Large-Scale Optimization of Complex Separator and Reactor Networks

A dissertation submitted in partial satisfaction of the Requirements for the degree Doctor of Philosophy
In Chemical Engineering

By

Paul G. Ghougassian

2013
The generation of globally optimal designs which can minimize capital and/or operating cost expenditures is a highly sought after objective within the chemical industry. A methodology which can systematically generate such globally optimal solutions to objective functions commonly encountered in the chemical industry is the IDEAS framework. The IDEAS framework decomposes a process network into an operator, OP network, where the unit operations (reactors, distillation columns, heat exchangers, etc.) occur, and a distribution, DN network, where the flow operations (mixing, splitting, recycling, and bypass) occur. The optimal process network structure is identified through solution of an infinite linear program (ILP) that is formulated within the IDEAS framework. The ILP’s solution is approximated by finite dimensional linear programs of ever increasing size. The global optimization of complex, multi-pressure distillation networks for the separation of azeotropic mixtures using the IDEAS framework, is presented in chapter 1. The objective function in this case aims at minimizing total network flow in an effort to directly (indirectly) reduce capital (operating) costs. The global
optimization of chemical reactor networks is presented in chapter 2-4. There, interesting properties relating to energy consumption and entropy generation for isothermal/isobaric reactor networks are described in the context of the attainable region (AR). Given certain assumptions, namely that all reactors are either of the endothermic or exothermic kind, a proof is presented that energy consumption and entropy generation can be rigorously identified in the infinite space of chemical reactors, independently of the network’s internals (chapter 2). For the case of isothermal/isobaric chemical reactor networks where both endothermic and exothermic reactors participate in delivering the desired outlet product composition, entropy generation minimization is synonymous with an objective function of minimum hot/cold utility cost, with the cost coefficient of hot (cold) streams being the inverse of the temperature of the cold (hot) reservoir to which it adds (removes) energy. For this scenario, the network’s internal structure plays a key role in determining the optimal reactor network, which is determined using the IDEAS framework (chapter 3). A novel method to identify the sequence of isothermal mixed flow reactors (CSTR’s) which globally minimizes a reactor residence time dependent objective function (able to represent such objectives as capital cost, volume, or total annualized cost), subject to a constraint dependent on the reactor sequence’s exit concentrations, is presented in chapter 4. Finally, chapter 5 discusses a novel, heat-integrated, pressure-temperature-swing-adsorption (PTSA) process for the capture of CO₂ from the flue gas of fossil-fueled power plants using MgO sorbents.
The dissertation of Paul G. Ghougassian is approved.

Tatiana Segura

Adnan Darwiche

Jim Davis

Vasilios Manousiouthakis, Committee Chair

University of California, Los Angeles

2013
# TABLE OF CONTENTS

## Chapter 1: Globally Optimal Networks for Multi-Pressure Distillation of Homogeneous Azeotropic Mixtures

1.1. Abstract ......................................................................................................................... 1

1.2. Introduction .................................................................................................................. 2

1.3. Applicability and Mathematical Formulation of IDEAS for Multi-Pressure Flash Separator Network Synthesis ........................................................................................................... 5

1.3.1 IDEAS Property 1 ...................................................................................................... 10

1.3.2 IDEAS Property 2 ...................................................................................................... 10

1.3.3 IDEAS Property 3 ...................................................................................................... 10

1.3.4 LP Formulation ......................................................................................................... 14

1.3.5 Proposition 1 ............................................................................................................. 17

1.3.6 Proposition 2 ............................................................................................................. 18

1.4. Case Study 1: Dual-Pressure Distillation of a Binary Mixture of Methyl Acetate (1) and Methanol (2) ........................................................................................................ 20

1.4.1. Optimized Traditional Two-Column PSD Design .................................................. 22

1.4.2. IDEAS-Generated Globally Optimal Azeotropic Separation Design ...................... 25

1.4.2.1. Uniform Temperature Grid Discretization Strategy .......................................... 28

1.4.2.2. Non-uniform Temperature Grid Discretization Strategy ................................... 33

1.4.3. Effects of Pressure and Purity on the Total Flash Inlet Flow .................................. 35
1.5. Case Study 2: Dual-Pressure Distillation of a Ternary Mixture of Water (1), Methanol (2), and Acetone (3) .................................................................37
1.5.1. Optimized Traditional Two-Column Design .......................................39
1.5.2. IDEAS-Generated Globally Optimal Azeotropic Separation Design ....41
1.6. Conclusions .........................................................................................43
1.7. Nomenclature .....................................................................................44
1.8. Appendices .........................................................................................48
1.9. References ........................................................................................50

2. Chapter 2: Attainable Composition, Energy Consumption, and Entropy Generation Properties for Isothermal/Isobaric Reactor Networks

2.1. Abstract ...............................................................................................56
2.2. Introduction ..........................................................................................56
2.3. Motivation and Significance .................................................................59
2.4. Applicability of IDEAS to Isothermal Reactor Network Synthesis ....63
   2.4.1. Reactor Model – Variable Density Model (Mass Basis) ..................65
   2.4.2. Reactor Model – Constant Density Model (Molar Basis) ............66
   2.4.3. Entropy/Enthalpy Relations for Both VDF and CDF Models .........67
   2.4.4. IDEAS Property 1 .......................................................................70
   2.4.5. IDEAS Property 2 .......................................................................70
   2.4.6. LP Constraints Formulation .........................................................72
2.5. Reactor Network Utility Consumption and Entropy Generation Formulations ....76
   2.5.1. Theorem 1 ...................................................................................77
2.6. Attainable Region-Based Quantification of Entropy Generation and Utility Consumption for Isothermal Reactor Networks ................................................................. 82

2.7. Case Study ............................................................................................................ 84

2.8. Conclusions .......................................................................................................... 91

2.9. Nomenclature ....................................................................................................... 92

2.10. Appendices ......................................................................................................... 101

2.11. References .......................................................................................................... 103

3. Chapter 3: Minimum Entropy Generation for Isothermal Endothermic/Exothermic Reactor Networks

3.1. Abstract .................................................................................................................. 107

3.2. Introduction ............................................................................................................ 108

3.3. Applicability of IDEAS to Isothermal Reactor Network Synthesis ...................... 110

3.3.1. Reactor Model – Variable Density Model (Mass Basis) ................................. 110

3.3.2. Reactor Model – Constant Density Model (Molar Basis) ......................... 111

3.4. Entropy/Enthalpy Relations for both VDF and CDF Models ......................... 112

3.5. Applicability of IDEAS to VDF model .............................................................. 113

3.5.1. IDEAS Property 1 ............................................................................................ 114

3.5.2. IDEAS Property 2 ............................................................................................ 114

3.5.3. IDEAS Property 3 ............................................................................................ 114

3.6. Mathematical Formulation .................................................................................... 116

3.7. Objective Function Formulation: Reactor Entropy Generation ....................... 121
3.7.1. Theorem 1................................................................................................................121
3.8. Case Study..................................................................................................................125
3.9. Discussion-Conclusions............................................................................................135
3.10. Nomenclature..........................................................................................................136
3.10. References................................................................................................................144

4. Chapter 4: Global Minimization of Capital Cost/Volume/Total Annualized Cost for
Isothermal Mixed-Flow Reactor Sequences with General Reaction Schemes

4.1. Abstract......................................................................................................................147
4.2. Introduction...............................................................................................................147
4.3. Mathematical Preliminaries.....................................................................................150
4.4. Mathematical Formulation.......................................................................................152
  4.4.1. Dimensionality Reduction Method A.................................................................154
  4.4.2. Dimensionality Reduction Method B.................................................................155
4.5. Optimization Problem Properties..........................................................................158
  4.5.1. Theorem 1: Existence..........................................................................................158
  4.5.2. Theorem 2: Regularity.......................................................................................160
  4.5.3. Theorem 3: Necessary Conditions for Optimality.............................................162
4.6. Properties for Optimization Problems with Linear Kinetics.................................163
  4.6.1. Theorem 4: Local Optimality of Equal-Reactor Sequences...............................164
  4.6.2. Theorem 5: Global Optimality of Equal Reactor Sequences..............................164
4.7. General Solution Procedure....................................................................................166
  4.7.1. Interval-Analysis Based Algorithm.................................................................166
4.7.2. Graphical Method

4.8. Case Study – Linear Kinetics – Application of Theorem 5

4.9. Case Study – Trambouze Kinetics

   4.9.1. Trambouze Case Study 1: Non-Linear Objective Function (TAC)

   4.9.2. Trambouze Case Study 2: Linear Objective Function (Total Volume)

4.10. Conclusions

4.11. Nomenclature

4.12. Appendices A-F

   4.12.1. Appendices A-C

   4.12.2. Appendices D-F

4.13. References

5. Chapter 5: CO₂ Capturing from Power Plant Flue Gases: Energetic Comparison of Heat Integrated, Pressure-Temperature-Swing Adsorption with Amine Absorption

   5.1. Abstract

   5.2. Introduction & Background

   5.3. Steam-Cycle without Carbon Capture

   5.4. Steam-Cycle with Amine-Based Capture

   5.5. Gibbs Minimization Analysis

   5.6. Steam-Cycle with Sorbent (MgO) – Based Capture

      5.6.1. Block 1: Modified Boiler Tri-Sector Heat Exchanger

      5.6.2. Block 2: Adsorber-Desorber Circuit
5.6.2.1. General Description of Proposed PTSA and its Time-Dependent Operation…………………………………………………………238

5.6.2.2………………………………………………………………………………239

5.6.3. Block 3: Vapor-Compression Refrigeration Circuit………………………………246

5.6.4. Block 4: Heat-Exchanger Network Structure…………………………………248

5.6.5. Block 5: Separation Network Structure…………………………………………251

5.7. Discussion…………………………………………………………………………253

5.8. Conclusions………………………………………………………………………254

5.9. Nomenclature………………………………………………………………………255

5.10. References…………………………………………………………………………259
ACKNOWLEDGMENTS

Financial support for this work through NSF grant NSF-CBET 0829211 & 0943264 is gratefully acknowledged. The author would like to thank Vasilios Manousiouthakis for his guidance, insight, and friendship.


Chapter 2 is a version of "Attainable Composition, Energy Consumption and Entropy Generation Properties for Isothermal/Isobaric Reactor Networks”, by Paul G. Ghougassian & Vasilios Manousiouthakis, Industrial & Engineering Chemistry Research, 2013, 52 (9), pp. 3225-3238
Vita

2008
B.S. in Chemical Engineering
University of California, Riverside
Graduated with Honors (Cum Laude)

2011
M.S. in Chemical Engineering
University of California, Los Angeles
Thesis: “Global Minimization of Total Annualized Cost for Mixed Flow Reactor Sequences”

Presentations & Publications

- Presented two preliminary research papers at the American institute of Chemical Engineers (AIChE) annual meeting in Nashville, TN (2009) titled: “Optimal Synthesis of Azeotropic Reactive Distillation Networks”, and “Hydrogen Production Plant with Urea co-production”
- Presented two preliminary research papers at the American institute of Chemical Engineers (AIChE) annual meeting in Salt Lake City, UT (2010) titled: “Optimal Synthesis of Liquid-Liquid Extraction Networks”, and “Optimal Synthesis of Sequence of CSTR with Non-Linear Cost Objective Function”
- Presented two preliminary research papers at the American institute of Chemical Engineers (AIChE) annual meeting in Minneapolis, MN (2011) titled: “Optimal Synthesis of Pressure Swing Distillation Columns for the Separation of Azeotropic Mixtures”, and “An Energetic Comparison between Heat Integrated Pressure-Temperature-Swing Adsorption using Alkaline-Earth Oxide Sorbents and Amines for the Capture of CO₂ from Coal-Fired Plants”
- Presented two preliminary research papers at the American institute of Chemical Engineers (AIChE) annual meeting in Pittsburgh, PA (2012) titled: “IDEAS Minimization of Entropy Generation for Isothermal/Isobaric/Constant Density Reactor Networks with Bounded Utility Consumption”, and “Globally Optimal Networks for Multi-Pressure Distillation of Homogeneous Azeotropic Mixtures: Application to Ternary Mixtures”

1. CHAPTER 1

Globally Optimal Networks for Multi-Pressure Distillation of Homogeneous Azeotropic Mixtures

1.1. Abstract

In this paper, a methodology for the globally optimal synthesis of a network of vapor-liquid equilibrium flash separators that can operate at multiple pressures and separate an azeotropic mixture is presented. The objective function minimized is the total flow entering the network flashes. The proposed synthesis methodology employs the Infinite DimEnsionAl State-Space (IDEAS) conceptual framework, which is shown to be applicable to the problem under consideration. The resulting infinite linear programming (ILP) IDEAS formulation is shown to possess several properties that allow its simplification. The approximate solution of this IDEAS ILP is pursued through the solution of a number of finite dimensional linear programs (FLP) of ever increasing size, whose optimum values form a sequence that converges to the ILP’s infimum. The proposed optimal design methodology is general in nature and can be used to separate any number of pressure-sensitive azeotropic mixtures, with or without using an entrainer. The method is demonstrated on a first case study involving the dual pressure separation of a Methyl-acetate/ Methanol binary mixture, which exhibits a minimum boiling azeotrope, without using an entrainer, and a second case study involving the dual pressure separation of a ternary mixture of Water/Methanol/Acetone which also exhibits a minimum boiling azeotrope for the Methanol/Acetone binary mixture, again without using an entrainer. The IDEAS-generated globally optimal design is shown to be 31.54 % better than an optimized,
dual pressure, traditional, two-column design for the binary mixture (case 1), and 15.15 % for the
ternary mixture (case 2).

1.2. Introduction

Knowledge regarding the sensitivity of azeotropes to pressure effects dates back to the 19th
century\textsuperscript{1-3}. Azeotropic mixtures are typically separated by either homogeneous or heterogeneous
azeotropic distillation, batch\textsuperscript{4} or continuous\textsuperscript{5}. The separation process requires the addition of an
entrainer and/or the use of pressure swing distillation (PSD), which exploits the azeotrope
dependence on pressure\textsuperscript{5}. The main advantage of the PSD process is that it does not require an
entrainer, i.e. a substance which facilitates the considered separation but requires additional
separation steps downstream, and may itself be a toxic chemical, or may degrade into byproducts
harmful to the environment. The systematic generation process synthesis paradigm has been
predicted to expand in the foreseeable future\textsuperscript{6}, with the separation of an azeotropic mixture listed
as an important problem to address in the 21st century\textsuperscript{7}. A large list of pressure-sensitive binary
azeotropes prevalent in the chemical industry that can be separated through the PSD process has
been tabulated\textsuperscript{8}. The PSD process involves the operation of multiple columns at different
pressures to bypass pressure-dependent azeotropic pinch points and recover high purity products.
A two-column PSD is an especially interesting process, since its two columns operate at two
different pressures and can be readily thermally integrated, by matching the heat removed by the
high pressure condenser with the heat required by the low pressure boiler, or with the heat
required by the feed preheater\textsuperscript{9-10}. Several algorithms have been developed to optimize
azeotropic columns based on energy and cost considerations, using trial-and-error simulations at
specific design parameters\textsuperscript{5,11-16}. However, these techniques do not guarantee global optimality
and only consider a limited number of alternatives. Geometric approaches to identify and
optimize azeotropic separation processes, through homotopy, arc length continuation, residue curve maps, distillation boundaries, shortcut methods and distillation lines have also been proposed\textsuperscript{17-22}, but possess visualization limitations and also do not guarantee global optimality. Unusual and non-traditional variant designs have also emerged\textsuperscript{23-24}. Recently, researchers have begun using more refined optimization techniques relying on the formulation of complex Mixed Integer Non-linear Programs (MINLPs)\textsuperscript{25-33}. While the MINLP methodology provides improvements, solutions are locally optimal and only as good as the initially supplied superstructure, due to the non-linearity and non-convexity that naturally arises from the superstructure-based MINLP problem formulation. In addition, commercially available globally optimal non-linear programming software cannot handle the large number of variables resulting from the complexity of distillation column (super) structures.

This paper demonstrates the use of the IDEAS framework in simultaneously synthesizing a network that can separate azeotropic mixtures, and minimizing the total flash inlet flow in the aforementioned network. The IDEAS framework is a generalized methodology that allows for the generation of globally optimal flow sheet designs. The IDEAS framework decomposes a process network into an operator, OP network, where the unit operations (reactors, distillation columns, heat exchangers, etc.) occur, and a distribution, DN network, where the flow operations (mixing, splitting, recycling, and bypass) occur. The optimal process network structure is identified through solution of an infinite linear program (ILP) that is formulated within the IDEAS framework. The ILP’s solution is approximated by finite dimensional linear programs of ever increasing size. The solution of these linear programs is guaranteed to be globally optimal. IDEAS has been successfully applied to numerous globally optimal process network synthesis problems, such as: mass exchange network synthesis\textsuperscript{34}, complex distillation network synthesis\textsuperscript{35}.
In this work, IDEAS is shown to be applicable to the globally optimal synthesis of networks that employ steady state vapor-liquid equilibrium flash separators, operating at multiple pressures, to separate azeotropic mixtures. The representation of a theoretical tray of a distillation column as a combination of two separate devices: a mixer that can receive vapor and liquid inlets at different temperatures, and an equilibrium (flash) separator that has as inlet the mixer’s outlet, and as outlets a vapor and a liquid stream that are in equilibrium with one another, has been suggested.

A schematic representation of this concept is shown below in figure 1. Since the possibility of mixing is incorporated in the DN of the IDEAS framework, and the equilibrium separator can be made part of the OP of IDEAS, the above suggest that a distillation network can be represented within the IDEAS framework as a network of vapor-liquid equilibrium flash separators. Thus, IDEAS can employ this representation to synthesize distillation networks.

**Figure 1.1:** Mixer + Flash Separator representation of a distillation column tray.
The rest of the paper is structured as follows: first, the applicability of IDEAS to the multi-pressure flash separator network synthesis problem is established, and the resulting IDEAS mathematical formulation is presented. Properties that facilitate the solution of this mathematical formulation are then presented. This is followed by two case studies in which the IDEAS framework is used to generate an optimal network for the separation of a binary mixture (case study 1), and ternary mixture (case study 2). The obtained results are then discussed and conclusions are drawn.

1.3. Applicability and mathematical formulation of IDEAS for multi-pressure flash separator network synthesis

In this work, the isothermal, isobaric flash separator shown in figure 2 is considered. The flash separator’s vapor and liquid exit streams are considered to be in phase equilibrium with one another. Since the main goal of the synthesis task to be undertaken is to establish the feasibility of separation of an azeotropic mixture using multi-pressure distillation, and to identify a reasonably sized distillation network design that can carry out the aforementioned separation, only mass/component balance and phase equilibrium relations are incorporated in the flash separator’s mathematical model, and the considered optimization goal is the minimization of the total flow entering the network’s flashes. This objective function can be thought of to directly be minimizing network capital cost (flash separator total volume) by considering that each flash separator has the same residence time. It can also be thought of to indirectly minimize energy consumption, since distillation network energy costs are typically related to the network’s flows. As long as there are no constraints imposed on the network’s energy consumption, energy balances need not be incorporated in the flash separator and distribution network models, for the minimum total network flow to be correctly identified over all feasible networks. Indeed, by
omitting all energy balances the optimization problem has a larger feasible region than if the energy balances are included. Thus the obtained minimum is less than or equal to the minimum obtained with the energy balances included. The two aforementioned minima are actually equal, since energy balances can always be written a posteriori for the network minimizing total flow, to identify the network’s heating and cooling needs. The lack of any specifications on these needs suggests that the network would be feasible even if energy balances were considered. On the other hand, the synthesis of an optimally heat integrated multi-pressure distillation network would require that energy consumption specifications be imposed on the optimization problem, thus necessitating the use of energy balances. This latter problem will be the subject of future research efforts.

It is true that distillation is an inherently nonlinear process with nonlinear constraints. The beauty of IDEAS is exactly that it overcomes the inherently nonlinear nature of the distillation process optimization problem, not via some kind of Taylor series approximate linearization, but rather by exploiting the decomposition and linearity properties that naturally exist in the distillation process model, based on knowledge of the intensive properties and design parameters, and independently of the extensive properties.

The considered equilibrium separator model employs the Gamma-Phi vapor liquid equilibrium formulation\textsuperscript{49} (p. 545) and mass and component balances.

\[ f_k^P - x_k^L F^L - y_k^V F^V = 0 \quad \forall k = 1, n \quad (1.1) \]

\[ \sum_{k=1}^{n} x_k^L = 1 \quad (1.2) \]
\[
\sum_{k=1}^{n} y_k^V = 1 \quad (1.3)
\]

\[
y_k^V \phi_k \left( \left\{ y_j^V \right\}_{j=1}^{n}, T, P \right) P - x_k^L \gamma_k \left( \left\{ x_j^L \right\}_{j=1}^{n}, T \right) P_{sat} \left( T \right) = 0 \quad \forall k = 1, n \quad (1.4)
\]

**Figure 1.2:** Representation of a flash separator

A variety of thermodynamic models can be employed in quantifying the functions

\[
\phi_k \left( \left\{ y_j^V \right\}_{j=1}^{n}, T, P \right), \gamma_k \left( \left\{ x_j^L \right\}_{j=1}^{n}, T \right), P_{sat} \left( T \right) \quad \forall k = 1, n.
\]

In the illustrative case studies outlined below, ideal gas behavior is assumed \( \phi_k \left( \left\{ y_j^V \right\}_{j=1}^{n}, T, P \right) = 1 \quad \forall k = 1, n \); the Wilson equations \( (1.5)-(1.6) \) are used to model the non-ideal liquid phase coefficients \( \gamma_k \left( \left\{ x_j^L \right\}_{j=1}^{n}, T \right) \quad \forall k = 1, n \),

and the extended Antoine equation \( (1.7) \) is used to model the vapor pressure \( P_{sat} \left( T \right) \quad \forall k = 1, n \).

\[
\ln \left( \gamma_k \left( \left\{ x_j^L \right\}_{j=1}^{n}, T \right) \right) = 1 - \ln \left( \sum_{j=1}^{n} x_j^L \Lambda_{k,j} \left( T \right) \right) - \sum_{j=1}^{n} \left( \frac{x_j^L \Lambda_{k,j} \left( T \right)}{\sum_{j=1}^{n} x_j^L \Lambda_{i,j} \left( T \right)} \right) \quad \forall k = 1, n \quad (1.5)
\]

\[
\Lambda_{k,j} \left( T \right) = \frac{V_k^L}{V_k} \exp \left( \frac{-A_{k,j}}{RT} \right) \quad \forall k = 1, n; \quad \forall j = 1, n \quad (1.6)
\]
\[ \ln \left( P_{k}^{\text{sat}}(T) \right) = A_k + \frac{B_k}{T+C_k} + D_k \cdot \ln(T) + E_k \cdot T^{F_k} \quad \forall k = 1, n \] (1.7)

The above lead us to conclude that the aforementioned flash separator model can be employed to construct the following input-output information map:

\[ \Phi : \mathbb{R}^{n+2} \times \mathbb{R}^{n+2} \to \mathbb{R}^{2n+2} \times \mathbb{R}^{n+2}, \quad \Phi : \ u \to y = \Phi(u) = \left[ \left[ \Phi_1(u_1, u_2)^T \right] \left[ \Phi_2(u_1, u_2)^T \right]^T \right] \]

Where:

\[ u = \left[ u_1^T \left| u_2^T \gamma^T \right. \right] = \left[ P \ T \ x_1^L \ ... \ x_n^L \ | \ f_1 \ f_2 \ ... \ f_n \ F^L \ F^V \right] \]

\[ u \in D = \left\{ u = (u_1, u_2) \in \mathbb{R}^{n+2} \times \mathbb{R}^{n+2} : \Psi_1(u_1) = 0 \land \Psi_2(u_1, u_2) = 0 \land u_1 \geq 0 \land u_2 \geq 0 \right\} \]

\[ \Psi_1 : \mathbb{R}^{n+2} \to \mathbb{R}^2, \quad \Psi_1 : u_1 = \left[ \begin{array}{c} P \\ T \\ x_1^L \\ \vdots \\ x_n^L \end{array} \right] \to \Psi_1(u_1) = \left[ \begin{array}{c} \sum_{k=1}^{n} x_k^L - 1 \\ \sum_{k=1}^{n} x_k^L \gamma_k \left( \{x_i^L\}_{i=1}^{n}, T \right) P_{k}^{\text{sat}}(T) P \end{array} \right] \]

\[ \Psi_2 : \mathbb{R}^{n+2} \times \mathbb{R}^{n+2} \to \mathbb{R}^n, \quad \Psi_2 : \left[ \begin{array}{c} u_1 \\ u_2 \end{array} \right] \to \Psi_2 \left( \left[ \begin{array}{c} u_1 \\ u_2 \end{array} \right] \right) = \left[ \begin{array}{c} f_1^P - x_1^L F^V - \frac{x_1^L \gamma_1 \left( \{x_i^L\}_{i=1}^{n}, T \right) P_{1}^{\text{sat}}(T)}{P} F^V \\ \vdots \\ f_n^P - x_n^L F^V - \frac{x_n^L \gamma_n \left( \{x_i^L\}_{i=1}^{n}, T \right) P_{n}^{\text{sat}}(T)}{P} F^V \end{array} \right] \]

\[ y = \left[ y_1^T \left| y_2^T \right. \right] = \left[ T \ y_1^V \ ... \ y_n^V \ P \ x_1^L \ ... \ x_n^L \ | \ f_1 \ f_2 \ ... \ f_n \ F^L \ F^V \right]^T \]
\[
\Phi_1 : \mathbb{R}^{n+2} \times \mathbb{R}^{n+2} \to \mathbb{R}^{2n+2}, \quad \Phi_1 : (u_1, u_2) \mapsto y_1 = \Phi_1(u_1, u_2) = \begin{bmatrix}
T \\
x_1^L, y_1 \left( \{ x_i^L \}_{i=1}^n, T \right) P^\text{sat} (T) \\
\vdots \\
x_n^L, y_n \left( \{ x_i^L \}_{i=1}^n, T \right) P^\text{sat} (T) \\
P \\
x_1^L \\
\vdots \\
x_n^L
\end{bmatrix}
\]

\[
\Phi_2^T : \mathbb{R}^{n+2} \times \mathbb{R}^{n+2} \to \mathbb{R}^{n+2}, \quad \Phi_2^T : [u_1^T \quad u_2^T]^T \mapsto y_2^T = \Phi_2^T \left( [u_1^T \quad u_2^T]^T \right) = [f_1 \quad \cdots \quad f_n \quad F^L \quad F^V]^T
\]

The engineering importance of the above information maps can best be understood as follows.

Consider that \( u_i = [P \quad T \quad x_i^L \quad \cdots \quad x_n^L]^T \) such that \( \Psi_1(u_i) = 0 \land u_i \geq 0 \) is known. This can be ascertained by first considering \( [P \quad T \quad x_1^L \quad \cdots \quad x_{n-2}^L]^T \geq [0 \quad 0 \quad 0 \quad \cdots \quad 0]^T \) to be known, and by then solving for all \( q \) physically meaningful solutions \( [x_{n-1}^L \quad x_n^L]^T \geq [0 \quad 0]^T \) of the system of equations \( \sum_{k=1}^n x_k^L - 1 = 0, \sum_{k=1}^n \frac{x_k^L}{\gamma_k} \left( \{ x_i^L \}_{i=1}^n, T \right) P^\text{sat} (T) - 1 = 0 \). \( q \) may be either zero or a positive integer. For each of the \( q \), resulting physically meaningful vectors \( u_i = [P \quad T \quad x_1^L \quad \cdots \quad x_n^L]^T \{ y_i^V \}_{i=1}^q \) can then be computed through (1.4). In turn, this suggests that for any \( u_i \) such that \( \Psi_1(u_i) = 0 \land u_i \geq 0 \) one can actually evaluate the image \( \Phi_1(u) \).

Having defined the maps \( \Psi_1, \Psi_2, \Phi_1, \Phi_2 \), we can now readily verify the following properties:
1.3.1. IDEAS property 1

\[ \exists \Phi_3 : \mathbb{R}^{n+2} \rightarrow \mathbb{R}^{2n+2} \] such that \( \Phi_1(u_1, u_2) = \Phi_3(u_1) \) \( \forall (u_1, u_2) \in D \). This map is:

\[
\Phi_3 : u_1 = \begin{bmatrix} T \\ P \\ x_1^L \\ \vdots \\ x_n^L \end{bmatrix} \rightarrow \Phi_3(u_1) = \begin{bmatrix} T \\ x_1^L \gamma_1 \left( \left\{ x_i^L \right\}_{i=1}^n, T \right) P_1^{m_1}(T) \\ \vdots \\ P \\ x_n^L \gamma_n \left( \left\{ x_i^L \right\}_{i=1}^n, T \right) P_n^{m_n}(T) \end{bmatrix}
\]

This implies that \( y_1 \doteq \Phi_1(u_1, u_2) = \Phi_3(u_1) \) can be evaluated based only on knowledge of \( u_1 \) (intensive properties and design parameters) and independently of \( u_2 \) (extensive properties).

1.3.2. IDEAS property 2

\[ \exists \Phi_4 : \mathbb{R}^{n+2} \rightarrow \mathbb{R}^{(n+2)\times(n+2)} \] such that \( \Phi_2(u_1, u_2) = \Phi_4(u_1)u_2 \) \( \forall (u_1, u_2) \in D \). Indeed this map is:

\[ \Phi_4 : u_1 \rightarrow \Phi_4(u_1) = I \in \mathbb{R}^{(n+2)\times(n+2)} \], and thus \( y_2 \doteq \begin{bmatrix} f_1 & f_2 & \cdots & f_n & F^L & F^V \end{bmatrix}^T = Iu_2 = u_2 \)

This implies that, for fixed \( u_1 \), \( \Phi_4(u_1) \) is a linear operator (the identity operator), and

\[ y_2 \doteq \Phi_2(u_1, u_2) = \Phi_4(u_1)u_2 \] is linear in \( u_2 \).

1.3.3. IDEAS property 3:
\[ \exists \Psi_3 : \mathbb{R}^{n+2} \rightarrow \mathbb{R}^{n(n+2)} \text{ such that } \Psi_2(u_1, u_2) = \Psi_3(u_1)u_2 \quad \forall (u_1, u_2) \in D \]

Indeed this map is:

\[
\begin{bmatrix}
1 & 0 & \cdots & 0 & -x_1^L & - \frac{x_1^L \gamma_1 \left( \{x_i^L \}_{i=1}^n, T \} P_{1\text{sat}}(T) \right)}{P} \\
\vdots & 1 & \cdots & 0 & -x_2^L & - \frac{x_2^L \gamma_2 \left( \{x_i^L \}_{i=1}^n, T \} P_{2\text{sat}}(T) \right)}{P} \\
0 & \ddots & \cdots & 0 & \vdots \\
0 & 0 & \cdots & 1 & -x_n^L & - \frac{x_n^L \gamma_n \left( \{x_i^L \}_{i=1}^n, T \} P_{n\text{sat}}(T) \right)}{P}
\end{bmatrix}
\]

This implies that \( \Psi_3(u_1) \) can be evaluated based only on knowledge of \( u_1 \), and independently of \( u_2 \), and that, for fixed \( u_1 \), \( \Psi_3(u_1) \) is a linear operator, and thus \( \Psi_2(u_1, u_2) = \Psi_3(u_1)u_2 \) is linear in \( u_2 \).

At this point, it should be noted for future reference that the incorporation of energy balances in the problem formulation does not change the above characteristics of the flash separator model. Indeed, given a predictive thermodynamic model that accounts not only for phase equilibrium but also for molar enthalpy, calculation of all the vapor/liquid product mole fractions and molar enthalpies, only requires knowledge of the flash \( P, T \), and \( \{x_i^L \}_{i=1}^{n-2} \), and does not require any knowledge of either the feed component flows or the feed enthalpy flows or the total product molar flows.
It has been established that, for a fixed vector \( u_1 \), the employed flash-separator model is defined by an input-output map \( \Phi_3(u_i) \) whose domain is defined as the set

\[
\begin{equation}
\begin{bmatrix}
P & T & x_i^L & \cdots & x_n^L
\end{bmatrix}^T \in \mathbb{R}^{n+2} : \Psi_1(u_i) = 0
\end{equation}
\]

and by an identity operator \( \Phi_4(u_i) \) whose domain is the null space of \( \Psi_3(u_i) \) which, for fixed \( u_1 \), is a linear operator. To incorporate the variation of \( u_1 \) in the optimization process, so as to avoid suboptimal solutions, an infinite number of flash-separator units each with a fixed value of \( u_1 \) is considered such that the union of the considered \( u_1 \) values is dense in the set over which \( u_1 \) can vary. A one-to-one correspondence is then created between the infinite sequence \( \{u_i(i)\}_{i=1}^{\infty} \) consisting of all possible values of \( u_1 \) and the infinite sequence \( \{\Psi_3(u_i(i))\}_{i=1}^{\infty} \) of corresponding linear maps used to define the domain of the identity operator for each flash-separator unit. These sequences are then used to define the domain and action of a linear operator (termed IDEAS OP) that quantifies the effect of all flash-separator units, and has its domain and range be subsets of infinite-dimensional spaces. This relation gives rise to the linear OP constraints, which hold true around every OP unit.

To account for all possible multi-pressure distillation flowsheets the (OP) operator needs to be interfaced with a distribution network (DN) where all stream splitting, mixing and pressure adjustment occurs, as shown in figure 3. Each of the cross-flow streams in the DN is characterized by a flow rate variable, and fixed destination and origin conditions. This information takes the form of the following sequence triplets respectively: DN inlet to DN outlet, \( (F'^O_L, z^O, z^l) \), DN inlet to OP inlet, \( (F'^P_L, z^P, z^l) \), OP liquid outlet to DN outlet, \( (F'^O_L, z^O, x^L) \).
OP vapor outlet to DN outlet, \( (F_{OV}, z^0, y^V) \), OP liquid outlet to OP inlet, \( (F_{PL}, z^p, x^L) \), and OP vapor outlet to OP inlet, \( (F_{PV}, z^p, y^V) \).

\[ \text{Figure 1.3: IDEAS representation for (multi-pressure) flash separator network} \]
1.3.4. LP Formulation

A linear objective is considered in the proposed IDEAS formulation. It can be generally presented as:

\[
\sum_{i=1}^{\infty} \sum_{j=1}^{M} \alpha_{i,j} F_{PL}^{i} (i, j) + \sum_{i=1}^{\infty} \sum_{j=1}^{M} \beta_{i,j} F_{PL}^{j} (i, j) + \sum_{i=1}^{\infty} \sum_{j=1}^{M} \gamma_{i,j} F_{PV}^{i} (i, j)
\]

The above objective function can be used to realize a wide array of objectives, through appropriate selection of the cost coefficients \(\alpha_{i,j}\), \(\beta_{i,j}\), and \(\gamma_{i,j}\), associated with each of the problem’s flow variables. In the case study below, the minimization of total flash volume is considered. Under the assumption that each flash has the same residence time as any other flash (i.e. assuming that the same time is needed to reach equilibrium), the common residence time shared by all flashes can be factored out. This yields \(\alpha_{i,j} = \beta_{i,j} = \gamma_{i,j} = 1\), which then yields the following objective function:

\[
\sum_{i=1}^{\infty} \sum_{j=1}^{M} F_{PL}^{i} (i, j) + \sum_{i=1}^{\infty} \sum_{j=1}^{M} F_{PL}^{j} (i, j) + \sum_{i=1}^{\infty} \sum_{j=1}^{M} F_{PV}^{i} (i, j)
\]

which represents the total flow entering the network’s flashes (total network unit inlet flow).

The resulting mathematical formulation of IDEAS (I.F.1) is:
\[ \nu \geq \inf \sum_{i=1}^{\infty} \sum_{j=1}^{M} F^p_l(i, j) + \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} F^{p_l}(i, j) + \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} F^{p_v}(i, j) \]

\[ s.t. \]

\[ F^l(j) - \sum_{i=1}^{N} F^{o_l}(i, j) + \sum_{i=1}^{\infty} F^{p_l}(i, j) = 0 \quad (1.8) \quad \forall j = 1, \ldots, M \]

\[ F^{o_l}(i) - \sum_{j=1}^{M} F^{o_l}(i, j) - \sum_{j=1}^{\infty} F^{o_l}(i, j) - \sum_{j=1}^{\infty} F^{o_v}(i, j) = 0 \quad (1.9) \quad \forall i = 1, \ldots, N \]

\[ F^{l}(j) - \sum_{i=1}^{N} F^{o_l}(i, j) - \sum_{i=1}^{\infty} F^{p_l}(i, j) = 0 \quad (1.10) \quad \forall j = 1, \ldots, \infty \]

\[ F^{v}(j) - \sum_{i=1}^{N} F^{o_v}(i, j) + \sum_{i=1}^{\infty} F^{p_v}(i, j) = 0 \quad (1.11) \quad \forall j = 1, \ldots, \infty \]

\[ \left( z^o_k(i) \right)^j F^o_l(i) \leq \sum_{j=1}^{M} z^o_k(j) F^{o_l}(i, j) + \sum_{j=1}^{\infty} x^o_k(j) F^{o_l}(i, j) \\
+ \sum_{j=1}^{\infty} y^o_k(j) F^{o_v}(i, j) \leq \left( z^o_k(i) \right)^n F^o_l(i) \quad (1.12) \quad \forall i = 1, \ldots, N; \forall k = 1, \ldots, n \]

\[ f^p_k(i) - x^l_k(i) F^l(i) - y^l_k(i) F^v(i) = 0 \quad (1.13) \quad \forall i = 1, \ldots, \infty; \forall k = 1, \ldots, n \]

\[ f^p_k(i) - F^p(i) \cdot z^p_k(i) = 0 \Rightarrow \]

\[ f^p_k(i) - \sum_{j=1}^{M} z^p_k(j) F^{p_l}(i, j) - \sum_{j=1}^{\infty} x^l_k(j) F^{p_l}(i, j) - \sum_{j=1}^{\infty} y^l_k(j) F^{p_v}(i, j) = 0 \quad (1.14) \quad \forall i = 1, \ldots, \infty; \forall k = 1, \ldots, n \]

\[ F^l \geq 0; F^o \geq 0; F^p \geq 0; F^v \geq 0; F^{o_l} \geq 0; F^{p_l} \geq 0; F^{o_v} \geq 0; F^{p_v} \geq 0; f^p_k \geq 0; \]

\[ F^{o_v} \geq 0; F^{p_l} \geq 0; F^{p_v} \geq 0; f^p \geq 0; \]
Constraints (1.8) and (1.9) represent the DN inlet (splitting) and outlet (mixing) total flow balances respectively, graphically appearing on the left and top of the DN block in figure 3. Constraints (1.10) and (1.11) correspond to the OP total liquid and vapor outlet flow balances respectively, which undergo splitting operations in the DN, and graphically appear on the bottom of the DN. Constraint (1.12) correspond to the bounds on the quality variables of the DN outlet and is represented by component balances, which undergo mixing operations in the DN, and graphically appear on the top of the DN. Constraint (1.13) represents the separator model, and finally constraint (1.14) correspond to the OP inlet component flow balances, which undergo mixing operations in the DN, and graphically appear on the right of the DN. In addition, all flow variables are nonnegative.

Close examination of the above formulation reveals that it gives rise to an infinite linear program (ILP). The aforementioned linearity of the infinite program stems from the linearity of the IDEAS OP established earlier, and the linearity of the constraints that quantify the IDEAS DN as shown below:

1- The DN total flow mixing and splitting balances appearing in constraints (1.8)–(1.11) are inherently linear.

2- The DN component flow mixing balances appearing in constraint (1.12) and (1.14) are linear, because the vapor (liquid) composition of vapor (liquid) streams entering or leaving the DN at any junction are known and fixed.
Two propositions are next presented to simplify the structure of the above IDEAS formulation by reducing the number of variables considered without compromising optimality.

1.3.5. Proposition 1

The OP inlet and outlet flow variables $f^P_k(i), F^L(i), F^V(i) \ \forall i = 1, \infty$ can be eliminated from the IDEAS formulation (I.F.1) via variable substitution without compromising optimality.

Proof:

Substitution of $f^P_k(i) \ \forall i = 1, \infty$ from (1.13) to (1.14) and subsequent substitution of $F^L(i), F^V(i) \ \forall i = 1, \infty$ from (1.10) and (1.11) into the resulting equation, yields:

$$
\sum_{j=1}^M z^L_k(j) F^{PL}(i,j) + \sum_{j=1}^\infty x^L_k(j) F^{PL}(i,j) + \sum_{j=1}^\infty y^V_k(j) F^{PV}(i,j) - x^L_k(i) F^L(i) - y^V_k(i) F^V(i) = 0 \ \Rightarrow (1.10),(1.11)
$$
\[
\sum_{j=1}^{M} z_{k}^{j}(j)F_{PL}^{j}(i,j) + \sum_{j=1}^{\infty} x_{k}^{j}(j)F_{PL}^{j}(i,j) + \sum_{j=1}^{\infty} y_{k}^{j}(j)F_{PV}^{j}(i,j) - x_{k}^{j}(i) \left[ \sum_{j=1}^{N} F_{OL}^{j}(j,i) + \sum_{j=1}^{\infty} F_{PL}^{j}(j,i) \right] \\
- y_{k}^{j}(i) \left[ \sum_{j=1}^{N} F_{OV}^{j}(j,i) + \sum_{j=1}^{\infty} F_{PV}^{j}(j,i) \right] = 0
\]

(1.15) \quad \forall i = 1, \ldots, \infty ; \quad \forall k = 1, \ldots, n

Constraint (1.15) only involves the flow variables occurring inside the DN, i.e.

\[ F_{PL}^{j}(i,j), F_{PL}^{j}(i,j), F_{PV}^{j}(i,j), F_{OL}^{j}(i,j), F_{OV}^{j}(i,j) , \]

and replaces equations (1.10), (1.11), (1.13), and (1.14). Furthermore, the non-negativity constraints

\[ f_{k}^{p}(i) \geq 0, f_{k}^{L}(i) \geq 0, f_{k}^{V}(i) \geq 0 \quad \forall i = 1, \infty , \]

are ensured by the non-negativity of

\[ F_{PL}^{j}(i,j), F_{PV}^{j}(i,j), F_{OL}^{j}(i,j), F_{OV}^{j}(i,j), x_{k}^{j}(i), y_{k}^{j}(i) \quad \forall i = 1, \infty ; \quad \forall j = 1, \infty ; \quad \forall k = 1, \ldots, n . \]

In addition, the variables \( f_{k}^{p}(i), f_{k}^{L}(i), f_{k}^{V}(i) \quad \forall i = 1, \infty \) do not appear in the objective function.

Thus, they can be omitted. O.E.D.

**1.3.6. Proposition 2**

The self-recycling liquid flows and vapor flows \( F_{PL}^{j}(i,i), F_{PV}^{j}(i,i) \quad \forall i = 1, \infty \)

respectively can be eliminated from the IDEAS formulation (I.F.1) without compromising optimality.

