI. It is clear from the figure that the surface of the Pareto front is very steep around both anchor points. This provides a useful insight that the economic performance of the process, for example, can be significantly improved by making a small loss in power generation. In contrast, the analysis of the Pareto front generated by SD suggests that there limited trade-offs that can achieve a large improvement in one objective by sacrificing very little in another.

At the termination of the SDNBI algorithm, the objective space is decomposed into a total of eight subspaces, and they are shown in Figure 7.7, where the Pareto points included in each subspace are depicted with different colours. As denoted with cross markers, two subspaces are successfully eliminated from consideration by solving problems (mNBI $\bar{n}(a)$) and (mNBI $\bar{n}(b)$), while such regions are only partially screened out when using mNBI. The discontinuity of the Pareto front observed at $0.8022 < f_2 < 0.8547$ is misinterpreted and a sub-optimal, i.e., dominated solution, z^{44} , is produced. The facets represented by $F_S^1(z^1, z^{46})$ and $F_S^2(z^{46}, z^{44})$ in Figure 7.7, which are constructed by the convex hull generation are discarded from the search space in a subsequent iteration, as they satisfy the quality tolerances rather than because an empty part of the Pareto front has been recognised. Similarly, mNBI and SD each produce one dominated solution. This suboptimality is identified by comparing the set of Pareto points generated by each algorithm with the elements of the best-known Pareto front, not within the approximated set. Overall, the comparative analysis confirms that the SDNBI algorithm shows excellent performance in generating a well-spaced and accurate set of Pareto-optimal working fluids and



Figure 7.6: Pareto points generated by the (a) SD (\times), (b) mNBI (\diamond), and (c) SDNBI (\triangle) algorithms for CS5. Grey markers (\bigcirc) indicate best-known Pareto points



Figure 7.7: Schematic of the solutions (\triangle) generated by SDNBI in a bi-objective space for CS5. Each colour denotes each of eight different sub-search spaces. The empty regions between the cross marker(\times) are identified by solving SDNBI subproblems ($\underline{mNBI\bar{n}}(a)$) and ($\underline{mNBI\bar{n}}(b)$). Solution z^{46} is identified as a dominated solution after investigating if it is a member of the best-known Pareto front.

process conditions within a reasonable CPU time compared to other approaches.

7.6 Conclusions

In this chapter, we have extended the comparative study of the performance of the proposed BOO algorithm, SDNBI, in order to examine the effectiveness and applicability of the algorithm to CAM(P)D problems. One CAMD problem, where the solvent structures are optimised with respect to thermal performance and CO₂ solubility criterion, i.e., RED and one CAMPD problem, where the best thermo-economic performance of the ORC process is identified as a function of working fluids, were formulated for a test purpose. In order to avoid the algorithmic failure arising from the infeasibilities of the property or process model, we employed an OA-based framework where tailored feasibility tests are introduced as a precursor to the primal problem solution to eliminate infeasible molecules and process conditions. Several modifications of the SOO solution approach have been made to adapt the SOO algorithm to the SDNBI/mNBI subproblems. Having demonstrated the efficiency of the global search algorithms in chapter 5, the MLSL algorithm is combined with each MOO algorithm to prevent the algorithm from convergence to dominated points.

For the CAMD case, comparative results highlighted the robustness of the SDNBI algorithm, relative to mNBI and SD, in generating the Pareto-optimal solutions along the discrete Pareto front. The algorithm captures the disconnected regions where no new Pareto points exist, allowing the algorithm to stop without relying on the userprovided termination criteria. Although the mNBI method successfully generated the Pareto points, it was found to encounter difficulties in determining the next scalarisation parameters that can guide the search towards Pareto points that have not yet been identified, in particular when many disconnect parts of the Pareto front are involved. Similar trends were observed for the CAMPD case, while the differences in the values of each quality criterion are less striking. Such small deviations in the

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performance metrics is due to the fact that most of the best-known Pareto points are characterised as convex, and the algorithms developed based on the nonconvex assumption of Pareto front can generate fairly good quality of the Pareto points. The greater confidence in the quality of the solutions produced by SDNBI comes with the capability to recognise nonconvex and disconnected parts of the Pareto front such that a more diverse and accurate set of trade-offs is achieved without expending effort in fruitless area of bi-objective space. Careful attention must be paid to the choice of an appropriate (feasible) starting point to avoid numerical difficulties during the solution of the primal problem.

Further work could be directed at testing the proposed SDNBI algorithm on additional engineering problems to derive more general conclusions of its performance. It would be useful to explore the effect of adding additional objective functions to the problem.

CHAPTER 8

Conclusions

"The study of origins is the art of drawing sufficient conclusions from insufficient evidence."

– Allan Sandage

8.1 Concluding remarks

In this thesis, robust algorithms for the integrated molecular and process design problems, which inherently involve mixed-integer and nonlinear model equations, have been developed focusing on two main aspects: the simultaneous optimisation of molecular- and process-level variables, with special attention on amine-based CO₂ chemical absorption processes; and the development of multi-objective optimisation (MOO) techniques that facilitate the approximation of the Pareto front over the molecular design domain.

In Chapter 3, an equilibrium-based model of the CO_2 absorption-desorption process has been developed and validated on existing pilot plant data using a sophisticated thermodynamic model, the SAFT- γ Mie equation of state, that is useful in the general area of computer-aided molecular design (CAMD) and computer-aided molecular and process design (CAMPD) due to its predictive capabilities. The simulation results have shown that the model is in overall good quantitative agreement with the experimental data, allowing one to evaluate the economic performance of the process for a wide range of process conditions and solvents molecular structures. In order to improve the convergence behaviour of the process model, a tailored initialisation strategy has been established by incorporating the concept of the inside-out algorithm. The performance tests conducted for a set of solvents have shown that the initialisation approach provides a reliable way of achieving convergence without the need for good initial guesses on process conditions. The resulting numerical stability has made it possible to undertake a parametric study, which was carried out to identify the impact of key operating parameters on the economic, environmental and thermal performance of the CO₂ absorption process using an aqueous MEA solution. The results of this study have been used to formulated process optimisation problems that can be integrated into the CAMPD framework. Process optimisations carried out for two solvents have shown that a large reduction in total annualised cost (TAC) and energy penalty can be made by tuning the operating conditions for each solvent considered. The optimisation results have suggested a strong link between solvent types and process performance criteria. These results also have emphasised that the choice of a suitable solvent is key to achieving better economic performance and thermal efficiency of the process.

Building on the process modelling and optimisation approach, the next step was to develop a robust CAMPD algorithm aiming to identify a list of optimal solvents that can enhance the economic value of the chemical absorption process. This required addressing the numerical challenges inherent in solving CAMPD problem with highly nonconvex feasible regions. In Chapter 4, motivated by the work of Buxton et al. (1999); Gopinath et al. (2016), improved feasibility tests have been proposed by focusing on the identification of infeasible combinations of solvent structures and process operating conditions, with a views to enhance the applicability and computational reliability to the more complex setting of CO₂. In order to overcome the difficulties associated with the phase equilibrium calculations for CO₂-watersolvent systems, alternative strategies, namely, tangent plane distance analysis and the Helmholtz free energy Lagrangian Dual (HELD) algorithm have been investigated to replace the previously-used flash calculations in the feasibility tests. By comparing the reliability of these approaches in modelling the correct phase behaviour of the mixtures that present vapour-liquid-liquid splits, it has been shown that the HELD algorithm provides is best suited for integration in the feasibility tests. The resulting CAMPD framework with feasibility tests has been applied to three case studies and has demonstrated the robustness and efficiency of the proposed algorithm. The benefits of the simultaneous solution approach have been highlighted by comparing the results with those produced by the conventional CAMD approach and a decomposition-based CAMPD approach.