Proof:

The variables \( F_{PL}^{j}(i,i), F_{PV}^{j}(i,i) \quad \forall i = 1, \infty \) only appear in the equality constraint (1.15) and in their respective non-negativity inequalities. Constraint (1.15) can be rewritten as:
\[
\sum_{j=1}^{M} z^l_k(j) F^{pl}(i,j) + \sum_{j=1}^{N} x^l(k)(j) F^{pl}(i,j) + \sum_{j=1}^{N} y^v(j) F^{pv}(i,j) + x^l_k(i) F^{pl}(i,i) + y^v_k(i) F^{pv}(i,i)
\]

\[
-x^l_k(i) \left[ \sum_{j=1}^{N} F^{ol}(j,i) + \sum_{j=1}^{N} F^{pl}(j,i) + F^{pl}(i,i) \right] - y^v_k(i) \left[ \sum_{j=1}^{N} F^{ov}(j,i) + \sum_{j=1}^{N} F^{pv}(j,i) + F^{pv}(i,i) \right] = 0
\]  
\[\text{(1.15)} \quad \forall i=1,\ldots, \infty \quad ; \quad \forall k=1,\ldots, n\]

\[
\Leftrightarrow \sum_{j=1}^{M} z^l_k(j) F^{pl}(i,j) + \sum_{j=1}^{N} x^l_k(j) F^{pl}(i,j) + \sum_{j=1}^{N} y^v(j) F^{pv}(i,j)
\]

\[
-x^l_k(i) \left[ \sum_{j=1}^{N} F^{ol}(j,i) + \sum_{j=1}^{N} F^{pl}(j,i) \right] - y^v_k(i) \left[ \sum_{j=1}^{N} F^{ov}(j,i) + \sum_{j=1}^{N} F^{pv}(j,i) \right] = 0
\]  
\[\text{(1.16)} \quad \forall i=1,\ldots, \infty \quad ; \quad \forall k=1,\ldots, n\]

Eq. (1.16) no longer contains the variables \(F^{pl}(i,i), F^{pv}(i,i)\) \(\forall i=1, \infty\). This is also the case for all other equality constraints. Thus these variables appear only in the objective function and in their respective non-negativity constraints. In addition, the weight coefficient of each of these variables in the objective function is positive (actually equal to one). Since \(V\) is a minimization problem, then the value of each of these variables at the optimum is zero. O.E.A.

Based on the above two properties, the mathematical formulation of IDEAS (I.F.2) becomes:

\[
\nu \geq \inf \sum_{i=1}^{M} \sum_{j=1}^{N} F^{pl}(i,j) + \sum_{i=1}^{M} \sum_{j=1}^{N} F^{pl}(i,j) + \sum_{i=1}^{M} \sum_{j=1}^{N} F^{pv}(i,j)
\]

\[s.t.\]

\[
(1.8), (1.9), (1.12) \& (1.16)
\]

\[
F^l \geq 0; F^o \geq 0; F^{ol} \geq 0; F^{pl} \geq 0; F^{ov} \geq 0; F^{pv} \geq 0; F^{pl} \geq 0; F^{pv} \geq 0
\]  
\[\text{(1.17)}\]
An infinite dimensional linear program cannot be explicitly solved. However, its solution can be approximated by a series of finite linear programs of increasing size, whose sequence of optimum values converges to the infinite dimensional problem’s infimum. In particular, consider the aforementioned IDEAS formulation with optimum value \( V \), which aims at the synthesis of a multi-pressure flash distillation network with \( M \) inlets, and \( N \) outlets and allows for the possible use of an infinite number of multi-pressure flash-separator units. By considering an ever increasing number \( G \) of multi-pressure flash-separator units, the optimum objective function values of the resulting finite linear programs form a non-increasing sequence \( \{ v_G \}^\infty_1 \) which converges to \( V \). The DN of these finite dimensional formulations contains \((M + 2G) \cdot (N + G)\) cross-flow streams. Proposition 2 reduces the number of those streams to \((M + 2G) \cdot (N + G) - 2G\) streams. These cross-flow streams are distributed as follows: \( M \cdot N \) DN inlet to DN outlet streams, \( M \cdot G \) DN inlet to OP inlet streams, \( G \cdot N \) OP liquid outlet to DN outlet streams, \( G \cdot N \) OP vapor outlet to DN outlet streams, \( G^2 - G \) OP liquid outlet to OP inlet streams, and \( G^2 - G \) OP vapor outlet to OP inlet streams.

Next, the proposed IDEAS framework is illustrated on a case-study involving the dual-pressure distillative separation of an azeotropic mixture.

1.4. Case Study 1: Dual-pressure distillation of a binary mixture of M-Acetate (1)/
Methanol (2)

In this case study, the dual-pressure (1 and 3 bar) distillative separation of an equimolar mixture of M-Acetate (species 1) and Methanol (species 2) is considered. Indeed, mixtures of M-Acetate (1) and Methanol (2) exhibit azeotropic behavior at 65.5% mole fraction of M-
Acetate at 1 bar, and 56.1% mole fraction of M-Acetate at 3 bars. This behavior is captured by the Gamma-Phi vapor liquid equilibrium model outlined in section 2. The vapor phase is considered to be an ideal gas, while the liquid phase activity coefficients are quantified by the Wilson equations (1.5)–(1.6), and the vapor pressure of the various species is quantified by the Antoine equation (1.7). The molar flow rate of the stream to be separated is 2 mol/s. The specifications of the two desired product streams are 20% (1) mole fraction for the first product, and 80% (1) mole fraction for the second product.

<table>
<thead>
<tr>
<th>Wilson Coefficients</th>
<th>( A_{11} ) (cal/mol)</th>
<th>( A_{12} ) (cal/mol)</th>
<th>( A_{21} ) (cal/mol)</th>
<th>( A_{22} ) (cal/mol)</th>
<th>( V_1 ) (cm³/mol)</th>
<th>( V_2 ) (cm³/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gmehling et al</td>
<td>0</td>
<td>-31.19</td>
<td>813.18</td>
<td>0</td>
<td>79.84</td>
<td>40.73</td>
</tr>
<tr>
<td>UniSim</td>
<td>0</td>
<td>9.117</td>
<td>776.6</td>
<td>0</td>
<td>80.26</td>
<td>40.76</td>
</tr>
</tbody>
</table>

**Table 1.1**: Wilson equation coefficients from UniSim and Gmehling et al.

A traditional two-column PSD design method and the aforementioned IDEAS design method will be compared. To this end, both design methods will aim to minimize the total network unit inlet flow. The traditional design will be pursued within the UniSim software platform, while the IDEAS design will be carried out with in-house developed IDEAS software. Both UniSim and IDEAS will employ the aforementioned Wilson and Antoine equation thermodynamic models. Associated coefficient values are already built-in UniSim, and can also be found in the literature (Gmehling et al. ⁵⁰ for the Wilson equation coefficients, and Poling et al. ⁵¹ for the Antoine equation coefficients). The values of these coefficients are summarized in Tables 1 and 2 below. The thermodynamic behavior of these models is captured in figure 4 below, which illustrates the
T-x-y diagram for the mixture under study, at the two pressures considered. Given that UniSim’s coefficients are already built-in the software, and for purposes of a fair comparison between the traditional and IDEAS methods, UniSim’s values will also be employed in IDEAS.

<table>
<thead>
<tr>
<th>Coefficients</th>
<th>Poling ($k = 1$)</th>
<th>UniSim ($k = 1$)</th>
<th>Poling ($k = 2$)</th>
<th>UniSim ($k = 2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_i$</td>
<td>14.240</td>
<td>96.52</td>
<td>16.578</td>
<td>59.84</td>
</tr>
<tr>
<td>$B_i$</td>
<td>-2662.78</td>
<td>-7050</td>
<td>-3638.27</td>
<td>-6283</td>
</tr>
<tr>
<td>$C_i$</td>
<td>219.69</td>
<td>0</td>
<td>239.50</td>
<td>0</td>
</tr>
<tr>
<td>$D_i$</td>
<td>0</td>
<td>-12.38</td>
<td>0</td>
<td>-6.379</td>
</tr>
<tr>
<td>$E_i$</td>
<td>0</td>
<td>1.137e-5</td>
<td>0</td>
<td>4.617e-6</td>
</tr>
<tr>
<td>$F_i$</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 1.2: Antoine equation coefficients from UniSim and Poling et al., UniSim (T(K), P(kPa)), Poling et.al (T(°C), P(kPa))

$\Delta$: UniSim built-in thermodynamic data
●: Literature thermodynamic data
Next, the optimization of a traditional two-column PSD design is carried out (sec. 1.4.1), followed by the IDEAS optimization method (sec. 1.4.2).

1.4.1. Optimized Traditional Two-Column PSD Design

A traditional two-column PSD design and its UniSim representation are shown in figures 5a, and 5b respectively. The objective function minimized here \((F_{\text{Total}})\) is the total network unit inlet flow, which is \(F_{\text{Total}} = F_{T_1} + F_{T_2}\), where \(F_{T_1}\) and \(F_{T_2}\) are the sums of vapor and liquid molar flow rates entering each plate in columns \(T_1\) and \(T_2\) respectively.

To determine the number of degrees of freedom associated with the flow structure of the separation system in figure 5, the mass, and component mass balance equations (using M-Acetate as the reference species) outside columns \(T_1\) and \(T_2\), and the inlet and outlet specifications, are considered:

\[
\begin{align*}
F &= B_1 + B_2 \\
D_1 &= D_2 + B_2 \\
F_{T_1} &= D_1 + B_1 \\
F_{z} &= B_1x_{B1} + B_2x_{B2} \\
D_1x_{D_1} &= D_2x_{D_2} + B_2x_{B2} \\
F_{T_1}z_1 &= D_1x_{D_1} + B_1x_{B1}
\end{align*}
\]

This is a set of 10 equations involving 12 variables. Therefore, there are 2 degrees of freedom, (that can be chosen as \(x_{D_1}\), and \(x_{D_2}\)), that are associated with the traditional design’s flow structure. These are augmented by 4 degrees of freedom associated with column internals, namely the number of plates and the feed plate location for each of the two columns, thus giving rise to 6 degrees of freedom in total for the traditional design.
The solution to the minimization problem is carried out using an exhaustive search in the triangular feasible region of the \( (x_{D_1}, x_{D_2}) \) 2-D space defined by the physical inequality constraints \( x_{AZ_1} \geq x_{D_1} \geq x_{D_2} \geq x_{AZ_2} \). For every \( (x_{D_1}, x_{D_2}) \) in this region, the aforementioned mass and component mass balances are solved and the input-output flow/composition information for each of the two columns is determined. Then, the optimization problem is reduced to two

**Figure 1.5:** a) Traditional two-column azeotropic separation system

b) UniSim representation of azeotropic separation system
separate single column optimization problems, each of which involves identifying the optimum number of plates and optimum feed plate location, and is carried out by systematically varying these integer valued variables in UniSim. Every time the number of plates or the location of the feed plate changes, UniSim automatically adjusts the reflux and reboil ratio to ensure feasible column operation. Following this procedure, the globally minimum $F_{Total}$ as a function of $x_{D1}$ and $x_{D2}$ is shown in figure 6 and is found to be 202.93 mol/s at $(x_{D1}, x_{D2})_{optim} = (0.629, 0.586)$. 

![Figure 1.6: Two views of iso- $x_{D1}$ lines of $F_{Total}$ as a function of $x_{D2}$ in $(x_{D1}, x_{D2})$ space](image)

1.4.2. IDEAS-Generated Globally Optimal Azeotropic Separation Design

According to the phase rule\(^{49}\) (pp. 339-340) for binary mixtures in equilibrium at a fixed pressure, knowledge of temperature can yield a finite number of corresponding mole fractions, thus in the context of IDEAS $u_1 = [P \ T]^T$. Using the procedure outlined below, it can be determined that for $P = 1$ bar, if $T \leq 330$ there exist two $x_i^L$ solutions ($q = 2$), while if $T > 330$
there exists only one solution \( x_{1}^{L} (q = 1) \). Similarly, for \( P = 3 \) bars, if \( T \leq 365.7 \) K there exist two \( x_{1}^{L} \) solutions \((q = 2)\), while if \( T > 365.7 \) K there exists only one solution \( x_{1}^{L} (q = 1) \).

The following numerical/graphical procedure captures all feasible flash separators corresponding to the two operating pressures considered, and a discretization of the feasible temperature range.

1- For each pressure, select a temperature \( T \) from the considered temperature grid, and then evaluate \( P_{k}^{sat} \) \( \forall k = 1, 2 \) from (1.7)

2- Express first \( \gamma_{k} \) \( \forall k = 1, 2 \), and subsequently \( y_{k}^{V} \) \( \forall k = 1, 2 \), as a function of \( x_{1}^{L} \) from (1.5) & (1.6), and from (1.4) respectively

3- Generate the graph of the function \( \sum_{k=1}^{2} y_{k}^{V} \) vs. \( x_{1}^{L} \) plot for the chosen \( P \) and \( T \), and identify all values of \( x_{1}^{L} \in [0, 1] \) at which \( \sum_{k=1}^{2} y_{k}^{V} = 1 \) holds (as illustrated in figure 7 below). Each of these values corresponds to a feasible flash separator, with known values \( \{ x_{k}^{L} \}_{k=1}^{2}, \{ y_{k}^{V} \}_{k=1}^{2} \)

4- Return to step 1, and repeat steps 1-3 until all temperatures and pressures are considered
All flashes created for a given pressure are part of an ensemble of flash separator units called a pressure universe. The above procedure is therefore repeated for several different pressure levels, in order to create as many pressure universes as desired. At least two pressure universes are required for the separation of a binary azeotropic mixture. The grid discretization used for the temperature range can be selected to be uniform or non-uniform. A uniform grid generates flashes at equal temperature intervals, while a non-uniform grid generates more flashes for some, and less flashes for other, temperature intervals. Both uniform and non-uniform grids will be used in the following development to acquire globally optimal solutions.

Exact product specifications on the network outlet are achieved by setting the upper and lower bound of the outlet composition vector to be the same for each of the outlet streams 1 and 2 such that $\left(z^o(1)\right)^I = \bar{z}^o(1) = \left(z^o(1)\right)^U$, and $\left(z^o(2)\right)^I = \bar{z}^o(2) = \left(z^o(2)\right)^U$ respectively. Where $\bar{z}^o$
and \( \bar{z}^O (2) \) are vectors of fixed mole fractions for the network outlet streams 1 and 2 corresponding to \( \bar{z}^O (1) = [0.8 \ 0.2] \), and \( \bar{z}^O (2) = [0.2 \ 0.8] \). The network’s two outlet flows are such that \( F^O (1) = F^O (2) = 1 \), while the network’s inlet mole fractions and flow are \( \bar{z}^I (1) = [0.5 \ 0.5]^T \), and \( F^I (1) = 2 \). The solution process for the IDEAS formulation involves the sequential solution of finite linear programs of increasing size \( G \), until the values of the finite optima do not change significantly (less than 0.25%).

1.4.2.1. Uniform Temperature Grid Discretization Strategy

Figure 8 shows the convergence of the IDEAS optimum objective function \( \nu_c \) as \( G \) increases. As previously mentioned, the number of units made available to IDEAS depends on the level of discretization of the temperature space. Starting with an initial discretization level of 0.15 K, the discretization levels chosen are uniform, cover the entire temperature space, and correspond to \( \frac{0.15K}{i} \) \( \forall T (G = 193 \) units for \( i = 1 \); \( G = 386 \) units for \( i = 2 \), and \( G = 772 \) for \( i = 4 \).
At the smallest temperature discretization (0.0375K) the generated flow sheet has a converged total network unit inlet flow value of 138.9072 (mol/s). Since a temperature discretization of 0.0375K contains as a subset in its universe of flashes all the flashes generated at a temperature discretization of 0.075K, and since the total network unit inlet flow between these last two points differs by only 0.2 % convergence can be declared. This represents a 31.54 % reduction over the optimized two-column design.

The actual number of units employed at the IDEAS optimum is only a small fraction of the number of units made available to the IDEAS formulation. Indeed, the IDEAS-generated flow sheet corresponding to 193 available units (0.15K) is shown below in figure 9 and consists of a

![IDEAS convergence](image-url)
total of 16 units. This particular IDEAS design has an optimum objective function corresponding to 152.4843 (mol/s), which represents a 24.85% decrease over the optimized two-column design. Every flow and corresponding quality vector for that design is detailed in Table 3.

**Figure 1.9**: IDEAS optimum for $G = 193$ available units (uniform discretization)

*Liquid and vapor states only indicate the phase of flash outlets but not inlets solution and associated objective function values $\{v_G\}$ is guaranteed. Thus, the IDEAS infimum $V$ provides the globally optimal solution to the posed optimal design problem, and hence represents a lower bound to the cost of any alternative design employing the same technologies (flash separators) and operating pressures. This is confirmed in figure 8 above where the optimum value of the traditional design (202.93 mol/s) is seen to be above the IDEAS $v_G = 138.9072$ (mol/s) for $G = 772$ available units.
When a stream portion is indicated as leaving a flash and entering another flash, its thermal condition is known at the point of departure but not known at the point of arrival. The model considers that an appropriate cooling/heating apparatus, and possibly an appropriate pressure altering apparatus are associated with each DN flow from one flash to another. What is important to realize is that the networks identified by the present formulation can always be realized a posteriori through the use of the aforementioned apparatuses, and as previously mentioned the identified minimum total flow is correct over all networks whether the formulation includes energy balances or not.

<table>
<thead>
<tr>
<th>Unit #</th>
<th>X^c (M-Acetate)</th>
<th>Flow</th>
<th>Destination</th>
<th>Y^c (M-Acetate)</th>
<th>Flow</th>
<th>Destination</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5628</td>
<td>13.992</td>
<td>2</td>
<td>0.6047</td>
<td>14.827</td>
<td>9</td>
</tr>
<tr>
<td>2</td>
<td>0.5117</td>
<td>7.690</td>
<td>3</td>
<td>0.5792</td>
<td>14.977</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>0.4444</td>
<td>4.860</td>
<td>4</td>
<td>0.5454</td>
<td>8.682</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>0.3751</td>
<td>3.320</td>
<td>6</td>
<td>0.5082</td>
<td>3.857</td>
<td>3</td>
</tr>
<tr>
<td>5</td>
<td>0.2957</td>
<td>0.209</td>
<td>7</td>
<td>0.4590</td>
<td>0.248</td>
<td>4</td>
</tr>
<tr>
<td>6</td>
<td>0.2830</td>
<td>0.795, 0.876</td>
<td>7, 8</td>
<td>0.4501</td>
<td>2.071</td>
<td>4</td>
</tr>
<tr>
<td>7</td>
<td>0.2035</td>
<td>0.548</td>
<td>Out 1</td>
<td>0.3844</td>
<td>0.456</td>
<td>5</td>
</tr>
<tr>
<td>8</td>
<td>0.1956</td>
<td>0.452</td>
<td>Out 1</td>
<td>0.3766</td>
<td>0.423</td>
<td>6</td>
</tr>
<tr>
<td>9</td>
<td>0.6249</td>
<td>18.449</td>
<td>10</td>
<td>0.5894</td>
<td>13.856</td>
<td>1</td>
</tr>
<tr>
<td>10</td>
<td>0.6653</td>
<td>5.263</td>
<td>11</td>
<td>0.6143</td>
<td>17.466</td>
<td>9</td>
</tr>
<tr>
<td>11</td>
<td>0.6938</td>
<td>4.536</td>
<td>12</td>
<td>0.6333</td>
<td>4.267</td>
<td>10</td>
</tr>
<tr>
<td>12</td>
<td>0.7360</td>
<td>2.729</td>
<td>14</td>
<td>0.6631</td>
<td>3.540</td>
<td>11</td>
</tr>
<tr>
<td>13</td>
<td>0.7681</td>
<td>0.206</td>
<td>15</td>
<td>0.6883</td>
<td>0.195</td>
<td>12</td>
</tr>
<tr>
<td>14</td>
<td>0.7818</td>
<td>0.750, 0.446</td>
<td>16, Out 2</td>
<td>0.6997</td>
<td>1.536</td>
<td>12</td>
</tr>
</tbody>
</table>
Close examination of the generated optimum IDEAS networks reveals that they possess a number of properties:

1- They employ only a small percentage (< 10%) of the available units.

2- They exhibit a small degree of interconnectedness, despite the high degree of interconnectedness inherent in the IDEAS framework.

3- They exhibit countercurrent structures in some parts of the network, but not in others.

4- They exhibit only two interconnections between the high and low pressure parts of the network.

This suggests that although a very large number of units and interconnections is made available for consideration, only a select few participate in the optimal network. In addition, the optimal networks are physically meaningful and can be realistically constructed. Other interesting similarities between the IDEAS optimum networks representation and the traditional azeotropic separation structure are as follows:

1- High purity M-Acetate leaves the high pressure (3 bars) sequence, while high purity Methanol leaves the low pressure (1 bar) sequence, both in liquid form.

2- There exists only one stream connecting the low pressure sequence to the high pressure sequence, and only one recycle stream connecting the high pressure sequence back to the low pressure sequence.

### Table 1.3: Flash outlet flow rates and mole fractions for IDEAS design

<p>| | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.8060</td>
<td>0.113</td>
<td>Out 2</td>
<td>0.7211</td>
<td>0.0926</td>
</tr>
<tr>
<td>16</td>
<td>0.8167</td>
<td>0.441</td>
<td>Out 2</td>
<td>0.7312</td>
<td>0.309</td>
</tr>
<tr>
<td>Inlet</td>
<td>0.500</td>
<td>2.00</td>
<td>3</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
3- The feed enters the low pressure sequence at a single unit, whose exit compositions straddle the feed composition.

4- Vapor streams always flow against the temperature gradient of flashes (hot to cold) belonging to a pressure universe, while liquid streams always flow in the direction of the temperature gradient (cold to hot) of flashes belonging to a pressure universe.

In contrast, interesting differences between the IDEAS representation and the traditional azeotropic separation structure are as follows:

1- Communication between low and high pressure sequences occurs at the last stage of each sequence in IDEAS designs, while it occurs at intermediate stages in the traditional design.

2- The high pressure sequence has no rectifying section.

Analysis of the above flow sheet indicates that flash inlet flow quantity is largest for network flashes within close proximity of the azeotropic pinch point (lower temperatures). Therefore, a non-uniform temperature grid is introduced in the next section to allow the generation of more flashes around to the azeotropic pinch point. This will considerably reduce the problem size while still resulting in globally optimal flow sheets.

1.4.2.2. Non-uniform Temperature Grid Discretization Strategy

Starting with an initial discretization level of 0.3 K, the discretization level chosen is non-uniform, with its specifics displayed in table 4 corresponding to $G = 150$ units. The resulting objective function is equal to 138.6528 mol/s, which is effectively identical to the converged globally optimal value of 138.9072 mol/s determined in the previous section using a uniform temperature grid discretization strategy and $G = 772$ units. The IDEAS-generated flow sheet
corresponding to this number of flashes is shown in figure 10 below, with flow and corresponding quality vector detailed in table 5. Therefore, employing a non-uniform temperature grid discretization can potentially serve as an intelligent allocation of limited computational resources while still yielding globally optimal designs.

<table>
<thead>
<tr>
<th>P (bar)</th>
<th>$T$ range (K)</th>
<th>$T$ discretization</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$T \leq 327, K$</td>
<td>0.01875 K ($i = 16$)</td>
</tr>
<tr>
<td>1</td>
<td>$T &gt; 327, K$</td>
<td>0.3 K ($i = 1$)</td>
</tr>
<tr>
<td>3</td>
<td>$T \leq 359.6, K$</td>
<td>0.01875 K ($i = 16$)</td>
</tr>
<tr>
<td>3</td>
<td>$T &gt; 359.6, K$</td>
<td>0.3 K ($i = 1$)</td>
</tr>
</tbody>
</table>

Table 1.4: Non-uniform grid discretization of $T$ for the two pressure levels considered
In the next section, the effect of the operating pressure of the second universe of flashes (while the operating pressure of the first universe of flashes is kept equal to atmospheric) and product purity, on the IDEAS optimum, is quantified.

<table>
<thead>
<tr>
<th>Unit #</th>
<th>$X^c$ (M-Acetate)</th>
<th>Flow</th>
<th>Destination</th>
<th>$Y^c$ (M-Acetate)</th>
<th>Flow</th>
<th>Destination</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5654</td>
<td>8.831</td>
<td>3</td>
<td>0.6060</td>
<td>14.794</td>
<td>15</td>
</tr>
<tr>
<td>2</td>
<td>0.5365</td>
<td>3.396</td>
<td>4</td>
<td>0.5915</td>
<td>4.440</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>0.5303</td>
<td>3.444</td>
<td>4</td>
<td>0.5884</td>
<td>5.380</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>0.4890</td>
<td>5.739</td>
<td>5</td>
<td>0.5679</td>
<td>7.833</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>0.4256</td>
<td>4.518</td>
<td>7</td>
<td>0.5357</td>
<td>6.732</td>
<td>4</td>
</tr>
<tr>
<td>6</td>
<td>0.3809</td>
<td>0.107</td>
<td>8</td>
<td>0.5114</td>
<td>0.1308</td>
<td>5</td>
</tr>
<tr>
<td>7</td>
<td>0.3443</td>
<td>2.211, 0.244</td>
<td>10, 11</td>
<td>0.4902</td>
<td>3.247</td>
<td>5</td>
</tr>
<tr>
<td>8</td>
<td>0.3134</td>
<td>0.149</td>
<td>12</td>
<td>0.4708</td>
<td>0.136</td>
<td>5</td>
</tr>
<tr>
<td>9</td>
<td>0.2866</td>
<td>0.231</td>
<td>13</td>
<td>0.4526</td>
<td>0.238</td>
<td>6</td>
</tr>
<tr>
<td>10</td>
<td>0.2630</td>
<td>1.165</td>
<td>14</td>
<td>0.4353</td>
<td>1.044</td>
<td>7</td>
</tr>
<tr>
<td>11</td>
<td>0.2420</td>
<td>0.102</td>
<td>Out 1</td>
<td>0.4187</td>
<td>0.141</td>
<td>7</td>
</tr>
<tr>
<td>12</td>
<td>0.2231</td>
<td>0.0741</td>
<td>Out 1</td>
<td>0.4025</td>
<td>0.0754</td>
<td>8</td>
</tr>
<tr>
<td>13</td>
<td>0.2059</td>
<td>0.127</td>
<td>Out 1</td>
<td>0.3866</td>
<td>0.103</td>
<td>8</td>
</tr>
<tr>
<td>14</td>
<td>0.1902</td>
<td>0.695</td>
<td>Out 1</td>
<td>0.3711</td>
<td>0.469</td>
<td>9</td>
</tr>
<tr>
<td>15</td>
<td>0.6272</td>
<td>9.857</td>
<td>16</td>
<td>0.5907</td>
<td>13.823</td>
<td>1</td>
</tr>
<tr>
<td>16</td>
<td>0.6539</td>
<td>6.609</td>
<td>17</td>
<td>0.6071</td>
<td>8.866</td>
<td>15</td>
</tr>
<tr>
<td>17</td>
<td>0.6852</td>
<td>5.751</td>
<td>18</td>
<td>0.6272</td>
<td>5.615</td>
<td>16</td>
</tr>
</tbody>
</table>
1.4.3. Pressure & Purity Effects on Total Flash Inlet Flow:

The IDEAS framework makes it possible to systematically and rigorously evaluate the effect that product purity and pressure have on the optimum objective function value of total inlet flash flow. Consider the traditional azeotropic separation structures described above in sec. 1.4.1. For a given pressure, a design specifying lower product purity requires less total unit inlet flow than a design specifying higher product purity. Similarly, for a given product purity, a design operating at lower pressure will require more total unit inlet flow than a design operating at a higher pressure. This intuitive trend manifests itself in IDEAS designs as well. Figure 11 shows the total unit inlet flow as a function of pressure at three different product purities for a uniform discretization of 0.15K. This discretization level was selected because it leads to readily realizable flow sheets, and a smaller computational burden than that needed for smaller discretization levels.

The obtained IDEAS optimization results indicate that after an initial sharp decrease in total unit inlet flow at low pressures, the impact of further increasing pressure is minimal. This trend repeats itself at all product purities, albeit at lower product purities the curves begin to level off at lower pressures (earlier) than for higher product purities. Therefore, IDEAS can help determine not only optimal design structures and the optimal total unit inlet flow, but also appropriate levels of operating pressure for a desired level of product purity.
1.5. Case Study 2: Dual-pressure distillation of a ternary mixture of Water (1)/ Methanol (2)/ Acetone (3)

In this case study, the dual pressure distillative separation of a mixture of Water (species 1) Methanol (species 2), and Acetone (species 3) is considered. The mixture’s molar flow rate, and mole fractions of species 1, 2, and 3 are 3 mol/s, 0.3, 0.35 and 0.35 respectively. Binary mixtures of Methanol (2) and Acetone (3) exhibit a minimum boiling azeotrope at 79.07% mole fraction of Acetone (3) at 1 bar and 328.5 K, and 97.5% mole fraction of Acetone (3) at 0.2 bar and 288.7 K. Similarly to the previous case study, the mixture’s thermodynamic behavior is captured by a Gamma-Phi vapor liquid equilibrium model. The vapor phase is considered to be an ideal gas,

![Figure 1.11: Iso-purity lines of total flow entering network flashes as a function of pressure](image-url)
while the liquid phase activity coefficients are quantified by the Wilson equations (1.5)–(1.6),
and the vapor pressure of the various species is quantified by the Antoine equation (1.7).

<table>
<thead>
<tr>
<th>Wilson Coefficients</th>
<th>$A_1$</th>
<th>$A_2$</th>
<th>$A_3$</th>
<th>$A_{21}$</th>
<th>$A_{22}$</th>
<th>$A_{23}$</th>
<th>$A_{32}$</th>
<th>$A_{31}$</th>
<th>$A_{33}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>0</td>
<td>469.55</td>
<td>1448.01</td>
<td>107.33</td>
<td>0</td>
<td>583.11</td>
<td>-161.88</td>
<td>291.27</td>
<td>0</td>
</tr>
</tbody>
</table>

**Table 1.6.A: Wilson equation coefficients**

<table>
<thead>
<tr>
<th>Wilson Coefficients</th>
<th>$V_1$</th>
<th>$V_2$</th>
<th>$V_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>17.88</td>
<td>40.76</td>
<td>74.47</td>
</tr>
</tbody>
</table>

**Table 1.6.B: Wilson equation coefficients**

Similarly to case study 1, a traditional two-column PSD design method and the aforementioned IDEAS design method will be compared. To this end, both design methods will aim to minimize the total network unit inlet flow. The traditional design will be pursued within the UniSim software platform, while the IDEAS design will be carried out with in-house developed IDEAS software. Both UniSim and IDEAS will employ the aforementioned Wilson and Antoine equation thermodynamic models. The coefficient values employed in both methods are summarized in Tables 6 and 7. The ability of these thermodynamic models to capture the azeotropic behavior of the Methanol (2)/Acetone (3) mixture is shown in figure 12, which illustrates the mixture’s T-x-y equilibrium diagram, at the two pressures considered.
Two sets of design specifications are considered, as shown in table 8 below.

<table>
<thead>
<tr>
<th>Specification Set #</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Component-Mole Fraction-Flow Rate</td>
<td>Component-Mole Fraction-Flow Rate</td>
<td></td>
</tr>
<tr>
<td>Product 1</td>
<td>Water-0.80 - 1.0 mol/s</td>
<td>Water-0.80-Free</td>
</tr>
<tr>
<td>Product 2</td>
<td>Methanol-0.80-1.0 mol/s</td>
<td>Methanol-0.80-Free</td>
</tr>
<tr>
<td>Product 3</td>
<td>Acetone-0.80-1.0 mol/s</td>
<td>Acetone-0.80-1.2 mol/s</td>
</tr>
</tbody>
</table>

Table 1.8: Design specifications

For each set of specifications, a traditional two-column design is compared to the IDEAS-generated optimal design. The traditional design is carried out in UniSim, and the aforementioned thermodynamic data are used in both the UniSim and IDEAS designs.
1.5.1. Optimized Traditional Two-Column Design

A UniSim representation of the considered two-column design is shown in figure 13. This traditional design has been shown to be suitable for the separation of the water-methanol-acetone mixture. The objective function to be minimized is again the same as for the first case study (total network unit inlet flow), $F_{Total} = F_{T1} + F_{T2}$, where $F_{T1}$ and $F_{T2}$ are the sums of vapor and liquid molar flow rates entering each plate in columns $T_1$ (P=0.2 bar) and $T_2$ (P=1 bar) respectively. The first distillation column in the considered design has a known feed. Thus, it possesses four degrees of freedom, two of them integer variables (number of plates, and feed plate location), and the other two continuous. In this case study, and for both specification sets, the two continuous degrees of freedom are chosen to be the specified top product flowrate and specified acetone mole fraction. Once the first column’s degrees of freedom are specified, the second column’s feed is also specified. Thus again, the second column possesses two integer,
and two continuous degrees of freedom. For the first set of specifications, the second column
must meet four specifications: namely the flowrates of both of its products are known and the
methanol mole fraction in its distillate and the water mole fraction in its bottom are known.
Given the continuous nature of the specifications, and the integer nature of two of the four
degrees of freedom, it is likely that the considered traditional design may not be able to meet the
first set of specifications, since it possesses four integer degrees of freedom and must meet two
continuous specifications. On the other hand, for the second set of specifications, the first
column again has only two integer degrees of freedom. The second column however must meet
two specifications: namely the methanol mole fraction in its distillate and the water mole fraction
in its bottom are known. By selecting these variables as the second column’s continuous degrees
of freedom, the second column has two integer degrees of freedom. Therefore the traditional
design possesses no unmet continuous specifications, and four integer degrees of freedom that
can be used to optimize the design’s total network flow.

An exhaustive search over all possible values of the four integer degrees of freedom is carried
out through repeated UniSim simulations. For specification set 1, which must meet two
continuous specifications, there exists no two-column design capable of delivering the desired
specifications. For specification set 2 (figure 13), which has no unmet continuous specifications,
the optimized two-column design yields distillate and bottom streams flows of value equal to
0.7634 mol/s and 1.037 mol/s respectively. Optimized total network flow is equal to
44.487 mol/s.
1.5.2. IDEAS-Generated Globally Optimal Azeotropic Separation Design

According to the phase rule (pp. 339-340) for ternary mixtures in equilibrium at a fixed pressure, knowledge of temperature, and species (1) mole fraction can yield a finite number of corresponding mole fractions for the other two species, thus in the context of IDEAS, \( u_1 \) can be chosen as \( u_1 = \begin{bmatrix} P & T & x_1^L \end{bmatrix}^T \). Superscript \( q \), when needed, is used to indicate multiple \( x_2^L \) solutions corresponding to a fixed \( T, x_1^L \).

A similar numerical/graphical procedure to the one outlined in the first case study is employed to capture all feasible flash separators corresponding to the two operating pressures considered, by discretizing the feasible range of both temperature \( T \) and the first species’ liquid phase mole fraction \( x_1^L \). Figure 14 illustrates how feasible separators are generated, by identifying the \( x_2^L \) values for which \( \sum_{k=1}^{3} y_k^V = 1 \) at any given values of \( x_1^L, T \) and \( P \).
In this case, a non-uniform grid, with an increased refinement strategy at low temperatures, to better capture the change in composition around the azeotropic pinch point, is used. The grid sizes for $T$ and $x_i^L$ are displayed in table 9 for different temperature ranges and pressures.

![Figure 1.14: $\sum_{k=1}^{3} y_k^V$ vs. $x_2^L$ plots for a $x_i^L$ discretization of 0.125, at $T = 336$ K, $P = 1$ bar](image)

▲ indicates a feasible flash separator

<table>
<thead>
<tr>
<th>P ( bar )</th>
<th>$T$ range ( C )</th>
<th>$T$ discretization</th>
<th>$x_i^L$ discretization</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$T \leq 60$</td>
<td>1 K</td>
<td>0.03125 (1/32)</td>
</tr>
<tr>
<td>1</td>
<td>$T &gt; 60$</td>
<td>2 K</td>
<td>0.0625 (1/16)</td>
</tr>
<tr>
<td>0.2</td>
<td>$T \leq 18$</td>
<td>0.5 K</td>
<td>0.03125 (1/32)</td>
</tr>
<tr>
<td>0.2</td>
<td>$T &gt; 18$</td>
<td>1 K</td>
<td>0.0625 (1/16)</td>
</tr>
</tbody>
</table>

**Table 1.9:** Non-uniform grid discretization of $T$ and $x_i^L$ for the two pressure levels considered
• For the first set of specifications, which is unattainable by the traditional two-column method, IDEAS is able to identify a feasible design. The optimum solution obtained features a total network flow of 43.785 mol/s. The identities of the flashes participating in the optimum network, as well as the optimal interconnecting flows, are shown in Appendices A, B respectively.
• For the second set of specifications, which is attainable by the traditional two-column method with a minimum total network flow of 44.487 mol/s, the IDEAS optimum design features a total network flow of 37.738 mol/s, which is 15.15% lower than the traditional design’s optimum value.

1.6. Conclusions:

A methodology is demonstrated for the global minimization of total network flash inlet flow for pressure swing distillation (PSD) systems using the IDEAS framework. IDEAS yields globally optimal designs, that minimize the total network flow required to break an azeotrope achieving the desired level of separation. This allows for a rigorous comparison of alternative designs. The IDEAS framework is able to successfully generate optimal distillation networks using flash units as building blocks, and without any preconception of a network structure. Only VLE data information is provided a priori to the IDEAS design procedure. Two case studies consisting of a binary and a ternary mixture are considered, and the obtained IDEAS designs indicate that the traditional two-column design can be significantly improved upon (by 31.54% for the binary case, and 15.15% for the ternary case). IDEAS-generated designs surpass the two-column PSD traditional designs, because the flexibility of the IDEAS framework allows the
consideration of all possible flow and unit combinations. IDEAS can not only lead to improvements when compared to optimized traditional designs, but it can also provide vital information in other areas. Indeed, for the binary mixture, the obtained IDEAS designs indicate that, following an initial sharp decrease, the dependence of the optimum objective function value on pressure is minimal, and higher purity level requirements lead to increased optimum objective function values with similar pressure dependence. Also, for ternary mixtures, IDEAS can deliver compositions and outlet flow rates unattainable using the rigid two-column design structure.