Given the inherently conflicting nature of the objectives considered in molecular design problems, it is beneficial in many cases frame the problem as multi-objective optimisation (MOO) formulation. In Chapter 5, we explored the performance of five MOO solution approaches on the selection of two CAMD problems and one CAMPD problem, aiming to gain a better understanding of the performance of different algorithms in identifying the Pareto front efficiently. The five methods included: weighted-sum method (WS) with simulated annealing (SA), WS with multi-level single linkage algorithm (MLSL), sandwich (SD) algorithm with MLSL, and the nondominated genetic algorithm-II (NSGA-II). These algorithms have been derived by combining different techniques for multi-objective and single objective optimisation in order to address the discrete and nonlinear nature of the problem, with the aim of generating an accurate approximation of the Pareto front. The results have shown that the SD algorithm combined with MLSL offers the best performance in generating an accurate representation of the Pareto front.

In Chapter 6, a novel bi-objective optimisation (BOO) algorithm, the SDNBI algo-

rithm, has been proposed for an accurate approximation of nonconvex and combinatorial Pareto fronts. The development of the approach has focused on the interplay between the modified normal boundary intersection (mNBI) method and the SD algorithm, exploiting the strengths of both. Three main modifications presented were: 1) the characterisation of inner and outer approximations such that the accuracy of the given set of Pareto points can be assessed during the course of the algorithm, 2) a systematic way of setting the scalarisation parameters of the mNBI subproblem, 3) a decomposition of the objective space based on determining the convexity and nonconvexity of parts of the Pareto front, and 4) the refinement of the scalarised subproblem to avoid unnecessary iterations over disconnected or empty regions of the objective space.

The performance of the algorithm as measured by the accuracy of the resulting approximation of the Pareto front in the disconnected and nonconvex domain of Pareto points has been assessed relative to two other MOO approaches: the SD algorithm and the mNBI method. The features of these MOO algorithms have been evaluated using two published benchmark problems and, in Chapter 7, two molecular design problems. Initial results have demonstrated that the proposed algorithm outperforms the SD and the mNBI method in convex, nonconvex-continuous, combinatorial problems, in terms of the overall quality of the Pareto-optimal set.

8.2 Summary of the key contributions

The key contributions presented in this thesis include:

 The development and validation of a predictive and transferable equilibriumbased model of CO₂ chemical absorption-desorption processes with the SAFT-γ
 Mie EOS. The development of a robust initialisation strategy for the solution of this complex process model that improves the convergence behaviour over a large set of the molecular possibilities and process conditions without the need for good initial guesses;

- A techno-economic analysis of the CO₂ chemical absorption process that provides a better understanding of the relationship between process operating parameters and overall process performance such as economic criteria, energy efficiency, and environmental impact.
- The development of a robust CAMPD framework for the simultaneous design of optimal solvents and CO₂ chemical absorption processes that can overcome numerical complexities arising from infeasibilities in the process conditions and the dependence of the feasible operating region with each combination of integer variables. This required improving a set of feasibility tests designed to characterise the feasible process domain as a function of solvent structure. The effectiveness of the tests in the complex setting of CO₂ chemical absorption have been demonstrated through the study of over 4000 molecules;
- A systematic analysis of the performance of optimal solvents obtained by the proposed CAMPD algorithm and a comparison of the results generated by a conventional CAMD approach and a decomposition-based CAMPD approach with those from the proposed CAMPD algorithm;
- A systematic comparative study of the performance of different classes of MOO algorithms in solving several literature MOO CAM(P)D problems, including the introduction of several modifications to the algorithms in order to handle the discrete nature of the molecular structure and nonconvex equations. The successful application of the MOO algorithms and their results have provided initial guidance on the suitability of the algorithms in generating an accurate and diverse set of Pareto fronts and also highlighted the importance of targeting nonconvex parts of the Pareto front.
- The development of a novel deterministic optimisation approach (SDNBI) for

nonconvex and combinatorial bi-objective programming that can tackle theoretical and numerical challenges arising from the solution of general nonconvex and discrete BOO problems. Having validated its performance, the approximation capability of the SDNBI algorithm has been found to allow the solution of MOO CAM(P)D problems to produce an accurate and diverse set of Pareto points along nonconvex or disconnected parts of the Pareto front using few optimisations runs.