1.7. Nomenclature:

\[ P \quad \text{Flash unit pressure} \]

\[ T \quad \text{Flash unit temperature} \]

\[ y_k^V (i) \quad k^{th} \text{ Species equilibrium vapor composition leaving the } i^{th} \text{ unit} \]

\[ x_k^L (i) \quad k^{th} \text{ Species equilibrium liquid composition leaving the } i^{th} \text{ unit} \]

\[ P_{k}^{sat} (T) \quad k^{th} \text{ Species temperature dependent saturated vapor pressure} \]

\[ \phi_k \left( \left\{ y_i^V \right\}_{i=1}^n, T, P \right) \quad k^{th} \text{ Species non-ideal fugacity coefficient} \]

\[ \gamma_k \left( \left\{ x_i^L \right\}_{i=1}^n, T \right) \quad k^{th} \text{ Species non-ideal liquid activity coefficient} \]

\[ \Lambda_{k,j} (T) \quad \text{Wilson equation temperature dependent parameters} \]

\[ A_{i,j} \quad \text{Wilson equation interaction parameters between } i^{th} \text{ and } j^{th} \text{ species} \]
Antoine equation \( k^{th} \) species parameters

\( V_k(V_j) \) \( k^{th} \left( j^{th} \right) \) species molar volume

\( R \) Universal gas constant

\( F \) Inlet flow rate to PSD system

\( F_1 \) Inlet flow rate to first distillation column, sum of \( F \) and \( D_2 \)

\( D_1 \) Distillate stream leaving first distillation column for second column

\( D_2 \) Distillate stream leaving second distillation column, recycle back to first column

\( B_1 \) Bottom flow rate leaving first distillation column

\( B_2 \) Bottom flow rate leaving second distillation column

\( F_{T_2} \) Total flow of vapor and liquid inside second (high pressure) distillation column

\( F_{T_1} \) Total flow of vapor and liquid inside first (low pressure) distillation column

\( F_{Total} \) Sum of flow rates entering each plate inside each column in PSD system

\( z \) Composition of M-Acetate in inlet flow rate to PSD system

\( z_1 \) Composition of M-Acetate in inlet flow rate to first distillation column

\( x_{D1} \) Composition of M-Acetate in distillate stream leaving first distillation column
$x_{D2}$ Composition of M-Acetate in distillate stream leaving second distillation column

$x_{B1}$ Composition of M-Acetate in bottom flow rate leaving first distillation column

$x_{B2}$ Composition of M-Acetate in bottom flow rate leaving second distillation column

$x_{AZ1}$ Azeotropic composition of M-Acetate in low-pressure column (column $T_1$)

$x_{AZ2}$ Azeotropic composition of M-Acetate in high-pressure column (column $T_2$)

IDEAS Variables:

$I_F^i$ $i^{th}$ DN inlet stream

$O_F^i$ $i^{th}$ DN outlet stream

$L_F^i$ $i^{th}$ OP liquid outlet

$V_F^i$ $i^{th}$ OP vapor outlet

$F_{ij}^O$ $j^{th}$ DN inlet stream to $i^{th}$ DN outlet

$F_{ij}^P$ $i^{th}$ OP inlet stream from $j^{th}$ DN network inlet

$F_{ij}^{OL}$ $i^{th}$ DN outlet stream from $j^{th}$ OP liquid outlet

$F_{ij}^{OV}$ $i^{th}$ DN outlet stream from $j^{th}$ OP vapor outlet
\( F^{PL}(i, j) \) \( \text{\(i^{th}\) OP inlet stream from \(j^{th}\) OP liquid outlet} \\
\( F^{PV}(i, j) \) \( \text{\(i^{th}\) OP inlet stream from \(j^{th}\) OP vapor outlet} \\
\( z^j_k(i) \) \( k^{th}\) species, \(i^{th}\) DN inlet stream composition \\
\( z^o_k(i) \) \( k^{th}\) species, \(i^{th}\) DN outlet stream composition \\
\( z^o(i), (z^o(i))^l, (z^o(i))^u \) \( i^{th}\) DN outlet stream composition vector, lower bound, upper bound \\
\( x^L_k(i) \) \( k^{th}\) species, \(i^{th}\) OP liquid outlet composition \\
\( y^V_k(i) \) \( k^{th}\) species, \(i^{th}\) OP vapor outlet composition \\
\( G \) Total number of flashes generated in all pressure universes, for different discretizations \\
\( M \) Number of IDEAS network inlets \\
\( N \) Number of IDEAS network outlets \\

1.8. Appendices:

Appendix A

P=1 bar; T(°C) – Optimal Network Flashes:
### Appendix B

P=0.2 bar; T(°C) – Optimal Network Flashes:

<table>
<thead>
<tr>
<th>T</th>
<th>x1</th>
<th>x2</th>
<th>y1</th>
<th>y2</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.0</td>
<td>0.105</td>
<td>0.110</td>
<td>0.0138</td>
<td>0.00976</td>
</tr>
<tr>
<td>16.5</td>
<td>0.108</td>
<td>0.1630</td>
<td>0.0236</td>
<td>0.1250</td>
</tr>
<tr>
<td>17.0</td>
<td>0.113</td>
<td>0.1980</td>
<td>0.0315</td>
<td>0.1452</td>
</tr>
<tr>
<td>17.5</td>
<td>0.120</td>
<td>0.2270</td>
<td>0.0382</td>
<td>0.1617</td>
</tr>
<tr>
<td>18.0</td>
<td>0.125</td>
<td>0.4550</td>
<td>0.0095</td>
<td>0.3074</td>
</tr>
<tr>
<td>18.0</td>
<td>0.129</td>
<td>0.2520</td>
<td>0.0441</td>
<td>0.1763</td>
</tr>
<tr>
<td>18.0</td>
<td>0.130</td>
<td>0.2020</td>
<td>0.0518</td>
<td>0.1432</td>
</tr>
<tr>
<td>19.5</td>
<td>0.135</td>
<td>0.5530</td>
<td>0.0173</td>
<td>0.3747</td>
</tr>
<tr>
<td>19.5</td>
<td>0.138</td>
<td>0.3200</td>
<td>0.0597</td>
<td>0.2106</td>
</tr>
<tr>
<td>19.5</td>
<td>0.139</td>
<td>0.2270</td>
<td>0.0704</td>
<td>0.1616</td>
</tr>
<tr>
<td>20.5</td>
<td>0.144</td>
<td>0.6260</td>
<td>0.0171</td>
<td>0.4342</td>
</tr>
<tr>
<td>20.5</td>
<td>0.147</td>
<td>0.3880</td>
<td>0.0589</td>
<td>0.2744</td>
</tr>
<tr>
<td>20.5</td>
<td>0.148</td>
<td>0.3125</td>
<td>0.0696</td>
<td>0.2271</td>
</tr>
<tr>
<td>20.5</td>
<td>0.149</td>
<td>0.2490</td>
<td>0.0788</td>
<td>0.1804</td>
</tr>
<tr>
<td>20.5</td>
<td>0.150</td>
<td>0.1890</td>
<td>0.0865</td>
<td>0.1431</td>
</tr>
<tr>
<td>21.5</td>
<td>0.159</td>
<td>0.3125</td>
<td>0.0702</td>
<td>0.2833</td>
</tr>
<tr>
<td>21.5</td>
<td>0.160</td>
<td>0.3750</td>
<td>0.0797</td>
<td>0.2393</td>
</tr>
<tr>
<td>22.5</td>
<td>0.167</td>
<td>0.7550</td>
<td>0.0175</td>
<td>0.5405</td>
</tr>
<tr>
<td>22.5</td>
<td>0.168</td>
<td>0.6570</td>
<td>0.0334</td>
<td>0.4914</td>
</tr>
<tr>
<td>22.5</td>
<td>0.171</td>
<td>0.4370</td>
<td>0.0717</td>
<td>0.3359</td>
</tr>
<tr>
<td>22.5</td>
<td>0.172</td>
<td>0.3750</td>
<td>0.0816</td>
<td>0.2901</td>
</tr>
<tr>
<td>23.5</td>
<td>0.181</td>
<td>0.7000</td>
<td>0.0342</td>
<td>0.5474</td>
</tr>
<tr>
<td>23.5</td>
<td>0.185</td>
<td>0.3750</td>
<td>0.0842</td>
<td>0.3385</td>
</tr>
<tr>
<td>23.5</td>
<td>0.186</td>
<td>0.3470</td>
<td>0.0933</td>
<td>0.2936</td>
</tr>
<tr>
<td>23.5</td>
<td>0.190</td>
<td>0.6875</td>
<td>0.1199</td>
<td>0.1311</td>
</tr>
<tr>
<td>23.5</td>
<td>0.195</td>
<td>0.1875</td>
<td>0.0506</td>
<td>0.5448</td>
</tr>
<tr>
<td>24.5</td>
<td>0.199</td>
<td>0.4375</td>
<td>0.0970</td>
<td>0.3388</td>
</tr>
<tr>
<td>24.5</td>
<td>0.200</td>
<td>0.5000</td>
<td>0.1055</td>
<td>0.2930</td>
</tr>
<tr>
<td>25.5</td>
<td>0.206</td>
<td>0.6560</td>
<td>0.0191</td>
<td>0.7269</td>
</tr>
<tr>
<td>25.5</td>
<td>0.207</td>
<td>0.7680</td>
<td>0.0366</td>
<td>0.6615</td>
</tr>
<tr>
<td>25.5</td>
<td>0.213</td>
<td>0.5000</td>
<td>0.1102</td>
<td>0.3349</td>
</tr>
<tr>
<td>26.5</td>
<td>0.219</td>
<td>0.1250</td>
<td>0.0380</td>
<td>0.7209</td>
</tr>
<tr>
<td>26.5</td>
<td>0.220</td>
<td>0.1875</td>
<td>0.0545</td>
<td>0.6569</td>
</tr>
<tr>
<td>26.5</td>
<td>0.225</td>
<td>0.5000</td>
<td>0.1154</td>
<td>0.3768</td>
</tr>
<tr>
<td>27.5</td>
<td>0.230</td>
<td>0.8210</td>
<td>0.0395</td>
<td>0.7825</td>
</tr>
<tr>
<td>27.5</td>
<td>0.231</td>
<td>0.7450</td>
<td>0.0568</td>
<td>0.7145</td>
</tr>
<tr>
<td>27.5</td>
<td>0.236</td>
<td>0.3440</td>
<td>0.1210</td>
<td>0.6194</td>
</tr>
<tr>
<td>28.5</td>
<td>0.243</td>
<td>0.3750</td>
<td>0.1041</td>
<td>0.5790</td>
</tr>
<tr>
<td>29.5</td>
<td>0.247</td>
<td>0.1250</td>
<td>0.0830</td>
<td>0.9117</td>
</tr>
<tr>
<td>29.5</td>
<td>0.248</td>
<td>0.1875</td>
<td>0.0619</td>
<td>0.8373</td>
</tr>
<tr>
<td>29.5</td>
<td>0.249</td>
<td>0.3125</td>
<td>0.0949</td>
<td>0.6965</td>
</tr>
<tr>
<td>29.5</td>
<td>0.253</td>
<td>0.6250</td>
<td>0.1537</td>
<td>0.3860</td>
</tr>
<tr>
<td>30.5</td>
<td>0.256</td>
<td>0.7290</td>
<td>0.0829</td>
<td>0.8258</td>
</tr>
<tr>
<td>30.5</td>
<td>0.257</td>
<td>0.6550</td>
<td>0.0994</td>
<td>0.7534</td>
</tr>
<tr>
<td>30.5</td>
<td>0.258</td>
<td>0.5120</td>
<td>0.1280</td>
<td>0.6171</td>
</tr>
<tr>
<td>31.5</td>
<td>0.261</td>
<td>0.2500</td>
<td>0.0869</td>
<td>0.8891</td>
</tr>
<tr>
<td>31.5</td>
<td>0.262</td>
<td>0.6700</td>
<td>0.1043</td>
<td>0.8120</td>
</tr>
<tr>
<td>31.5</td>
<td>0.263</td>
<td>0.3750</td>
<td>0.1201</td>
<td>0.7384</td>
</tr>
<tr>
<td>33.5</td>
<td>0.270</td>
<td>0.4375</td>
<td>0.1486</td>
<td>0.7753</td>
</tr>
<tr>
<td>35.5</td>
<td>0.273</td>
<td>0.5000</td>
<td>0.1808</td>
<td>0.8044</td>
</tr>
<tr>
<td>36.5</td>
<td>0.276</td>
<td>0.6250</td>
<td>0.2213</td>
<td>0.6784</td>
</tr>
<tr>
<td>38.5</td>
<td>0.279</td>
<td>0.7500</td>
<td>0.2766</td>
<td>0.5600</td>
</tr>
<tr>
<td>39.5</td>
<td>0.280</td>
<td>0.6875</td>
<td>0.2751</td>
<td>0.7189</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>T</th>
<th>x1</th>
<th>x2</th>
<th>y1</th>
<th>y2</th>
</tr>
</thead>
<tbody>
<tr>
<td>69.0</td>
<td>0.3125</td>
<td>0.6760</td>
<td>0.125</td>
<td>0.8319</td>
</tr>
<tr>
<td>77.0</td>
<td>0.3987</td>
<td>0.2050</td>
<td>0.367</td>
<td>0.273</td>
</tr>
<tr>
<td>77.0</td>
<td>0.100</td>
<td>0.8750</td>
<td>0.3771</td>
<td>0.2261</td>
</tr>
<tr>
<td>79.0</td>
<td>0.101</td>
<td>0.8750</td>
<td>0.4083</td>
<td>0.2722</td>
</tr>
<tr>
<td>81.0</td>
<td>0.102</td>
<td>0.8750</td>
<td>0.4417</td>
<td>0.3209</td>
</tr>
<tr>
<td>85.0</td>
<td>0.104</td>
<td>0.8750</td>
<td>0.5160</td>
<td>0.4249</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>T</th>
<th>x1</th>
<th>x2</th>
<th>y1</th>
<th>y2</th>
</tr>
</thead>
<tbody>
<tr>
<td>69.0</td>
<td>0.3125</td>
<td>0.6760</td>
<td>0.125</td>
<td>0.8319</td>
</tr>
<tr>
<td>77.0</td>
<td>0.3987</td>
<td>0.2050</td>
<td>0.367</td>
<td>0.273</td>
</tr>
<tr>
<td>77.0</td>
<td>0.100</td>
<td>0.8750</td>
<td>0.3771</td>
<td>0.2261</td>
</tr>
<tr>
<td>79.0</td>
<td>0.101</td>
<td>0.8750</td>
<td>0.4083</td>
<td>0.2722</td>
</tr>
<tr>
<td>81.0</td>
<td>0.102</td>
<td>0.8750</td>
<td>0.4417</td>
<td>0.3209</td>
</tr>
<tr>
<td>85.0</td>
<td>0.104</td>
<td>0.8750</td>
<td>0.5160</td>
<td>0.4249</td>
</tr>
</tbody>
</table>
1.9. References:


2. CHAPTER 2

Attainable Composition, Energy Consumption, and Entropy Generation Properties for
Isothermal/Isobaric Reactor Networks

2.1. Abstract

A methodology for the quantification of entropy generation and energy consumption in
isothermal, isobaric reactor networks is presented. The proposed methodology employs the
Infinite DimEnsionAl State-space (IDEAS) conceptual framework, which is shown to be
applicable to the problem under consideration. The IDEAS framework considers all possible
reactor units, and all possible mixing and splitting interconnections among them. It will be
shown mathematically that, under certain conditions, entropy generation and energy
consumption are functions of only the inlet and outlet stream compositions and flow rates and do
not depend on the reactor network structure, as long as there exists a network able to deliver the
considered outlets from the known inlets. This theoretical result provides the foundation for a
graphical method that can quantify entropy generation and energy consumption, by first
identifying the reactor network’s Attainable Region (AR) and then depicting the behavior of the
entropy generation and energy consumption functions within the AR. The proposed methodology
is demonstrated on a case study featuring reversible reactions both in series and parallel. Finally,
conclusions are drawn.

2.2. Introduction

Quantifying the entropy generation and energy consumption for a given process is the first
step towards its energetic optimization. According to Bejan, entropy generation minimization
(EGM) is the method of thermodynamic optimization of real systems that owe their
thermodynamic imperfection due to heat transfer, fluid flow, and mass transfer irreversibility. Identifying processes that feature minimum entropy generation is highly desirable, since such processes can be thought of as realizable approximations to ideal reversible processes, and can thus be expected to be highly efficient.

A multitude of approaches have been proposed for the study of EGM problems depending on the type of “thermodynamic imperfection” under consideration. Minimizing the entropy generation in a reactor is analogous to maximizing the obtainable work associated with the driving force of the chemical reaction occurring in the process. This is elaborated further in the next section.

Several authors have presented work on the minimization of the entropy generated in a reactor for a variety of industrially relevant reactions using optimal control theory. While interesting and insightful, the method of optimal control of a single reactor suffers from clear limitations. Most importantly, combinations of reactors and reactor networks are not explored as potentially better alternatives to single reactor systems, and the solutions are locally, rather than globally optimal.

Similarly, several authors have discussed the topic of energetically optimizing a network of non-isothermal reactors through the use of locally optimizing mixed-integer non-linear program (MINLP) formulations, and targeting strategies, though with no mention of entropy generation considerations.

This work employs the IDEAS framework for the quantification of both entropy generation and energy consumption for isothermal, isobaric reactor networks. The flow sheet is decomposed into two types of operations: flow operations (mixing, splitting, recycling, and bypass) and unit operations (reactors, distillation columns, heat exchangers, etc.). The IDEAS framework decomposes a process network into an operator, OP network, where the unit operations (reactors, distillation columns, heat exchangers, etc.) occur, and a distribution, DN network, where the
flow operations (mixing, splitting, recycling, and bypass) occur. IDEAS has been successfully applied to numerous globally optimal process network synthesis problems, such as: mass exchange network synthesis\textsuperscript{11}, complex distillation network synthesis\textsuperscript{12-14}, power cycle synthesis\textsuperscript{15}, reactor network synthesis\textsuperscript{16-17}, reactive distillation network synthesis\textsuperscript{18}, separation network synthesis\textsuperscript{19}, attainable region construction\textsuperscript{20-23}, and batch attainable region construction\textsuperscript{24}.

The novelty of this work is two-fold. First, it pursues for the first time the quantification of multiple parameters, namely entropy generation and energy consumption for networks of unit operations rather than individual units. Given that appropriately designed reactor networks can be superior (either in terms of network volume, attainable outlet concentrations, or other criteria) to optimally designed single reactor units, it is highly desirable for a method that systematically quantifies network entropy generation and energy consumption for reactor networks to be developed. To this end, the second item of novelty brought about by this work is the discovery of an important network property that allows for the systematic quantification of the network entropy generation and energy consumption to be based solely on network input and output information.

The rest of the paper is structured as follows: first, the motivation behind this work and its significance are presented, reactor models employing both mass and molar basis are developed, the network synthesis methodology is established, the applicability of IDEAS to the entropy generation and energy consumption quantification problem is demonstrated, and the resulting IDEAS mathematical formulation is presented. Next, the entropy generation and energy consumption functions are quantified and then simplified based on theorem 1, which establishes the functions’ dependence only on network inlet and outlet information. Subsequently, the
attainable region (AR) concept is used as a platform within which the property quantification problem is solved. Finally, a case study is used to illustrate the proposed global method, and conclusions are drawn.

2.3. Motivation and Significance

Application of the first law of thermodynamics for an open, steady-state, isothermal, isobaric, process with one input, one output, and no work production/consumption\(^{25}\), yields:

\[
H(T, P; \{N_{k}^{o}\}_{k=1}^{n}) - H(T, P; \{N_{k}^{i}\}_{k=1}^{n}) = Q
\]  

(2.1)

where \(\{N_{k}^{o}\}_{k=1}^{n}\) and \(\{N_{k}^{i}\}_{k=1}^{n}\) represent the outlet and inlet number of moles of all \(k\) species respectively \(\forall k = 1, n\).

In the presence of heat transfer irreversibility between system (at \(T\)) and surroundings (at \(T_{\sigma}\)), an entropy balance for the same process\(^{25}\), yields:

\[
S^{G} = S\left(T, P; \{N_{k}^{o}\}_{k=1}^{n}\right) - S\left(T, P; \{N_{k}^{i}\}_{k=1}^{n}\right) - \frac{Q}{T_{\sigma}}
\]  

(2.2 - a)

where heat is exchanged with an infinite reservoir at temperature \(T_{\sigma}\). Equation \((2.2 - a)\) denotes the general case of entropy generation for a process under the restrictions introduced at the beginning of this section. A model to which this equation corresponds is shown in figure 1, with matching equations \((2.10 - a)\), and \((2.10 - b)\) indicating mass and molar entropy balances respectively. All subsequent proofs and derivations included herein will also be based on this general representation.
For the special case of heat transfer reversibility between the system and surroundings \( T_a = T \), that same entropy balance \((2.2-a)\) becomes:

\[
S^G = S\left(T, P, \{N_k^o\}_{k=1}^n\right) - S\left(T, P, \{N_k^i\}_{k=1}^n\right) - \frac{Q}{T} \tag{2.2-b}
\]

Since the Gibbs free energy can be defined in terms of entropy and energy as

\[
G\left(T, P, \{N_k^o\}_{k=1}^n\right) - G\left(T, P, \{N_k^i\}_{k=1}^n\right) = H\left(T, P, \{N_k^o\}_{k=1}^n\right) - H\left(T, P, \{N_k^i\}_{k=1}^n\right) - T \left(S\left(T, P, \{N_k^o\}_{k=1}^n\right) - S\left(T, P, \{N_k^i\}_{k=1}^n\right)\right) \tag{2.3}
\]

for the reversible heat transfer case it then holds:

\[
S^G = \left\{G\left(T, P, \{N_k^i\}_{k=1}^n\right) - G\left(T, P, \{N_k^o\}_{k=1}^n\right) \right\} \frac{H\left(T, P, \{N_k^o\}_{k=1}^n\right) - H\left(T, P, \{N_k^i\}_{k=1}^n\right)}{T} \Rightarrow \tag{3}
\]

\[
S^G = \left\{\frac{G\left(T, P, \{N_k^i\}_{k=1}^n\right) - G\left(T, P, \{N_k^o\}_{k=1}^n\right)}{T} \right\} \tag{2.4}
\]

From the above it is clear that entropy generation for an isothermal, isobaric reactor, with reversible heat transfer, is related to the change in Gibbs energy between the inlet and outlet composition. At the equilibrium state, the total Gibbs energy is at a minimum with respect to all possible changes at the given \( T \) and \( P \). It then becomes clear that for a fixed reactor inlet \( \{N_k^i\}_{k=1}^n \), the entropy generated by the isothermal, isobaric reactor process, with reversible heat transfer, approaches its supremum value, when the reactor outlet \( \{N_k^o\}_{k=1}^n \) approaches the equilibrium state \( \{N_k^E\}_{k=1}^n \) that the underlying reaction scheme possesses at the reactor’s operating temperature.

61
and pressure. Since $\left\{N^E_k\right\}_{k=1}^R$ is approached for an infinite reactor size, one can loosely associate a general trend of increasing reactor network entropy generation with increasing reactor network volume, though this by no means implies that there is a unique correspondence between the two measures (i.e. there can exist multiple reactor networks with identical total network volume and different values of entropy generation, and vice-versa there can exist multiple reactor networks with identical entropy generation and different values of total network volume).

A more exact physical interpretation of entropy generation by a process is related to the thermodynamic efficiency of that process. Consider a complex manufacturing process that generates/consumes work and involves a number of sub-processes, including a reactor network sub-process. The efficiency of such a process can be assessed by quantifying as lost work the difference between real work generated/consumed when its sub-processes are irreversible and the ideal work generated/consumed when its sub-processes are reversible. Summing up the lost work for each of its sub-processes yields the lost work for the entire manufacturing process. It becomes apparent from the above that the synthesis of the most thermodynamically efficient overall process is equivalent to the minimization of the lost work sum for all sub-processes comprising the considered process. However, the lost work $W_{\text{lost}}$ for a sub-process is equal to the product of the temperature of the surroundings $T_\sigma(K)$ times the sub-process’s entropy generation $S^G$, i.e.

$$W_{\text{lost}} = T_\sigma \cdot S^G \quad (2.5)$$

Thus, the synthesis of the most thermodynamically efficient overall process is equivalent to the minimization of the sum of entropy generation terms for each sub-process comprising the considered process. The focus of this effort is on the quantification of entropy generation for an
isothermal, isobaric reactor network as a first step towards the quantification of entropy generation for general complex manufacturing processes. Subsequent research efforts will also focus on other network types, such as non-isothermal, non-isobaric reactor networks, distillation networks, etc. Representing such networks as systems containing some subsystems which are isothermal, isobaric networks operating at different temperatures and pressures, will allow the results obtained here to serve as building blocks for the quantification of these properties for general manufacturing processes. This will be the subject of future work.

Having provided physical interpretations of entropy generation for isothermal, isobaric reactor networks, it becomes apparent that it is advantageous to identify the energy consumption, and entropy generation for such a network at the early conceptual design stage, namely before a particular network structure is chosen. Given the wide array of choices for the reactor network selection it is clear that no single value for the aforementioned two quantities can be identified. It would nevertheless be highly desirable to identify ranges of values for these quantities over all feasible reactor networks, and how other network design specifications may affect these ranges. Commonly employed reactor network design specifications are related to the network’s outlet concentrations. Examples include reactant conversion, alternative product selectivity, upper and/or lower bounds on outlet concentrations of particular species, etc. All these specifications can be readily represented in reactor network outlet concentration space. In that same space, the set of all attainable outlet concentration points, termed the Attainable Region (AR) can be readily quantified using a variety of techniques. A representation of all these attributes (attainable region, entropy generation, energy consumption, design specifications) on a common diagram would allow for a rigorous tradeoff analysis among all these considerations while selecting an optimal reactor network structure.
It will be subsequently demonstrated in this paper how the IDEAS framework described above can be used to establish that the entropy generation and energy consumption of an isothermal, isobaric reactor network with irreversible heat transfer and known feed can be quantified as a function of only network outlet concentrations and independently of the network’s internal structure (Theorem 1). This will allow for all the attributes discussed above to be represented on a single AR diagram, thus facilitating rigorous tradeoff analysis during reactor network design optimization. For energy-intensive processes, with high heating/cooling costs, it can be expected that minimization of lost work (which is equivalent to minimization of entropy generation) will lead to designs that are close to the economic optimum. This may not be the case for non-energy intensive processes for which other objectives should be sought, such as maximizing profitability, including the installed equipment cost. Nevertheless, even in these latter cases, the simultaneous depiction of all these network properties on a single diagram can facilitate the design engineer in arriving at an economic optimum.

The strength of the new methodology is illustrated in the case study below.

2.4. Applicability of IDEAS to Isothermal Reactor Network Synthesis

For this work, the following assumptions are considered:

- Reactor network is isothermal i.e. all the reactors, streams are at the same temperature $T$
- Reactor network is isobaric i.e. all the reactors, streams are at the same pressure $P$
- No work is consumed or generated
- Reactor network consists of both CSTR and PFR reactor units
- The universe of considered isothermal, isobaric reactors either consists only of units that accept heat or consists only of units that reject heat. This allows the consideration of
reactors in which both endothermic and exothermic reactions occur, as long as the reactor’s overall energy flow is in the same direction as the energy flow for every reactor in the network.

- An infinite reservoir at constant temperature $T_\sigma$ is considered to provide heat to each reactor in the former case (net endothermic, $T_\sigma > T$), or to remove heat from each reactor in the latter case (net exothermic, $T_\sigma < T$).

It should be noted that isothermal reactor networks are not infrequent. Particularly, it is known that for reactors in which multiple reactions are carried out, the operating temperature should be the highest allowable temperature, if the activation energies of the various reactions are such that the favorable product distribution is obtained at a high temperature\(^{27}\). Thus these reactor networks should naturally be isothermal with all reactors operating at the maximum allowable temperature.

The reactor model resulting from the aforementioned assumptions is illustrated in Figure 1, and the associated modeling equations for PFR ($\lambda = 0$) and CSTR ($\lambda = 1$) reactor units are listed below. Equations \(2.6 - a(b)\) and \(2.7 - a(b)\) correspond to total and component mass (molar) balances respectively. Equation \(2.8\) clarifies the relation between the \(i^{th}\) species concentration $c_i$ and the system’s mass fractions $\{z_k\}_{k=1}^{a}$. Equations \(2.9 - a(b)\) and \(2.10 - a(b)\) are the energy and entropy balances around the reactor, involving the mass (volumetric) heat generation and mass (volumetric) entropy generation functions respectively. Equations \(2.11 - a(b)\) and \(2.12 - a(b)\) relate the heat generation and entropy generation rate functions to their mass
(volumetric) counterparts, respectively. Equations (2.13) and (2.14) quantify molar entropy and molar enthalpy in terms of excess molar entropy and enthalpy for any mixture, and will be applied to both the reactor unit’s inlet and outlet streams\textsuperscript{25}. Finally equations (2.15) and (2.16) quantify excess molar entropy and enthalpy in terms of liquid phase activity coefficients, which are presumed available from some thermodynamic model like Wilson, NRTL, etc. The derivation of the excess molar enthalpy and entropy equations (2.15) and (2.16) can be found in appendix A.

2.4.1. Reactor Model – Variable Density Model (Mass Basis)

\[ \dot{m}_{in} = \dot{m}_{out} = \ddot{m} \quad (2.6 - a) \]

\[
\begin{aligned}
\left\{ \frac{dz_k}{d\dot{\sigma}} = M_k \rho_k \left( \left\{ \frac{C^\text{out}}{C^i} \left( \sum_{i=1}^{n} \frac{z_j}{z_i} \right) \right\} \right)_{i=1}^{n} \right\} & \forall k = 1, n \\
\left\{ z_k^{in} = z_k^{out}, \quad z_k^{in}_{\sigma=0} = z_k^{out}_{\sigma=1} \forall k = 1, n \right\} & \dot{\lambda} = 0 \\
\left\{ z_k^{in} - z_k^{out} + \sigma M_k \rho_k \left( \left\{ \frac{C^\text{out}}{C^i} \left( \sum_{i=1}^{n} \frac{z_j}{z_i} \right) \right\} \right)_{i=1}^{n} = 0 \right\} & \forall k = 1, n \quad \dot{\lambda} = 1 \\
\sigma = \frac{V}{\ddot{m}} \\
\end{aligned}
\]

\[ C^\text{out}_i = C^i \left( \left\{ \frac{z_j}{z_i} \right\} \right)_{i=1}^{n-1} T, P \quad \forall i = 1, n \quad (2.8 - a) \]
Equation \((8-a)\) aims to capture the thermodynamic model of the underlying mixture. Several models can be brought into the form of \((8-a)\). For example if a compressibility factor model \((Z)\) is employed, then:

\[
C_i = x_i \left( \frac{P}{RT} \right) \left( \frac{1}{Z \{x_j\}_{j=1}^{n-1}, T, P} \right) \tag{2.8-b}
\]

\[
x_i = \frac{z_i}{M_i \sum_{k=1}^{n} \left( \frac{z_k}{M_k} \right)} \quad \forall i = 1, n-1 \tag{2.8-c}
\]

where \(R\) is the universal gas constant and \(x_i, z_i \quad \forall i = 1, n\) designate the \(i^{th}\) species mole fraction and mass fraction respectively.

\[
\sum_{i=1}^{n} \left( \frac{z_i^{in}}{M_i} \right) H \left( T, P, \left\{ C_i \left( \{z_j^{in}\}_{j=1}^{n-1}, T, P \right) \right\}_{j=1}^{n} \right) - \sum_{i=1}^{n} \left( \frac{z_i^{out}}{M_i} \right) H \left( T, P, \left\{ C_i \left( \{z_j^{out}\}_{j=1}^{n-1}, T, P \right) \right\}_{j=1}^{n} \right) + Q_m = 0 \tag{2.9-a}
\]

\[
\sum_{i=1}^{n} \left( \frac{z_i^{in}}{M_i} \right) S \left( T, P, \left\{ C_i \left( \{z_j^{in}\}_{j=1}^{n-1}, T, P \right) \right\}_{j=1}^{n} \right) - \sum_{i=1}^{n} \left( \frac{z_i^{out}}{M_i} \right) S \left( T, P, \left\{ C_i \left( \{z_j^{out}\}_{j=1}^{n-1}, T, P \right) \right\}_{j=1}^{n} \right) + \frac{Q_m}{T} + S^m = 0 \tag{2.10-a}
\]

\[
\dot{Q} = Q_m \dot{m} \tag{2.11-a}
\]

\[
\dot{S}_G = S^m \dot{m} \tag{2.12-a}
\]

2.4.2. Reactor Model – Constant Density Model (Molar Basis)
\( F^{in} = F^{out} = F \quad (2.6-b) \)

\[
\begin{aligned}
\left\{ \begin{array}{l}
dC_k = R_k \left( \{C_k\}_{k=1}^{n} \right) & \forall k = 1, n \\
d\tau = C_k^{in} \quad C_k^{out} = C_k & \forall k = 1, n \\
C_k^{in} - C_k^{out} + R_k \left( \{C_k^{out}\}_{k=1}^{n} \right) \tau = 0 & \forall k = 1, n \\
\tau = \frac{V}{F} 
\end{array} \right\} \lambda = 0
\end{aligned}
\]

\[
\left( \sum_{l=1}^{n} C_l^{in} \right) H \left( T, P, \{C_k^{in}\}_{k=1}^{n} \right) - \left( \sum_{l=1}^{n} C_l^{out} \right) H \left( T, P, \{C_k^{out}\}_{k=1}^{n} \right) + Q_F = 0 \quad (2.9-b)
\]

\[
\left( \sum_{l=1}^{n} C_l^{in} \right) S \left( T, P, \{C_k^{in}\}_{k=1}^{n} \right) - \left( \sum_{l=1}^{n} C_l^{out} \right) S \left( T, P, \{C_k^{out}\}_{k=1}^{n} \right) + \frac{Q_L}{T} + S_G^F = 0 \quad (2.10-b)
\]

\[
\dot{Q} = Q_F F \quad (2.11-b)
\]

\[
\dot{S}_G = S_G^F F \quad (2.12-b)
\]

2.4.3. Entropy/Enthalpy relations for both VDF and CDF models

\[
S \left( T, P, \{C_k\}_{k=1}^{n} \right) = \sum_{k=1}^{n} \frac{C_k}{\sum_{l=1}^{n} C_l} S_k \left( T, P \right) + S^E \left( T, P, \{C_k\}_{k=1}^{n} \right) - R \sum_{k=1}^{n} \frac{C_k}{\sum_{l=1}^{n} C_l} \ln \left( \frac{C_k}{\sum_{l=1}^{n} C_l} \right) \quad (2.13)
\]

\[
H \left( T, P, \{C_k\}_{k=1}^{n} \right) = \sum_{k=1}^{n} \frac{C_k}{\sum_{l=1}^{n} C_l} H_k \left( T, P \right) + H^E \left( T, P, \{C_k\}_{k=1}^{n} \right) \quad (2.14)
\]

68
\[
H^E(T, P, \{C_k \}_k) = -RT \sum_{k=1}^{n} \frac{C_k}{\sum_{l=1}^{n} C_l} \left. \frac{\partial \ln \gamma_k(T, P, \{C_k\}_k)}{\partial T} \right|_{P, C_k}
\]

\[
S^E(T, P, \{C_k \}_k) = -RT \sum_{k=1}^{n} \frac{C_k}{\sum_{l=1}^{n} C_l} \left. \frac{\partial \ln \gamma_k(T, P, \{C_k\}_k)}{\partial T} \right|_{P, C_k} - R \sum_{k=1}^{n} \frac{C_k}{\sum_{l=1}^{n} C_l} \ln \gamma_k(T, P, \{C_k\}_k)
\]

Having presented isothermal CSTR/PFR reactor models for the constant density (molar model) and variable density (mass model) cases, the applicability of IDEAS to the constant density reactor models is next demonstrated. In a similar manner, IDEAS can be readily shown to be applicable to the variable density reactor models as well, though this is not shown here in the interest of space.

\[\begin{align*}
F^{in} & \rightarrow \text{Reactor} \rightarrow F^{out} \\
C^{in} & \rightarrow \text{Reactor} \rightarrow C^{out} \\
S(T, P, \{C^{in}_k \}_k) & \rightarrow \text{Reactor} \rightarrow S(T, P, \{C^{out}_k \}_k) \\
H(T, P, \{C^{in}_k \}_k) & \rightarrow \text{Reactor} \rightarrow H(T, P, \{C^{out}_k \}_k)
\end{align*}\]

\textbf{Figure 2.1:} Reactor model (Molar Basis)

The aforementioned reactor model can be employed to construct the following input-output information map:
\( \Phi : D \rightarrow R^{2n+7} \times R^3, \Phi : u \rightarrow y \) such that:

\[
\Phi : u = \begin{bmatrix} u_1 \\ u_2 \end{bmatrix} \rightarrow y = \begin{bmatrix} y_1 \\ y_2 \end{bmatrix} = \Phi(u_1, u_2) = \begin{bmatrix} \Phi_1(u_1, u_2) \\ \Phi_2(u_1, u_2) \end{bmatrix}
\]

where \( D = \{ u \in R^{n+2} \times R : u_1 \geq 0 \land u_2 \geq 0 \} \subset \{ R^{n+2} \times R \} \),

\[
u^T = \begin{bmatrix} u_1^T \mid u_2^T \end{bmatrix} = \begin{bmatrix} C_1^{\text{in}} & C_1^{\text{out}} & \ldots & C_n^{\text{out}} & \lambda & F \end{bmatrix},
\]

\[
y^T = \begin{bmatrix} y_1^T \mid y_2^T \end{bmatrix} = \Phi^T(u_1, u_2) = \begin{bmatrix} \tau & C_1^{\text{in}} & \ldots & C_n^{\text{in}} & C_1^{\text{out}} & \ldots & C_n^{\text{out}} & S_1^{\text{in}} & H_1^{\text{in}} & S_1^{\text{out}} & H_1^{\text{out}} & Q_F & S_G^F & F \dot{Q} & \dot{S}_G \end{bmatrix}
\]

The evaluation of the image \( \Phi^T(u_1, u_2) \), given \( u_1 \) and \( u_2 \), is illustrated next for the constant density reactor case.

Consider that \( u_1 \) is known. For the CSTR model, \( \lambda = 1, \tau \) can first be evaluated by solving equation \( 2.7 - b \) for the first species \( (k = 1) \). From the solution of equations \( 2.7 - b \) for all other species \( k, \forall k = 2, n, \{ C_k^{\text{in}} \}_{k=2}^n \) can be evaluated. For the PFR model, \( \lambda = 0, \tau \) and \( \{ C_k^{\text{in}} \}_{k=2}^n \) can be evaluated through backward integration of equation \( 2.7 - b \) until \( C_1 \) is equal to \( C_1^{\text{in}} \). With knowledge of the outlet/inlet species concentrations, since the network is isothermal and isobaric, the molar outlet/inlet entropy, and molar outlet/inlet enthalpy for each stream can be obtained from equations \( (2.13), (2.16), (2.14), (2.15) \) respectively. Given the temperature of the environment \( T_{\sigma} \), volumetric utility consumption rate \( Q_F \) and volumetric entropy generation rate \( S_G^F \) can then be evaluated from equations \( 2.9 - b \) and \( 2.10 - b \) respectively. Evaluation of the
reactor flowrate, $F$, heating/cooling rate, $Q$, and entropy generation rate $\dot{S}_G$, requires knowledge of both $u_1$ and $u_2$ and is carried out using equations 2.11–b and 2.12–b.

The above decompositions of the input vector $u$ to $u_1$ and $u_2$, of the output vector $y$ to $y_1$ and $y_2$, and of the map $\Phi$ to $\Phi_1$ and $\Phi_2$ are carried out so that the following IDEAS properties can be shown to hold:

2.4.4. IDEAS property 1

$$\exists \Phi_3: \mathbb{R}^{n+2} \rightarrow \mathbb{R}^{2n+7} \text{ such that } \Phi_1(u_1, u_2) = \Phi_3(u_1) \forall (u_1, u_2) \in D.$$ 

This implies that $y_1 = \Phi_1(u_1, u_2) = \Phi_3(u_1)$ can be evaluated based only on knowledge of $u_1$, and independently of $u_2$.

2.4.5. IDEAS property 2

$$\exists \Phi_4: \mathbb{R}^{n+2} \rightarrow \mathbb{R}^3 \text{ such that } \Phi_2(u_1, u_2) = \Phi_4(u_1) \cdot u_2 \forall (u_1, u_2) \in D.$$ This map is:
\[
\Phi_4: \mathbf{u}_1 \rightarrow \Phi_4(\mathbf{u}_1) = \begin{bmatrix}
C_{i}^{\text{in}} \\
C_{i}^{\text{out}} \\
\vdots \\
C_{n}^{\text{out}} \\
\lambda
\end{bmatrix}. \quad \text{From equations} \ (2.10-b) \text{ and } (2.11-b) \text{ it can be readily verified that:} \]

\[
y_2 \approx \begin{bmatrix} F \hat{Q} \hat{S}_G \end{bmatrix}^T = \begin{bmatrix} 1 & Q_F & F^T \end{bmatrix} \cdot F = \Phi_4(\mathbf{u}_1) \cdot \mathbf{u}_2
\]

This implies that for fixed \( \mathbf{u}_1 \), \( \Phi_4(\mathbf{u}_1) \) is a linear operator, and \( y_2 \approx \Phi_2(\mathbf{u}_1, \mathbf{u}_2) = \Phi_4(\mathbf{u}_1) \cdot \mathbf{u}_2 \) is linear in \( \mathbf{u}_2 \). Therefore, for a fixed \( \mathbf{u}_1 \) the employed reactor model is defined by a linear input-output map \( \Phi_4(\mathbf{u}_1) \). An infinite sequence \( \{\mathbf{u}_1(i)\}_{i=1}^{\infty} \), consisting of all possible values of \( \mathbf{u}_1 \) is then considered, such that the union of the considered \( \mathbf{u}_1 \) values is dense in the set over which \( \mathbf{u}_1 \) can vary. The map \( \Phi_4 \) is then used to create the sequence \( \{\Phi_4(\mathbf{u}_1(i))\}_{i=1}^{\infty} \) of linear maps, each element of which is the image of an element of \( \{\mathbf{u}_1(i)\}_{i=1}^{\infty} \) under the map \( \Phi_4 \). These sequences are then used to define the domain and action of a linear operator (IDEAS OP) that quantifies the effect of all reactor units, and has its domain and range be subsets of infinite dimensional spaces. The IDEAS representation is illustrated in figure 2.2 for a reactor network with \( n \) components, \( M \) network inlet streams and \( N \) network outlet streams.
2.4.6. LP Constraints Formulation

Under the previously mentioned assumptions that the network is homogeneous, isothermal and isobaric, the resulting IDEAS feasible region is defined by the total mass, component mass, energy, and entropy balance constraints given below:

\[
F^I (j) = \sum_{i=1}^{N} F^{Oj} (i, j) + \sum_{j=1}^{\infty} F^{Hj} (i, j) \quad \forall j = 1, M \quad (2.17)
\]

\[
F^{Oj} (i) = \sum_{j=1}^{M} F^{Oj} (i, j) + \sum_{j=1}^{\infty} F^{Oj} (i, j) \quad \forall i = 1, N \quad (2.18)
\]
\[ F^i(i) = \sum_{j=1}^{M} F^{ii}(i, j) + \sum_{i=1}^{\infty} F^{i\delta}(i, j) \quad \forall i = 1, \infty \quad (2.19) \]

\[ F^{\delta}(j) = \sum_{i=1}^{N} F^{\delta\delta}(i, j) + \sum_{i=1}^{\infty} F^{i\delta}(i, j) \quad \forall j = 1, \infty \quad (2.20) \]

\[ F^{\delta}(i) = F^i(i) \quad \forall i = 1, \infty \quad (2.21) \]

\[ C^i_k(i) F^i(i) = \sum_{j=1}^{M} C^i_k(i) F^{ii}(i, j) + \sum_{j=1}^{\infty} C^i_k(j) F^{i\delta}(i, j) \quad \forall i = 1, \infty; \forall k = 1, n \quad (2.22) \]

\[ (C^o_k(i))^l F^o(i) \leq \left[ \sum_{j=1}^{M} C^o_k(j) F^{o\delta}(i, j) + \sum_{j=1}^{\infty} C^o_k(j) F^{o\delta}(i, j) \right] \leq (C^o_k(i))^u F^o(i) \quad \forall i = 1, N; \forall k = 1, n \quad (2.23) \]

\[ (F^o(i))^L \leq F^o(i) \leq (F^o(i))^U \quad \forall i = 1, N \quad (2.24) \]

\[ \hat{Q}^o(i) = \left[ H^o(i) \left( \sum_{k=1}^{n} C^0_k(i) \left( \sum_{j=1}^{N} F^{o\delta}(j, i) + \sum_{j=1}^{\infty} F^{i\delta}(j, i) \right) \right) - H^i(i) \left( \sum_{k=1}^{n} C^i_k(i) F^i(i) \right) \right] \quad \forall i = 1, \infty \quad (2.25) \]
\[
\dot{Q}^M(i) = \left[ H^i(i) \left( \sum_{k=1}^n C^i_k(i) \right) F^i(i) - \sum_{j=1}^\infty \left( H^{\hat{o}}(j) \left( \sum_{k=1}^n C^{\hat{o}}_k(j) \right) F^{i\hat{o}}(i,j) \right) \right] - \sum_{j=1}^M \left( H^i(j) \left( \sum_{k=1}^n C^i_k(j) \right) F^{i\hat{o}}(i,j) \right)
\]

\[
\dot{Q}(i) = \dot{Q}^M(i) + \dot{Q}^\hat{o}(i) \Rightarrow
\]

\[
\dot{Q}(i) = \sum_{j=1}^N \left( H^{\hat{o}}(j) \left( \sum_{k=1}^n C^{\hat{o}}_k(j) \right) F^{i\hat{o}}(i,j) \right) - \sum_{j=1}^\infty \left( F^{i\hat{o}}(j) \right) \quad \forall i = 1, \infty
\]

\[
\dot{Q}^\hat{o}(j) = \sum_{i=1}^N \left( H^{\hat{o}}(j) \left( \sum_{k=1}^n C^{\hat{o}}_k(i) \right) F^{i\hat{o}}(j,i) \right) - \sum_{i=1}^M \left( F^{i\hat{o}}(j) \right) \quad \forall j = 1, N
\]
\[
\hat{S}_G(i) = \sum_{j=1}^{\infty} \left[ S^O(j) \left( \sum_{k=1}^{n} C^O_k(j) \right) F^{0\dot{O}}(j,i) + \sum_{j=1}^{\infty} F^{i\dot{O}}(j,i) \right] - \sum_{j=1}^{\infty} \left[ S^O(j) \left( \sum_{k=1}^{n} C^O_k(j) \right) F^{i\dot{O}}(i,j) \right]
\]
\[
\hat{S}_G(j) = \sum_{i=1}^{N} \left[ S^O(i) \left( \sum_{k=1}^{n} C^O_k(i) \right) F^{0\dot{O}}(i,j) - \sum_{i=1}^{N} \left[ S^O(i) \left( \sum_{k=1}^{n} C^O_k(i) \right) F^{i\dot{O}}(i,j) \right] - \frac{\dot{Q}(i)}{T_\sigma} \right] \quad \forall i = 1, \infty \quad (2.29)
\]

\[
\hat{S}_G^O(j) = \sum_{i=1}^{\infty} \left[ S^O(j) \left( \sum_{k=1}^{n} C^O_k(j) \right) F^O(j) \right] - \sum_{i=1}^{\infty} \left[ S^O(i) \left( \sum_{k=1}^{n} C^O_k(i) \right) F^{0\dot{O}}(i,j) \right] - \frac{\dot{Q}(i)}{T_\sigma} \quad \forall j = 1, N \quad (2.30)
\]

\[
\left\{ \begin{array}{l}
\frac{dC_k(i)}{d\tau} = R_k \left( \left\{ C_k(i) \right\}_{k=1}^{n} \right) \quad \forall k = 1, n \\
C_k(i) \mid_{\tau=0} = C^I_k(i) C_k(i) \mid_{\tau=\tau} = C^O_k(i) \\
C^I_k(i) - C^O_k(i) + R_k \left( \left\{ C^O_k(i) \right\}_{k=1}^{n} \right) \tau = 0 \\
\end{array} \right\} \quad \lambda(i) = 0 \quad (a)
\]

\[
\left\{ \begin{array}{l}
C_k(i) \mid_{\tau=0} = C^I_k(i) C_k(i) \mid_{\tau=\tau} = C^O_k(i) \\
C^I_k(i) - C^O_k(i) + R_k \left( \left\{ C^O_k(i) \right\}_{k=1}^{n} \right) \tau = 0 \\
\end{array} \right\} \quad \lambda(i) = 1 \quad (b)
\]

\[
\begin{array}{c}
F^I \geq 0; F^O \geq 0; F^{0\dot{O}} \geq 0; F^{i\dot{O}} \geq 0; F^{i\dot{O}} \geq 0; F^{i\dot{O}} \geq 0; F^{i\dot{O}} \geq 0
\end{array}
\]
Equations (2.17) – (2.20) correspond to mixing and splitting total mass balances in the DN. Equation (2.21) represents the action of the OP unit. Equation (2.22) represents a component mass balance at the OP inlet; while equation (2.23) represents a component mass balance at the DN outlet combined with stream composition related specifications on the network outlets. Equation (2.24) represents upper and lower bounds on each DN network outlet flow variable. Equations (2.25) and (2.26) are based on energy balances at each reactor inlet and at each reactor to help quantify the utility consumption around the $i^{th}$ reactor due to reaction, $\dot{Q}^R(i)$ $\forall i = 1, \infty$, and the utility consumption due to the mixing of the DN streams that constitute the inlet stream of the $i^{th}$ reactor, $\dot{Q}^M(i) \forall i = 1, \infty$. These two utility consumptions are considered together to always have either a heating or cooling effect, releasing or absorbing heat to the infinite reservoir that interacts energetically with the reactor network. In this case, both utility consumptions can be combined into one term, quantifiable by equation (2.27), which yields the total utility consumption around the augmented $i^{th}$ reactor $\dot{Q}(i) \forall i = 1, \infty$. Equation (2.28) is based on an energy balance that helps quantify the utility consumption $\dot{Q}^O(j)$ $\forall j = 1, N$ due to mixing at the $j^{th}$ outlet at the DN network outlet. Similarly, equations (2.29) and (2.30) are based on entropy balances that help quantify the entropy generation around the augmented $i^{th}$ reactor, $\dot{S}_G(i) \forall i = 1, \infty$ and the entropy generation due to mixing at the $j^{th}$ outlet of the IDEAS DN network, $\dot{S}_G^O(j)$ $\forall j = 1, N$ respectively. Finally, the inlet and outlet compositions
$C_k^i(i), C_k^0(i)$ of every OP unit must satisfy relation (2.31–a) for PFR reactors and (2.31–b) for CSTR reactors.