8.3 Directions for future work

In this thesis, an algorithm for the integrated design of optimal solvents and CO_2 chemical absorption processes has been developed, and its robustness has been demonstrated for a set of acyclic amine solvents focusing on their economic values. In recent years, cyclic amines and binary amine mixtures such as AMP (2-amino-2-methyl-1-propanol) or, PZ (piperazine), and AMP/PZ mixture have been receiving increasing attention to address shortcomings of conventional amines associated with a high regeneration heat duty, slower reaction kinetics, and low absorption capacity (Brúder et al., 2011; Zarogiannis et al., 2016; Bernhardsen & Knuutila, 2017; Bui et al., 2018). Given the predictive power of the SAFT- γ Mie approach and the availability of the group parameters, one possible research avenue could be directed at applying the proposed CAMPD framework to a larger molecular design space such that the overall performance of cyclic amine functionalities and binary amine mixtures is examined systematically.

Another important aspect in developing CAMPD approaches is their the reliability, in terms of generating promising solvent candidates, primarily relies on the accuracy of the predicted physical properties. The property prediction models, however, may exhibit deviations in their predictions compared with experimental data, particularly for caloric properties and transport properties. It is therefore of interest to account for the uncertainty present in the model parameters. In this context, a second direction to improve the applicability of CAM(P)D would be to assess the sensitivity of key property model parameters under different operating conditions and to incorporate systematic uncertainty quantification methods directly into the CAMPD framework. In addition, it would be useful to investigate the potential use of the feasibility pump algorithm (Fischetti et al., 2005; Bonami et al., 2009; Bernal et al., 2020) with the proposed CAMPD framework by which an initial feasible solution for MINLPs is quickly identified by solving the feasible pump subproblem at the start of the outer approximation algorithm (OA) and when the NLP subproblem is infeasible (Bonami et al., 2009) or only once before the OA procedure starts (Bernal et al., 2020).

As a second part of the thesis, a novel BOO has been developed, focusing on the exploration of the nonconvex and combinatorial Pareto front. Having demonstrated the robustness of the algorithm in approximating a Pareto front where many disconnected and nonconvex regions are involved, it would be interesting to implement BOO for the design of optimal solvents for the CO₂ absorption process in order to generate trade-offs between the economic performance and energy efficiency or the environmental impact of the solvents. In order to derive a general conclusion on the reliability and applicability of the SDNBI algorithm, an extension of the performance tests on additional engineering and benchmark problems would be a useful research avenue for future work.

The performance of the sandwich algorithm that makes use of the weighted-sum subproblem has been studied for the high-dimensional objective space ($m \ge 4$) (Lee et al., 2020; Rennen et al., 2011) and has shown their efficiency in terms of generating an accurate approximation of the Pareto front. However, the computational time taken to approximate an error between inner and outer approximation and convex hull generation may increase drastically. For the mNBI method, Burachik et al. (2017) reported the difficulty of generating well-distributed Pareto points for three

or more objective function space and proposed the grid generation method that can replace the convex hull individual minima. Therefore, another important area of research would be to explore the theoretical properties and algorithmic behaviour of the SDNBI algorithm when adding objective functions to the problem so as to extend its applicability to dimensions higher than two and investigate its computational performance when many additional constraints are added to the problem.

8.4 Publications and presentation

8.4.1 Publications

- Lee, Y.S., Galindo, A., Jackson, G. and Adjiman, C.S., (2022). The SDNBI Algorithm: A deterministic optimization approach for nonconvex and combinatorial bi-objective programming. (in preparation, will be submitted to Eur J Oper Res)
- Lee, Y.S., Galindo, A., Jackson, G. and Adjiman, C.S., (2022). Development of a deterministic bi-objective optimisation algorithm and application to computer-aided molecular design problems. (in preparation, will be submitted to Comput Chem Eng)
- Lee, Y.S., Galindo, A., Jackson, G. and Adjiman, C.S., (2022). Integrated amine solvent and process design using a SAFT-γ Mie equation of state: chemical absorption of carbon dioxide. (in preparation, will be submitted to Comput Chem En)
- Lee, Y.S., Galindo, A., Jackson, G. and Adjiman, C.S., (2021). Development of a bi-objective optimisation framework for mixed-integer nonlinear programming problems and application to molecular design (submitted to Computaided Chem En)