2.5. Reactor Network Utility Consumption and Entropy Generation Formulations

The heat generation (or consumption) rate of the reactor network is equal to the sum of heat generation (or consumption) rate at every reactor, and every overall network outlet mixing junction. Similarly, the entropy generation rate of the network is equal to the sum of entropy generation rates at every reactor and every overall network outlet mixing junction. This yields the following mathematical expressions for these entities:

$$Q^T = \sum_{i=1}^{\infty} Q(i) + \sum_{j=1}^{N} Q^O(j) \tag{2.32}$$

$$S_G^T = \sum_{i=1}^{\infty} S_G(i) + \sum_{j=1}^{N} S_G^O(j) \tag{2.33}$$

The above equations can be used to define network utility consumption and entropy generation constraints in IDEAS formulations of the reactor network synthesis problem. However, the theoretical development below will demonstrate that when all feasible reactors exhibit heat generation (or consumption) the above derived formulas can be simplified to the point where both utility consumption and entropy generation are only related to the overall network’s inlets and outlets.

2.5.1. Theorem 1

Consider the homogeneous, isothermal, isobaric, reactor network illustrated in figure 2.2, featuring $N$ components, $M$ network inlet streams and $N$ network outlet streams. Under the
assumptions that all feasible reactors and network outlet mixing junctions exhibit heat generation (or consumption), that all network concentrations are bounded, that the molar enthalpy and entropy functions are bounded over their domain in temperature-pressure-composition space, and that the total mass flow in the network is finite, the network’s utility consumption and entropy generation satisfy the following:

\[
\tilde{Q}^T = \left[ \sum_{j=1}^{N} \left( H^O (j) \left( \sum_{k=1}^{n} C_k^O (j) \right) F^O (j) \right) - \sum_{i=1}^{M} \left( H^I (i) \left( \sum_{k=1}^{n} C_k^I (i) \right) F^I (i) \right) \right]
\]

(2.34)

\[
\tilde{S}^T_G = \left[ \sum_{j=1}^{N} \left( S^O (j) - \frac{H^O (i)}{T_\sigma} \left( \sum_{k=1}^{n} C_k^O (j) \right) F^O (j) \right) - \sum_{i=1}^{M} \left( S^I (i) - \frac{H^I (i)}{T_\sigma} \left( \sum_{k=1}^{n} C_k^I (i) \right) F^I (i) \right) \right]
\]

(2.35)

**Proof:**

Equations (2.27), (2.28) and (2.32) imply:

\[
\tilde{Q}^T = \left[ \sum_{i=1}^{\infty} \left( H^\sigma (j) \left( \sum_{k=1}^{n} C_k^\sigma (i) \right) F^{O\sigma} (j,i) + \sum_{j=1}^{\infty} F^{i\sigma} (j,i) \right) - \sum_{j=1}^{\infty} \left( H^\sigma (j) \left( \sum_{k=1}^{n} C_k^\sigma (j) \right) F^{i\sigma} (i,j) \right) - \sum_{i=1}^{\infty} \left( H^\sigma (i) \left( \sum_{k=1}^{n} C_k^\sigma (i) \right) F^{i\sigma} (i,j) \right) \right] + \left[ \sum_{j=1}^{\infty} \left( H^\sigma (j) \left( \sum_{k=1}^{n} C_k^\sigma (j) \right) F^{O\sigma} (j,i) - \sum_{i=1}^{\infty} \left( H^\sigma (i) \left( \sum_{k=1}^{n} C_k^\sigma (i) \right) F^{i\sigma} (i,j) \right) \right) \right]
\]

\[
\leftrightarrow
\]

\[
\sum_{j=1}^{\infty} \left( H^\sigma (j) \left( \sum_{k=1}^{n} C_k^\sigma (j) \right) F^{O\sigma} (j,i) - \sum_{i=1}^{\infty} \left( H^\sigma (i) \left( \sum_{k=1}^{n} C_k^\sigma (i) \right) F^{i\sigma} (i,j) \right) \right) \]

\[
\sum_{i=1}^{\infty} \left( H^\sigma (j) \left( \sum_{k=1}^{n} C_k^\sigma (i) \right) F^{i\sigma} (j,i) + \sum_{j=1}^{\infty} F^{i\sigma} (j,i) \right)
\]
Given the theorem’s assumptions that all network concentrations are bounded, that the molar enthalpy and entropy functions are bounded over their domain in temperature-pressure-composition space, and that the total mass flow in the network is finite, all seven sums in the right hand side of the above equation for $\dot{Q}^r$ are absolutely summable. Then, all these sums are finite, and Fubini’s theorem for infinite sums suggests that the order of summation can be switched for each sum. It then becomes apparent that the first and second terms cancel with the sixth and third terms respectively. Then

$$
\dot{Q}^r = \left[ \sum_{j=1}^{\infty} \sum_{i=1}^{n} \left( H^o (i) \left( \sum_{k=1}^{n} C_k^o (j) \right) F^{o} (j, i) \right) + \sum_{j=1}^{\infty} \sum_{i=1}^{n} \left( H^i (i) \left( \sum_{k=1}^{n} C_k^i (j) \right) F^{i} (j, i) \right) \\
- \sum_{j=1}^{\infty} \sum_{i=1}^{n} \left( H^o (j) \left( \sum_{k=1}^{n} C_k^o (i) \right) F^{o} (j, i) \right) - \sum_{j=1}^{M} \sum_{i=1}^{N} \left( H^i (j) \left( \sum_{k=1}^{n} C_k^i (j) \right) F^{i} (i, j) \right) \\
+ \sum_{j=1}^{N} \left( H^o (j) \left( \sum_{k=1}^{n} C_k^o (j) \right) F^{o} (j) \right) - \sum_{j=1}^{M} \sum_{i=1}^{N} \left( H^i (j) \left( \sum_{k=1}^{n} C_k^i (j) \right) F^{i} (j, i) \right) \\
- \sum_{j=1}^{N} \sum_{i=1}^{n} \left( H^i (i) \left( \sum_{k=1}^{n} C_k^i (i) \right) F^{i} (j, i) \right) \\
\right] \\
$$

Use of equation (2.17) then establishes the desired formula for $\dot{Q}^r$. 

80
Next consider entropy generation. Equations (2.29), (2.30) and (2.33) imply:

\[
S_G^T = \left[ \sum_{i=1}^{\infty} \left( S^\circ (i) \left( \sum_{k=1}^{n} C_k^\circ (i) \right) \right) \left( \sum_{j=1}^{N} F^{\circ \circ} (j, i) + \sum_{j=1}^{\infty} F^i (j, i) \right) \right] - \\
+ \sum_{j=1}^{N} \left( S^\circ (j) \left( \sum_{k=1}^{n} C_k^\circ (j) \right) F^i (j, i) \right) - \sum_{i=1}^{\infty} \left( S^\circ (i) \left( \sum_{k=1}^{n} C_k^\circ (i) \right) F^{\circ \circ} (j, i) \right) - \frac{\dot{Q}(i)}{T_{\sigma}} \right] 
\]

Employing again Fubini’s theorem for infinite sums, and based on similar arguments to the ones provided above, allows us to cancel the first and second terms with the sixth and third terms respectively in the right hand side of the above expression. Then, using equation (2.32), and the newly established equation (2.34), yields:
The importance of the above theorem is best realized when considering a non-isothermal reactor network. In that case, entropy generation cannot be quantified solely based on the inlets and outlets of the reactor network but also depends on the internal network structure. The reason is that some of the network’s reactors may be exothermic, while others are endothermic and thus some of the reactors may be heat integrated, exchanging heat with one another. In fact, as the Theorem demonstrates, even for an isothermal reactor network, entropy generation cannot be quantified solely based on the inlets and outlets of the reactor network but also depends on the internal network structure. Indeed, if some reactors are exothermic and others endothermic and/or if the mixing unit that yields the overall reactor network outlet is exothermic (endothermic) and the network reactors are endothermic (exothermic), then entropy generation

Use of equation (2.17) then establishes the desired formula for $\dot{S}_G$. O.E.Δ.
depends on the network structure. The exothermic reactors would provide heat to a reservoir whose temperature \( T_c \) is below the network temperature \( T \), while the endothermic would receive heat from a reservoir whose temperature \( T_h \) is above the network temperature \( T \). The resulting contributions to overall network energy generation/consumption can thus not be added, rendering in this case the network structure essential to the calculation. On the other hand, when all reactors are exothermic (endothermic) and the product mixer unit is also exothermic (endothermic), then the above theorem establishes that the network’s total utility consumption \( Q^r \) and entropy generation \( S_G^T \) depend only on the network inlet and outlet information and do not depend on the network structure. In turn, this implies that the synthesis of isothermal, isobaric reactor networks where entropy generation and utility consumption levels are quantified can be pursued within the Attainable Region (AR) conceptual framework\(^{29}\). Even though the development leading to this result employed the constant density reactor model case, a similar result where total network utility consumption and entropy generation depend only on the network inlet and outlet information and not on the network structure can be readily obtained by using the variable density reactor model case.

2.6. Attainable Region-Based Quantification of Entropy Generation and Utility Consumption for Isothermal Reactor Networks

It has been determined above that entropy generation and utility consumption network properties are dependent only on the reactor network’s inlet and outlet compositions. Consider a single inlet-single outlet reactor network with known inlet composition and known reaction kinetics. Then, the collection of all feasible reactor network outlet concentration vectors is a convex subset of concentration space called the Attainable Region (AR). Since any point of the AR represents a feasible reactor network’s outlet composition vector, and given that the reactor
network’s inlet composition vector is known, the above theorem suggests that a value of entropy generation and a value of utility consumption can be associated with each AR point.

The AR can be quantified either by using a linear programming approach\(^{20}\), a bounding plane approach\(^{26}\), or by using the Shrink-Wrap algorithm\(^{21}\). The latter procedure is cursorily described as follows: Starting with an initial convex superset guaranteed to contain the AR, a finite collection of points approximating the set is considered. At each extreme point of this approximated set, backward PFR and CSTR trajectories are generated and their intersection with the approximated superset is examined. If such an intersection exists, the current extreme point is kept; otherwise it is discarded thus reducing the set. The procedure continues by identifying the list of extreme points for the reduced set, and repeating the extreme point elimination process. The procedure concludes if all extreme points satisfy the PFR/CSTR trajectory criterion, or represent a feed point. The final list of extreme points constitutes an approximation of the true AR, which can be refined by considering a larger number of points to approximate the initial convex superset.

The dimension of the concentration space in which the AR is constructed can be reduced, if linear dependence relations are satisfied by the generation rates of the species involved in the reaction scheme\(^{22}\). In particular, for a single inlet/single outlet reactor network, if relation (36) holds true, then relation (2.37) holds true as well for any stream in the reactor network.

\[
\sum_{k=1}^{n} \eta_k R_k = 0 \quad (2.36)
\]

\[
\sum_{k=1}^{n} \eta_k (C_k - C'_{k}) = 0 \quad (2.37)
\]
Where \( \eta_k \) is a scalar, \( R_k \) is the generation rate of species \( k \), \( \forall k = 1, n \), \( C_k \) is the concentration of species \( k \), \( \forall k = 1, n \) in any stream, and \( C_k^f \) is the concentration of species \( k \), \( \forall k = 1, n \) in the network inlet stream.

The above results for AR construction and dimensionality reduction, coupled with the results of the theorem will be next utilized in a case study which quantifies entropy generation and energy consumption for feasible reactor networks.

### 2.7. Case Study

Consider the following reversible reaction scheme, taking place at \( T = 400K \) and \( P = 10^5 \) Pa, in a homogeneous, isothermal, isobaric, constant density, and single inlet/outlet reactor network, with a feed concentration of 1 mol/m³ of pure reactant A and volumetric feed flow rate of 1 m³/s.

The reaction scheme is as follows:

\[
A \rightleftharpoons B \rightleftharpoons C
\]

\[
k_1^f \quad k_2^f
\]

\[
k_1^i \quad k_2^i
\]

\[
2A \rightleftharpoons 2C
\]

All reactions obey simple elementary rate laws such that the resulting species generation rates can be written as:

\[
R_A = -k_1^f \left( C_A - \frac{C_B}{K_1} \right) - k_3^f \left( \frac{C_A^2}{K_1^2K_2^2} - \frac{C_C^2}{K_1^2K_2^2} \right)
\]

\[
R_B = k_1^i \left( C_A - \frac{C_B}{K_1} \right) - k_2^i \left( \frac{C_B}{K_2} - \frac{C_C}{K_2} \right)
\]
\[ R_C = k_f^f \left( \frac{C_B - C_C}{K_2} \right) + k_f^r \left( \frac{C^2_A - C_C^2}{K_1^2 K_2^2} \right) \]

Where \( K_1 = \frac{C_{Be}}{C_{Ae}} = \frac{k_f^f}{k_f^r}, \ K_2 = \frac{C_{Ce}}{C_{Be}} = \frac{k_f^r}{k_f^r}, \ K_3 = \frac{C_{Ce}^2}{C_{Ae}} = K_1 K_2^2 = \frac{k_f^f}{k_f^r} \)

Close examination of the above reaction scheme reveals that:

\[ R_A + R_B + R_C = 0 \]

Thus application of the aforementioned dimensionality reduction principle, for single inlet and single outlet reactor networks, yields that for any reactor network stream it holds:

\[ C_A + C_B + C_C = C_A^0 + C_B^0 + C_C^0 = C_A^0 = 1 \text{ mol/m}^3 \]

At equilibrium it holds that \( R_B = 0 \), and \( R_C = 0 \). Therefore, \( R_A + R_C = 0 \iff \)

\[ -k_f^f \left( \frac{C_{Ae}}{K_1} \right) + k_f^r \left( \frac{C_{Ce}}{K_2} \right) = 0 \iff C_{Be} = \frac{\left( \frac{k_f^f}{k_f^r} \right)}{\left( \frac{k_f^f}{K_1} + \frac{k_f^r}{K_2} \right)} C_{Ae} + \frac{\frac{k_f^f}{k_f^r} C_A^0}{\left( \frac{k_f^f}{K_1} + \frac{k_f^r}{K_2} \right)} \]

Defining \( \alpha \equiv \frac{\left( \frac{k_f^f}{k_f^r} \right)}{\left( \frac{k_f^f}{K_1} + \frac{k_f^r}{K_2} \right)} \), and \( \beta \equiv \frac{\frac{k_f^f}{k_f^r} C_A^0}{\left( \frac{k_f^f}{K_1} + \frac{k_f^r}{K_2} \right)} \), then yields \( C_{be} = \alpha C_{Ae} + \beta \);

Combining with \( R_A = 0 \) yields:
\[
k_3^f \left( \frac{(\alpha +1)^2}{K_1^2 K_2^2} - 1 \right) C_{Ae}^2 - \left( k_f^f \left( 1 - \frac{\alpha}{K_1} \right) + 2k_3^f \left( \frac{C_A^0 - \beta}{K_1^2 K_2^2} \right) \right) C_{Ae} + \left( k_f^f \frac{\beta}{K_1} + k_3^f \left( \frac{C_A^0 - \beta}{K_1^2 K_2^2} \right)^2 \right) = 0
\]

For given kinetic and equilibrium constants and given network feed composition \(C_A^0\), the above quadratic equation can determine the equilibrium concentration of species A. The equilibrium concentration of species B and C can then be trivially obtained.

The reactor network’s inlet and outlet are considered to be at the reactor network’s operating temperature and pressure \(T = 400K\) and \(P = 10^5 Pa\), and the reacting mixture is considered to be ideal, i.e. mixing effects are neglected and excess entropy/enthalpy terms are set to zero. The three pure species’ molar entropy, \(S_k\) and molar enthalpy, \(H_k\) at \(T = 400K\) and \(P = 10^5 Pa\) are shown in table 1. These values suggest that each reactor in the reactor network requires cooling, which is provided by an infinite reservoir at \(T_\sigma = 298K\). For this reservoir temperature, the quantity \(\alpha_k\) defined as \(\alpha_k(T, P) \equiv S_k(T, P) - \frac{H_k(T, P)}{T_\sigma}\), can be evaluated for each species.

Considering no pressure dependence of the enthalpy and entropy functions allows evaluation of the pure species Gibbs free energy at standard state (liquid at \(P = 10^5 Pa\)) and at the reactor network temperature \(T = 400K\) as:

\[
G_k^0 \left( T = 400K, P = 10^5 Pa \right) \equiv H_k \left( T = 400K, P = 10^5 Pa \right) - 400 \cdot S_k \left( T = 400K, P = 10^5 Pa \right).
\]

<table>
<thead>
<tr>
<th>(k)</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(S_k) (J/(mol.K))</td>
<td>-451</td>
<td>-443</td>
<td>-435</td>
</tr>
<tr>
<td>(H_k) (J/mol)</td>
<td>-24,437</td>
<td>-25,429</td>
<td>-25,125</td>
</tr>
</tbody>
</table>
![Table 2.1: Pure species molar entropy and enthalpy at $T = 400K$ and $P = 10^5 Pa$](image)

From the pure species Gibbs free energy values in table 1, the reaction Gibbs free energies for reactions 1, 2 are:

$$
\Delta G_{\text{React.1}}^0 = G_B^0 - G_A^0 = -4.192 \text{ J/mol, and } \Delta G_{\text{React.2}}^0 = G_C^0 - G_B^0 = -2.897 \text{ J/mol.}
$$

In turn, the equilibrium constants for the three reactions can be evaluated as

$$
K_1 = \exp\left(\frac{-\Delta G_{\text{React.1}}^0}{RT}\right) = \frac{k_f^1}{k_b^1} = 3.527, \quad K_2 = \exp\left(\frac{-\Delta G_{\text{React.2}}^0}{RT}\right) = \frac{k_f^2}{k_b^2} = 2.389 \quad \text{and}
$$

$$
K_3 = \exp\left(\frac{-\Delta G_{\text{React.3}}^0}{RT}\right) = K_1^2K_2^2 = \frac{k_f^3}{k_b^3} = 70.99 \text{ respectively.}
$$

Considering the forward kinetic constants of the three reactions to be

$$
k_f^1 = 1 \text{s}^{-1}; k_f^2 = 0.1 \text{s}^{-1}; k_f^3 = 2 \left(\text{m}^3/\text{mol}\right)^2 \cdot \text{s}^{-1} \quad \text{yields} \quad \frac{k_f^1}{K_1} = 0.2835 \text{s}^{-1}, \quad \frac{k_f^2}{K_2} = 0.04185 \text{s}^{-1} \quad \text{and}
$$

$$
\frac{k_f^3}{K_1K_2^2} = 0.0281 \left(\text{m}^3/\text{mol}\right)^2 \cdot \text{s}^{-1}, \quad \text{and} \quad \alpha = 2.252 \quad \text{and} \quad \beta = 0.0983 \text{ for } C_A^0 = 1 \text{ mol/m}^3. \text{ In turn, this}
$$

yields the quadratic equation $-1.7C_{Ae}^2 - 0.52C_{Ae} + 0.05 = 0$, which has a single physically meaningful positive root $C_{Ae} = 0.0768 \text{ mol/m}^3$. The corresponding equilibrium concentration of species B can then be evaluated $C_{Be} = 0.2712 \text{ mol/m}^3$, which is consistent with the AR results shown in figure 3-4 obtained using the Shrink-Wrap algorithm. (The $C_1, C_2$ axes correspond to $C_A$ and $C_B$ respectively in figure 3, while it corresponds to $C_C$ and $C_B$ respectively.)
Figure 2.3: Attainable region and CSTR/PFR trajectories that determine the AR (discretization 3000 x 3000; $C_1, C_2$ correspond to $C_A$ and $C_B$ respectively).

Figure 2.4: Attainable region and CSTR/PFR trajectories that determine the AR (discretization 3000 x 3000; $C_1, C_2$ correspond to $C_C$ and $C_B$ respectively).
As can be seen in figure 2.3 (2.4), the upper attainable region boundary can be formed by a CSTR followed by a PFR, for small concentrations of A (high concentrations of C), and by mixing of the feed with a CSTR outlet, for high concentrations of A (small concentrations of C). Since the reactor network’s inlet consists of pure A, it then holds \( S' = -451 \text{ J/(mol.K)} \) and \( H' = -24,437 \text{ J/mol} \). Since the reacting mixture is considered ideal, the network outlet stream’s entropy and enthalpy are:

\[
S^O = \sum_{k \in \{A,B,C\}} \left( \sum_{l \in \{A,B,C\}} \frac{C_k}{C_l} S_k(T,P) \right), \quad \text{and} \quad H^O = \sum_{k \in \{A,B,C\}} \left( \sum_{l \in \{A,B,C\}} \frac{C_k}{C_l} H_k(T,P) \right).
\]

Then, the network entropy generation and utility consumption can be evaluated as

\[
\hat{S}^T_G = (C^O_A + C^O_B + C^O_C) \cdot F \cdot \left( S^O - \frac{H^O}{T_\sigma} \right) - \left( S^I - \frac{H^I}{T_\sigma} \right) \left( \frac{J}{s \cdot K} \right) \Rightarrow \\
\hat{Q}^T = \left( C^O_A + C^O_B + C^O_C \right) \cdot F \cdot \left[ H^O - H^I \right] \left( \frac{J}{s} \right) \Rightarrow \hat{Q}^T = \left[ \sum_{k \in \{A,B,C\}} C_k H_k(T,P) + 24,437 \right] \left( \frac{J}{s} \right).
\]

Therefore, \( \text{iso} - \hat{S}^T_G \left( \frac{J}{s \cdot K} \right) \) and \( \text{iso} - \hat{Q}^T \left( \frac{J}{s} \right) \) lines are linear and can be drawn on an AR diagram as shown in figure 4 (C_B vs. C_A) and figure 5 (C_B vs. C_C). The AR diagrams equipped with
$iso - \dot{S}_G^T \left( \frac{J}{s \cdot K} \right)$, and $iso - \dot{Q}_s^T \left( \frac{J}{s} \right)$ lines can be used to quantify attainable region composition, entropy generation, and utility consumption properties simultaneously. As expected from the above discussion, it can be verified that entropy generation is zero for an outlet concentration of pure reactant A (no reaction) and increases as the outlet composition approaches the equilibrium value.

**Figure 2.5:** Entropy generation ($\dot{S}_G^T$) and utility consumption ($\dot{Q}_s^T$) isoclines on a $C_B$ vs. $C_A$ AR Diagram
Figure 2.6: Entropy generation ($\dot{S}_G^T$) and utility consumption ($\dot{Q}^T$) isoclines on a $C_B$ vs. $C_C$ AR Diagram
2.8. Conclusions

This work presents a method to quantify entropy generation, utility consumption, and composition using AR information for isothermal, isobaric reactor networks. The IDEAS framework is shown to apply to this synthesis problem. A theorem is proved which establishes that, under certain assumptions, an isothermal, isobaric reactor network’s entropy generation and utility consumption properties depend only on the network outlet streams’ composition, regardless of the network’s internal structure. In turn, this implies that quantifying entropy generation and energy consumption can be achieved by simply quantifying the AR for the considered reaction kinetic scheme from known network inlet. While for energy intensive processes tradeoffs between entropy generation, energy consumption and outlet composition will lead to a final design that is close to an entropy generation minimizing design, the final design may not possess minimal entropy generation characteristics for energy non-intensive processes.

2.9. Nomenclature

\[ \{ N_k^o \}_{k=1}^n \] : Number of \( k^{th} \) species moles in process outlet stream

\[ \{ N_k^i \}_{k=1}^n \] : Number of \( k^{th} \) species moles in process inlet stream

\[ \{ N_k^E \}_{k=1}^n \] : Equilibrium number of \( k^{th} \) species moles

\[ H(T, P, \{ N_k^o \}_{k=1}^n) \] : Enthalpy associated with a general outlet stream of temperature, pressure, and moles \( T, P \) and \( \{ N_k^o \}_{k=1}^n \) respectively (J)
$H(T, P, \{N_k^i\}_{k=1})$: Enthalpy associated with a general inlet stream of temperature, pressure, and moles $T$, $P$ and $\{N_k^i\}_{k=1}$ respectively (J)

$S(T, P, \{N_k^o\}_{k=1})$: Entropy associated with a general outlet stream of temperature, pressure, and moles $T$, $P$ and $\{N_k^o\}_{k=1}$ respectively (J/K)

$S(T, P, \{N_k^i\}_{k=1})$: Entropy associated with a general inlet stream of temperature, pressure, and moles $T$, $P$ and $\{N_k^i\}_{k=1}$ respectively (J/K)

$G(T, P, \{N_k^o\}_{k=1})$: Gibbs free energy associated with a general outlet stream of temperature, pressure, and moles $T$, $P$ and $\{N_k^o\}_{k=1}$ respectively (J)

$G(T, P, \{N_k^i\}_{k=1})$: Gibbs free energy associated with a general inlet stream of temperature, pressure, and moles $T$, $P$ and $\{N_k^i\}_{k=1}$ respectively (J)

$T_\sigma$: Temperature of infinite heat reservoir (K)

$W_{\text{lost}}$: Lost work due to process irreversibility (J)

$F$: Volumetric flow rate (m$^3$/s)

$F^m$: Inlet volumetric flow rate (m$^3$/s)
\( R^{\text{out}} \): Outlet volumetric flow rate \((\text{m}^3/\text{s})\)

\( M_k \): \(k^{th}\) Species molecular weight \((\text{g/mol})\)

\( \dot{m} \): Mass flow rate \((\text{kg/s})\)

\( \dot{m}^{\text{out}} \): Outlet mass flow rate \((\text{kg/s})\)

\( \dot{m}^{\text{in}} \): Inlet mass flow rate \((\text{kg/s})\)

\( C_i \): \(i^{th}\) Component molar concentration \((\text{mol/m}^3)\)

\( C_i^{\text{in}} \): \(i^{th}\) Component inlet molar concentration to IDEAS unit model \((\text{mol/m}^3)\)

\( C_i^{\text{out}} \): \(i^{th}\) Component outlet molar concentration from IDEAS unit model \((\text{mol/m}^3)\)

\( z_k \): \(k^{th}\) Species mass fraction

\( z_i^{\text{in}} \): \(i^{th}\) Component inlet mass fraction

\( z_i^{\text{out}} \): \(i^{th}\) Component outlet mass fraction

\( x_i \): \(i^{th}\) Component mole fraction

\( R_k \): \(k^{th}\) Component generation rate, molar model \((\text{mol}/(\text{m}^3 \cdot \text{s}))\)

\( r_i \): \(k^{th}\) Component generation rate, mass model \((\text{mol}/(\text{m}^3 \cdot \text{s}))\)
$\bar{\sigma}$: Design specification variable of mass model reactor \((\text{m}^3 \cdot \text{s})/\text{kg}\)

$\sigma'$: Design specification final value of mass model reactor \((\text{m}^3 \cdot \text{s})/\text{kg}\)

$\bar{\tau}$: Design specification variable of molar model reactor \((\text{s})\)

$\tau'$: Design specification final value of mass model reactor \((\text{s})\)

$V$: Reactor volume \((\text{m}^3)\)

$T$: Temperature \((\text{K})\)

$P$: Pressure \((\text{Pa})\)

$\rho$: Density \((\text{kg}/\text{m}^3)\)

$\tau$: Residence time \((\text{s})\)

$R$: Universal gas constant \((\text{cal}/(\text{K} \cdot \text{mol}))\)

$\Phi$: Input-output information map for process model

$u$: Input vector of an information map

$y$: Output vector of an information map

$H^{in}$: Molar enthalpy inlet to IDEAS unit model \((\text{J/mol})\)

$H^{out}$: Molar enthalpy outlet from IDEAS unit model \((\text{J/mol})\)
\( S^{in} \): Molar entropy inlet to IDEAS unit model \((J/(\text{mol} \cdot \text{K}))\)

\( S^{out} \): Molar entropy outlet from IDEAS unit model \((J/(\text{mol} \cdot \text{K}))\)

\( k \): Reaction rate constants \((s^{-1})\)

\[ H \left( T, P, \{C_i \{z_k^{in} \}_{k=1}^{n-1}\} \right), H \left( T, P, \{C_j \{z_k^{out} \}_{k=1}^{n-1}\} \right), H \left( T, P, \{C_k \}_{k=1}^{n} \right) \]: Enthalpy associated with a general stream of temperature, pressure, and composition \( T \), \( P \) and \( \{C_k \}_{k=1}^{n} \) respectively, where

\( \{C_k \}_{k=1}^{n} \) can be a function of mass fractions \( \{z_k \}_{k=1}^{n} \) \((J/\text{mol})\)

\[ S \left( T, P, \{C_i \{z_k^{in} \}_{k=1}^{n-1}\} \right), S \left( T, P, \{C_j \{z_k^{out} \}_{k=1}^{n-1}\} \right), S \left( T, P, \{C_k \}_{k=1}^{n} \right) \]: Entropy associated with a general stream of temperature, pressure, and composition \( T \), \( P \) and \( \{C_k \}_{k=1}^{n} \) respectively, where

\( \{C_k \}_{k=1}^{n} \) can be a function of mass fractions \( \{z_k \}_{k=1}^{n} \) \((J/(\text{mol} \cdot \text{K}))\)

\[ H^{id} \left( T, P, \{C_k \}_{k=1}^{n} \right) \]: Ideal enthalpy associated with a temperature, pressure, and composition \( T \), \( P \) and \( \{C_k \}_{k=1}^{n} \) respectively \((J/\text{mol})\)

\[ S^{id} \left( T, P, \{C_k \}_{k=1}^{n} \right) \]: Ideal entropy associated with a general stream of temperature, pressure, and composition \( T \), \( P \) and \( \{C_k \}_{k=1}^{n} \) respectively \((J/(\text{mol} \cdot \text{K}))\).

\[ H^{E} \left( T, P, \{C_k \}_{k=1}^{n} \right) \]: Excess enthalpy associated with a general stream of temperature, pressure, and composition \( T \), \( P \) and \( \{C_k \}_{k=1}^{n} \) respectively \((J/\text{mol})\).
$S^E(T, P, \{C_k\}_{k=1}^n)$: Excess entropy associated with a general stream of temperature, pressure, and composition $T$, $P$ and $\{C_k\}_{k=1}^n$ respectively ($J/(\text{mol} \cdot \text{K})$).

$H_k(T, P)$: Pure component enthalpy associated with a general stream of temperature and pressure $T$, $P$ respectively ($J/\text{mol}$).

$S_k(T, P)$: Pure component entropy associated with a general stream of temperature and pressure $T$, $P$ respectively ($J/(\text{mol} \cdot \text{K})$).

$G^E(T, P, \{C_k\}_{k=1}^n)$: Excess Gibbs free energy associated with a general stream of temperature, pressure and composition $T$, $P$ and $\{C_k\}_{k=1}^n$ respectively ($J/\text{mol}$).

$\gamma_k(T, P, \{C_k\}_{k=1}^n)$: Liquid phase activity coefficient function associated with a liquid stream of temperature, pressure and composition $T$, $P$ and $\{C_k\}_{k=1}^n$ respectively ($J/\text{mol}$).

$Q_F$: Volumetric heat input in IDEAS unit model ($J/\text{m}^3$)

$Q_m$: Mass basis heat input in IDEAS unit model ($J/\text{kg}$)

$\dot{Q}$: Rate of heat input in IDEAS unit model ($J/\text{s}$)

$S^F_G$: Volumetric entropy generation rate in IDEAS unit model ($J/(\text{m}^3 \cdot \text{K})$)

$S^m_G$: Mass basis entropy generation rate in IDEAS unit model ($J/(\text{kg} \cdot \text{K})$)
\[ \dot{S}_G \] : Rate of entropy generation in IDEAS unit model \((J/(s \cdot K))\)

\[ \dot{Q}^R (i) \] : Heat consumption rate due to reaction for \(i^{th}\) reactor in IDEAS reactor network \(\forall i = 1, \infty\) \((J/s)\)

\[ \dot{Q}^M (i) \] : Heat consumption rate due to mixing of stream entering \(i^{th}\) reactor in IDEAS reactor network \(\forall i = 1, \infty\) \((J/s)\)

\[ \dot{Q}(i)\left(\dot{Q}^R (i) + \dot{Q}^M (i)\right) \] : Heat consumption rate for augmented \(i^{th}\) reactor in IDEAS reactor network \(\forall i = 1, \infty\) \((J/s)\)

\[ \dot{Q}^O (i) \] : Heat of mixing rate at \(i^{th}\) DN network outlet \(\forall i = 1, N\) \((J/s)\)

\[ \dot{Q}^T \] : Total network energy consumption rate \((J/s)\)

\[ \dot{S}_G (i) \] : Entropy generation rate for augmented \(i^{th}\) reactor in IDEAS reactor network \(\forall i = 1, \infty\) \((J/(s \cdot K))\)

\[ \dot{S}_G^O (i) \] : Entropy generation rate at \(i^{th}\) DN network outlet \(\forall i = 1, N\) \((J/(s \cdot K))\)

\[ \dot{S}_G^T \] : Total network entropy generation rate \((J/(s \cdot K))\)

IDEAS Variables

\(M\) : Number of IDEAS network inlets

\(N\) : Number of IDEAS network outlets
\( C_k^I (j) \): \( k^{th} \) Component concentration in the \( j^{th} \) network inlet \( \forall k = 1, n; \forall j = 1, M \)

\( C_k^O (i) \): \( k^{th} \) Component concentration in the \( i^{th} \) network outlet \( \forall k = 1, n; \forall i = 1, N \)

\( C_k^I (i) \): \( k^{th} \) Component concentration in the \( i^{th} \) OP inlet \( \forall k = 1, n; \forall i = 1, \infty \)

\( C_k^O (i) \): \( k^{th} \) Component concentration in the \( i^{th} \) OP outlet \( \forall k = 1, n; \forall i = 1, \infty \)

\( F^I (j) \): \( j^{th} \) Network inlet flow rate \( \forall j = 1, M \)

\( S^I (j) \): Entropy associated with \( j^{th} \) network inlet stream \( \forall j = 1, M \)

\( H^I (j) \): Enthalpy associated with \( j^{th} \) network inlet stream \( \forall j = 1, M \)

\( F^O (i) \): \( i^{th} \) Network outlet flow rate \( \forall i = 1, N \)

\( S^O (i) \): Entropy associated with \( i^{th} \) network outlet stream \( \forall i = 1, N \)

\( H^O (i) \): Enthalpy associated with \( i^{th} \) network outlet stream \( \forall i = 1, N \)

\( F^I (j) \): \( j^{th} \) OP inlet flow rate \( \forall j = 1, \infty \)

\( H^I (j) \): Enthalpy associated with \( j^{th} \) OP inlet stream \( \forall j = 1, \infty \)

\( F^O (i) \): \( i^{th} \) OP outlet flow rate \( \forall i = 1, \infty \)

\( S^O (i) \): Entropy associated with \( i^{th} \) OP outlet stream \( \forall i = 1, \infty \)
$H^O(i)$: Enthalpy associated with $i^{th}$ OP outlet stream $\forall i = 1, \infty$

$F^{Oj}(i, j)$: $j^{th}$ Network inlet flow rate to the $i^{th}$ network outlet $\forall j = 1, M; \forall i = 1, N$

$F^{Hi}(i, j)$: $j^{th}$ Network outlet flow rate to the $i^{th}$ OP inlet $\forall j = 1, M; \forall i = 1, \infty$

$F^{OO}(i, j)$: $j^{th}$ OP outlet flow rate to the $i^{th}$ network outlet $\forall j = 1, \infty; \forall i = 1, N$

$F^{IO}(i, j)$: $j^{th}$ OP outlet flow rate to the $i^{th}$ OP network outlet $\forall j = 1, \infty; \forall i = 1, \infty$

$\tau(i)$: Residence time of the $i^{th}$ OP unit $\forall i = 1, \infty$

$\lambda(i)$: Technology flag of the $i^{th}$ OP unit (i.e. 0 for PFR and 1 for CSTR) $\forall i = 1, \infty$

$u(i)$: Input of the $i^{th}$ OP unit information map $\forall i = 1, \infty$

$y(i)$: Output of the $i^{th}$ OP unit information map $\forall i = 1, \infty$
2.10. Appendices

Appendix A:

The molar free energy, enthalpy and entropy of a multi-component liquid mixture are quantified from reference\textsuperscript{25} p. 414, as:

$$H(T,P,\{C_k^n\}_{k=1}^n) = H^E(T,P,\{C_k^n\}_{k=1}^n) + H^{id}(T,P,\{C_k^n\}_{k=1}^n)$$

$$S(T,P,\{C_k^n\}_{k=1}^n) = S^E(T,P,\{C_k^n\}_{k=1}^n) + S^{id}(T,P,\{C_k^n\}_{k=1}^n)$$

Ideal mixture molar enthalpy and entropy can be evaluated\textsuperscript{25} p. 412, as follows:

$$H^{id}(T,P,\{C_k^n\}_{k=1}^n) = \sum_{k=1}^n C_k \sum_{l=1}^n C_l H_k(T,P)$$

$$S^{id}(T,P,\{C_k^n\}_{k=1}^n) = \sum_{k=1}^n C_k \sum_{l=1}^n C_l S_k(T,P) - R \sum_{k=1}^n C_k \ln \left( \frac{C_k}{\sum_{l=1}^n C_l} \right)$$

Excess molar entropy, $S^E(T,P,\{C_k^n\}_{k=1}^n)$, and molar enthalpy, $H^E(T,P,\{C_k^n\}_{k=1}^n)$, can be evaluated from the excess Gibbs free energy, $G^E(T,P,\{C_k^n\}_{k=1}^n)$, which in turn is expressed in terms of liquid activity coefficients as shown in reference\textsuperscript{25} p. 415, p. 418:
\[
\frac{G^E(T, P, \{C_k\}_{k=1}^n)}{RT} = \sum_{k=1}^n \frac{C_k}{\sum_{l=1}^n C_l} \ln \gamma_k(T, P, \{C_k\}_{k=1}^n)
\]

\[
H^E(T, P, z_k) = -RT^2 \frac{\partial}{\partial T} \left[ \frac{G^E(T, P, \{C_k\}_{k=1}^n)}{RT} \right] = -RT^2 \sum_{k=1}^n \frac{C_k}{\sum_{l=1}^n C_l} \frac{\partial}{\partial T} \left[ \ln \gamma_k(T, P, \{C_k\}_{k=1}^n) \right]_{p, c_i}
\]

\[
S^E(T, P, \{C_k\}_{k=1}^n) = \frac{H^E(T, P, \{C_k\}_{k=1}^n) - G^E(T, P, \{C_k\}_{k=1}^n)}{T}
\]

\[
= -RT \sum_{k=1}^n \frac{C_k}{\sum_{l=1}^n C_l} \frac{\partial \ln \gamma_k(T, P, \{C_k\}_{k=1}^n)}{\partial T} \bigg|_{p, c_i} - R \sum_{k=1}^n \frac{C_k}{\sum_{l=1}^n C_l} \ln \gamma_k(T, P, \{C_k\}_{k=1}^n) \bigg|_{p, c_i}
\]

Several temperature dependent local composition models such as Wilson, NRTL, UNIFAC, and UNIQUAC, etc, can be used to define the liquid phase activity coefficient functions

\[
\ln \gamma_k(T, P, \{C_k\}_{k=1}^n) \quad \forall k = 1, n.
\]
2.11. References:


3. CHAPTER 3

Minimum Entropy Generation for Isothermal Endothermic/Exothermic Reactor Networks

3.1. Abstract

In our earlier work, it was shown that the entropy generation and energy consumption of isothermal, isobaric reactor networks only depend on the network’s inlet and outlet stream compositions and flow rates and are not dependent on the reactor network structure, as long as the universe of realizable reactor units and network outlet mixing units are either all endothermic, or all exothermic. In this work, it is shown that when the universe of realizable reactor/mixer units consists of both endothermic and exothermic units, the entropy generation and energy consumption of isothermal, isobaric reactor networks depends on both the network’s inlet and outlet stream compositions and flow rates and the reactor network structure. Thus, in this case, it is meaningful to consider the entropy generation minimization problem over all isothermal, isobaric reactor networks, with known inlet and outlet stream compositions and flow rates. The Infinite DimEnsionAl State-space (IDEAS) conceptual framework is employed for the problem’s mathematical formulation, which is then used to rigorously establish the problem’s equivalence to the hot/cold utility cost minimization problem. The proposed methodology is demonstrated on a case study featuring Trambouze kinetics for which the universe of realizable reactors consists of both endothermic and exothermic units. The IDEAS-generated optimal network generates 28% less entropy than a baseline design. Finally, conclusions are drawn.
3.2. Introduction

This work is a continuation of a previously published contribution by the authors on the synthesis of reactor networks with known entropy generation\(^1\). In this earlier work, it was rigorously demonstrated, using the IDEAS framework, that if the universe of reactors that could possibly help realize the reactor network consists of either only endothermic reactors or only exothermic reactors, then the quantification of entropy generation and utility consumption can be performed irrespective of the network’s internal structure, and depends only on reactor network inlet and outlet compositions. In turn, this allows the creation of entropy and energy consumption isoclines within an attainable region diagram, allowing reactor network design to be pursued based on rigorous tradeoffs among entropy generation, energy consumption, and other reactor network performance specifications (such as conversion, yield, selectivity, etc.). This work relaxes the aforementioned assumption that the universe of feasible reactors consists of either only endothermic reactors or only exothermic reactors, and considers the existence of both exothermic and endothermic reactors in the reactor universe. It is shown that while net energy consumption remains a function of only network inlet/outlet compositions, entropy generation and energy consumption are also strong functions of the network’s internals. Thus, it is desirable and meaningful to quantify minimum entropy generation over all reactor networks that meet predefined performance specifications. To this end, the IDEAS conceptual framework will be employed.
The method of entropy generation minimization has been applied to several industrial reactions to determine the optimal reactor temperature profile\(^2-^6\) using optimal control theory. Unfortunately, this technique only allows for the identification of a locally optimal solution rather than a globally optimal one. In addition, only single reactors are considered in those studies. Other authors have relied on MINLP formulations\(^7\), and references therein to energetically optimize networks of non-isothermal reactors, but with no entropy generation considerations.