- Lee, Y. S., Galindo, A., Jackson, G., and Adjiman, C. S. (2021). An approach for simultaneous computer-aided solvent design and process design for CO2 chemical absorption processes. In Comput-aided Chem En, vol. 50, (pp. 167–172)
- Lee, Y. S., Graham, E. J., Galindo, A., Jackson, G., and Adjiman, C. S. (2020). A comparative study of multi-objective optimization methodologies for molecular and process design. Comput Chem Eng, 136, 106802

8.4.2 Conferences presentation and posters

- A Modified Sandwich Algorithm for Nonconvex Multi-Objective Mixed-Integer Nonlinear Programming, International Federation of Operational Research Societies conference 2021, July 2021, Seoul, South Korea (virtual).
- An approach for simultaneous computer-aided solvent design and process design for CO2 chemical absorption processes, European Symposium on Computer Aided Process Engineering 2021, June 2021, Virtual.
- Integrated solvent and chemical absorption process design for the separation of CO₂ from flue gas, AIChE Annual Meeting 2020, Nov 2020, San Francisco, US (virtual).
- On the Performance of Multi-objective Optimization Methods Applied to a Mixed-Integer Solvent Design Problem. Fundamental of Computer Aided Process Design 2019, July 2019 Colorado, US. (poster session)
- A Comparison of the Performance of Multi-Objective Optimization Methodologies for Solvent Design. European Symposium of Computer Aided Process Engineering. European Symposium on Computer Aided Process Engineering 2018, June 2018, Eindhoven, Netherlands.

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Appendix

A.1 Appendix A. Implementation of the proposed CAMPD algorithm to the CO₂ chemical absorption process

ID	DS1	DS2	DS3
s1	[1-0-0-0-0-0-0-0-1-0-0-1]	[1-0-0-0-0-0-0-0-1-0-0-1]	[1-0-0-0-0-0-0-0-1-0-0-1]
s2	[0-0-0-0-1-0-0-0-3-0-0-2]	[0-0-0-0-1-0-0-0-3-0-0-2]	[0-0-0-0-1-0-0-0-3-0-0-2]
s3	[0-0-0-0-0-1-0-0-4-0-0-2]	[0-0-0-0-0-1-0-0-4-0-0-2]	[0-0-0-0-0-1-0-0-4-0-0-2]
s4	[0-0-0-0-1-0-0-0-5-0-0-2]	[0-1-0-0-0-0-0-0-2-0-0-2]	[1-0-0-0-1-0-0-0-2-0-0-1]
s5	[1-0-0-0-0-0-0-0-3-0-0-1]	[0-0-0-1-0-0-0-0-2-0-0-1]	[1-0-0-0-1-0-0-0-3-0-0-1]
s6	[0-0-0-0-0-0-1-3-3-1-0-1]	[1-0-0-0-1-0-0-0-2-0-0-1]	[0-0-1-0-1-0-0-2-0-0-0-1]
s7	[0-1-0-0-0-0-0-0-2-0-0-2]	[1-0-0-0-0-0-1-0-5-0-0-2]	[2-0-0-0-1-0-0-0-0-0-1]
s8	[0-1-0-0-0-0-0-1-3-0-0-1]	[0-0-1-0-1-0-0-2-0-0-1]	[0-0-1-1-1-0-0-0-2-1-0-0-0]
s9	[0-0-0-0-0-1-0-1-1-0-0-1]	[0-1-0-0-0-0-0-1-3-0-0-1]	[0-0-1-0-2-0-0-3-2-0-0-0]
s10	[0-0-0-1-0-0-0-0-2-0-0-1]	[0-0-0-0-0-1-0-1-1-0-0-1]	[0-0-1-0-1-0-3-1-0-0-0]

Table A.1: Molecular starting points given for each case study

Table A.2: Results of the solution of the integrated solvent and chemical absorption process design for each case study. The molecules are presented in the order of high to low rank with their molecular code. Test column represents the results of evaluating the molecules in the feasibility tests.