This work employs the IDEAS framework for the quantification of both entropy generation and energy consumption for isothermal, isobaric reactor networks whose universe of feasible reactor units include units of both the exothermic and endothermic type. The IDEAS framework decomposes a reactor network into an operator, OP network, where the reactor unit operations occur, and a distribution, DN network, where the flow operations (mixing, splitting, recycling, and bypass) occur. IDEAS has been successfully applied to numerous globally optimal process network synthesis problems, such as: mass exchange network synthesis\(^8\), complex distillation network synthesis\(^9-^{11}\), power cycle synthesis\(^12\), reactor network synthesis\(^13-^{14}\), reactive distillation network synthesis\(^15\), separation network synthesis\(^16\), attainable region construction\(^17-^{20}\), and batch attainable region construction\(^21\).

The rest of the paper is structured as follows: CSTR models employing a mass basis and a molar basis are presented, the applicability of IDEAS to the entropy generation and energy consumption quantification problem is demonstrated, and the resulting IDEAS mathematical formulation is presented. Next, properties of the entropy generation and net energy consumption functions are rigorously established in a theorem, which establishes the net energy consumption function’s dependence on only network inlet and outlet information, and the entropy generation
function’s dependence on both network inlet and outlet information and network cold/hot utility consumption. A case study involving Trambouze kinetics is used to illustrate the proposed reactor network synthesis method, and conclusions are drawn.

3.3. Applicability of IDEAS to Isothermal Reactor Network Synthesis

For this work, the following assumptions are considered:

- Reactor network is isothermal i.e. all the reactors, streams are at the same temperature $T$
- Reactor network is isobaric i.e. all the reactors, streams are at the same pressure $P$
- No work is consumed or generated
- Reactor network consists only of CSTR units
- The universe of isothermal, isobaric reactors consists of reactors of both the exothermic or endothermic types.
- An infinite reservoir at constant temperature $T_H$ ($T_H > T$) is considered to provide heat to any endothermic reactor, and an infinite reservoir at constant temperature $T_C$ ($T_C < T$) is considered to provide heat to the exothermic reactor.

3.3.1. Reactor Model – Variable Density Model (Mass Basis)

$$F^{\text{in}} = F^{\text{out}} = F$$ (3.1–a)

$$\left\{ \begin{align*}
\bar{z}_k^{\text{in}} - \bar{z}_k^{\text{out}} + \sigma M_k r_k \left( \left\{ C_i \left( \left\{ \bar{z}_j^{\text{out}} \right\}_{j=1}^n , T, P \right) \right\}_{j=1}^n \right) &= 0 \quad \forall k = 1, n \\
\sigma &= \frac{V}{F} 
\end{align*} \right\}$$ (3.2–a)

$$C_i^{\text{out}} = C_i \left( \left\{ \bar{z}_j^{\text{out}} \right\}_{j=1}^n , T, P \right) \quad \forall i = 1, n$$ (3.3–a)
Where:

\[
\sum_{j=1}^{n} z_{j}^{\text{in}} = 1, \quad z_{j}^{\text{in}} \geq 0 \quad \forall i = 1, n; \quad \sum_{j=1}^{n} z_{j}^{\text{out}} = 1, \quad z_{j}^{\text{out}} \geq 0 \quad \forall i = 1, n \quad (3.3' - a)
\]

Equation \((3.3 - a)\) aims to capture the thermodynamic model of the underlying mixture. Several models can be brought into the form of \((3.3 - a)\). For example if a compressibility factor model \((Z)\) is employed, then:

\[
C_{i}^{\text{out}} = C_{i} \left( \left\{ z_{j}^{\text{out}} \right\}_{j=1}^{n}, T, P \right) = x_{i}^{\text{out}} \left( \frac{P}{RT} \right) \left( \frac{1}{Z \left( \left\{ x_{j}^{\text{in}} \right\}_{j=1}^{n}, T, P \right)} \right) \quad \forall i = 1, n \quad (3.4 - a)
\]

\[
x_{i}^{\text{out}} = \frac{z_{i}^{\text{out}}}{M_{i} \sum_{k=1}^{n} \left( \frac{z_{k}^{\text{out}}}{M_{k}} \right)} \quad \forall i = 1, n \quad (3.5 - a)
\]

Where \(R\) is the universal gas constant, \(x_{i}, z_{i} \forall i = 1, n\) designate the \(i\)th species mole fraction and mass fraction respectively, and \(\sum_{j=1}^{n} x_{j}^{\text{out}} = 1, \quad x_{j}^{\text{out}} \geq 0 \quad \forall i = 1, n \quad (3.5' - a)\)

\[
\left\{ h^{\text{arr}} - F \sum_{j=1}^{n} \left( \frac{z_{j}^{\text{out}}}{M_{j}} \right) H \left( T, P, \left\{ C_{i} \left( \left\{ z_{j}^{\text{out}} \right\}_{j=1}^{n-1}, T, P \right) \right\}_{i=1}^{n} \right) + \dot{Q}^{R} = 0 \right\} \quad (3.6 - a)
\]

\[
\dot{Q}^{R} > 0 \iff \lambda = 1; \quad \dot{Q}^{R} < 0 \iff \lambda = 0
\]

\[
\left\{ S^{\text{arr}} - F \sum_{j=1}^{n} \left( \frac{z_{j}^{\text{out}}}{M_{j}} \right) S \left( T, P, \left\{ C_{i} \left( \left\{ z_{j}^{\text{out}} \right\}_{j=1}^{n-1}, T, P \right) \right\}_{i=1}^{n} \right) + \dot{Q}^{R} \left( \frac{\lambda}{T_{H}} + \frac{1 - \lambda}{T_{C}} \right) + \dot{S}_{G}^{R} = 0 \right\} \quad (3.7 - a)
\]

\[
\dot{Q}^{R} > 0 \iff \lambda = 1; \quad \dot{Q}^{R} < 0 \iff \lambda = 0
\]

3.3.2. Reactor Model – Constant Density Model (Molar Basis):

\[
q^{\text{in}} = q^{\text{out}} = q \quad (3.1 - b)
\]
\[
\begin{aligned}
C_k^\text{in} - C_k^\text{out} + R_k \left( \left\{ C_k^\text{out} \right\}_{k=1}^n \right) \tau = 0 \quad \forall k = 1, n \\
\tau = \frac{V}{q} 
\end{aligned}
\]  
(3.2–b)

\[
\begin{aligned}
 h^{\text{arr}} - q \left( \sum_{l=1}^n C_l^\text{out} \right) H \left( T, P, \left\{ C_k^\text{out} \right\}_{k=1}^n \right) + \dot{Q}^R = 0 \\
\dot{Q}^R > 0 \iff \lambda = 1; \quad \dot{Q}^R < 0 \iff \lambda = 0 
\end{aligned}
\]  
(3.6–b)

\[
\begin{aligned}
 S^{\text{arr}} - q \left( \sum_{l=1}^n C_l^\text{out} \right) S \left( T, P, \left\{ C_k^\text{out} \right\}_{k=1}^n \right) + \dot{Q}^R \left( \frac{\lambda}{T_H} + \frac{(1-\lambda)}{T_C} \right) + \dot{S}_C^R = 0 \\
\dot{Q}^R > 0 \iff \lambda = 1; \quad \dot{Q}^R < 0 \iff \lambda = 0 
\end{aligned}
\]  
(3.7–b)

3.4. **Entropy/Enthalpy relations for both VDF and CDF models**

\[
S \left( T, P, \left\{ C_k \right\}_{k=1}^n \right) = \sum_{k=1}^n \frac{C_k}{\sum_{l=1}^n C_l} S_k \left( T, P \right) + S^E \left( T, P, \left\{ C_k \right\}_{k=1}^n \right) - R \sum_{k=1}^n \frac{C_k}{\sum_{l=1}^n C_l} \ln \left( \frac{C_k}{\sum_{l=1}^n C_l} \right) 
\]  
(3.10)

\[
H \left( T, P, \left\{ C_k \right\}_{k=1}^n \right) = \sum_{k=1}^n \frac{C_k}{\sum_{l=1}^n C_l} H_k \left( T, P \right) + H^E \left( T, P, \left\{ C_k \right\}_{k=1}^n \right) 
\]  
(3.11)

\[
H^E \left( T, P, \left\{ C_k \right\}_{k=1}^n \right) = -RT^2 \sum_{k=1}^n \frac{C_k}{\sum_{l=1}^n C_l} \left. \frac{\partial \ln \gamma_k \left( T, P, \left\{ C_k \right\}_{k=1}^n \right) }{\partial T} \right|_{P,C_k} 
\]  
(3.12)

\[
S^E \left( T, P, \left\{ C_k \right\}_{k=1}^n \right) = -RT \sum_{k=1}^n \frac{C_k}{\sum_{l=1}^n C_l} \ln \gamma_k \left( T, P, \left\{ C_k \right\}_{k=1}^n \right) 
\]  
(3.13)

Having presented isothermal CSTR reactor models for the variable density (mass model) and constant density (molar model) cases, the applicability of IDEAS to the variable density reactor models is next demonstrated. In a similar manner, IDEAS can be readily shown to be applicable to the constant density reactor model as well, though this is not shown here in the interest of space.
3.5. Applicability of IDEAS to VDF model

The aforementioned reactor model can be employed to construct the following input-output information map:

$$\Phi : D \rightarrow R^{m+2} \times R, \Phi : u \rightarrow y \text{ such that:}$$

$$\Phi : u = \begin{bmatrix} u_1 \\ u_2 \end{bmatrix} \rightarrow y = \begin{bmatrix} y_1 \\ y_2 \end{bmatrix} = \Phi(u_1, u_2) = \begin{bmatrix} \Phi_1(u_1, u_2) \\ \Phi_2(u_1, u_2) \end{bmatrix},$$

$$u^T = [u_1^T | u_2^T] = [T \ P \ \tilde{z}_1^{in} \ z_1^{out} \ \ldots \ z_{n}^{out} \ \lambda \ | \ F \ h^{arr} \ \hat{Q}^R \ s^{arr} \ \hat{S}_G],$$

$$y^T = [y_1^T | y_2^T] = \Phi^T(u_1, u_2) \triangleq$$

$$[\sigma \ \tilde{z}_2^{in} \ \ldots \ \tilde{z}_n^{in} \ \tilde{x}_1^{out} \ \ldots \ \tilde{x}_n^{out} \ C_1^{out} \ \ldots \ C_n^{out} \ H(T, P, \{C_i^{out}\}_{i=1}^n) \ S(T, P, \{C_i^{out}\}_{i=1}^n) \ | \ F]$$

Where:

$$D = \left\{ u \in R^{m+3} \times \{0, 1\} \times R^3 : \Phi_3(u_1, u_2) = 0 \land \sum_{i=1}^n z_i^{out} - 1 = 0 \land u_1 \geq 0 \land F \geq 0 \land \hat{S}_G \geq 0 \right\},$$

and

$$\Phi_3(u_1, u_2) \triangleq$$

$$\begin{bmatrix} h^{arr} - F \sum_{i=1}^n \left( \frac{z_i^{out}}{M_i} \right) H(T, P, \{C_i^{out}\}_{i=1}^n) + \hat{Q}^R \\ s^{arr} - F \sum_{i=1}^n \left( \frac{z_i^{out}}{M_i} \right) S(T, P, \{C_i^{out}\}_{i=1}^n) + \hat{Q}^R \left( \frac{\lambda}{T_H} + \frac{1-\lambda}{T_C} \right) + \hat{S}_G \end{bmatrix}$$

The evaluation of the images $\Phi^T(u_1, u_2)$, $\Phi_3(u_1, u_2)$ given $u_1$ and $u_2$, is illustrated next for the variable density reactor case.
Consider that \( u_1 \) is known. The residence time \( \sigma \) can first be evaluated by solving equation \((3.2-a)\) for the first species \((k = 1)\). From the solution of equations \((3.2-a)\) for all other species \(k, \forall k = 2, n\), \({z_i^{in}}^{k}\) can be evaluated. Knowledge of the network’s temperature and pressure, and of the outlet species mass fractions, yields the outlet species mole fractions and concentrations, and the outlet molar enthalpy and molar entropy, from equations \((3.10),(3.13)\), and \((3.11),(3.12)\) respectively. Knowledge of \( \lambda \in \{0,1\} \) determines the sign of \( \dot{Q}^R \), since according to equations \((3.6-a)\) and \((3.7-a)\), \( \dot{Q}^R > 0 \Leftrightarrow \lambda = 1; \dot{Q}^R < 0 \Leftrightarrow \lambda = 0 \)

The above decompositions of the input vector \(u\) to \(u_1\) and \(u_2\), of the output vector \(y\) to \(y_1\) and \(y_2\), and of the map \(\Phi\) to \(\Phi_1\) and \(\Phi_2\) are carried out, so that the following IDEAS properties can be shown to hold for the maps \(\Phi_1, \Phi_2\) and for the domain defining map \(\Phi_3\).

### 3.5.1. IDEAS property 1

\( \exists \Phi_4 : \{R^{n+3} \times \{0,1\}\} \to R^{3n+2} \), such that \(\Phi_4 (u_1, u_2) = \Phi_4 (u_1) \forall (u_1, u_2) \in D\). This implies that 

\(\Phi_1 (u_1, u_2)\) can be evaluated based on knowledge of \(u_1\) alone, and independently of \(u_2\).

### 3.5.2. IDEAS property 2

\( \exists \Phi_5 : \{R^{n+3} \times \{0,1\}\} \to R^{5n+2} \), such that \(\Phi_5 (u_1, u_2) = \Phi_5 (u_1) \cdot u_2 \forall (u_1, u_2) \in D\). This map is:

\[
\Phi_5 : u_1 = \begin{bmatrix} T & P & z_1^{in} & z_1^{out} & \cdots & z_n^{out} & \lambda \end{bmatrix}^T \to \Phi_5 (u_1) = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \end{bmatrix}.
\]

It can be readily verified that: \(y_2 = \begin{bmatrix} F \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} F & h^{arr} & \dot{Q}^R & s^{arr} & \dot{S}^R \end{bmatrix}^T = \Phi_5 (u_1) \cdot u_2\)

### 3.5.3. IDEAS property 3
\[ \exists \Phi_6 : \{ \mathbb{R}^{n+3} \times \{0,1\} \} \rightarrow \mathbb{R}^{2s5} , \text{ such that } \Phi_3 (u_1, u_2) = \Phi_6 (u_1) \cdot u_2 \]

\[ \forall (u_1, u_2) \in \mathbb{R}^{n+3} \times \{0,1\} \times \mathbb{R}^5 : \sum_{i=1}^{n} z_i^\text{out} - 1 = 0 \land u_1 \geq 0 \land F \geq 0 \land \delta^R_G \geq 0 \] . This map is:

\[
\Phi_6 : u_1 \equiv \begin{bmatrix} T & P & z_1^\text{in} & z_1^\text{out} & \ldots & z_n^\text{out} & \lambda \end{bmatrix}^\top \rightarrow \\
\Phi_6 (u_1) = \begin{bmatrix}
- \sum_{i=1}^{n} \left( \frac{z_i^\text{out}}{\mathcal{M}_i} \right) H \left( T, P, \{ C_i^\text{out} \}_{i=1}^{n} \right) & 1 & 1 & 0 & 0 \\
- \sum_{i=1}^{n} \left( \frac{z_i^\text{out}}{\mathcal{M}_i} \right) S \left( T, P, \{ C_i^\text{out} \}_{i=1}^{n} \right) & 0 & \left( \frac{\lambda}{T_H} + \frac{1-\lambda}{T_C} \right) & 1 & 1
\end{bmatrix} .
\]

It can be readily verified that:

\[
\Phi_3 (u_1, u_2) = \begin{bmatrix}
- \sum_{i=1}^{n} \left( \frac{z_i^\text{out}}{\mathcal{M}_i} \right) H \left( T, P, \{ C_i^\text{out} \}_{i=1}^{n} \right) & 1 & 1 & 0 & 0 \\
- \sum_{i=1}^{n} \left( \frac{z_i^\text{out}}{\mathcal{M}_i} \right) S \left( T, P, \{ C_i^\text{out} \}_{i=1}^{n} \right) & 0 & \left( \frac{\lambda}{T_H} + \frac{1-\lambda}{T_C} \right) & 1 & 1
\end{bmatrix} \Phi_6 (u_1) \cdot u_2
\]

The above imply that for fixed \( u_1 \), \( \Phi_5 (u_1) \) and \( \Phi_6 (u_1) \) are linear operators. In turn this implies that \( y_2 = \Phi_2 (u_1, u_2) = \Phi_5 (u_1) \cdot u_2 \) is linear in \( u_2 \) and the domain defining constraint

\[ \Phi_3 (u_1, u_2) = \Phi_6 (u_1) \cdot u_2 = 0 \] is also linear in \( u_2 \) . Therefore, for a fixed \( u_1 \) the employed reactor model is defined by a linear input-output map \( \Phi_5 (u_1) \) with domain defined also through the linear map \( \Phi_6 (u_1) \) .

An infinite sequence \( \{ u_1(i) \}_{i=1}^{\infty} \), consisting of all possible values of \( u_1 \) is then considered, such that the union of the considered \( u_1 \) values is dense in the set over which \( u_1 \) can vary. The map \( \Phi_5 \) is then used to create the sequence \( \{ \Phi_5 (u_1(i)) \}_{i=1}^{\infty} \) of linear maps from \( \mathbb{R}^5 \) to \( \mathbb{R} \) , each of which has its domain defined as a subset of the null space of a corresponding linear map from \( \mathbb{R}^5 \).
to \( R \), the collection of which forms the sequence \( \{ \Phi_{\delta} \left( u_i(i) \right) \}_{i=1}^{\infty} \). These sequences are then used to define the domain and action of a linear operator (IDEAS OP) that quantifies the effect of all reactor units, and has its domain and range be subsets of infinite dimensional spaces.

The IDEAS representation is illustrated in figure 1 for a variable density reactor network with \( n \) components, \( M \) network inlet streams and \( N \) network outlet streams.

![Figure 3.1: IDEAS Representation for Isothermal Variable Density Reactor Network](image)

3.6. IDEAS Mathematical Formulation (Variable Density Reactor Network):

Under the previously mentioned assumptions that the network is homogeneous, isothermal and isobaric, and assuming that all reactors and mixers are perfectly mixed, the resulting IDEAS feasible region is defined by the total mass, component mass, energy, and entropy balance.
constraints given below. Let $S_1^R$ and $S_2^R$ denote the index sets corresponding to all realizable exothermic and endothermic reactors, respectively. Let also $S_1^O$ and $S_2^O$ denote the index sets corresponding to all realizable exothermic and endothermic overall network outlet mixers, respectively. Then $S_1^R \cup S_2^R = \{1, \cdots, \infty\}$, $S_1^O \cup S_2^O = \{1, \cdots, N\}$ and the aforementioned constraints can be written as:

$$F^i (i) = \sum_{j=1}^{N} F^{O_i} (j,i) + \sum_{j \in S_1^R} F^{\hat{R}_i} (j,i) + \sum_{j \in S_2^R} F^{\hat{I}_i} (j,i) \quad \forall i = 1, M \quad (3.14)$$

$$F^O (i) = \sum_{j=1}^{M} F^{O_i} (i,j) + \sum_{j \in S_1^O} F^{\hat{O}_i} (i,j) + \sum_{j \in S_2^O} F^{\hat{O}_i} (i,j) \quad \forall i = 1, N \quad (3.15)$$

$$F^i (i) = \sum_{j=1}^{M} F^{R_i} (i,j) + \sum_{j \in S_1^I} F^{\hat{R}_i} (i,j) + \sum_{j \in S_2^I} F^{\hat{I}_i} (i,j) \quad \forall i \in S_1^R \quad (3.16)$$

$$F^I (i) = \sum_{j=1}^{M} F^{R_i} (i,j) + \sum_{j \in S_1^O} F^{\hat{R}_i} (i,j) + \sum_{j \in S_2^O} F^{\hat{I}_i} (i,j) \quad \forall i \in S_2^R \quad (3.17)$$

$$F^{\hat{O}} (j) = \sum_{i=1}^{N} F^{O_i} (i,j) + \sum_{i \in S_1^O} F^{\hat{O}_i} (i,j) + \sum_{i \in S_2^O} F^{\hat{O}_i} (i,j) \quad \forall j \in S_1^R \quad (3.18)$$

$$F^{\hat{O}} (j) = \sum_{i=1}^{N} F^{O_i} (i,j) + \sum_{i \in S_1^O} F^{\hat{O}_i} (i,j) + \sum_{i \in S_2^O} F^{\hat{O}_i} (i,j) \quad \forall j \in S_2^R \quad (3.19)$$

$$F^{\hat{O}} (i) = F^{\hat{I}} (i) \quad \forall i \in S_1^R \cup S_2^R \quad (3.20)$$

$$z_k^i (i) F^i (i) = \sum_{j=1}^{M} z_k^i (j) F^{R_i} (i,j) + \sum_{j \in S_1^R} z_k^\hat{R} (j) F^{\hat{R}_i} (i,j) + \sum_{j \in S_2^R} z_k^\hat{O} (j) F^{\hat{O}_i} (i,j) \quad \forall i \in S_1^R; \forall k = 1, n \quad (3.21)$$

$$z_k^i (i) F^i (i) = \sum_{j=1}^{M} z_k^i (j) F^{R_i} (i,j) + \sum_{j \in S_1^R} z_k^\hat{R} (j) F^{\hat{R}_i} (i,j) + \sum_{j \in S_2^R} z_k^\hat{O} (j) F^{\hat{O}_i} (i,j) \quad \forall i \in S_2^R; \forall k = 1, n \quad (3.22)$$
\[ z_k^O (i) F^O (i) = \sum_{j=1}^{M} z_k^t (j) F^{\text{Ol}} (i, j) + \sum_{j \in S_1^R} z_k^\omega (j) F^{\text{Ol}} (i, j) + \sum_{j \in S_2^R} z_k^\omega (j) F^{\text{Ol}} (i, j) \quad \forall i = 1, N; \quad \forall k = 1, n \quad (3.23) \]

\[ \dot{Q}_R^O (i) = \sum_{l=1}^{n} \left( \frac{z_l (i)}{M_l} \right) H^\omega (i) F^\omega (i) - h^{\text{arr}} (i) \quad \forall i = 1, \infty \quad (3.24) \]

\[ h^{\text{arr}} (i) = \left[ \sum_{j=1}^{M} \sum_{l=1}^{n} \left( \frac{z_l (j)}{M_l} \right) H^t (j) F^{\text{H}} (i, j) + \sum_{j \in S_1^R} \sum_{l=1}^{n} \left( \frac{z_l (j)}{M_l} \right) H^\omega (j) F^{\text{Ho}} (i, j) + \right] \quad \forall i \in S_1^R \cup S_2^R \quad (3.24') \]

\[ \dot{Q}_R^O (i) = \sum_{l=1}^{n} \left( \frac{z_l (i)}{M_l} \right) H^\omega (i) F^\omega (i) - \sum_{j \in S_1^R} \sum_{l=1}^{n} \left( \frac{z_l (j)}{M_l} \right) H^\omega (j) F^{\text{Ho}} (i, j) + \]

\[ \sum_{j \in S_2^R} \sum_{l=1}^{n} \left( \frac{z_l (j)}{M_l} \right) H^\omega (j) F^{\text{Ho}} (i, j) \quad \forall i = 1, N \quad (3.25) \]

\[ S_{G}^R (i) = \sum_{l=1}^{n} \left( \frac{z_l (i)}{M_l} \right) S^\omega (i) F^\omega (i) - S^{\text{arr}} (i) - \frac{\dot{Q}_R^O (i)}{T_c} \quad \forall i \in S_1^R \quad (3.26) \]

\[ S_{G}^R (i) = \sum_{l=1}^{n} \left( \frac{z_l (i)}{M_l} \right) S^\omega (i) F^\omega (i) - S^{\text{arr}} (i) - \frac{\dot{Q}_R^O (i)}{T_h} \quad \forall i \in S_2^R \quad (3.27) \]

\[ S^{\text{arr}} (i) = \left[ \sum_{j=1}^{M} \sum_{l=1}^{n} \left( \frac{z_l (j)}{M_l} \right) S^t (j) F^{\text{H}} (i, j) + \sum_{j \in S_1^R} \sum_{l=1}^{n} \left( \frac{z_l (j)}{M_l} \right) S^\omega (j) F^{\text{Ho}} (i, j) + \right] \quad \forall i \in S_1^R \cup S_2^R \quad (3.27') \]
\[ S_G^O(i) = \sum_{l=1}^{n} \left( \frac{z_i(i)}{M_i} \right) S_0^O(i) F^O(i) - \left[ \sum_{j=1}^{M} \sum_{l=1}^{n} \left( \frac{z_i(j)}{M_j} \right) S^l(j) F^{O,l}(i,j) + \sum_{j \in S^O} \sum_{l=1}^{n} \left( \frac{z_i(j)}{M_j} \right) S^{O,l}(j) F^{O,O,l}(i,j) + \sum_{j \in S^O} \sum_{l=1}^{n} \left( \frac{z_i(j)}{M_j} \right) S^{O,O,l}(j) F^{O,O,O,l}(i,j) \right] - \frac{\dot{Q}^O(i)}{T_c} \quad \forall i \in S_1^O \] (3.28)

\[ S_G^O(i) = \sum_{l=1}^{n} \left( \frac{z_i(i)}{M_i} \right) S_0^O(i) F^O(i) - \left[ \sum_{j=1}^{M} \sum_{l=1}^{n} \left( \frac{z_i(j)}{M_j} \right) S^l(j) F^{O,l}(i,j) + \sum_{j \in S^O} \sum_{l=1}^{n} \left( \frac{z_i(j)}{M_j} \right) S^{O,l}(j) F^{O,O,l}(i,j) + \sum_{j \in S^O} \sum_{l=1}^{n} \left( \frac{z_i(j)}{M_j} \right) S^{O,O,l}(j) F^{O,O,O,l}(i,j) \right] - \frac{\dot{Q}^O(i)}{T_h} \quad \forall i \in S_2^O \] (3.29)

\[ F^l \geq 0; F^O \geq 0; F^{i,l} \geq 0; F^{O,l} \geq 0; F^{i,O} \geq 0; F^{i,O,l} \geq 0 \] (3.30)

\[ \dot{Q}^R(i) \leq 0 \quad \forall i \in S_1^R; \quad \dot{Q}^O(i) \geq 0 \quad \forall i \in S_2^R; \quad \dot{Q}^O(i) \leq 0 \quad \forall i \in S_1^O; \quad \dot{Q}^O(i) \geq 0 \quad \forall i \in S_2^O \] (3.31)

4. Equations (3.14)–(3.19) correspond to mixing and splitting total mass balances in the DN.

Equations (3.20)–(3.22) represent the action of the OP unit. Equation (3.23) represents a component mass balance at the DN outlet combined with stream composition related specifications on the network outlets. Equation (3.24) and (3.25) are based on energy balances at each reactor inlet and at each network outlet respectively. Equation (3.24') describes the enthalpy arriving at the \( i^{th} \) reactor, and equation (3.27') describes the entropy arriving at the \( i^{th} \) reactor. Equations (3.26) and (3.27) are based on reactor entropy generation balances of exothermic and endothermic reactors. Equations (3.28) and (3.29) are exothermic and
endothermic network outlet entropy generation balances respectively. Finally, equations (3.30) and (3.31) are inequalities which denote the physical properties of mass flows and the direction of heat transfer (exothermic and endothermic).

Then the reactor network’s cold utility consumption, hot utility consumption, and total entropy generation can be written as:

$$\dot{Q}_{CU}^c = - \left( \sum_{i \in S_1^R} \dot{Q}_R^R (i) + \sum_{i \in S_1^O} \dot{Q}_O^O (i) \right) \geq 0 \quad (3.32)$$

$$\dot{Q}_{HU}^h = \sum_{i \in S_2^R} \dot{Q}_R^R (i) + \sum_{i \in S_2^O} \dot{Q}_O^O (i) \geq 0 \quad (3.33)$$

$$S_T^G = \sum_{i \in S_1^R} S_{G}^R (i) + \sum_{i \in S_1^O} S_{G}^O (i) + \sum_{i \in S_2^R} S_{G}^R (i) + \sum_{i \in S_2^O} S_{G}^O (i) \geq 0 \quad (3.34)$$
3.7. Objective Function Formulation: Reactor Network Entropy Generation

The entropy generation rate/utility consumption rate of the network is equal to the sum of entropy generation rates/utility consumption rates at every reactor and every overall network outlet mixing junction. The theoretical development below will demonstrate that the above derived formulas can be simplified to the point where utility consumption only depends on the reactor’s network inlet and outlet composition, while entropy generation depends on the network’s internal structure only through the network’s endothermic reactors absorbing heat from a reservoir at $T_H$, and exothermic reactors rejecting heat to a reservoir $T_C$.

3.7.1. Theorem 1

Consider the homogeneous, isothermal, isobaric, reactor network illustrated in figure 2, featuring $n$ components, $M$ network inlet streams and $N$ network outlet streams. Under the assumptions that all feasible reactors and network outlet mixing junctions exhibit heat generation and consumption, that all network concentrations are bounded, that the mass enthalpy and entropy functions are bounded over their domain in temperature-pressure-composition space, and that the total mass flow in the network is finite, the network’s utility consumption, and entropy generation satisfy the following:

$$Q^{HU} - Q^{CU} = \sum_{j=1}^{M} \sum_{l=1}^{n} \left( \frac{z_l(j)}{M_l} \right) H^o(j) F^o(j) - \sum_{j=1}^{M} \sum_{l=1}^{n} \left( \frac{z_l(j)}{M_l} \right) H^l(j) F^l(j) \quad (3.35)$$
\[
\dot{Q}^\text{CU} = - \left[ \sum_{i \in S^R} \dot{Q}^R (i) + \sum_{i \in S^O} \dot{Q}^O (i) \right] 
\]
(3.32)

\[
\dot{Q}^\text{HU} = \sum_{i \in S^R} \dot{Q}^R (i) + \sum_{i \in S^O} \dot{Q}^O (i) 
\]
(3.33)

\[
\dot{S}_T^G = \sum_{i \in S^R} \dot{S}^R_G (i) + \sum_{i \in S^O} \dot{S}^O_G (i) + \sum_{i \in S^R} \dot{S}^R_G (i) + \sum_{i \in S^O} \dot{S}^O_G (i) 
\]
(3.34)

\[
(3.24) \land (3.24') \Rightarrow 
\]

\[
\dot{Q}^R (i) = \sum_{l=1}^{n} \left( \frac{z_l (i)}{M_l} \right) H^\circ (i) F^\circ (i) - \sum_{j=1}^{M} \sum_{l=1}^{n} \left( \frac{z_l (j)}{M_l} \right) H^i (j) F^i (i, j) + \sum_{j=1}^{M} \sum_{l=1}^{n} \left( \frac{z_l (j)}{M_l} \right) H^\circ (j) F^\circ (i, j) + \sum_{j=1}^{M} \sum_{l=1}^{n} \left( \frac{z_l (j)}{M_l} \right) H^\circ (j) F^\circ (i, j) \quad \forall i = 1, \infty 
\]
(3.24"
\[
\dot{Q}^O (i) = \sum_{l=1}^{n} \left( \frac{z_l (i)}{M_l} \right) H^O (i) F^O (i) - \sum_{j=1}^{M} \sum_{l=1}^{n} \left( \frac{z_l (j)}{M_l} \right) H^I (j) F'^{O_l} (i, j) + \sum_{j=1}^{N} \sum_{l=1}^{n} \left( \frac{z_l (j)}{M_l} \right) \hat{H}^O (j) F'^{O_l} (i, j) \quad \forall i = 1, N \quad (3.25)
\]

Using the above equations, it holds that:

\[
\dot{Q}^H - \dot{Q}^{CU} = \sum_{i=1}^{N} \dot{Q}^R (i) + \sum_{i=1}^{N} \dot{Q}^O (i) + \sum_{i=1}^{N} \dot{Q}^R (i) + \sum_{i=1}^{N} \dot{Q}^O (i) = \sum_{i=1}^{N} \dot{Q}^R (i) + \sum_{i=1}^{N} \dot{Q}^O (i)
\]

Using Fubini’s theorem for infinite sums\(^{22}\), the above is equivalent to:

\[
= \sum_{i=1}^{N} \left( \sum_{l=1}^{n} \left( \frac{z_l (i)}{M_l} \right) H^O (i) F^O (i) - \sum_{j=1}^{M} \sum_{l=1}^{n} \left( \frac{z_l (j)}{M_l} \right) H^I (j) F'^{O_l} (i, j) + \sum_{j=1}^{N} \sum_{l=1}^{n} \left( \frac{z_l (j)}{M_l} \right) \hat{H}^O (j) F'^{O_l} (i, j) \right) + \\
= \sum_{i=1}^{N} \left( \sum_{l=1}^{n} \left( \frac{z_l (i)}{M_l} \right) H^O (i) F^O (i) - \sum_{j=1}^{M} \sum_{l=1}^{n} \left( \frac{z_l (j)}{M_l} \right) H^I (j) F'^{O_l} (i, j) + \sum_{j=1}^{N} \sum_{l=1}^{n} \left( \frac{z_l (j)}{M_l} \right) \hat{H}^O (j) F'^{O_l} (i, j) \right)
\]
\[
\begin{align*}
\sum_{i=1}^{N} \sum_{l=1}^{n} \left( z_i(i) / M_i \right) H^\circ(i) F^\circ(i) &= \left( \sum_{j=1}^{M} \sum_{l=1}^{n} \left( z_j(j) / M_j \right) H^I(j) \sum_{i=1}^{\infty} F^i(i, j) \right) - \\
&\quad \left( \sum_{j=1}^{\infty} \sum_{l=1}^{n} \left( z_j(j) / M_j \right) H^\circ(j) \sum_{i=1}^{\infty} F^i(i, j) \right) + \\
&\quad \sum_{j=1}^{N} \sum_{l=1}^{n} \left( z_l(l) / M_l \right) F^\circ(i) - \sum_{j=1}^{N} \sum_{l=1}^{n} \left( z_l(l) / M_l \right) H^I(j) \sum_{i=1}^{\infty} F^i(i, j) + \sum_{i=1}^{\infty} F^i(i, j) \\
&= \sum_{j=1}^{N} \sum_{l=1}^{n} \left( z_j(j) / M_j \right) H^\circ(j) F^\circ(j) - \sum_{j=1}^{M} \sum_{l=1}^{n} \left( z_l(l) / M_l \right) H^I(j) F^I(j) \Omega \Delta
\end{align*}
\]

From the above, equation (3.35) is satisfied.

Similarly, network total entropy generation can be evaluated from equation (3.34) as:

\[
S^T_G = \sum_{i \in S^R_2} S^R_G(i) + \sum_{i \in S^O_2} S^O_G(i) + \sum_{i \in S^R_1} S^R_G(i) + \sum_{i \in S^O_1} S^O_G(i)
\]
\begin{align*}
\sum_{i \in \mathcal{S}_i^1} & \left[ \sum_{t=1}^{n} \left( \frac{z_t(i)}{M_t} \right) S^\circ(i) F^\circ(i) - \sum_{j=1}^{M} \sum_{t=1}^{n} \left( \frac{z_t(j)}{M_t} \right) S^I(j) F^\circ(i, j) + \right. \\
& \left. - \sum_{j \in \mathcal{S}_j^2} \sum_{t=1}^{n} \left( \frac{z_t(j)}{M_t} \right) S^\circ(j) F^\circ(i, j) - \sum_{j=1}^{M} \sum_{t=1}^{n} \left( \frac{z_t(j)}{M_t} \right) S^I(j) F^\circ(i, j) - \frac{\dot{Q}^R(i)}{T_C} \right] + \\
\sum_{i \in \mathcal{S}_i^1} & \left[ \sum_{t=1}^{n} \left( \frac{z_t(i)}{M_t} \right) S^\circ(i) F^\circ(i) - \sum_{j=1}^{M} \sum_{t=1}^{n} \left( \frac{z_t(j)}{M_t} \right) S^I(j) F^O(i, j) - \\
& \sum_{j \in \mathcal{S}_j^2} \sum_{t=1}^{n} \left( \frac{z_t(j)}{M_t} \right) S^\circ(j) F^\circ(i, j) - \sum_{j=1}^{M} \sum_{t=1}^{n} \left( \frac{z_t(j)}{M_t} \right) S^I(j) F^\circ(i, j) - \frac{\dot{Q}^O(i)}{T_C} \right] + \\
\sum_{i \in \mathcal{S}_i^2} & \left[ \sum_{t=1}^{n} \left( \frac{z_t(i)}{M_t} \right) S^\circ(i) F^\circ(i) - \sum_{j=1}^{M} \sum_{t=1}^{n} \left( \frac{z_t(j)}{M_t} \right) S^I(j) F^O(i, j) - \\
& \sum_{j \in \mathcal{S}_j^2} \sum_{t=1}^{n} \left( \frac{z_t(j)}{M_t} \right) S^\circ(j) F^\circ(i, j) - \sum_{j=1}^{M} \sum_{t=1}^{n} \left( \frac{z_t(j)}{M_t} \right) S^I(j) F^\circ(i, j) - \frac{\dot{Q}^O(i)}{T_H} \right]
\end{align*}

Using a similar argument of Fubini’s theorem\textsuperscript{24}:

\begin{align*}
= \sum_{i=1}^{N} \sum_{j=1}^{n} \left( \frac{z_t(i)}{M_t} \right) S^\circ(i) F^O(i) + \sum_{j=1}^{M} \sum_{t=1}^{n} \left( \frac{z_t(j)}{M_t} \right) S^\circ(i) F^O(i) - \\
M \sum_{j=1}^{M} \sum_{t=1}^{n} \left( \frac{z_t(j)}{M_t} \right) S^I(j) \left( \sum_{i=1}^{N} F^O_i(j) + \sum_{i=1}^{N} F^O_i(j) \right) - \\
\sum_{i=1}^{N} \sum_{j=1}^{M} \sum_{t=1}^{n} \left( \frac{z_t(j)}{M_t} \right) S^\circ(j) F^i(j, i) - \sum_{j=1}^{M} \sum_{t=1}^{n} \sum_{i=1}^{N} \left( \frac{z_t(j)}{M_t} \right) S^\circ(j) F^O(i, j) - \\
\left[ \sum_{i \in \mathcal{S}_i^1} \frac{\dot{Q}^R(i) + \sum_{i \in \mathcal{S}_i^1} \dot{Q}^O(i)}{T_C} + \sum_{i \in \mathcal{S}_i^2} \frac{\dot{Q}^R(i) + \sum_{i \in \mathcal{S}_i^2} \dot{Q}^O(i)}{T_H} \right]
\end{align*}

\begin{align*}
= \sum_{i=1}^{N} \sum_{j=1}^{n} \left( \frac{z_t(i)}{M_t} \right) S^\circ(i) F^O(i) - \sum_{j=1}^{M} \sum_{t=1}^{n} \left( \frac{z_t(j)}{M_t} \right) S^I(j) F^O(j) + \frac{\dot{Q}^{CU}}{T_C} + \frac{\dot{Q}^{HU}}{T_H}
\end{align*}
\[
= \sum_{i=1}^{N} \sum_{j=1}^{n} \left( \frac{z_i (i)}{M_i} \right) \left( \frac{S^o (i) - \frac{H^o (i)}{T_H}}{F^o (i)} \right) - \sum_{j=1}^{M} \sum_{l=1}^{n} \left( \frac{z_j (j)}{M_l} \right) \left( S^i (j) - \frac{H^i (j)}{T_H} \right) F^i (j) + \frac{1}{T_C} \frac{1}{T_H}
\]

O.E.Δ.

From the above, equation (3.36) is satisfied.

### 3.8. Case Study

Consider the following Trambouze reaction scheme, taking place at \( T = 400K \) and \( P = 10^5 Pa \), in a homogeneous, isothermal, isobaric, constant density, and single inlet/outlet reactor network, with a feed concentration of 1 mol/m³ of pure reactant A and volumetric feed flow rate of 1 m³/s. The reaction scheme is as follows:

\[
A (1) \xrightarrow{k_1=0.025 \text{ mol/m}^3\text{s}} B (2)
\]

\[
A (1) \xrightarrow{k_2=0.2 \text{ s}^{-1}} C (3)
\]

\[
A (1) \xrightarrow{k_3=0.4 \text{ m}^3\text{mol/s}} D (4)
\]

Reaction rates for all species are as follows:

\[
R_1 \left( \frac{\text{mol}}{\text{m}^3\cdot\text{s}} \right) = -k_1 - k_2 C_1^{\text{out}} - k_3 \left( C_1^{\text{out}} \right)^2
\]

\[
R_2 \left( \frac{\text{mol}}{\text{m}^3\cdot\text{s}} \right) = k_1
\]
\( \frac{mol}{m^3 \cdot s} \) = \( k_2 C_1^{out} \)

\( \frac{mol}{m^3 \cdot s} \) = \( k_3 (C_1^{out})^2 \)

The reactor network’s inlet and outlet are considered to be at the reactor network’s operating temperature and pressure \( T = 400K \) and \( P = 10^5 Pa \), and the reacting mixture is considered to be ideal, i.e. mixing effects are neglected and excess entropy/enthalpy terms are set to zero. The three pure species’ molar entropy, \( S_k \) and molar enthalpy, \( H_k \) at \( T = 400K \) and \( P = 10^5 Pa \) are shown in table 1. These values suggest that some reactors in the reactor network require cooling, which is provided by an infinite reservoir at \( T_C = 350K \), while other reactors in the reactor network require heating, which is provided by an infinite reservoir at \( T_H = 450K \).

<table>
<thead>
<tr>
<th>( k )</th>
<th>A (1)</th>
<th>B (2)</th>
<th>C (3)</th>
<th>D (4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S_k ) (J/(mol.K))</td>
<td>-451</td>
<td>-445</td>
<td>-439</td>
<td>-440</td>
</tr>
<tr>
<td>( H_k ) (J/mol)</td>
<td>-24000</td>
<td>-16000</td>
<td>-35000</td>
<td>-15300</td>
</tr>
</tbody>
</table>

**Table 3.1:** Pure species molar entropy and enthalpy at \( T = 400K \) and \( P = 10^5 Pa \)

Close examination of the above reaction scheme reveals that:

\[ R_1 + R_2 + R_3 + R_4 = 0 \]
Thus, application of the dimensionality reduction principle for single inlet and single outlet reactor networks\textsuperscript{19}, yields that for any reactor network stream it holds that:

\[ C_1^{\text{i}} = C_1 + C_2 + C_3 + C_4 \Rightarrow 1 \text{ mol/m}^3 = C_1 + C_2 + C_3 + C_4 \]

The desired network outlet concentration vector is chosen as

\[
\begin{bmatrix}
C_A^O \\
C_B^O \\
C_C^O \\
C_D^O
\end{bmatrix} = \begin{bmatrix}
0.0625 \\
0.2958 \\
0.4195 \\
0.2222
\end{bmatrix},
\]

which satisfies the above condition.

In addition, as will be subsequently demonstrated, since the reaction rates of components 3 and 4 depend only on \( C_1^{\text{out}} \), the change in the concentrations of components 2, 3 and 4 across each reactor can be determined only as a function of the residence time \( \tau \), and possibly \( C_1^{\text{out}} \).

Under the aforementioned mixture properties, equations (3.10)--(3.14) can be simplified into equations (3.10')--(3.14') as follows:

\[
S(T, P, \{C_k\}_{k=1}^n) = \sum_{l=1}^n \frac{C_k}{\sum_{l=1}^n C_l} S_k(T, P) \tag{3.10'}
\]

\[
H(T, P, \{C_k\}_{k=1}^n) = \sum_{l=1}^n \frac{C_k}{\sum_{l=1}^n C_l} H_k(T, P) \tag{3.11'}
\]

\[
H^E(T, P, \{C_k\}_{k=1}^n) = 0 \tag{3.12'}
\]

\[
S^E(T, P, \{C_k\}_{k=1}^n) = 0 \tag{3.13'}
\]

In turn, the vectors \( u \) and \( y \), which describe the information map under consideration, can be defined (from the development in sec. 3.2.4) as:
\[ \Phi : u = \begin{bmatrix} u_1 \\ u_2 \end{bmatrix} \rightarrow y = \begin{bmatrix} y_1 \\ y_2 \end{bmatrix} = \Phi(u_1, u_2) = \begin{bmatrix} \Phi_1(u_1, u_2) \\ \Phi_2(u_1, u_2) \end{bmatrix} \]

\[ u^T \triangleq [u_1^T \mid u_2^T] \triangleq \begin{bmatrix} T & P & C_{i1} & C_{i2} & \lambda & q & \hat{Q}^R & \hat{S}_G^R \end{bmatrix} , \]

\[ y^T \triangleq [y_1^T \mid y_2^T] \triangleq \Phi^T(u_1, u_2) \triangleq \begin{bmatrix} \tau \left( C_{22} - C_{21} \right) \left( C_{33} - C_{31} \right) \left( C_{44} - C_{41} \right) & q \end{bmatrix} \]

Where:

\[ D = \left\{ u \in \mathbb{R}^4 \times \{0,1\} \times \mathbb{R}^3 : \Phi_3(u_1, u_2) = 0 \land \sum_{i=1}^{n} C_{i}^{out} - C_{i}^{in} = 0 \land u_i \geq 0 \land F \geq 0 \land \hat{S}_G \geq 0 \right\} , \text{ and} \]

\[ \Phi_3(u_1, u_2) \triangleq \begin{bmatrix} -q \sum_{i=1}^{n} \left( C_{i}^{out} - C_{i}^{in} \right) H_i(T, P) + \hat{Q}^R \\ -q \sum_{i=1}^{n} \left( C_{i}^{out} - C_{i}^{in} \right) S_i(T, P) + \hat{Q}^R \left( \frac{\lambda}{T_H} + \frac{1-\lambda}{T_C} \right) + \hat{S}_G \end{bmatrix} \]

for which all the properties described in sec. 3.2.4 hold true.

Knowing \( U_1 \), the reactor model then allows us to first determine the residence time \( \tau \) as follows:

\[ C_{11} - C_{12} = \tau \left( -k_1 - k_2 C_{1}^{out} - k_3 \left( C_{1}^{out} \right)^2 \right) \Rightarrow \]

\[ \tau = \frac{C_{11} - C_{12}}{-k_1 - k_2 C_{1}^{out} - k_3 \left( C_{1}^{out} \right)^2} \tag{3.37} \]

The change in concentrations for species 2, 3 and 4 can then be determined from the following equations:

\[ C_{22}^{out} - C_{22}^{in} = \Delta C_2 = \tau k_1 \tag{3.38} \]

\[ C_{33}^{out} - C_{33}^{in} = \Delta C_3 = \tau k_2 C_{1}^{out} \tag{3.39} \]

\[ C_{44}^{out} - C_{44}^{in} = \Delta C_4 = \tau k_3 \left( C_{1}^{out} \right)^2 \tag{3.40} \]
The corresponding finite linear programming formulation of the reactor network synthesis consisting of a single inlet and single outlet and featuring minimum entropy generation for an ever increasing sequence of $L$ reactors is given below. Let $S_1^L$ and $S_2^L$ denote the index sets corresponding to all realizable exothermic and endothermic reactors, respectively within the considered set of $L$ reactors. Then $S_1^L \cup S_2^L = \{1, \cdots, L\}$, and the LP can be written as follows:

$$\inf \; \hat{S}_g$$

s.t.

$$\begin{align}
1 &= q^{oi} (1,1) + \sum_{j=1}^{L} q^{i,j} (i,1) \\
1 &= q^{oi} (1,1) + \sum_{j=1}^{L} q^{o\hat{o}} (1, j) \\
q^i (i) &= q^{i,j} (i,1) + \sum_{j=1}^{L} q^{i,j\hat{o}} (i, j) \quad \forall i = 1, L \\
q^{\hat{o}} (j) &= q^{o\hat{o}} (1, j) + \sum_{i=1}^{L} q^{i,j\hat{o}} (i, j) \quad \forall j = 1, L \\
q^{\hat{o}} (i) &= q^i (i) \quad \forall i = 1, L \\
C_i^i (i) q^i (i) &= C_i^i q^{i,j} (i,1) + \sum_{j=1}^{L} C_i^{\hat{o}} (j) q^{i,j\hat{o}} (i, j) \quad \forall i = 1, L \\
C_i^i q^{oi} (1,1) + \sum_{j=1}^{L} C_i^{\hat{o}} (j) q^{o\hat{o}} (1, j) &= C_i^o \\
\left[ \sum_{j=1}^{L} \Delta C_k (j) q^j (j) \right] &= C_k^o \quad \forall k = 2, 4 \\
\hat{Q}^i (i) &= q^i (i) \sum_{j=1}^{n} \left( C_i^{out} (i) - C_i^{in} (i) \right) H_i (T, P) \quad \forall i = 1, L
\end{align}$$
\[ \hat{S}_G^R (i) = q^i (i) \sum_{i=1}^{n} (c_{i, out}^o (i) - c_{i, in}^o (i)) S_i (T, P) - \frac{\dot{Q}_R^i (i)}{T_C} \quad \forall i \in S_1^L \quad (3.50) \]

\[ \hat{S}_G^R (i) = q^i (i) \sum_{i=1}^{n} (c_{i, out}^o (i) - c_{i, in}^o (i)) S_i (T, P) - \frac{\dot{Q}_R^i (i)}{T_H} \quad \forall i \in S_2^R \quad (3.51) \]

\[ \hat{S}_G^T = \left[ \sum_{i=1}^{n} (c_i^o - c_i^l) \left( S_i (T, P) - \frac{H_i (T, P)}{T_H} \right) - \sum_{i \in S_1^l} \dot{Q}_R^i (i) \left( \frac{1}{T_C} - \frac{1}{T_H} \right) \right] \quad (3.52) \]

\( q^i \geq 0; q^o \geq 0; q^{oi} \geq 0; q^{i} \geq 0; q^{i} \geq 0; q^{io} \geq 0; q^{io} \geq 0; \dot{Q}_R^i (i) \leq 0 \quad \forall i \in S_1^L; \dot{Q}_R^i (i) \geq 0 \quad \forall i \in S_2^L \)

**Figure 3.2:** Baseline reactor network design

A reactor network that delivers the specified outlet concentration vector

\[
\begin{bmatrix}
C_A^o & C_B^o & C_C^o & C_D^o
\end{bmatrix} = \begin{bmatrix}
0.0625 & 0.2958 & 0.4195 & 0.2222
\end{bmatrix}
\]

is considered as the baseline design. It consists of two CSTRs in series with residence \( \tau_1 = 5.432 \text{s} \) and \( \tau_2 = 6.4 \text{s} \) respectively, generates \( 1.20944 \frac{J}{K \cdot s} \) of entropy, and has exothermic and endothermic heat loads equal to -802 \( \frac{J}{s} \) and 487 \( \frac{J}{s} \) respectively. At a discretization of 1/32 (496 reactors) for each of \( C_{i, in}^o \) and \( C_{i, out}^o \), the IDEAS-generated network’s internals shown in figure 3 are found to generate \( 0.9477 \frac{J}{K \cdot s} \).
of entropy, compared to the baseline two reactor sequence shown in figure 2 which generates $1.20944 \frac{J}{K \cdot s}$ of entropy. This represents an improvement of 27.61% in reduced entropy generation. In comparison, the entropy generation contribution of the inlet/outlet flows is $9.2625 \frac{J}{K \cdot s}$. If the temperatures of the reservoirs (hot and cold) were infinitesimally away from the temperature of the reactor network, then entropy generation would become independent of the network structure. In this case, a reversible entropy generation lower bound can be quantified through an entropy balance around the network. If only the heat effect contribution to entropy generation is considered, to maintain consistency with the irreversible case discussed above, we would only generate $0.7875 \frac{J}{K \cdot s}$ through reversible heat transfer between the reactor network and its isothermal surroundings. Given that the outlet concentration specifications are the same, and based on the presented Theorem, minimization of entropy generation is equivalent to hot (or cold) utility minimization. If one were to compare the difference in exothermic and endothermic heat loads between the baseline and IDEAS designs, then the IDEAS-generated network is seen to generate 51% less exothermic heat load and to require 84% less endothermic heat load.

<table>
<thead>
<tr>
<th>From</th>
<th>To</th>
<th>Flow</th>
<th>From</th>
<th>To</th>
<th>Flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet</td>
<td>1</td>
<td>0.00188</td>
<td>2</td>
<td>1</td>
<td>0.05076</td>
</tr>
<tr>
<td>Inlet</td>
<td>2</td>
<td>0.00362</td>
<td>4</td>
<td>2</td>
<td>0.04713</td>
</tr>
<tr>
<td>Inlet</td>
<td>3</td>
<td>0.00631</td>
<td>1</td>
<td>3</td>
<td>0.05264</td>
</tr>
<tr>
<td>Inlet</td>
<td>4</td>
<td>0.00841</td>
<td>5</td>
<td>4</td>
<td>0.03871</td>
</tr>
<tr>
<td>Inlet</td>
<td>5</td>
<td>0.0870</td>
<td>6</td>
<td>5</td>
<td>0.4145</td>
</tr>
<tr>
<td>Inlet</td>
<td>6</td>
<td>0.0740</td>
<td>11</td>
<td>5</td>
<td>0.5371</td>
</tr>
<tr>
<td>Inlet</td>
<td>7</td>
<td>0.0153</td>
<td>7</td>
<td>6</td>
<td>0.2451</td>
</tr>
<tr>
<td>Inlet</td>
<td>8</td>
<td>0.05895</td>
<td>8</td>
<td>6</td>
<td>0.0987</td>
</tr>
<tr>
<td>Inlet</td>
<td>9</td>
<td>0.04308</td>
<td>9</td>
<td>7</td>
<td>0.2297</td>
</tr>
<tr>
<td>Inlet</td>
<td>10</td>
<td>0.09335</td>
<td>3</td>
<td>8</td>
<td>0.05895</td>
</tr>
</tbody>
</table>
### Table 3.2: Flow rate from-to nodes of IDEAS-generated network

<table>
<thead>
<tr>
<th>Reactor</th>
<th>$C_{A}^{in}$</th>
<th>$C_{A}^{out}$</th>
<th>$\Delta C_{B}$</th>
<th>$\Delta C_{C}$</th>
<th>$\Delta C_{D}$</th>
<th>$\dot{Q}(J/s)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.15625</td>
<td>0.125</td>
<td>0.01388</td>
<td>0.01388</td>
<td>0.00347</td>
<td>-0.603</td>
</tr>
<tr>
<td>2</td>
<td>0.1875</td>
<td>0.125</td>
<td>0.02777</td>
<td>0.02777</td>
<td>0.00694</td>
<td>-1.163</td>
</tr>
<tr>
<td>3</td>
<td>0.21875</td>
<td>0.125</td>
<td>0.04166</td>
<td>0.04166</td>
<td>0.01041</td>
<td>-2.026</td>
</tr>
<tr>
<td>4</td>
<td>0.28125</td>
<td>0.125</td>
<td>0.06944</td>
<td>0.06944</td>
<td>0.01736</td>
<td>-2.700</td>
</tr>
<tr>
<td>5</td>
<td>0.34375</td>
<td>0.125</td>
<td>0.09722</td>
<td>0.09722</td>
<td>0.02430</td>
<td>-83.315</td>
</tr>
<tr>
<td>6</td>
<td>0.5</td>
<td>0.125</td>
<td>0.1666</td>
<td>0.1666</td>
<td>0.04166</td>
<td>-57.459</td>
</tr>
<tr>
<td>7</td>
<td>0.53125</td>
<td>0.5</td>
<td>0.003472</td>
<td>0.01388</td>
<td>0.01388</td>
<td>-1.021</td>
</tr>
<tr>
<td>8</td>
<td>0.5625</td>
<td>0.125</td>
<td>0.1944</td>
<td>0.1944</td>
<td>0.04861</td>
<td>-18.915</td>
</tr>
<tr>
<td>9</td>
<td>0.59375</td>
<td>0.5</td>
<td>0.01041</td>
<td>0.04166</td>
<td>0.04166</td>
<td>-2.872</td>
</tr>
<tr>
<td>10</td>
<td>0.75</td>
<td>0.5</td>
<td>0.02777</td>
<td>0.1111</td>
<td>0.1111</td>
<td>-6.223</td>
</tr>
<tr>
<td>11</td>
<td>0.96875</td>
<td>0.40625</td>
<td>0.08163</td>
<td>0.2653</td>
<td>0.2151</td>
<td>-209.439</td>
</tr>
<tr>
<td>12</td>
<td>0.96875</td>
<td>0.5</td>
<td>0.05208</td>
<td>0.20833</td>
<td>0.20833</td>
<td>-5.834</td>
</tr>
<tr>
<td>13</td>
<td>0.125</td>
<td>0.09375</td>
<td>0.01652</td>
<td>0.01239</td>
<td>0.00232</td>
<td>16.089</td>
</tr>
<tr>
<td>14</td>
<td>0.09375</td>
<td>0.0625</td>
<td>0.02000</td>
<td>0.01000</td>
<td>0.00125</td>
<td>60.874</td>
</tr>
</tbody>
</table>

### Table 3.3: Species concentration change across each reactor of IDEAS network

### Table 3.4: Exothermic and endothermic heat loads for IDEAS and baseline designs

<table>
<thead>
<tr>
<th>Total 193Heat Transfered</th>
<th>$\sum_{i} \dot{Q}(i)$(Exothermic)</th>
<th>$\sum_{i} \dot{Q}(i)$(Endothermic)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline Network</td>
<td>-802.082</td>
<td>486.999</td>
</tr>
<tr>
<td>IDEAS Network</td>
<td>-391.570</td>
<td>76.963</td>
</tr>
</tbody>
</table>

Table 3.2: Flow rate from-to nodes of IDEAS-generated network

Table 3.3: Species concentration change across each reactor of IDEAS network

Table 3.4: Exothermic and endothermic heat loads for IDEAS and baseline designs
The IDEAS-generated reactor network, as compared to the baseline network, exhibits several characteristics not known in advance, and worthy of elaboration. The most striking of these characteristics is the splitting of the network feed, in varying quantities, so it can help form the feed to each and every exothermic reactor in the IDEAS network (reactors 1-12). On the other hand, the network feed does not contribute to the feed of any endothermic reactor in the IDEAS network. Another network characteristic is that it employs two clusters of exothermic reactors; one cluster with $C^{out}_A = 0.5$ (reactors 7, 9-10, and 12), and another cluster with $C^{out}_A = 0.125$ (reactors 1-6, and 8). The feed to each one of the reactors in those two clusters is generated by mixing part of the network feed with an outlet from some other exothermic reactor. In contrast, the endothermic reactors (reactor 13-14) form a sequence which outlet is the outlet of the network.
Discussion - Conclusions

This work demonstrated the importance of the internal structure of an isothermal reactor network featuring both endothermic and exothermic reactors, in determining the entropy generated by the network. This stands contrary to the case where the feasible reactor universe consists of either only endothermic or only exothermic reactors, where entropy generation is uniquely determined by the network’s inlet and outlet specifications and is independent of the network structure. A Theorem is rigorously established suggesting that the synthesis of isothermal reactor networks featuring minimum entropy generation and having known and fixed

Figure 3.3: IDEAS-generated minimum entropy generation network

3.9. Discussion - Conclusions

This work demonstrated the importance of the internal structure of an isothermal reactor network featuring both endothermic and exothermic reactors, in determining the entropy generated by the network. This stands contrary to the case where the feasible reactor universe consists of either only endothermic or only exothermic reactors, where entropy generation is uniquely determined by the network’s inlet and outlet specifications and is independent of the network structure. A Theorem is rigorously established suggesting that the synthesis of isothermal reactor networks featuring minimum entropy generation and having known and fixed
inlet and outlet specifications, is equivalent to the synthesis of isothermal reactor networks featuring minimum hot (or cold) utility consumption and having known and fixed inlet and outlet specifications. A case study is used to illustrate the proposed IDEAS-based network synthesis methodology. The network generated by IDEAS demonstrates several unique characteristics. The network feed contributes to the formation of the feed of each exothermic reactor unit of the network. The outlets of all exothermic reactors of the network (except reactor 11) have species A composition equal to either $C_A^{\text{out}} = 0.5$ or $C_A^{\text{out}} = 0.125$. The entropy generation of a baseline traditional design is shown to be 28% greater than that of the IDEAS design.

3.10. Nomenclature

$T_H$: Temperature of hot infinite heat reservoir (K)

$T_C$: Temperature of cold infinite heat reservoir (K)

$q$: Volumetric flow rate (m$^3$/s)

$q^{\text{in}}$: Inlet volumetric flow rate (m$^3$/s)
$q^{\text{out}}$: Outlet volumetric flow rate (m$^3$/s)

$M_k$: $k^{th}$ Species molecular weight (g/mol)

$F$: Mass flow rate (kg/s)

$F^{\text{out}}$: Outlet mass flow rate (kg/s)

$F^{\text{in}}$: Inlet mass flow rate (kg/s)

$C_i$: $i^{th}$ Component molar concentration (mol/m$^3$)

$C_i^{\text{in}}$: $i^{th}$ Component reactor inlet molar concentration (mol/m$^3$)

$C_i^{\text{out}}$: $i^{th}$ Component reactor outlet molar concentration (mol/m$^3$)

$z_k$: $k^{th}$ Component mass fraction

$z_i^{\text{in}}$: $i^{th}$ Component reactor inlet mass fraction

$z_i^{\text{out}}$: $i^{th}$ Component reactor outlet mass fraction

$x_i$: $i^{th}$ Component mole fraction

$R_k$: $k^{th}$ Component generation rate, molar model (mol/(m$^3$.s))

$r_k$: $k^{th}$ Component generation rate, mass model (mol/(m$^3$.s))
\( \tau \): Residence time for constant density fluid reactor \( (s) \)

\( \sigma \): Volume to mass flowrate rat for variable density fluid reactor \( ((m^3 \cdot s)/kg) \)

\( V \): Reactor volume \( (m^3) \)

\( k_1 : 0.025 \frac{mol}{m^3 \cdot s}, \) 0\(^{\text{th}}\) order Trambouze kinetics constant

\( k_2 : 0.2 \text{ s}^{-1}, \) 1\(^{\text{st}}\) order Trambouze kinetics constant

\( k_3 : 0.4 \frac{m^3}{mol \cdot s}, \) 2\(^{\text{nd}}\) order Trambouze kinetics constant

\( T \): Temperature \( (K) \)

\( P \): Pressure \( (Pa) \)

\( \rho \): Density \( (kg/m^3) \)

\( R \): Universal gas constant \( (J/(K \cdot mol)) \)

\( \Phi \): Input-output information map for process model

\( \mu \): Input vector of an information map

\( \gamma \): Output vector of an information map
\( h^{arr} \): Enthalpy arriving at reactor inlet (J/s). This is different than the reactor’s inlet enthalpy, since it does not account for stream mixing heat effects which are directly incorporated into the reactor’s overall heating/cooling need.

\( s^{arr} \): Entropy arriving at reactor inlet (J/(K·s)). This is different than the reactor’s inlet entropy, since it does not account for stream mixing heat effects which are directly incorporated into the reactor’s overall heating/cooling need, and entropy generation.

\[ H(T, P, \{ C_k \}_{k=1}^n) \]: Molar enthalpy associated with a stream of temperature, pressure, and composition \( T, P \) and \( \{ C_k \}_{k=1}^n \) (J/mol).

\[ S(T, P, \{ C_k \}_{k=1}^n) \]: Molar entropy associated with a stream of temperature, pressure, and composition \( T, P \) and \( \{ C_k \}_{k=1}^n \) (J/(mol·K)).

\[ H^{id}(T, P, \{ C_k \}_{k=1}^n) \]: Ideal molar enthalpy associated with a temperature, pressure, and composition \( T, P \) and \( \{ C_k \}_{k=1}^n \) (J/mol).

\[ S^{id}(T, P, \{ C_k \}_{k=1}^n) \]: Ideal molar entropy associated with a general stream of temperature, pressure, and composition \( T, P \) and \( \{ C_k \}_{k=1}^n \) (J/(mol·K)).

\[ H^E(T, P, \{ C_k \}_{k=1}^n) \]: Excess molar enthalpy associated with a general stream of temperature, pressure, and composition \( T, P \) and \( \{ C_k \}_{k=1}^n \) (J/mol).
\[ S^E(T, P, \{C_k\}_{k=1}^n) \]: Excess molar entropy associated with a general stream of temperature, pressure, and composition \(T, P\) and \(\{C_k\}_{k=1}^n \) \( (J/(mol \cdot K)) \).

\[ H_k(T, P) \]: Pure component ideal molar enthalpy associated with a constant density stream of temperature and pressure \(T, P\) respectively \( (J/mol) \).

\[ S_k(T, P) \]: Pure component ideal molar entropy associated with a general stream of temperature and pressure \(T, P\) respectively \( (J/(mol \cdot K)) \).

\[ G^E(T, P, \{C_k\}_{k=1}^n) \]: Excess Gibbs free energy associated with a general stream of temperature, pressure and composition \(T, P\) and \(\{C_k\}_{k=1}^n \) respectively \( (J/kg) \).

\[ \gamma_k(T, P, \{C_k\}_{k=1}^n) \]: Liquid phase activity coefficient function associated with a liquid stream of temperature, pressure and composition \(T, P\) and \(\{C_k\}_{k=1}^n \) respectively \( (J/kg) \).

\[ Q^R(i) \]: Heat consumption rate due to reaction for \(i^{th}\) reactor in IDEAS reactor network \( \forall i = 1, \infty \) \( (J/s) \)

\[ Q^O(i) \]: Heat of mixing rate at \(i^{th}\) DN network outlet \( \forall i = 1, N \) \( (J/s) \)

\[ \dot{Q}^T \]: Total network energy consumption rate \( (J/s) \)

\[ \dot{Q}^{HU} \]: Hot utility consumption rate \( (J/s) \)
\[ \dot{Q}_{CU}^{\text{CU}} \]: Cold utility consumption rate \((\text{J/s})\)

\[ S_1^R, S_1^L \]: Entropy generation in exothermic reactor \((\text{J/(s \cdot K)})\)

\[ S_2^R, S_2^L \]: Entropy generation in endothermic reactor \((\text{J/(s \cdot K)})\)

\[ S_1^O \]: Entropy generation in exothermic network mixing outlet \((\text{J/(s \cdot K)})\)

\[ S_2^O \]: Entropy generation in endothermic network mixing outlet \((\text{J/(s \cdot K)})\)

\[ \dot{S}_T^R \]: Total network entropy generation rate \((\text{J/(s \cdot K)})\)

\[ \dot{S}_G^R \]: Reactor entropy generation rate \((\text{J/(s \cdot K)})\)

IDEAS Variables

\[ M \]: Number of IDEAS network inlets

\[ N \]: Number of IDEAS network outlets

\[ C_{k}^{j}(\hat{)}): k^{\text{th}} \text{ Component concentration in the } j^{\text{th}} \text{ network inlet } \forall k = 1, n; \forall j = 1, M \left( \text{mol/m}^3 \right) \]

\[ C_{k}^{i}(\hat{)}): k^{\text{th}} \text{ Component concentration in the } i^{\text{th}} \text{ network outlet } \forall k = 1, n; \forall i = 1, N \left( \text{mol/m}^3 \right) \]

\[ C_{k}^{i}(\hat{)}): k^{\text{th}} \text{ Component concentration in the } i^{\text{th}} \text{ OP inlet } \forall k = 1, n; \forall i = 1, \infty \left( \text{mol/m}^3 \right) \]

\[ C_{k}^{i}(\hat{)}): k^{\text{th}} \text{ Component mass fraction in the } i^{\text{th}} \text{ OP outlet } \forall k = 1, n; \forall i = 1, \infty \left( \text{mol/m}^3 \right) \]
$z_k^I(j)$: $k^{th}$ Component mass fraction in the $j^{th}$ network inlet $\forall k = 1, n; \forall j = 1, M$

$z_k^O(i)$: $k^{th}$ Component mass fraction in the $i^{th}$ network outlet $\forall k = 1, n; \forall i = 1, N$

$z_k^I(i)$: $k^{th}$ Component mass fraction in the $i^{th}$ OP inlet $\forall k = 1, n; \forall i = 1, \infty$

$z_k^O(i)$: $k^{th}$ Component mass fraction in the $i^{th}$ OP outlet $\forall k = 1, n; \forall i = 1, \infty$

$F^I(j)$: $j^{th}$ Network inlet mass flow rate $\forall j = 1, M$ (kg/s)

$q^I(j)$: $j^{th}$ Network inlet volumetric flow rate $\forall j = 1, M$ (m³/s)

$S^I(j)$: Entropy associated with $j^{th}$ network inlet stream $\forall j = 1, M$ (J/(mol·K))

$H^I(j)$: Enthalpy associated with $j^{th}$ network inlet stream $\forall j = 1, M$ (J/mol)

$q^O(i)$: $i^{th}$ Network outlet volumetric flow rate $\forall i = 1, N$ (m³/s)

$F^O(i)$: $i^{th}$ Network outlet mass flow rate $\forall i = 1, N$ (kg/s)

$S^O(i)$: Entropy associated with $i^{th}$ network outlet stream $\forall i = 1, N$ (J/(mol·K))

$H^O(i)$: Enthalpy associated with $i^{th}$ network outlet stream $\forall i = 1, N$ (J/mol)

$q^I(j)$: $j^{th}$ OP inlet volumetric flow rate $\forall j = 1, \infty$ (m³/s)

$F^I(j)$: $j^{th}$ OP inlet mass flow rate $\forall j = 1, \infty$ (kg/s)
\( S^i (j) \): Entropy associated with \( j^{th} \) OP inlet stream \( \forall j = 1, \infty \) (J/(mol·K))

\( H^i (j) \): Enthalpy associated with \( j^{th} \) OP inlet stream \( \forall j = 1, \infty \) (J/mol)

\( q^O (i) \): \( i^{th} \) OP outlet volumetric flow rate \( \forall i = 1, \infty \) (m\(^3\)/s)

\( \dot{F}^O (i) \): \( i^{th} \) OP outlet mass flow rate \( \forall i = 1, \infty \) (kg/s)

\( S^O (i) \): Entropy associated with \( i^{th} \) OP outlet stream \( \forall i = 1, \infty \) (J/(mol·K))

\( H^O (i) \): Enthalpy associated with \( i^{th} \) OP outlet stream \( \forall i = 1, \infty \) (J/mol)

\( q^{OL} (i, j) \): \( j^{th} \) Network inlet volumetric flow rate to the \( i^{th} \) network outlet \( \forall j = 1, M; \forall i = 1, N \) (m\(^3\)/s)

\( q^{HL} (i, j) \): \( j^{th} \) Network outlet volumetric flow rate to the \( i^{th} \) OP inlet \( \forall j = 1, M; \forall i = 1, \infty \) (m\(^3\)/s)

\( q^{OOL} (i, j) \): \( j^{th} \) OP outlet volumetric flow rate to the \( i^{th} \) network outlet \( \forall j = 1, \infty; \forall i = 1, N \) (m\(^3\)/s)

\( q^{IO} (i, j) \): \( j^{th} \) OP outlet volumetric flow rate to the \( i^{th} \) OP network outlet \( \forall j = 1, \infty; \forall i = 1, \infty \) (m\(^3\)/s)

\( F^{OL} (i, j) \): \( j^{th} \) Network inlet mass flow rate to the \( i^{th} \) network outlet \( \forall j = 1, M; \forall i = 1, N \) (kg/s)

\( F^{H} (i, j) \): \( j^{th} \) Network outlet mass flow rate to the \( i^{th} \) OP inlet \( \forall j = 1, M; \forall i = 1, \infty \) (kg/s)
\( F^{\text{O\dot{o}}} (i, j): j^{th} \text{ OP outlet mass flow rate to the } i^{th} \text{ network outlet } \forall j = 1, \infty; \forall i = 1, N \left( \text{kg/s} \right) \)

\( F^{\text{I\dot{o}}} (i, j): j^{th} \text{ OP outlet mass flow rate to the } i^{th} \text{ OP network outlet } \forall j = 1, \infty; \forall i = 1, \infty \left( \text{kg/s} \right) \)

\( \tau (i): \text{Residence time of the } i^{th} \text{ OP unit } \forall i = 1, \infty \left( \text{s} \right) \)

\( \lambda (i): \text{Exothermic reactor flag identifier} \)

\( u (i): \text{Input of the } i^{th} \text{ OP unit information map } \forall i = 1, \infty \)

\( y (i): \text{Output of the } i^{th} \text{ OP unit information map } \forall i = 1, \infty \)

3.11. References:


CHAPTER 4

Global Minimization of Capital Cost/Volume/Total Annualized Cost for Isothermal Mixed-Flow Reactor Sequences with General Reaction Schemes

4.1. Abstract:

This work presents a novel method to identify the sequence of isothermal mixed flow reactors (CSTR’s) which globally minimizes a reactor residence time dependent objective function (able to represent such objectives as capital cost, volume, or total annualized cost), subject to a constraint dependent on the reactor sequence’s exit concentrations. Following a review of the relevant literature, the mathematical problem formulation is presented, and proofs for the existence of the global optimum and for the applicability of the first order necessary conditions of optimality are provided. The special structure of the resulting equations is then exploited in creating graphical and computational algorithms that guarantee global optimality of the obtained solution. For reaction schemes involving generation rates linear in species concentrations, both local and global optimality analytical results are established. Finally, the advantages of the proposed solution methodology are illustrated with several case studies.

4.2. Introduction:

Optimizing a sequence of mixed flow reactors has been of interest to chemical engineers for many decades. Denbigh\(^1\) showed that a decrease of the total volume used in a mixed flow reactor can be achieved by replacing a single mixed flow reactor with a fixed terminal yield, with two or more smaller reactors having the same terminal yield but a smaller total volume compared to the
single mixed flow reactor. The result obtained by Denbigh, and later reiterated by Leclerc through a graphical trial-and-error method is that there exists an optimal volumetric ratio for a series of two CSTRs which is proportional to the reaction order. Aris proposed solving the optimization problem of minimization of overall residence time for general kinetics through the use of dynamic programming, to find the optimal control policy. Horn proposed solving that same problem with Lagrange multipliers. Several authors followed up on Aris’s and Horn’s work. These authors relied on one of the two techniques which always included a trial-and-error “guessing” solution procedure. Unfortunately, such a procedure contains a bottle-neck on the number of reactors considered and complexity of the reaction scheme.

The focus of this work is on the optimization of sequences of mixed flow reactors, rather than on the general reactor network synthesis problem. The literature contains numerous references on the reactor network synthesis problem, which however will not be reviewed here since they are deemed outside the scope of this paper. Nevertheless, the reader is referred elsewhere for a more comprehensive literature review of the area of reactor network synthesis.

Before proceeding any further, it should be noted that while the optimization of a sequence of CSTRs may sound restrictive or limited in nature, the solution obtained in this work is globally optimal, unlike other more general reactor network synthesis methodologies that yield at best locally optimal solutions which are only as good the initially provided superstructure. In addition, while global NLP solver such as BARON®, perform well in solving small sequencing problems with few variables, they quickly break down and lose their efficiency once the number of reactors considered increases, as will be shown later in the case study to follow. This justifies the need to develop advanced, tailor-made algorithms which can easily outperform generic solvers.
Several novel results set this paper apart from the aforementioned literature review with respect to the optimization of a sequence of CSTRs in series. The general nature of the objective function considered can account for total residence (linear) or total annualized cost (TAC, non-linear). In addition, computational and theoretical advances make possible the development of a computationally intensive, general purpose algorithm based on advanced interval-analysis techniques applicable in lower dimension concentration space. This eliminates the need to use a trial-and-error procedure, reduces the size of the problem considered, and guarantees finding all solutions to a non-linear set of equations. In the remainder of this paper, several variable definitions are first introduced, and the mathematical formulation of the problem is presented. Dimensionality reduction is then briefly reviewed, since it allows us to work in a lower dimension concentration space. Next, proofs regarding existence, continuity, regularity, and 1st order conditions of optimality are formalized. A section covering the special case of linear kinetics follows. Here two theorems, pertaining to local and global optimality of equal-size reactors are presented. An interval-based solution procedure and a graphical procedure are then described in detail, followed by two case studies applying the Trambouze kinetic scheme for the minimization of two different objective functions which are total annualized cost/capital cost and total residence time. Finally, conclusions regarding the work’s results are drawn.
4.3. Mathematical Preliminaries:

Let:

\[
A_i \triangleq \left[ a_{i,1}, a_{i,2}, \ldots, a_{i,m} \right]^T; \quad l = 1, n; \quad \Lambda_i \triangleq \left[ \lambda_i^1, \lambda_i^2, \ldots, \lambda_i^m \right]^T; \quad i = 1, n; \quad C_i \triangleq \left[ C_i^1, C_i^2, \ldots, C_i^m \right]^T; \quad i = 1, n;
\]

\[
R_i \triangleq \begin{bmatrix}
R^1 \left( \{C_i^p \}^m_{p=1} \right) \\
R^2 \left( \{C_i^p \}^m_{p=1} \right) \\
\vdots \\
R^m \left( \{C_i^p \}^m_{p=1} \right)
\end{bmatrix}; \quad \forall l = 1, n \quad \frac{\partial R}{\partial C_i} \triangleq \begin{bmatrix}
\frac{\partial R^1 \left( \{C_i^p \}^m_{p=1} \right)}{\partial C_i^1} \\
\frac{\partial R^2 \left( \{C_i^p \}^m_{p=1} \right)}{\partial C_i^2} \\
\vdots \\
\frac{\partial R^m \left( \{C_i^p \}^m_{p=1} \right)}{\partial C_i^m}
\end{bmatrix}; \quad \forall k = 1, m, \forall l = 1, n
\]

\[
\frac{\partial \mathbf{f}}{\partial C_i} \triangleq \begin{bmatrix}
\frac{\partial \mathbf{f}}{\partial C_i^1} \\
\frac{\partial \mathbf{f}}{\partial C_i^2} \\
\vdots \\
\frac{\partial \mathbf{f}}{\partial C_i^m}
\end{bmatrix}; \quad \frac{\partial \mathbf{R}}{\partial C_i} \triangleq \begin{bmatrix}
\frac{\partial R^1 \left( \{C_i^k \}^m_{k=1} \right)}{\partial C_i^1} & \frac{\partial R^2 \left( \{C_i^k \}^m_{k=1} \right)}{\partial C_i^1} & \ldots & \frac{\partial R^m \left( \{C_i^k \}^m_{k=1} \right)}{\partial C_i^1} \\
\frac{\partial R^1 \left( \{C_i^k \}^m_{k=1} \right)}{\partial C_i^2} & \frac{\partial R^2 \left( \{C_i^k \}^m_{k=1} \right)}{\partial C_i^2} & \ldots & \frac{\partial R^m \left( \{C_i^k \}^m_{k=1} \right)}{\partial C_i^2} \\
\vdots & \vdots & \ddots & \vdots \\
\frac{\partial R^1 \left( \{C_i^k \}^m_{k=1} \right)}{\partial C_i^m} & \frac{\partial R^2 \left( \{C_i^k \}^m_{k=1} \right)}{\partial C_i^m} & \ldots & \frac{\partial R^m \left( \{C_i^k \}^m_{k=1} \right)}{\partial C_i^m}
\end{bmatrix}; \quad \forall l = 1, n
\]
When linear kinetics are considered, the following hold:

\[
R_i = \begin{bmatrix}
R^1 \left( \{ C_{i}^k \}_{k=1}^{m} \right) \\
R^2 \left( \{ C_{i}^k \}_{k=1}^{m} \right) \\
\vdots \\
R^m \left( \{ C_{i}^k \}_{k=1}^{m} \right)
\end{bmatrix}
= \begin{bmatrix}
R^{11} R^{12} \ldots R^{1m} \\
R^{21} R^{22} \ldots R^{2m} \\
\vdots \\
R^{m1} R^{m2} \ldots R^{mm}
\end{bmatrix}
\begin{bmatrix}
C_i^1 \\
C_i^2 \\
\vdots \\
C_i^m
\end{bmatrix}
\doteq R \cdot C_i \; ; \; l = 1, n
\]

\[
\frac{\partial R}{\partial C_i} \overset{T}{=} 
\begin{bmatrix}
\frac{\partial R^1}{\partial C_i} \\
\frac{\partial R^2}{\partial C_i} \\
\vdots \\
\frac{\partial R^m}{\partial C_i}
\end{bmatrix}
\begin{bmatrix}
\frac{\partial R^1}{\partial C_i} \\
\frac{\partial R^2}{\partial C_i} \\
\vdots \\
\frac{\partial R^m}{\partial C_i}
\end{bmatrix}
= R^T; \; \forall l = 1, n
\]

The mathematical formulation is next presented. A general objective function of residence times is being minimized subject to reactor component mass balance, and outlet concentration function specification.
4.4. Mathematical Formulation

In this work, the following optimization problem is considered:

\[
P_1: \min_x \sum_{i=1}^{n} (\beta \tau_i^a)
\]

\[
s.t:\]
\[
C_i^j - C_i^j + \tau_i \cdot R^j \left( \left\{ C^k_j \right\}_{k=1}^q \right) = 0; \ i = 1, n; \ j = 1, q
\]
\[
f \left( \left\{ C^k_j \right\}_{k=1}^q \right) - \delta = 0
\]
\[
-C_i^j \leq 0; \ i = 1, n; \ j = 1, q
\]
\[
-\tau_i \leq 0; \ i = 1, n
\]

Where \( R^j(\cdot) \) \( j = 1, q; \ f(\cdot); \left\{ C^k_j \right\}_{k=1}^q \); \( a; \beta_i, i = 1, n; \delta \) are known, and \( 0 \leq a \leq 1; \ \beta_i \geq 0 \ i = 1, n \).

\( n \) is the number of reactors in the sequence, constraint (4.1) is the \( j^{th} \) component mass balance around the \( i^{th} \) reactor, constraint (4.2) is the reactor sequence’s performance specification which is a function of the sequence’s outlet concentrations, and constraints (4.3)–(4.4) account for the non-negativity of the \( j^{th} \) species’ concentration in the \( i^{th} \) reactor and of the \( i^{th} \) reactor residence time, respectively.

Depending on the values given to the coefficients \( \beta_i \), this objective function can represent such objectives as reactor volume, capital cost, or total annualized cost as follows:
1- Total reactor volume (linear objective) for \( \beta_i = c_i F \) \( i = 1, n \), \( c_i = 1 \) \( i = 1, n \), and \( a = 1 \)

such that \( Obj = \sum_{i=1}^{n} F \tau_i \)

2- Capital cost (non-linear objective) for \( \beta_i = c_i' F^a \) \( i = 1, n \) and \( 0 < a < 1 \) such that

\[
Obj = \sum_{i=1}^{n} c_i' F^a \tau_i^a
\]

3- Total annualized cost (nonlinear objective) two components:

a. Amortization cost for \( \beta_i = c_i^* F^a \) \( i = 1, n \) and \( 0 < a < 1 \)

b. Operating cost for \( \beta_i = E \cdot F \) \( i = 1, n \) and \( a = 0 \)

Such that \( Obj = \sum_{i=1}^{n} c_i^* F^a \tau_i^a + E \cdot F \). Where \( F \) is the flow rate \( \left( \frac{\text{Unit Volume}}{\text{Time}} \right) \), \( c_i' \), \( c_i^" \) are scaling coefficients for capital cost and total annualized cost respectively \( \left( \frac{\$}{\text{Unit Volume}^a} \right) \), and \( E \) is the operating cost coefficient \( \left( \frac{\$ \cdot \text{Time}}{\text{Unit Volume}} \right) \)

Considering all \( q \) species during the optimization may be computationally burdensome. In certain circumstances however it may be advantageous. As an example, for the case of linear reaction kinetics, the summability to one property of species fractions to first establish that the overall input-output reactor map is a Markoff process\(^14\), and to then identify properties of the reactor sequence that minimize the sum of reactor residence times. This potential advantage however disappears if either the reaction kinetics or the objective function is nonlinear. It is therefore desired that \( q \), the number of species considered in the optimization, be made as small as possible. To this end, two approaches can be pursued: In dimensionality reduction method A,
the concept of reaction invariance which states that certain state variables are not affected by chemical reactions taking place in the system, is employed. Reaction invariance was formalized for single units\textsuperscript{15}. More recently, this concept was expanded to reaction networks\textsuperscript{16-17} and is therefore applicable to sequences of CSTRs. Dimensionality reduction method B on the other hand takes advantage of the fact that often only some of the components participating in a reaction scheme are of interest, and their generation rates may not depend on all component concentrations. A brief outline of these dimensionality reduction methods is provided below.