ID	Molecular code	Test
M1	[0-0-0-0-0-0-2-2-0-0-0-2]	Pass
M3	[0-0-0-0-0-1-0-1-4-0-1-0-1]	Fail
M7	[0-0-0-0-0-0-2-2-2-0-0-2]	Pass
M8	[0-0-0-0-0-0-1-2-0-0-1]	Fail
M10	[0-0-0-0-1-0-0-1-2-0-0-0-1]	Pass
M11	[0-0-0-0-2-0-0-1-2-0-0-0-1]	Fail
M12	[0-0-0-0-0-1-0-1-3-0-0-0-1]	Fail
M16	[0-0-0-0-1-0-0-0-2-4-0-0-0]	Fail
M17	[0-0-0-0-0-1-0-1-5-1-2-0-1]	Fail
M19	[0-0-0-0-0-1-0-1-6-3-3-0-1]	Fail
M21	[0-0-0-0-0-0-2-2-1-0-0-2]	Pass
M22	[0-0-0-0-2-0-0-0-1-0-0-0-1]	Pass
M23	[0-0-0-0-2-0-0-2-2-0-0-0]	Fail
M25	[0-0-0-0-0-1-0-1-5-0-0-1-1]	Fail
M26	[0-0-0-0-1-1-1-3-0-0-0-1]	Pass
M30	[0-0-0-0-0-0-1-3-0-1-0-1]	Fail
M31	[0-0-0-0-1-1-0-0-2-0-0-0-1]	Fail
M32	[0-0-0-0-1-0-0-0-1-0-0-0-1]	Pass
M36	[0-0-0-1-0-1-0-1-3-0-0-0-0]	Fail

A.2 Appendix B. Implementation of the SDNBI algorithm to the molecular design problems

Table A.3: A complete list of Pareto-optimal solvents for CS4. Each of the solvents is represented with a molecular code where each number represents the occurrences of a functional group in the following order: NH₂CH₂, NH₂CH, NH₂C, NHCH₃, NHCH₂, NHCH, NCH₃, NCH₂, CH₃, CH₂, CH, C, and OH.

Index	Molecular code	$f_1(C_p)$	f ₂ (<i>RED</i>)
S1	[1-0-0-0-0-0-0-0-0-0-0-1]	0.0000	1.0000
S2	[0-0-0-0-1-0-0-0-1-0-0-0-1]	0.0224	0.6947
S3	[2-0-0-0-0-0-0-0-0-0-0-0]	0.1022	0.6759
S4	[0-0-0-0-0-0-1-2-0-0-1]	0.1344	0.3426
S5	[0-0-0-0-0-0-1-2-1-0-0-1]	0.2495	0.3243
S6	[0-0-0-0-0-0-1-3-0-1-0-1]	0.3477	0.2736
S7	[1-0-0-0-0-0-0-1-4-0-0-0]	0.3922	0.1565
S8	[1-0-0-0-0-0-0-3-1-2-0-0]	0.4778	0.1100
S9	[1-0-0-0-0-0-0-3-2-0-1-0]	0.5012	0.0506
S10	[1-0-0-0-0-0-0-4-1-1-1-0]	0.5929	0.0265
S11	[1-0-0-0-0-0-0-4-2-1-1-0]	0.6922	0.0162
S12	[1-0-0-0-0-0-0-4-3-1-1-0]	0.7918	0.0103
S13	[1-0-0-0-0-0-0-3-5-0-1-0]	0.7999	0.0076
S14	[1-0-0-0-0-0-0-3-6-0-1-0]	0.8999	0.0005
S15	[1-0-0-0-0-0-0-3-7-0-1-0]	1.0000	0.0000

Table A.4: A list of Pareto-optimal working fluids for CS5. Each numbers in molecular code represents the occurrences of a functional group and the groups are given in following order: CH_3 , CH_2 , eO, cO, COO, -CH=, COOH, CH_2OH , $=CH_2$.

Index	Molecular code	Name	
W1	[1-0-0-0-1-0-0-1]	Propene	
W2	[1-1-0-0-0-1-0-0-1]	But-1-ene	
W3	[2-0-1-0-0-0-0-0]	Dimethyl ether	
W4	[2-1-0-0-0-0-0-0]	Propane	
W5	[2-1-1-0-0-0-0-0]	Methyl Ethyl Ether	
W6	[2-2-0-0-0-0-0-0]	n-Butane	