4.4.1. Dimensionality Reduction Method A\textsuperscript{16}:

Consider a reaction scheme involving \( p \) reactions and \( q \) species. Let \( r_j \) be the \( j^{\text{th}} \) reaction rate \( \forall j = 1, p \); \( R^i = \sum_{j=1}^{p} V_{i,j} r_j \) be the rate of generation of the \( i^{\text{th}} \) species \( \forall i = 1, q \); \( C_i^0 \) be the network inlet concentration of the \( i^{\text{th}} \) species \( \forall i = 1, q \); and \( V_j = \begin{bmatrix} V_{1,j} & V_{2,j} & \cdots & V_{q,j} \end{bmatrix}^T \) be the vector of component stoichiometric coefficients in the \( j^{\text{th}} \) reaction.

Let also \( X \) be the vector space of all continuous functions mapping \( [0, q] \) to \( \mathbb{R}^p \), and let \( r_j \in X \ \forall j = 1, p \). Then the set \( S = \{r_j, j = 1, p\} \) is a subset of \( X \). Let \( [S] \) be the subspace consisting of all linear combinations of elements of \( S \). An element \( r_x \in [S] \) is said to be linearly dependent upon a set \( S_x \subset [S] \) if \( r_x \) can be expressed as a linear combination of elements from \( S_x \). In this context, \( S_x \) is a linearly independent set if each vector in \( S_x \) is linearly independent of the remainder of the set. Set \( S_x \) is said to be a basis for the subspace \( [S] \) if \( S_x \) generates \( [S] \), i.e. if
any vector in \([S]\) can be expressed as a linear combination of the elements of \(S_x\). Since

\[
R^i = \sum_{j=1}^{p} V_{ij} R_j \quad \forall i = 1,q, \]

it then holds true that \(R^i \in [S] \quad \forall i = 1,q\). Let \(n_b\) be the smallest positive integer such that the set \(R = \{R^1, R^2, \ldots, R^k\}\), with \(k \in \{1, \ldots, q\}\), \(\forall k = 1,n_b\), is a basis of \([S]\).

Then all species generation rates \(R^i \quad \forall i = 1,q\) can be calculated as linear combinations of vectors in \(R\), i.e.:

\[
R^i = \sum_{k=1}^{n_b} \phi_k R^k \quad i = 1,q
\]

The above equation is combined with the reactor network mass balances to yield the following relationship which must hold at every node of a reactor network:

\[
C^i - C^i_0 = \sum_{k=1}^{n_b} \phi_k \left( C^k - C^k_0 \right) \quad i = 1,q
\]

These equations allow the reduction of the dimension of the concentration space within which reactor network synthesis can be pursued. This reduced dimension \(m\) must satisfy \(m \leq n_b\).

**4.4.2. Dimensionality Reduction Method B**: 

It is often the case that only some of the components participating in a reaction scheme are of interest, and their generation rates may not depend on all component concentrations. Consider a reaction scheme involving \(q\) species. Let \(J_x\) be the subset of \(\{j, j = 1,q\}\) containing the indices of all components of interest; and let \(J_z\) be the least subset of \(\{j, j = 1,\ldots,q\}\) such that \(J_x \subseteq J_z\) and \(R^i\) depends solely on \(\left\{C^i\right\}_{i \in J_z} \forall j \in J_z\). Let \(n_z\) be the cardinality (i.e. the number of elements) of
Then, the reduced dimension $m$ of the concentration space within which reactor network synthesis can be pursued must satisfy $m \leq n_e$.

For demonstration purposes, dimensionality reduction method A is applied around the $j^{th}$ reactor $\forall j = 1, n$, to the following general single reversible reaction consisting of $q = 4$ species:

$$\alpha A(1) + \beta B(2) \Leftrightarrow \sigma C(3) + \lambda D(4)$$

$\alpha, \beta, \sigma, \lambda$ : Stoichiometric coefficients.

The reaction rates of the different species for this reaction satisfy:

$$R^i = -k_1 (C_j^i)^\sigma (C_j^{i+1})^\beta + k_2 (C_j^i)^\sigma (C_j^{i-1})^\beta, \quad R^2 = \frac{\beta}{\alpha} R^1, \quad R^3 = -\left(\frac{\sigma}{\alpha}\right) R^1, \quad R^4 = -\left(\frac{\lambda}{\alpha}\right) R^1$$

Assuming the reactor sequence’s inlet concentration vector is known, i.e. $C_0^1, C_0^2, C_0^3, C_0^4$, the outlet concentration of each species for each reactor in the sequence satisfies

$$C_j^2 = C_0^2 - \frac{\beta}{\alpha} (C_0^1 - C_j^1), \quad C_j^3 = C_0^3 + \frac{\sigma}{\alpha} (C_0^1 - C_j^1) \quad \text{and} \quad C_j^4 = C_0^4 + \frac{\lambda}{\alpha} (C_0^1 - C_j^1); \quad j = 1, n \quad \text{in the positive orthant of the four dimensional concentration space of the species 1, 2, 3, 4. Therefore, a reactor sequence featuring this general kinetic scheme can be optimized using a reduced dimension } m = 1,$$

since all species concentrations throughout the sequence can be expressed at the outlet of every $j^{th}$ reactor $\forall j = 1, n$, in terms of the corresponding concentration of species 1: $C_j^1.$

Similarly, dimensionality reduction method B is applied around the $j^{th}$ reactor $\forall j = 1, n$, to the Trambouze reaction scheme also consisting of $q = 4$ species:

Consider the Trambouze reaction scheme below being carried out in the $i^{th}$ reactor of an $N$ - CSTR reactor sequence:

Reaction 1: $A(1) \rightarrow B(2) \quad R^i = k_i, \quad \forall i = 1, n \quad \text{zero-order}$
Reaction 2: \( A(1) \rightarrow C(3) \) \( R^3 = k_2 C_i^i \ \forall i = 1, n \) first-order

Reaction 3: \( A(1) \rightarrow D(4) \) \( R^4 = k_3 \left( C_i^i \right)^2 \ \forall i = 1, n \) second-order

It can be seen from examination of the reaction scheme that the generation rates \( R^2, R^3 \) and \( R^4 \) form a linearly independent set and that \( R^4 \), the rate of consumption of species A, is a linear combination of \( R^2, R^3, R^4 \), i.e. \( R^4 = -R^2 - R^3 - R^4 \). Since \( A(1) \) is considered to be the only component of interest, application of dimensionality reduction method B outlined earlier yields the dimensionality of the reduced concentration space to be \( m = 1 \).

Considering that the reaction kinetics and the problem specifications of \( P_1 \) are such that the problem’s dimensionality can be reduced from \( q \) to \( m \), \( P_1 \) can be rewritten as:

\[
P_1: \quad \nu = \min \sum_{i=1}^{n} \beta_i \tau_i^a \\
\text{s.t.:} \\
C_{i-1}^j - C_i^j + \tau_i \cdot R^j \left( \left\{ C_k^k \right\}_{k=1}^m \right) = 0; \ i = 1, n; \ j = 1, m \quad (4.1)
\]

\[
f \left( \left\{ C_k^k \right\}_{k=1}^m \right) - \delta = 0 \quad (4.2)
\]

\[
- C_i^j \leq 0; \ i = 1, n; \ j = 1, m \quad (4.3)
\]

\[
- \tau_i \leq 0; \ i = 1, n \quad (4.4)
\]

\[
x = \left[ \left\{ C_1^i \right\}_{j=1}^m, \left\{ C_2^i \right\}_{j=1}^m, \ldots, \left\{ C_n^i \right\}_{j=1}^m, \tau_1, \tau_2, \ldots, \tau_n \right]^T
\]
Where $R^j : j = 1, m; f(\cdot) ; \{C^{k}_{ij}\}_{k=1}^{q} ; a ; \beta ; i = 1, n ; \delta$ are known, and $0 \leq a \leq 1 ; \beta_i \geq 0 ; i = 1, n$.

The above optimization problem possesses a number of properties which are formally presented below in the form of theorems.

### 4.5. Optimization Problem Properties

#### 4.5.1. Theorem 1: Existence

Let the functions $f(\cdot) : R^m \to R$, $f(\cdot) ; \{C^{k}_{n}\}_{k=1}^{q}$ and

\[ R^j : j = 1, m; R^i : \{C^{k}_{ij}\}_{k=1}^{q} \to R^j \left( \{C^{k}_{ij}\}_{k=1}^{q} \right) \forall i = 1, n; \forall j = 1, m \]

be continuous in the nonnegative orthant of the concentration spaces over which they are defined. Then, if the above optimization problem $P_1$ is feasible, it has a minimum.

**Proof**

Appendix A

Having established the existence of the problem’s optimum, it is desired to develop conditions of optimality that can be subsequently used for its solution. To simplify the development of these conditions, it is considered that the inequality constraints

\[ \tau_i \geq 0 \ \forall i = 1, n; \ C^j_i \geq 0 \ \forall j = 1, m \ \forall i = 1, n \]

are inactive at the problem’s optimum. This assumption can essentially be thought of as an active constraint solution strategy for the problem, wherein if the globally optimum solution identified under the strategy satisfies the omitted constraints, then it is the global optimum for the overall problem. If, on the other hand, the
globally optimum solution identified under the strategy does not satisfy the omitted constraints, then one of the omitted constraints is incorporated in the problem formulation as an equality constraint and the process is repeated. Such a solution procedure is effective, if the likelihood of the omitted constraints being active is small. This is indeed the case, for the following reasons. In regard to the concentration non-negativity constraints, their likelihood of being active is low because typically reaction rates become small as species concentrations become small, and thus the concentrations may approach zero but never actually become equal to zero. If on the other hand, one of the residence time non-negativity constraints becomes active at an intermediate reactor, this can always be made equivalent to the residence time of the last reactor being zero.

Having simplified the problem formulation so that it only contains equality constraints, the reduced problem formulation becomes:

$$\text{P2: } \mu \doteq \min_x \sum_{i=1}^{n} (\beta_i \tau_i^a)$$

subject to:

$$C_{i-1}^j - C_i^j + \tau_i \cdot R^j \left( C_i^k \right) = 0; \ i = 1, n; \ j = 1, m \quad (4.1)$$

$$f \left( \left\{ C_n^k \right\} \right) - \delta = 0 \quad (4.2)$$

$$x = \left[ \left\{ C_1^j \right\}_{j=1}^{m} \left\{ C_2^j \right\}_{j=1}^{m} \ldots \left\{ C_n^j \right\}_{j=1}^{m} \tau_1 \tau_2 \ldots \tau_n \right]^T$$

Where $$R^j \left( \cdot \right) \ i = 1, m; \ f \left( \cdot \right); \ \left\{ C_0^k \right\}_{k=1}^{q}; \ a; \ \beta_i \ i = 1, n; \ \delta$$ are known, and $$0 \leq a \leq 1; \ \beta_i \geq 0 \ i = 1, n.$$

A sequential solution procedure is followed, namely the optimum is found for an ever increasing number of reactors (2, 3, etc.) for a given $$\delta$$. As soon as the optimum for $$n$$ reactors is inferior to the optimum for $$n-1$$ reactors, the optimization procedure can terminate. This
termination condition must always hold true; otherwise, to obtain a globally optimal $n$ reactor sequence, the residence time of the additional $n^{th}$ reactor must be equal to zero (i.e. $\tau_n = 0$), which activates the non-negativity residence time constraint, and prohibits the further addition of reactors.

By definition\(^{18}\), a point $x$ is a regular point of the equality constraints if the gradient vectors of the equality constraints evaluated at $x$ are linearly independent.

In this case, let:

$$h_{i,j}(x) = C_{i-1} - C_{i} + \tau_{i} \cdot R' \left( \left\{ C_{i}^{k} \right\}_{k=1}^{m} \right) = 0; \ \forall i = 1,n; \ \forall j = 1,m,$$

and $h_{n+1}(x) = f \left( \left\{ C_{n}^{k} \right\}_{k=1}^{m} \right) - \delta = 0$.

Then,

$x$ is a regular point of the equality constraints $h_{i,j}(x) = 0$ $\forall i = 1,n; \ \forall j = 1,m$ and $h_{n+1}(x) = 0$ if and only if

$$\sum_{i=1}^{n} \sum_{j=1}^{m} \alpha_{i,j} \left( \frac{\partial h_{i,j}}{\partial x} \right) + \alpha_{n+1} \left( \frac{\partial h_{n+1}}{\partial x} \right) = 0 \Rightarrow \alpha_{i,j} = 0; \ \forall i = 1,n; \ \forall j = 1,m; \ \alpha_{n+1} = 0.$$ 

The following regularity result listed below in theorem 2 can be established for the reduced problem $P2$.

\[4.5.2. \ \text{Theorem 2: Regularity}\]

Let $x$ belong to the positive orthant of $\mathbb{R}^{m(n+1)}$, and satisfy the equality constraints

$$h_{i,j}(x) = 0 \ \forall i = 1,n; \ \forall j = 1,m \text{ and } h_{n+1}(x) = 0$$

of the above optimization problem $P2$.

Assuming:
\[
\begin{bmatrix}
R_1^T \\
R_2^T \left[ I - \tau_1 \cdot \frac{\partial R}{\partial C_1} \right] \\
. \\
. \\
. \\
R_m^T \left[ I - \tau_{m-1} \cdot \frac{\partial R}{\partial C_{m-1}} \right] \cdots \left[ I - \tau_1 \cdot \frac{\partial R}{\partial C_1} \right]
\end{bmatrix}
\]

is invertible and that \( \exists k \in \{1, \ldots, m\} : \frac{\partial f}{\partial C_k} \neq 0 \), then \( x \) is a regular point of the aforementioned equality constraints.

**Proof**

Appendix B

Theorem 2 above allows for the application of the 1st order necessary conditions of optimality to the reduced optimization problem \( P_2 \). To this end, equation (4.5) is the Lagrangian associated with the reduced constrained problem \( P_2 \).

\[
L(x, \lambda) = \sum_{i=1}^{n} (\beta_i \tau_i^a) + \left[ \sum_{i=1}^{n} \sum_{j=1}^{m} \lambda_i^j \left( C^i_j - C^j_i + \tau_i \cdot R^j_i (\{ C_k^i \}_{k=1}^m) \right) \right] + \lambda_{n+1} \left[ f \left( \{ C_n^k \}_{k=1}^m \right) - \delta \right] 
\]

(4.5)

The 1st order necessary conditions of optimality for equality constraints are such that \( \nabla_x L = 0 \) and \( \nabla_\lambda L = 0 \).

The resulting conditions of optimality for \( P_2 \) are shown below in theorem 3.
4.5.3. Theorem 3: Necessary Conditions for Optimality

Let \( x \) belong to the positive orthant of \( \mathbb{R}^{n(m+1)} \), and satisfy the equality constraints

\[
h_{i,j}(x) = 0 \quad \forall i = 1,n; \quad \forall j = 1,m \quad \text{and} \quad h_{n+1}(x) = 0
\]

of the above optimization problem \( P2 \). Under the assumptions of Theorems 1 and 2, and the additional conditions that \( x \) is a regular point of the equality constraints of \( P2 \) and that the inequality constraints of \( P2 \)

\[
\tau_i \geq 0 \quad \forall i = 1,n; \quad C_i^j \geq 0 \quad \forall j = 1,m \quad \forall i = 1,n \quad \text{are inactive at} \ x, \text{then for} \ X \text{to be a local minimum of} \ P2 \text{ the following optimality relations must be satisfied:}
\]

\[
\begin{align*}
\left\{ \begin{array}{l}
C_i^{j-1} - C_i^j + \tau_i \cdot R^i(\{C_i^k\}_{k=1}^m) = 0; \quad \forall i = 1,n; \quad \forall j = 1,m \\
f \left( \{C_i^k\}_{k=1}^m \right) - \delta = 0 \\
\Lambda_{n+1} = \left( I - \tau_i \cdot \frac{\partial R}{\partial C_i} \right) \Lambda_i \quad \forall i = 1,n-1 \\
\left( I - \tau_n \cdot \frac{\partial R}{\partial C_n} \right) \Lambda_n = \lambda_{n+1} \frac{\partial f}{\partial C_n} \\
\alpha \beta \tau_i a^{-1} + R^T_i \Lambda_i = 0 \quad \forall i = 1,n
\end{array} \right. \\
\end{align*}
\]

Proof:

Appendix C

If \( n>m>1 \) the necessary conditions for optimality can be rewritten as:

\[
C_i^{j-1} - C_i^j + \tau_i \cdot R^i(\{C_i^k\}_{k=1}^m) = 0 \quad \forall i = 1,m; \quad \forall j = 1,m
\]

(4.6)
\[ \begin{bmatrix} R_1^T \\ R_2^T \cdot \left[ I - \tau_1 \cdot \frac{\partial R}{\partial C_1} \right] \\ \vdots \\ R_m^T \cdot \left[ I - \tau_{m-1} \cdot \frac{\partial R}{\partial C_{m-1}} \right] \end{bmatrix} \Lambda_1 = \begin{bmatrix} -\alpha \beta_1 \tau_1^{a-1} \\ \vdots \\ -\alpha \beta_m \tau_m^{a-1} \end{bmatrix} \] (4.7)

\[
\begin{cases}
\alpha \beta_i \tau_i^{a-1} + R_i^T \left( I - \tau_{i-1} \cdot \frac{\partial R}{\partial C_{i-1}} \right) \left( I - \tau_1 \cdot \frac{\partial R}{\partial C_1} \right) \Lambda_1 = 0 & \forall i = m+1, n \\
C_{i-1} - C_i^j + \tau_j \cdot R' \left( \{C_i^k\}_{k=1}^m \right) = 0; & \forall j = 1, m; \forall i = m+1, n
\end{cases}
\] (4.8)

\[
\begin{cases}
f \left( \{C_n^k\}_{k=1}^m \right) - \delta = 0 \\
\left( I - \tau_n \cdot \frac{\partial R}{\partial C_n} \right) \left( I - \tau_{n-1} \cdot \frac{\partial R}{\partial C_{n-1}} \right) \cdots \left( I - \tau_1 \cdot \frac{\partial R}{\partial C_1} \right) \Lambda_1 - \lambda_{n+1} \frac{\partial f}{\partial C_n} = 0
\end{cases}
\] (4.9)

Equations (4.7)–(4.9) will be used in discussing the interval-based solution procedure in sec. 4.7.1.

### 4.6. Properties for Optimization Problems with Linear Kinetics

As shown in the mathematical preliminaries section above, for the case of linear kinetics it holds that \( \frac{\partial R}{\partial C_i} \equiv R_i^T \) and \( R_i \equiv R \cdot C_i \); \( i = 1, n \). In turn, this modifies the mass balance equation (4.1) , which now becomes: \( C_{i-1} = (I - \tau_i \cdot R)C_i \); \( i = 1, n \) \Rightarrow

\[ C_0 = (I - \tau_1 \cdot R) \cdots (I - \tau_i \cdot R)C_i \quad ; \quad i = 1, n \] (4.10)
The special structure of the resulting matrix relating inlet to outlet concentrations \( C_0 \) to \( C_i \); \( i = 1, n \) in equation (4.10) can then be exploited, concurrently with optimality equation (3.8) to yield the following two theorems for the case of linear kinetics.

### 4.6.1. Theorem 4: Local Optimality of Equal-Reactor Sequences

For the case of linear kinetics, under the assumptions of Theorems 1, 2, and 3, and considering that \( \beta_i = \beta, \forall i = 1, n \) and the matrices \( (I - \tau_i R_i^T) \) \( i = 1, n \) are invertible, the equal size reactor sequence satisfies the necessary conditions of optimality identified in Theorem 3 above, and thus is a candidate local minimum for \( P_2 \).

**Proof:**

Appendix D

### 4.6.2. Theorem 5: Global Optimality of Equal-Reactor Sequences

For the case of linear kinetics, under the assumptions of Theorems 1, 2, and 3, and considering that \( m = 1, \beta_i = \beta, \forall i = 1, n ; \ a \in (0, 1), \ 0 < C_n < C_0, \ k \) is the overall kinetic constant, \( n_u \) is the maximum number of allowable reactors, and the scalars \( (I - \tau_i R_i^T) \) \( i = 1, n \) are invertible,
the global minimum for $P_2$ is an equal size reactor sequence featuring $\hat{p}$ reactors, where

$$\hat{p} \equiv \arg \min_{p \in \mathbb{N}} p \left( \frac{C_0}{C_n} \right)^{\frac{1}{p}} - 1$$

and where the following two cases holds:

Case 1:

If

$$\left\{ \begin{array}{l} \frac{C_0}{C_n} < 1 \\
\frac{C_0}{C_n} > 1 \end{array} \right\} \quad \Rightarrow \hat{p} = 1$$

Case 2:

If

$$\left\{ \begin{array}{l} \frac{C_0}{C_n} < 1 \\
\frac{C_0}{C_n} > 1 \end{array} \right\} \quad \Rightarrow \exists \text{unique } \hat{x} \in \left\{ \frac{\ln \left( \frac{C_0}{C_n} \right)}{\ln (a)} \right\}$$

$$\left( \frac{C_0}{C_n} \right)^{\frac{1}{n}} \left( a \ln \left( \frac{C_0}{C_n} \right) \right) - 1 = 0 \Rightarrow \left\{ \begin{array}{l} \hat{p} = n_u \text{ if } n_u < \text{int}(\hat{x}) \\
\hat{p} = \min(\text{int}(\hat{x}), n_u) \text{ if } \text{int}(\hat{x}) < n_u < \text{int}(\hat{x}) + 1 \\
\hat{p} = \min(\text{int}(\hat{x}), \text{int}(\hat{x}) + 1) \text{ if } \text{int}(\hat{x}) + 1 \leq n_u \end{array} \right\}$$

Proof:

Appendix E
4.7. General Solution Procedure

The above Theorems 1, 2 and 3 lead us to suggest an interval analysis based global solution method for $P_2$. For any $n$-reactor sequence, the procedure consists of the following steps, which allows for a search in the reduced $m$-dimensional space:

4.7.1. Interval-Analysis Based Algorithm:

Consider $n > m \geq 1$:

1- Assuming known values $C_0^j \ \forall j = 1, q$, instantiate the box list. Place an $m$-dimensional ($m$ intervals) box guaranteed to contain the values of $C_i^i \ \forall i = 1, m$ in the box list.

2-
   a. Subdivide the first $m$-dimensional box in the list into $2^m$ boxes by using bisection in each of the $m$ box sides (for the first iteration, there exists only one $m$-dimensional box in the list). Place subdivided boxes into subdivision list.
   b. Select a box from the subdivision list.
   c. Evaluate $m$ intervals containing the values of $\tau_i \ \forall i = 1, m$ using interval extensions of equations (4.6)
   d. Evaluate sequentially intervals containing the values of $C_i^i \ \forall i = 1, m; \ \forall j = 2, m$, using interval extensions of equations (4.6).
e. Evaluate intervals containing the values of \( \Lambda_i \), using interval extensions of equation (4.7).

f. Evaluate sequentially intervals containing the values of \( C_i^j \) \( \forall i = m+1, n; \forall j = 1, m \), and \( \tau_i \) \( \forall i = m+1, n \) using interval extensions of equations (4.8).

g. Evaluate an interval containing the values of \( \hat{\lambda}_{n+1} \), using an interval extension of one of equations (4.9).

h. Evaluate intervals containing the left hand sides of the remaining equations (4.9), using interval extensions of these remaining equations.

i. If one of these intervals found in step 2-h does not contain 0, then eliminate the considered box from subdivision list and return to step 2-b. If each of these intervals contains 0, then evaluate an interval containing the values of the objective function of \( P2 \), using an interval extension of \( \sum_{i=1}^{n}\left( \beta_i \tau_i^u \right) \). Associate the objective function interval calculated with the considered box from subdivision list.

j. If the lower bound of the objective interval calculated in step 2-i is greater than the upper bound of the union of objective function intervals in the box list eliminate the considered box. Else, add the considered box to the box list.

k. If all subdivisions have been considered, go on to step 3; otherwise, return to step 2-b.
3- If the size of the objective function interval is less than or equal to $\epsilon_1$, and the size of the union of objective function intervals over all boxes in the box list is less than or equal to $\epsilon_2$, then terminate the algorithm and declare the union of objective function intervals over all boxes in the list as the range of the globally optimum objective function value; otherwise proceed to step 4.

4- If at least one of the two aforementioned termination criteria ($\epsilon_1$ or $\epsilon_2$) is violated, then

Rank-order the box list according to the lower bound of the objective function interval and return to step 2-a.

Consider $m \geq n$:

Then the above solution procedure is simplified by first carrying out steps 1, 2, and 3 $\forall i = 1, n$, and then omitting steps 2-e, 2-f, and 2-g. Step 2-h is carried out only for

$$f \left( \left\{ \binom{k}{n}^{m} \right\}_{k=1}^{m} \right) - \delta = 0.$$ The remaining steps are carried out as outlined above.

In addition to the above general interval-analysis based methodology applicable $\forall m$, it is possible to employ a simpler, graphical method for the case of $m = 1$ as described below.
4.7.2. Graphical Method:

Consider $m = 1$:

Close examination of the necessary conditions identified in Theorem 3 suggests that for

$m = 1$ using equations $\Lambda_{i+1} = \left( I - \tau_i \cdot \frac{\partial R}{\partial C_i} \right) \Lambda_i \ \forall i = 1, n - 1$ and $\alpha \beta_i \tau_i^{-1} + R_i^t \Lambda_i = 0 \ \forall i = 1, n$, the following must hold true:

$$R_i \left( -a \beta_{i+1} \left( \frac{C_{i+1}^i - C_i^i}{R_{i+1}} \right)^{a-1} \right) = R_i \left( 1 - \left( \frac{C_i^i - C_{i-1}^i}{R_i} \right) \frac{\partial R}{\partial C_i} \right) \left( -a \beta_i \left( \frac{C_i^i - C_{i-1}^i}{R_i} \right)^{a-1} \right)$$

(4.11)

$$\forall i = 1, n - 1$$

The above equations can be used to identify sequentially the values of $C_i^i \ \forall i = 2, n$, assuming that $C_1^i$ is known. Then aside from the interval analysis based solution method outlined above, an alternative graphical procedure is applicable to the problem’s global solution. The procedure can be summarized as follows:

1. For $i = 1$, all values of $C_2^i$ satisfying the above equation for any given value of $C_1^i$ are quantified. The resulting functions $C_2^i \left( C_1^i \right)$ are then captured in graph form.

2. The process is repeated for $i = 2, n - 1$, and thus all the composite functions $C_i^i \left( C_1^i \right) \ \forall i = 2, n$ are captured in graph form.
3. All locally optimum points of $P_2$, for a value of $\delta$, are then quantified by first
identifying all corresponding $C_i^l$, then all matching $C_i^l$ values $\forall i = 2, n$ for which
condition $f \left( C_i^l \left( C_i^l \right) \right) - \delta = 0$ is satisfied.

4. Knowing every reactor’s outlet concentration, the globally optimum sequence of $P_2$ is
then easily identified as the one with the minimum objective function $\sum_{i=1}^{n} \left( \beta_i \tau_i^a \right)$ for a
given $\delta$.

Aside from the insight this method provides into the structure of the problem’s global
optimum, it also possesses the additional advantage that it solves multiple instances of the
optimization problem $P_2$ for different values of $\delta$ without any additional work, and determines
transition points in the globally optimal number of reactors $\forall \delta$ simultaneously.

The results of theorem 4.6.2 will be applied towards a case study (sec. 4.8), while
graphical and interval-based methods will be used in the first and second Trambouze kinetics
case study examples, (sec. 4.9.1, and sec. 4.9.2), respectively.

4.8. Case study – Linear kinetics – Multiple Reactions – Application of Theorem 4.6.2:

Consider the following reaction scheme with linear kinetics below being carried out in the
$i^{th}$ reactor of an $n$-CSTR reactor sequence:

Reaction 1: $A(1) \rightarrow B(2) \quad R^2 = k_i \quad \forall i = 1, n \quad \text{zero-order}$

Reaction 2: $A(1) \rightarrow C(3) \quad R^3 = k_i C_i \quad \forall i = 1, n \quad \text{first-order}$
It can be seen from examination of the reaction scheme that the generation rates $R^2$, and $R^3$ form a linearly independent set and that $R^1$, the rate of consumption of species A, is a linear combination of $R^2, R^3$ i.e. $R^1 = -R^2 - R^3$. Since species A(1) is considered to be the only component of interest, application of dimensionality reduction method B outlined earlier yields the dimensionality of the reduced concentration space to be $1 (m=1)$. The kinetic constants are such that $k_1 = 1 \text{ mol dm}^{-3} \text{s}^{-1}$, and $k_2 = 2 \text{ s}^{-1}$. It is desired to obtain a reactor network outlet concentration of $C_n = 0.1 \text{ mol dm}^{-3}$. To this end, and since the kinetics are linear with $m=1$, the results of theorem 4.6.2 will be applied for $\frac{C_0}{C_n} = 10$, and $n_u = 100$. Evaluating $\left(\frac{C_0}{C_n}\right)^a = 8$, and

$$\left(\frac{C_0}{C_n}\right)^{-1 - a \ln \left(\frac{C_0}{C_n}\right)} = -9.42 < 0$$

leads to case 2 of theorem 6.2 where the solution of

$$\left(\frac{C_0}{C_n}\right)^{\frac{1}{2}} \left[1 - \frac{a \ln \left(\frac{C_0}{C_n}\right)}{\tilde{x}}\right] - 1 = 0$$

yields $\tilde{x} = 4.9602$. In addition, $\int(\tilde{x}) + 1 \leq n_u$ implies that

$$\hat{p} = \min\left(\int(\tilde{x}), \int(\tilde{x}) + 1\right) = \min\left(4 \left(\frac{C_0}{C_n}\right)^{\frac{1}{3}} - 1\right)^{0.8}, 5 \left(\frac{C_0}{C_n}\right)^{\frac{1}{5}} - 1\right)^{0.8} = \min(3.273, 3.255)$.

Therefore, the optimal sequence consists of 5 equal size reactors. This is validated by figure 1 below. The cost of such a reactor sequence is
Case study – Trambouze Kinetics:

The dimensionality of the Trambouze kinetics scheme was described in sec.4, and will be used in the following two sections (4.9.1, 4.9.2).

4.9.1. Trambouze Case Study 1: Non-Linear Objective Function (TAC)

The objective function represents the reactor sequence’s total annualized cost and has the form $p \left( \frac{C_0}{C_n} \right)^{\frac{1}{p}} - 1 \right)^a$. The following parameters were assumed $a = 0.6, C_0 = \frac{1 \text{mol}}{\text{dm}^3}$,

$$F = 1 \frac{\text{dm}^3}{s}, \quad c_i'' = 10^4 \frac{\text{S}}{\left( \text{dm}^3 \right)^{0.6}}, \quad \beta_i = 10^4 \frac{\text{S} \cdot \text{s}^{-0.6}}{\text{dm}^3}, \quad \text{and } E = 10^5 \frac{\text{S} \cdot \text{s}}{\text{dm}^3} \forall i = 1, n.$$ For the specific
Trambouze scheme at hand, the kinetic constants\textsuperscript{19} and are such that

\[ k_1 = 0.0001 \text{mol dm}^{-3} \text{s}^{-1}; \quad k_2 = 0.0015 \text{s}^{-1}; \quad k_3 = 0.008 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}. \]

Figure 2 is obtained from application of the graphical method discussed in the general solution procedure above, through sequential solution of equation (4.11) \( \forall i = 2,4 \), and shows the outlet concentration of the second \( C_2^i \), third \( C_3^i \), and fourth \( C_4^i \) reactor as a function of the first reactor’s outlet concentration \( C_1^i \).

\[ \delta = 0.01 \]

**Fig. 4.2:** Composite functions \( C_i^i \left( C_1^i \right) \) \( \forall i = 2,4 \) captured in graph form
For a given outlet $\delta = 0.01 \text{ mol/dm}^3$, all the values $C_i^l$ corresponding to $f\left(C_i^l\left(C_i^l\right)\right) = C_i^l = \delta$ are graphically denoted. The second and third reactor outlet concentrations, $(C_2^l)$ and $(C_3^l)$ respectively, conforming to a particular $C_i^l$ value are denoted on the top two subplots of the figure as well. The work performed on a four-reactor sequence is repeated for a three-reactor sequence, albeit now with $C_3^l = \delta = 0.01 \text{ mol/dm}^3$. The resulting globally optimal three and four-reactor sequences are shown below in figure 4.3.

a)

![Diagram of four-reactor sequence]

b)

![Diagram of three-reactor sequence]

**Fig. 4.3:** Globally optimal three-reactor sequence (4.3–a), four-reactor sequence (4.3–b)

The globally optimal four and three-reactor sequences yield minimum objective function values

$$\sum_{i=1}^{4} \beta_i \tau_i^{0.6} + E \cdot F = 143.21 \cdot 10^4 \, \text{$/10^5$} = 15.321 \cdot 10^4 \, \text{$/10^5$} \, \text{and}$$

$$\sum_{i=1}^{3} \beta_i \tau_i^{0.6} + E \cdot F = 142.84 \cdot 10^4 \, \text{$/10^5$} = 15.284 \cdot 10^5 \, \text{$/10^5$} \, \text{respectively.}$$

This implies that the use of
more than three reactors is unwarranted, and the procedure can terminate since the optimum for 
\( n = 4 \) reactors is inferior to the optimum for \( n = 3 \) reactors. Indeed, the residence time of the 
additional \( n^{th} \) reactor must be equal to zero (i.e. \( \tau_n = 0 \)), which activates the non-negativity 
residence time constraint, and prohibits the further addition of reactors. A three-reactor sequence 
is the globally optimal reactor sequence among any \( n \)-reactor sequence for 
\[
\delta = 0.01 \frac{\text{mol}}{\text{dm}}; \ n = 1, \ldots, \infty.
\]

[Diagram showing transitions between reactor sequences]

**Fig. 4.4:** \( \min \sum_{i=1}^{n} \tau_{i,0.6}^{10^4} \) vs. \( C_n^l(\delta) \) globally optimal curves for \( n = 1, 2, 3, 4 \)

In addition, it is possible to graphically identify the globally optimal number of reactors 
depending on the desired outlet concentration. This is illustrated in figure 4 by plotting 
\[
\min \sum_{i=1}^{n} \tau_{i,0.6}^{10^4}
\] as a function of \( C_n^l(\delta) \). Four curves are displayed, one for every globally optimal \( n \)-
reactor sequence \( (n=1,2,3,4) \) for all values of \( \delta \). The transition points in the number of optimal reactors and the value of \( \delta \) where they occur is also demonstrated on figures 4-5, and gives rise to the following four possible scenarios:

1- \( \delta < 1.3918 \times 10^{-3} \): Four-reactor sequence is optimal.

2- \( 1.3918 \times 10^{-3} \leq \delta < 0.1214 \): Three-reactor sequence is optimal.

3- \( 0.1214 \leq \delta < 0.3462 \): Two-reactor sequence is optimal.

4- \( \delta \geq 0.3462 \): One reactor is optimal.
Fig. 4.5: $\min \sum_{i=1}^{n} \tau_i^{0.6}$ vs. $C_n^l(\delta)$, blowup of transition points in $\delta$ $(n = 1, 2, 3, 4)$
4.9.2. Trambouze Case Study 2: Linear Objective Function (Total Volume)

The objective function represents the reactor sequence’s total residence time and has the form \( \sum_{i=1}^{n} F \tau_i \). The following parameters were assumed \( C_0^i = 1 \frac{\text{mol}}{\text{L}} \), \( F = 1 \frac{\text{L}}{\text{min}} \).

For the specific Trambouze scheme at hand, the kinetic constants are such that \( k_1 = 0.025 \frac{\text{mol}}{\text{L} \cdot \text{min}} \), \( k_2 = 0.2 \text{ min}^{-1} \), \( k_3 = 0.4 \frac{\text{L}}{\text{mol} \cdot \text{min}} \). Interval analysis, as discussed in the solution procedure above, is used to sequentially solve an \( n \)-reactor sequence with outlet concentration \( C_n^i \in [0, 10^{-7}] \left( f \left( C_n^i \right) \simeq C_n^i = 0 \right) \). For a ten-reactor sequence with a tolerance \( \varepsilon_1 = 10^{-5} \) and \( \varepsilon_2 = 10^{-3} \), the objective function obtained in interval form is

\[
\sum_{i=1}^{10} F \tau_i \in [9.32674, 9.32675].
\]

The algorithm was implemented using MATLAB® 7.1.1.0 on an Intel Core 2 Quad CPU Q6600 @ 2.4 GHZ. Convergence took a total of 3.6350 s of CPU time.

For comparison purposes, formulation P2 was solved with identical terminal constraints on two state-of-the-art global NLP solvers, which are BARON® and LindoGlobal®, as part of the GAMS® package, with up to a five-reactor sequence (Demo limit on variables). Convergence time using these solvers was then compared to those obtained from the implementation of the above described algorithm in table 4.1. It takes approximately the same amount of time for interval analysis to solve a problem with twice the number of reactors as BARON®. The reader is invited to verify the superiority of the proposed method by trying to solve the ten-reactor sequence problem using BARON®. It should be noted that the convergence time growth rate for interval-analysis is much more favorable to optimizing large reactor
sequences compared to LindoGlobal® or BARON® as shown in figure 4.6. Table 4.2 displays individual reactor residence time intervals for the globally optimal 10 reactor sequence.

![Graph showing convergence time growth-rate as a function of the number of reactors for the three global Solvers considered.](image)

**Fig. 4.6:** Convergence time growth-rate as a function of the number of reactors for the three global Solvers considered.

<table>
<thead>
<tr>
<th>Number of Reactors (n)</th>
<th>Interval Analysis CPU time (s)</th>
<th>BARON® CPU time (s)</th>
<th>LindoGlobal® CPU time (s)</th>
<th>Interval Analysis Results: $\sum_{i=1}^{n} \tau_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>3.6350</td>
<td>*</td>
<td>*</td>
<td>[9.32674, 9.32675]</td>
</tr>
<tr>
<td>9</td>
<td>1.3410</td>
<td>*</td>
<td>*</td>
<td>[9.48793, 9.48794]</td>
</tr>
<tr>
<td>8</td>
<td>0.5610</td>
<td>*</td>
<td>*</td>
<td>[9.69359, 9.69360]</td>
</tr>
<tr>
<td>7</td>
<td>0.2650</td>
<td>*</td>
<td>*</td>
<td>[9.96498, 9.96499]</td>
</tr>
<tr>
<td>6</td>
<td>0.1240</td>
<td>*</td>
<td>*</td>
<td>[10.33948, 10.33949]</td>
</tr>
<tr>
<td>5</td>
<td>0.0780</td>
<td>3.702</td>
<td>42.510</td>
<td>[10.88913, 10.88914]</td>
</tr>
<tr>
<td>4</td>
<td>0.0310</td>
<td>0.977</td>
<td>7.150</td>
<td>[11.77274, 11.77275]</td>
</tr>
<tr>
<td>3</td>
<td>0.0310</td>
<td>0.452</td>
<td>1.453</td>
<td>[13.49183, 13.49184]</td>
</tr>
<tr>
<td>2</td>
<td>0.0310</td>
<td>0.238</td>
<td>0.359</td>
<td>[17.49999, 17.50000]</td>
</tr>
</tbody>
</table>

**Table 4.1:** Comparison of the CPU time elapsed for convergence using different solver packages.

Interval analysis is always superior to generic global optimization packages.

* Demo limit on variables
4.10. Conclusions:

The minimization of a general objective function dependent on reactor residence times, subject to a constraint involving the reactor sequence’s exit concentrations, was presented. Several theorems proving existence, continuity, regularity and first order conditions of optimality were presented. General solution procedures to solve the sequencing problem, both graphical and computational, were rigorously described and applied in several case studies. The time needed for global solution of MINLP formulations grows exponentially with the number of variables appearing in these formulations in a non-convex manner. In the context of this work on the CSTR optimal sequence problem, CSTR outlet concentrations and residence times appear in these MINLP formulations in a nonconvex manner, thus requiring unrealistically long times to

<table>
<thead>
<tr>
<th>$\tau_i$ $(i=1,10)$</th>
<th>Interval Analysis Results $(i=1,10)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_1$</td>
<td>[0.635356631, 0.6353256632]</td>
</tr>
<tr>
<td>$\tau_2$</td>
<td>[0.700143820, 0.700143822]</td>
</tr>
<tr>
<td>$\tau_3$</td>
<td>[0.76559810, 0.76559811]</td>
</tr>
<tr>
<td>$\tau_4$</td>
<td>[0.83153794, 0.83153796]</td>
</tr>
<tr>
<td>$\tau_5$</td>
<td>[0.89789771, 0.89789776]</td>
</tr>
<tr>
<td>$\tau_6$</td>
<td>[0.964623, 0.964624]</td>
</tr>
<tr>
<td>$\tau_7$</td>
<td>[1.0316724, 1.0316727]</td>
</tr>
<tr>
<td>$\tau_8$</td>
<td>[1.099006, 1.099007]</td>
</tr>
<tr>
<td>$\tau_9$</td>
<td>[1.166594, 1.166596]</td>
</tr>
<tr>
<td>$\tau_{10}$</td>
<td>[1.234410, 1.234414]</td>
</tr>
<tr>
<td>$\sum_{i=1}^{10} \tau_i$</td>
<td>[9.32674, 9.32675]</td>
</tr>
</tbody>
</table>

Table 4.2: Interval for residence time of each reactor in globally optimal 10 reactor sequence
identify the global solution for sequences whose optimal number of reactors is large. This behavior manifests itself clearly in section 9.2, where the MINLP algorithms take significantly longer to solve, and their solution time grows faster, than the algorithms proposed here. In this work, information about the problem’s optimality conditions is incorporated into the computational methods proposed, thus allowing the interval analysis algorithm to proceed by carrying out its in this work search in a variable space with dimension equal to the “reduced dimension” $m$, while the MINLP algorithms carry out their search in $(m + 1)n$ dimensions. The advantages of the graphical and analytical methods over MINLP methods are even more compelling. For $m = 1$, the graphical method allows identification of the global optimum through simple inspection of a number of graphs, irrespective of the number of reactors in the optimum sequence of CSTR’s. Finally, and most importantly, for linear kinetics and $m = 1$, an analytical solution to the globally minimum capital cost problem is provided.
4.11. Nomenclature:

\[ \Lambda_i; l = 1, n : \text{Vector of regular points coefficients, for the } i^{th} \text{ reactor with } m \text{ species entries.} \]

\[ \alpha_{i,j}; i = 1, n; j = 1, m : \text{Regular point coefficient, for the } j^{th} \text{ species and } i^{th} \text{ reactor, entry of } \Lambda_i. \]

\[ \Lambda_i; i = 1, n : \text{Lagrangian vector for the } i^{th} \text{ reactor with } m \text{ species entries.} \]

\[ \lambda^i_l; i = 1, n; j = 1, m : \text{Lagrangian multiplier of the } j^{th} \text{ species leaving the } i^{th} \text{ reactor, entry of } \Lambda_i. \]

\[ C_i; i = 1, n : \text{Concentration vector for the } i^{th} \text{ reactor with } m \text{ species entries.} \]

\[ C^i_j; i = 1, n; j = 1, m : \text{Concentration of the } j^{th} \text{ species leaving the } i^{th} \text{ reactor, entry of } C_i. \]

\[ R^i_l; l = 1, n : \text{Reaction rate vector for the } l^{th} \text{ reactor with } m \text{ species entries.} \]

\[ R^j \left( \{C^p_i\}_{p=1}^m \right); j = 1, m : \text{Reaction rate vector of the } j^{th} \text{ species, entry of } R_i. \]

\[ R : \text{Matrix of reaction rate coefficients for linear kinetics.} \]

\[ R^T : \text{Gradient of the matrix of reaction rate coefficients for linear kinetics.} \]

\[ \frac{\partial R}{\partial C^k_i}; k = 1, m; l = 1, n : \text{Gradient of reaction rate vector for the } k^{th} \text{ species and } l^{th} \text{ reactor with } m \text{ species entries.} \]

\[ \frac{\partial R}{\partial C_i}; l = 1, n : \text{Matrix of gradient of reaction rate vectors of all species for the } l^{th} \text{ reactor with } m \cdot m \text{ matrix entries.} \]

\[ \tau_i : \text{Residence time of the } i^{th} \text{ reactor.} \]

\[ f \left( \{C^k_n\}_{k=1}^m \right) : \text{Specification function that defines concentration specification } \delta \text{ at the sequence exit.} \]
\( \frac{\partial f}{\partial C_n} \): Gradient of the specification function with respect to the outlet concentration of the sequence.

4.12. Appendices A-F:

4.12.1. Appendices A-C

Appendix A
Given the finite dimensional nature of P1, application of the Weierstrass theorem requires the continuity of the objective function throughout the feasible region, and the closedness and boundedness of the feasible region. The objective function is continuous, since its constituent linear and power law functions are well defined continuous functions throughout the feasible region, given that the residence times are required to be non-negative \( \tau_i \geq 0; \; i = 1, n \). The closedness of the feasible region is readily established, since it is defined by equality constraints \( (= 0) \) and inequality constraints of the less than or equal type, \( (\leq 0) \) whose left hand side involves continuous functions according to the Theorem’s assumptions. Continuity of the species’ generation/consumption rates \( R'(\cdot) \; \forall j = 1, m \) is a realistic assumption, since reaction rates capture the collective behavior of molecular events which cannot exhibit discontinuities or singularities. The function \( f(\cdot) \) which defines concentration specifications at the reactor sequence exit is at the designer’s discretion and can always be assumed to be a continuous function. All other functions involved in the definition of the equality and inequality constraints are multinomial in nature and thus continuous. The boundedness of the feasible region is established as follows: All species concentrations and all reactor residence times involved in the problem are nonnegative, i.e. \( \tau_i \geq 0 \; \forall i = 1, n; \; C_{ij} \geq 0 \; \forall \; j = 1, m \; \forall i = 1, n \). Let \( M' \) be the
molecular weight of the species \( j; \ j = 1, m \) present in the problem’s constraints. Then, since the mass density \( \rho < \infty \) of the reacting mixture is assumed constant, and all the species concentrations involved in the problem are nonnegative, it then holds that the concentration of species \( j \) at the exit of reactor \( i \) is bounded, since

\[
\sum_{j=1}^{m} M^j C^j_i \leq \rho \Rightarrow C^j_i \leq \frac{\rho}{M^j} < \infty \ \forall j = 1, m; \ \forall i = 1, n.
\]

In addition, since the optimization problem is feasible, there exists at least one feasible reactor sequence (i.e. one that also satisfies the exit concentration specification). Let the objective function value corresponding to that sequence be \( \nu^* \). It then holds that \( \nu^* \geq \nu \). In turn, this implies that augmenting the above optimization problem with the constraint \( \sum_{i=1}^{n} (\beta \tau^* a_i ) \leq \nu^* \), does not alter its infimum. Since

\[
\tau_i \geq 0; \ \beta_i \geq 0; \ \beta_i > 0; \ \forall i = 1, n, \text{ it then holds } 0 \leq \tau_i \leq \left( \frac{\nu^*}{\beta_i} \right)^{\frac{1}{a}} < \infty \ \forall i = 1, n \text{ which implies that }
\]

\( \tau_i \) can be appropriately bounded above and below \( \forall i = 1, n \), without altering the optimization problem’s infimum. Thus, all problem variables are bounded above and below and the feasible region is bounded. O.E.A.

**Appendix B**

It holds that:
Then the following holds:

\[
\frac{\partial h_{i,j}}{\partial C_i^{k}} = \begin{cases} 
1 & \text{if } i = l + 1, j = k; \forall l = 1, n-1; \forall k = 1, m \\
0 & \text{if } i = l + 1, j \neq k; \forall j = 1, m; \forall l = 1, n-1; \forall k = 1, m
\end{cases}
\]

\[
\frac{\partial h_{i,j}}{\partial \tau_i} = \begin{cases} 
R^j \left( \left\{ C_i^p \right\}_{p=1}^m \right) & \text{if } i = l; \forall j = 1, m; \forall l = 1, n \\
0 & \text{if } i \neq l; \forall i = 1, n; \forall j = 1, m; \forall l = 1, n
\end{cases}
\]

\[
\frac{\partial h_{n+1}}{\partial C^{k}} = \begin{cases} 
\frac{\partial f \left( \left\{ C_i^k \right\}_{k=1}^m \right)}{\partial C_i^{k}}; l = n; \forall k = 1, m \\
\frac{\partial f \left( \left\{ C_i^k \right\}_{k=1}^m \right)}{\partial C_i^{k}} = 0; l \neq n; \forall k = 1, m
\end{cases}
\]

\[
\frac{\partial h_{n+1}}{\partial \tau_i} = 0; \forall l = 1, n
\]

Then the following holds:

\[
\sum_{i=1}^{n} \sum_{j=1}^{m} \alpha_{i,j} \left( \frac{\partial h_{i,j}}{\partial x} \right) + \alpha_{n+1} \left( \frac{\partial h_{n+1}}{\partial x} \right) = 0 \Leftrightarrow
\]

\[
\left\{ \begin{aligned}
\sum_{i=1}^{n} \sum_{j=1}^{m} \alpha_{i,j} \left( \frac{\partial h_{i,j}}{\partial C_i^{k}} \right) + \alpha_{n+1} \left( \frac{\partial h_{n+1}}{\partial C_i^{k}} \right) = 0 & \forall l = 1, n-1; \forall k = 1, m \\
\sum_{i=1}^{n} \sum_{j=1}^{m} \alpha_{i,j} \left( \frac{\partial h_{i,j}}{\partial C_n^{k}} \right) + \alpha_{n+1} \left( \frac{\partial h_{n+1}}{\partial C_n^{k}} \right) = 0 & \forall k = 1, m \\
\sum_{i=1}^{n} \sum_{j=1}^{m} \alpha_{i,j} \left( \frac{\partial h_{i,j}}{\partial \tau_i} \right) + \alpha_{n+1} \left( \frac{\partial h_{n+1}}{\partial \tau_i} \right) = 0 & \forall l = 1, n
\end{aligned} \right\}
\]
\[
\left\{ \begin{array}{l}
\sum_{i=1}^{n} \sum_{j=1}^{m} \alpha_{i,j} \cdot 0 + \sum_{j=1}^{m} \alpha_{i,j} \cdot \tau_{i} \frac{\partial R^i \left( \{ C^p_l \}_{p=1}^m \} \right)}{\partial C^k_l} - \alpha_{i,k} \cdot \left( 1 - \tau_{i} \frac{\partial R^k \left( \{ C^p_l \}_{p=1}^m \} \right)}{\partial C^k_l} \right) = \right.
\\
\left. \sum_{j=1}^{m} \alpha_{l+1,j} \cdot 0 + \alpha_{l+1,k} \cdot 1 + \alpha_{n+1} \cdot 0 = 0; \quad \forall l = 1, n-1; \quad \forall k = 1, m \right\}
\\
\left\{ \begin{array}{l}
\sum_{i=1}^{n} \sum_{j=1}^{m} \alpha_{i,j} \cdot 0 + \sum_{j=1}^{m} \alpha_{i,j} \cdot \tau_{n} \frac{\partial R^i \left( \{ C^p_n \}_{p=1}^m \} \right)}{\partial C^k_n} - \alpha_{n,k} \cdot \left( 1 - \tau_{n} \frac{\partial R^k \left( \{ C^p_n \}_{p=1}^m \} \right)}{\partial C^k_n} \right) = \right.
\\
\left. \sum_{j=1}^{m} \alpha_{n+1,j} \cdot 0 + \alpha_{n+1,j} \cdot R^i \left( \{ C^p_l \}_{p=1}^m \} \right) + \alpha_{n+1} \cdot 0 = 0; \quad \forall l = 1, n \right\}
\\
\left\{ \begin{array}{l}
\sum_{j=1}^{m} \alpha_{i,j} \cdot \tau_{j} \frac{\partial R^i \left( \{ C^p_l \}_{p=1}^m \} \right)}{\partial C^k_l} - \alpha_{i,k} + \alpha_{l+1,k} = 0; \quad \forall l = 1, n-1; \quad \forall k = 1, m \right\}
\\
\left\{ \begin{array}{l}
\sum_{j=1}^{m} \alpha_{n,j} \cdot \tau_{n} \frac{\partial R^i \left( \{ C^p_n \}_{p=1}^m \} \right)}{\partial C^k_n} - \alpha_{n,k} + \alpha_{n+1} \cdot \frac{\partial f \left( \{ C^k_n \}_{k=1}^m \} \right)}{\partial C^k_n} = 0; \quad \forall k = 1, m \right\}
\\
\left\{ \begin{array}{l}
\sum_{j=1}^{m} \sum_{j=1}^{m} \alpha_{i,j} \cdot 0 + \sum_{j=1}^{m} \alpha_{i,j} \cdot R^i \left( \{ C^p_l \}_{p=1}^m \} \right) + \alpha_{n+1} \cdot 0 = 0; \quad \forall l = 1, n \right\}
\end{array} \right.
\]
\[
\begin{align*}
A_{l+1} &= \left[ I - \tau \cdot \frac{\partial R}{\partial C} \right] \cdot A_l; \quad l = 1, n-1 \\
\alpha_{n+1} \frac{\partial f \left( \{ C_i^k \}_{k=1}^m \right)}{\partial C_n^k} &= \left( I - \tau_n \cdot \frac{\partial R}{\partial C_n} \right) \cdot A_n; \\
R_j^T \cdot A_j &= 0; \quad l = 1, n
\end{align*}
\]
Under the Theorem’s assumption that is an invertible matrix and that , the above statement implies that , and . This implies that the regular point definition is satisfied for all that belong to the positive orthant of , and satisfy the equality constraints , and of the above optimization problem P2, and the Theorem’s assumptions. O.E.D.

Appendix C

The 1st order necessary conditions of optimality to P2 are:

\[
\begin{align*}
\left\{ \nabla_L L = 0 \right\} & \iff \\
\left\{ \nabla_x L = 0 \right\}
\end{align*}
\]
\[ \begin{align*} 
\left\{ \begin{array}{l} 
C_{i-1}^j - C_i^j + \tau_i \cdot R^j (\{C^k_i\}_{k=1}^m) = 0; \; \forall i = 1, n; \; \forall j = 1, m \\
\left\{ \begin{array}{c} 
C_{n}^m \end{array} \right\} - \delta = 0 \\
\end{array} \right. \\
\end{align*} \]
For the case of linear kinetics, the following holds:

\[
\begin{align*}
C_{i-1}^j - C_i^j + \tau_i \cdot R_i^j \left( \left\{ C_i^k \right\}_{k=1}^m \right) = 0 & \quad \forall i = 1, n; \forall j = 1, m \\
f \left( \left\{ C_i^k \right\}_{k=1}^m \right) - \delta = 0 \\
\Lambda_{i+1} = \left( I - \tau_i \cdot \frac{\partial R}{\partial C_i} \right) \Lambda_i & \forall i = 1, n-1 \\
\left( I - \tau_n \cdot \frac{\partial R}{\partial C_n} \right) \Lambda_n = \lambda_{n+1} \frac{\partial f}{\partial C_n} \\
a \beta_i \tau_i^{a-1} + \tau_i^{T} \Lambda_i = 0 & \forall i = 1, n
\end{align*}
\]

O.E.A.

4.12.2. Appendices D-E

Appendix D

For the case of linear kinetics, the following holds:

\[
\begin{align*}
R_i = R \cdot C_i & \forall i = 1, n \\
\frac{\partial R}{\partial C_i} = R^T & \forall i = 1, n \\
C_{i-1} = \left( I - \tau_i \cdot R \right) C_i & \forall i = 1, n
\end{align*}
\]

Then, based on the optimality conditions identified in theorem 3, it holds that:

\[
\begin{align*}
\Lambda_{i+1} = \left( I - \tau_i \cdot R^T \right) \Lambda_i; & \quad i = 1, n-1; \\
\left( I - \tau_n \cdot R^T \right) \Lambda_n = \lambda_{n+1} \frac{\partial f}{\partial C_n}; \\
a \beta_i \tau_i^{a-1} + \tau_i^{T} \Lambda_i = 0 & \forall i = 1, n;
\end{align*}
\]

The last of the above optimality conditions can be equivalently stated as:

\[
a \beta_i \tau_i^{a-1} + \tau_i^{T} \Lambda_i = 0 & \forall i = 1, n; \\
a \beta_i \left( \tau_i^{a-1} - \tau_{i+1}^{a-1} \right) + \tau_i^{T} \Lambda_i - \tau_{i+1}^{T} R^T \left( I - \tau_i^{T} R^T \right) \Lambda_i = 0 & \forall i = 1, n-1
\]
\( a \beta \left( \tau_i^{a-1} - \tau_{i+1}^{a-1} \right) + C_i^T R \Lambda_i - C_{i+1}^T (I - \tau_i R)^T \Lambda_i = 0 \quad \forall i = 1, n-1 \)

\( a \beta \left( \tau_i^{a-1} - \tau_{i+1}^{a-1} \right) + C_{i+1}^T (I - \tau_{i+1} R)^T \Lambda_i - C_i^T (I - \tau_i R)^T \Lambda_i = 0 \quad \forall i = 1, n-1 \)

\( a \beta \left( \tau_i^{a-1} - \tau_{i+1}^{a-1} \right) + (\tau_i - \tau_{i+1}) C_i^T R^T \Lambda_i = 0 \quad \forall i = 1, n-1 \)

It is clear that the last \( n-1 \) of the above equations are satisfied when \( \tau_i = \tau_{i+1} = \tau \quad \forall i = 1, n-1 \).

Based on the assumption that the matrices \((I - \tau R) \forall i = 1, n\) are invertible, these equal residence times can be evaluated by solving the equation \( f \left( \left[ I - \tau R \right]^n C_0 \right) - \delta = 0 \). The concentrations \( C_i \quad \forall i = 1, n \) are then evaluated using the mass balances

\( C_{i+1} = (I - \tau_i R) C_i \quad \forall i = 1, n \).

The remaining necessary conditions of optimality can then be readily satisfied, by selecting \( \Lambda_1 \) and \( \lambda_{n+1} \) so that

\[
\begin{align*}
& \left[ I - \tau R^T \right]^n \Lambda_1 - \lambda_{n+1} \frac{\partial f}{\partial C_n} = 0 \\
& a \beta \tau^{a-1} + C_0^T \left[ I - \tau R^T \right] R^T \Lambda_1 = 0
\end{align*}
\]

simply evaluating \( \Lambda_2, \ldots, \Lambda_n \) using equations \( \Lambda_{i+1} = (I - \tau \cdot R^T) \Lambda_i \); \( i = 1, n-1 \). Then all necessary conditions of optimality are satisfied. O.E.D.

**Appendix E**

**Lemma 1**

Consider the following optimization problem:

\[
\begin{align*}
\min_{\tau_i \geq 0, \tau_j \geq 0} & \quad (n-1) \left( \tau_1 \right)^a + \left( \tau_2 \right)^a \\
\text{s.t.} & \\
& \frac{C_0}{C_{n-1}} = \left( k \tau_1 + 1 \right)^{n-1} \\
& \frac{C_{n-1}}{C_n} = \left( k \tau_2 + 1 \right)
\end{align*}
\]
Where \( a \in (0,1), 0 < C_n < C_0 \), \( C' = \frac{C_0}{C_n} \) are known parameters.

This optimization problem possesses either one or three extrema:

If \( C' \left( a \frac{(-n-a+1)}{(-an+a-1)} \right)^{n-1} < \frac{1}{C_n} \), then there exists only one extremum, the \( n \) equal reactor solution is a maximum, and the globally optimal sequence consists of \( n-1 \) equal reactor, or one reactor.

If \( C' \left( a \frac{(-n-a+1)}{(-an+a-1)} \right)^{n-1} > \frac{1}{C_n} \), then there exist three extrema, the \( n \) equal reactor solution is a minimum, and the globally optimal sequence consists of \( n \) equal reactors, \( n-1 \) equal reactor, or one reactor.

Therefore, the optimal solution always consists of equal reactors, or a single reactor.

**Proof:**

Consider:

\[
\begin{align*}
\text{min}_{\tau_1 \geq 0, \tau_2 \geq 0} \left( n-1 \right) \left( \tau_1 \right)^a + \left( \tau_2 \right)^a \\
\text{s.t.} \quad \frac{C_0}{C_{n-1}} = (k \tau_1 + 1)^{n-1} \\
\quad \frac{C_{n-1}}{C_n} = (k \tau_2 + 1)
\end{align*}
\]

\[\Leftrightarrow \quad \begin{align*}
\text{min}_{\tau_1 \geq 0, \tau_2 \geq 0} \left( n-1 \right) \left( \tau_1 \right)^a + \left( \tau_2 \right)^a \\
\text{s.t.} \quad \frac{C_0}{C_n} = \left( k \tau_1 + 1 \right)^{n-1} \left( k \tau_2 + 1 \right)
\end{align*}\]

Define \( \frac{C_0}{C_n} = C' \), \( x \geq k \tau_2 + 1 \)

The problem’s Lagrangian and associated necessary conditions of optimality are:
\[ L = (n-1)(\tau_1)^a + (\tau_2)^a + \lambda \left( C - (k\tau_1 + 1)^{a-1} (k\tau_2 + 1) \right) \]

\[
\begin{align*}
\frac{\partial L}{\partial \tau_1} &= (n-1)a(\tau_1)^{a-1} - \lambda (n-1)(k\tau_1 + 1)^{a-2} (k\tau_2 + 1) = 0 \\
\frac{\partial L}{\partial \tau_2} &= a(\tau_2)^{a-1} - \lambda (k\tau_1 + 1)^{a-1} = 0 \\
C' &= (k\tau_1 + 1)^{a-1} (k\tau_2 + 1) \quad \tau_1, \tau_2 > 0
\end{align*}
\]

\[
\begin{align*}
a(\tau_1)^{a-1} - \lambda (k\tau_1 + 1)^{a-2} (k\tau_2 + 1) &= 0 \\
\frac{a(\tau_2)^{a-1}(k\tau_2 + 1)}{(k\tau_1 + 1)} - \lambda (k\tau_1 + 1)^{a-2} (k\tau_2 + 1) &= 0 \quad a > 0 \\
C' &= (k\tau_1 + 1)^{a-1} (k\tau_2 + 1)
\end{align*}
\]

\[(\tau_1)^{a-1} = (\tau_2)^{a-1} \frac{(k\tau_2 + 1)}{(k\tau_1 + 1)} \iff x - 1 - \left( C^{(n-1)(a-1)} x^{(n-1)(a-1)} - C^{(n-1)(a-1)} x^{(n-1)(a-1)} \right) = 0
\]

Define the following function:

\[ g : \mathbb{R} \rightarrow \mathbb{R}; \; x \in (1, C') \rightarrow g(x) \equiv (n-1) \left( \frac{C x^{(n-1)(a-1)} - 1}{k} \right)^a + \left( \frac{x-1}{k} \right)^a \]

Where \[ \min_{\tau_1 > 0, \tau_2 > 0} (n-1)(\tau_1)^a + (\tau_2)^a \iff \min_{1 \leq x < C} \left( \frac{C x^{(n-1)(a-1)} - 1}{k} \right)^a + \left( \frac{x-1}{k} \right)^a \iff \min g(x) \]

Define the function

\[ f : \mathbb{R} \rightarrow \mathbb{R}; \; x \in (1, C') \rightarrow f(x) \equiv x - 1 - \left( C^{(n-1)(a-1)} x^{(n-1)(a-1)} - C^{(n-1)(a-1)} x^{(n-1)(a-1)} \right) \]

195
Evaluation of $f(x)$ at the bounds and equal reactor solution yields:

$$f(1) < 0; \quad f(C') > 0; \quad f\left(\frac{1}{C^n}\right) = 0$$

Lemmas 1.1, 1.2 and 1.3 are next introduced:

**Lemma 1.1:** $g'(x) > 0 \iff f(x) < 0$

Proof:

$$g'(x) = \left[ a(x-1)^{n-1} + (n-1)C^{\frac{1}{n-1}} \left(\frac{-1}{n-1}\right) x^{\frac{1}{n-1}} \cdot a \left( C^{\frac{1}{n-1}} \left(\frac{-1}{n-1}\right) x^{\frac{1}{n-1}} - 1\right) \right] \left(\frac{1}{k}\right)^a$$

$$g'(x) > 0 \iff a(x-1)^{n-1} - C^{\frac{n}{n-1}} \cdot a \left( C^{\frac{1}{n-1}} \left(\frac{-1}{n-1}\right) x^{\frac{1}{n-1}} - 1\right) \left(\frac{1}{k}\right)^a$$

$$\frac{C^{\frac{1}{n-1}} \left(\frac{-1}{n-1}\right) x^{\frac{1}{n-1}} - 1}{x-1} \leq 1$$

$$x - 1 - C^{\frac{1}{n-1}} x^{\frac{1}{n-1}} a_n < 0 \iff f(x) < 0$$

O.E.A.

**Lemma 1.2:** $f\left(\frac{a(-n+a+1)}{(-an+a-1)}\right)^{n-1} > 0 \iff C' < a^n (n-1) \left(\frac{-n+a+1}{(-an+a-1)}\right)^{n-1}$
Proof:

\[ f'(C \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1}) > 0 \Leftrightarrow 1 - \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{-an} \left( \frac{C^{(a-1)}}{(n-1)(a-1)} \right)^{-a} \left( \frac{2a-an-a^2+n-1}{(-an+a-1)} \right) < 0 \]

\[ C^{(a-1)} > \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{-an} \left( \frac{1}{(n-1)(a-1)} \right) \left( \frac{2a-an-a^2+n-1}{(-an+a-1)} \right) \]

Therefore: \( f'(C \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1}) < 0 \Leftrightarrow C < \left( \frac{an-a^2}{an-a+1} \right)^{-n} \left( \frac{n-1+a}{(n-1)(an-a+1)} \right)^{a-1} \)

O.E.A.

Lemma 1.3: The function \( f(x) \) is convex at the equal reactor solution \( x = C^{\frac{1}{n}} \) if \( a \leq C^{\frac{1}{n}} \)

Proof:

If \( f(x) \) is convex for \( x \in \left[ C \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1}, C \right] \), then \( f(x) \) is convex at the equal reactor solution if:
\[
C \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1} \leq C_n^1 \iff \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1} \leq \frac{-an+a-1}{(-n-a+1)} \iff a \leq \frac{(-an+a-1)}{(-n-a+1)}.
\]

Also:
\[
C_n^{-1} \left( \frac{-an+a-1}{(-n-a+1)} \right) \leq C_n^{-1} \iff \frac{-an+a-1}{(-n-a+1)} \leq 1 \iff -an+2a-2+n \geq 0 \iff (2-n)(a-1) \geq 0,
\]

which is true since \( n \geq 2 \), and \( a \in (0,1) \). Thus \( a \leq \frac{-an+a-1}{(-n-a+1)} \leq C_n^{-1} \Rightarrow a \leq C_n^{-1} \) O.E.Δ.

It holds that that the first and second derivative of \( f \) are such that:
\[
f'(x) = 1 - \left( \frac{-an+a-1}{(n-1)(a-1)} \right)^{n-1} x^{-an} \left( \frac{-n}{(n-1)(a-1)} \right)^{n-1} \left( \frac{-an+a-1}{(n-1)(a-1)} \right)^{n-2} \]
\[
f''(x) = -\left( \frac{-n}{(n-1)(a-1)} \right)^{n-1} x^{-an} \left( \frac{-an+a-1}{(n-1)(a-1)} \right)^{n-2} \]

Evaluation of the derivative \( f'(x) \) at the bounds and equal reactor solution yields:
\[
f'(1) = 1 - \frac{1}{(n-1)(a-1)} \left( C_n^{(n-1)}(-n-a+1) \right)
\]
\[
f'(C_n^{\frac{1}{n}}) = 1 - \frac{1}{(n-1)(a-1)} \left( -n-a+1 - C_n^{-1}(-n) \right) ;
\]
\[
f'(C_n^{\frac{1}{n}}) > 0 \iff a = C_n^{-1}
\]

198
\[ f'(C) = 1 + C^{(a-1)} \left( \frac{1}{(n-1)} \right) > 0 \]

The sign of the second derivative \( f''(x) \) varies only once at \( x = C \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1} \) such that:

\[ f''(x) > 0 \iff x = C \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1} \]

which means that \( f(x) \) is concave for and convex for \( x \in \left[ 1, C \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1} \right] \) and convex for \( x \in \left[ C \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1}, C \right] \).

It can be verified that at \( x = C \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1} \), \( f'(x) \) is such that:

\[ f' \left( C \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1} \right) = 1 - \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1} \left( \frac{2a-an-a^2 + n-1}{n-1(a-1)} \right) \left( C^{(a-1)} \right)^{-a} \]

Therefore, in addition to the results of lemma 4.1-4.3, it has been established that:

- \( f(1) < 0 \), \( f(C) > 0 \), \( f'(C) > 0 \), \( f \left( \frac{1}{C^n} \right) = 0 \)
- \( f' \left( \frac{1}{C^n} \right) > 0 \iff \frac{1}{a} > \frac{1}{C^n} \iff \frac{1}{a} = \frac{1}{\frac{1}{C^n}} \)
- \( f''(x) < 0 \ \forall x \in \left[ 1, C \left( \frac{a^2+an-a}{1+an-a} \right)^{n-1} \right] \); \( f''(x) > 0 \ \forall x \in \left[ C \left( \frac{a^2+an-a}{1+an-a} \right)^{n-1}, C \right] \)

Consider the following cases and associated sub-cases:
Case 1: $C\left(\frac{a(-n-a+1)}{(-an+a-1)}\right)^{n-1} < 1$

Then $f''(x) > 0 \ \forall x \in (1, C) \iff f(x)$ is convex $\forall x \in (1, C) \iff f'(x)$ is increasing throughout $\left(1, C\right)$. From lemma 1.3, it then holds that $a < C^{-\frac{1}{n}}$, which was earlier shown equivalent to $f'\left(C^{\frac{1}{n}}\right) > 0$. Since $f'(C) > 0$, consider the following two sub-cases:

Case 1.1: $f'(1) < 0$

Then there $\exists \beta \in \left(1, C^{\frac{1}{n}}\right) : f'(\beta) = 0$ Therefore $f$ is decreasing in $(1, \beta)$ and increasing in $(\beta, C)$. Since $f(1) < 0$ and $f$ is decreasing in $(1, \beta)$, then $f(\beta) < 0$ and $f$ has no roots in $(1, \beta)$.

In turn, $f(\beta) < 0$, $f(C) > 0$ and $f$ is increasing in $(\beta, C)$, imply that there is one and only one root in $(\beta, C)$. Since $f\left(C^{\frac{1}{n}}\right) = 0$ and $C^{\frac{1}{n}} \in (\beta, C)$, this single root is at $C^{\frac{1}{n}}$.

Case 1.2: $f'(1) > 0$

Therefore, $f'(x) > 0 \ \forall x \in (1, C) \Rightarrow f$ is increasing throughout $(1, C)$. Since $f\left(C^{\frac{1}{n}}\right) = 0$ and $C^{\frac{1}{n}} \in (1, C)$, $f$ has a single root in $(1, C)$ which is at $C^{\frac{1}{n}}$. 

200
For both sub-cases 1.1 and 1.2 the following holds true (from lemma 1.1):

\[
\begin{align*}
\begin{cases}
  f(x) < 0 & \forall x \in \left(1, C^\frac{1}{\alpha}\right) \\
  f(x) = 0 & x = C^\frac{1}{\alpha} \\
  f(x) > 0 & \forall x \in \left(C^\frac{1}{\alpha}, C\right)
\end{cases}
\end{align*}
\quad \Leftrightarrow
\begin{align*}
\begin{cases}
  g'(x) > 0 & \forall x \in \left(1, C^\frac{1}{\alpha}\right) \\
  g'(x) = 0 & x = C^\frac{1}{\alpha} \\
  g'(x) < 0 & \forall x \in \left(C^\frac{1}{\alpha}, C\right)
\end{cases}
\end{align*}
\]

Thus, \( g(x) \) is increasing in \( \left(1, C^\frac{1}{\alpha}\right) \), decreasing in \( \left(C^\frac{1}{\alpha}, C\right) \), and has a unique maximum at \( C^\frac{1}{\alpha} \).

The minimum of \( \nu \) occurs at either \( x = 1 \) or \( x = C' \), and its minimal objective function value is

\[ g(1) = (n-1) \left(C^\frac{1}{\alpha-1} - 1\right)^a \quad \text{or} \quad g(C') = (C' - 1)^a. \]

Thus in this case, the global minimum corresponds to either \( n-1 \) equal reactors or one reactor.

Case 2: \( C \left(\frac{a(-n-a+1)}{(-an+a-1)}\right)^{\alpha-1} > 1 \)

The following holds true:

\[
\begin{align*}
\begin{cases}
  f''(x) < 0 & \forall x \in \left[1, C \left(\frac{a(-n-a+1)}{(-an+a-1)}\right)^{\alpha-1}\right] \\
  f''(x) > 0 & \forall x \in \left[C \left(\frac{a(-n-a+1)}{(-an+a-1)}\right)^{\alpha-1}, C\right]
\end{cases}
\end{align*}
\]

Two sub-cases are then considered:
Case 2.1: \( C \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1} > C^n > 1 \)

Then \( f^n \left( C^n \right) < 0 \), \( f'(x) \) is decreasing in \( \left[ 1, C' \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1} \right) \) and \( f'(x) \) is increasing in \( \left[ C' \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1}, C \right) \). From lemma 1.3, \( C' \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1} > C^n \Rightarrow a > C^{-1} \), which in turn is equivalent to \( f^n \left( C^{-1} \right) < 0 \). Since \( f'(x) \) is increasing in \( \left[ C' \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1}, C \right) \),

\( f^n \left( C^{-1} \right) < 0 \), and \( f'(C) > 0 \), this implies \( f'(x) \) has one root in \( \left[ C' \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1}, C \right) \), call it \( \beta_2 \). Then \( f'(\beta_2) = 0 \), and \( \beta_2 \in \left[ C' \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1}, C \right) \). Consider sub-cases 2.1.1 and 2.1.2:

Case 2.1.1: \( f'(1) < 0 \)

Since \( f'(1) < 0 \), \( f^n \left( C^{-1} \right) < 0 \), \( f'(x) \) is decreasing in \( \left[ 1, C' \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1} \right) \), and

\( C' \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1} > C^{-1} > 1 \), then \( f'(x) < 0 \) \( \forall x \in \left[ 1, C' \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1} \right) \). Since,
\[ f'(C) \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1} < 0, \quad C > \beta_2 > C' \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1} \] and \( f'(x) \) is increasing in

\[ C' \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1}, C' \], then \( f'(\beta_2) = 0 \). It follows that:

\[ f'(x) < 0 \quad \forall x \in \left[ C' \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1}, \beta_2 \right], \text{ and } f'(x) > 0 \quad \forall x \in (\beta_2, C'). \] Combining then above results suggests that \( f \) is decreasing in \((1, \beta_2)\) and increasing in \((\beta_2, C')\). However, it is known that \( f(1) < 0, \quad f \left( C^n \right) = 0, \quad C > \beta_2 > C' \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{1/n} > C'^n > 1, \) and since \( f \) is decreasing in \((1, \beta_2)\), then \( f \) is decreasing in \((1, C'^n)\). This is in contradiction with the continuity of \( f(x) \) on \((1, C')\) making this case impossible.

**Case 2.1.2: \( f'(1) > 0 \)**

Since \( f'(1) > 0, \quad f' \left( C^n \right) < 0, \quad f'(x) \) decreasing in \([1, C \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1}] \), and

\[ C > \beta_2 > C' \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1} > C'^n > 1, \text{ then } f'(x) \text{ has one root in } \left(1, C'^n \right), \text{ call it } \beta_i \text{ such that the following holds true:} \]

\[ C > \beta_2 > C' \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1} > C'^n > \beta_i > 1, \text{ and } f'(\beta_i) = 0, \text{ and } f'(\beta_2) = 0. \]
Since, in addition, \( f'(x) \) is increasing in \( \left[ C \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1}, C' \right) \), then \( f'(x) > 0 \ \forall x \in (1, \beta_1) \), \( f'(x) < 0 \ \forall x \in (\beta_1, \beta_2) \), and \( f'(x) > 0 \ \forall x \in (\beta_2, C') \). In turn, this implies \( f \) is increasing in \( (1, \beta_1) \), decreasing in \( (\beta_1, \beta_2) \), and increasing in \( (\beta_2, C') \). Since \( f \left( \frac{1}{n} \right) = 0 \) and

\[ \beta_1 < C_{\frac{1}{n}} < C \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1} < \beta_2 < C' \]

must hold true, \( f(\beta_1) > 0 \), and \( f(\beta_2) < 0 \). Since

\[ f(1) < 0, \ f(x) \text{ is increasing in } (1, \beta_1), \text{ and } f(\beta_1) > 0, \ f \text{ possesses one root in } (1, \beta_1) \text{ call it } \rho_1. \]

In addition, since \( \beta_1 < C_{\frac{1}{n}} < \beta_2 \), \( f(x) \) is decreasing in \( (\beta_1, \beta_2) \), and \( f \left( \frac{1}{n} \right) = 0 \), \( f \) possesses one root in \( (\beta_1, \beta_2) \), that at \( C_{\frac{1}{n}} \). Finally, since \( f(\beta_2) < 0 \), \( f(x) \) is increasing in \( (\beta_2, C') \), and \( f(C) > 0 \), \( f \) possesses one root in \( (\beta_2, C') \) call it \( \rho_2 \). Therefore, the function \( f \) has three roots in \( (1, C') \), one of which is at \( C_{\frac{1}{n}} \).

The above discussion can be summarized as follows:
The above implies \( g(x) \) is increasing in \((1, \rho_1)\), decreasing in \(\rho_1, C^{\frac{1}{n}}\), increasing in \(C^{\frac{1}{n}}, \rho_2\), and decreasing in \((\rho_2, C)\). Thus, \( \rho_1 \) is a local maximum, \( C^{\frac{1}{n}} \) is a local minimum, and \( \rho_2 \) is a local maximum. Thus, the global minimum is either at \( x = C^{\frac{1}{n}} \) with objective function value

\[
g\left(C^{\frac{1}{n}}\right) = (n-1) \left(\left(C^{\frac{1}{n}}\right)^{\frac{1}{n-1}} - 1\right)^a + \left(C^{\frac{1}{n}} - 1\right)^a = n\left(C^{\frac{1}{n}} - 1\right)^a,
\]

or at \( x = 1 \vee x = C \) with objective function value \( g(1) = (n-1)\left((C)^{\frac{1}{n-1}} - 1\right)^a \), or \( g(C') = (C' - 1)^a \). In this case, the global minimum becomes \( n \) -equal reactors, \( n-1 \) equal reactors, or one reactor.
Case 2.2: \(1 < C \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1} < C_n \)

\(f'(x)\) is decreasing in \([1, C \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1}]\) and increasing in

\(C \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1}, C'\). Based on lemma 1.3, \(C \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1} < C_n^{-1}\) implies that

\(a < C_n^{-1}\), equivalent to \(f'(C_n^{-1}) > 0\). Given that \(f'(x)\) is increasing in \(C \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1}, C'\)

\(C \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1} < C_n, f'(C_n^{1}) > 0, \text{ and } f'(C') > 0\), it then holds

\(f'(x) > 0 \quad \forall x \in \left( C_n^{1}, C' \right)\).

Case 2.2.1: \(f' \left( C \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1} \right) > 0\)

Since \(f' \left( C \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1} \right) > 0, f'(C') > 0\) and \(f'(x)\) is increasing in

\(C \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1}, C'\), it then holds \(f'(x) > 0 \quad \forall x \in \left( C \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1}, C' \right)\). Since

\(f'(x)\) is decreasing in \([1, C \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1}]\), and \(f' \left( C \left( \frac{a(-n-a+1)}{(-an+a-1)} \right)^{n-1} \right) > 0\), then
\[
f'(x) > 0 \quad \forall x \in \left(1, C \left(\frac{a(-n-a+1)}{-an+a-1}\right)^{-1}\right).
\]
Combining the above results then yields
\[
f'(x) > 0 \quad \forall x \in (1, C^{-1}).\]

Therefore, \( f \) is increasing in \((1, C^{-1})\) and since \( f \left(C^{-1}\right) = 0 \) then \( f \)
possesses one and only one root in \((1, C^{-1})\).

The above discussion can be summarized as follows:

\[
\begin{align*}
& \begin{cases} f(x) < 0 \quad \forall x \in \left(1, C^{-1}\right) \\
f(x) = 0 \quad x = C^{-1} \\
f(x) > 0 \quad \forall x \in \left(C^{-1}, C\right) 
\end{cases} \quad \Leftrightarrow \quad \begin{cases} g'(x) > 0 \quad \forall x \in \left(1, C^{-1}\right) \\
g'(x) = 0 \quad x = C^{-1} \\
g'(x) < 0 \quad \forall x \in \left(C^{-1}, C\right) 
\end{cases}
\end{align*}
\]

Case 2.2.2: \( f' \left(C \left(\frac{a(-n-a+1)}{-an+a-1}\right)^{-1}\right) < 0 \)

From the proof of lemma 1.3, \( a \leq C^{-1} \left(\frac{-an+a-1}{-n-a+1}\right) \Leftrightarrow C^{-1} \leq \left(\frac{an-a+1}{an-a+a^2}\right)^n \)

In addition, \( \left(\frac{n-1+a}{(n-1)(an-a+1)}\right) \leq 1 \Leftrightarrow 0 \leq an(n-2) \), which is always true for \( n \geq 2 \), and

\( a \in (0,1) \). This leads to the conclusion that \( C^{-1} < \left(\frac{an-a+1}{an-a+a^2}\right)^n \left(\frac{n-1+a}{(n-1)(an-a+1)}\right)^{\frac{a-1}{a}}. \)
Nevertheless, lemma 1.2 stipulates that \( f^* \left( \frac{a(-n-a+1)^{n-1}}{(-an+a-1)} \right) \leq 0 \)

\[ \Leftrightarrow C = \left( \frac{an-a+a^2}{an-a+1} \right)^{-n} \left( \frac{(n-1+a)}{(n-1)(an-a+1)} \right)^{a-1} \, . \]

Therefore this case is impossible.

O.E.Δ.

Having concluded that the optimal reactor sequence always consists of equal reactors or one reactor, lemma 2 is used to determine the number of equal reactors required in a globally optimal sequence.

**Lemma 2**

\[ \mu_n \triangleq \inf_{\tau \in \mathbb{R}, \; \tau \neq 1} \sum_{i=1}^{n} \tau_i^a \]

Let \( a \in (0,1), \; C' > 1, \; n \in \mathbb{N} \), \( s.t. \)

\[ C' = \prod_{i=1}^{n} (k\tau_i + 1) \]

Define \( \tau^*_\rho \triangleq \left\{ \tau^{*\rho}_i \right\}_{i=1}^{n} \triangleq \left\{ \frac{1}{k} \left( \frac{C'-1}{k} \right)^{\rho} \right\}_{i=1}^{n} \), \{0\}_{i=p+1}^{n} \forall i = 1, n, \mu_{\rho} \triangleq \left( \frac{1}{k} \right)^a p \left( C'^a - 1 \right)^a \) and

\[ \hat{\rho} \triangleq \arg \min_{\rho \in \mathbb{R}} \mu_{\rho} = \arg \min_{\rho \in \mathbb{R}} p \left( C'^a - 1 \right)^a , \text{ and } n_u \text{ to be the maximum number of allowable reactors.} \]

Then:
a. For any \( n \) \( \exists p \in \{1, \cdots, n\}; \{\tau_i^p\}_{i=1}^n \) is a global minimum of \( \mu \).

b. \( \inf_{n \in \mathbb{N}} \mu_n = \mu_p = \arg \min \left( \frac{1}{C^p} - 1 \right)^n \) where:

\[
\text{If } \{ C'a \leq 1 \lor \{ C'a > 1 \land C' - 1 - a \ln (C')C' > 0 \}\} \Rightarrow \hat{p} = 1
\]

\[
\text{If } \{ C'a > 1 \land C' - 1 - a \ln (C')C' < 0 \} \Rightarrow \begin{cases} \text{if } n_u < \text{int} (\hat{x}) \Rightarrow \hat{p} = n_u \\ \text{if } \text{int} (\hat{x}) < n_u < \text{int} (\hat{x}) + 1 \Rightarrow \hat{p} = \min (\text{int} (\hat{x}), n_u) \\ \text{if } \text{int} (\hat{x}) + 1 \leq n_u \Rightarrow \hat{p} = \min (\text{int} (\hat{x}), \text{int} (\hat{x}) + 1) \end{cases}
\]

\[
a > \max \left( \frac{1}{C'}, \frac{C' - 1}{\ln (C')C'} \right) \Rightarrow \exists \text{ unique } \hat{x} \in \left( 1, -\frac{\ln (C')}{\ln (a)} \right); \left( C' \hat{x} \right)^{1 - \frac{a \ln (C')}{\hat{x}}} - 1 = 0
\]

**Proof:**

a. Let \( \bar{\tau} = \{\bar{\tau}_i\}_{i=1}^n \) be a global minimum of \( \mu \) such that the cardinality \( N_{0_0}^\tau \) of the set

\[
S_{0_0}^\tau = \{i = 1, n: \bar{\tau}_i = 0\}, \text{ is the maximum possible over all the cardinalities of such sets corresponding to global minima of } \mu \text{. Then define } \bar{p} = n - N_{0_0}^\tau \text{. Therefore}
\]

\[
\mu = \sum_{i=1}^\bar{p} (\bar{\tau}_i)^\mu \land C' = \prod_{i=1}^\bar{p} (k\bar{\tau}_i + 1) \text{. By the definition of } \bar{p} \text{ it holds that } \bar{\tau}_i \neq 0 \forall i = 1, \bar{p} \text{ If all
\( \bar{\tau}, i = 1, \bar{\mu} \) are equal to each other, and since \( C' = \prod_{i=1}^{p} (k\bar{\tau}_i + 1) \), then it holds

\[
\bar{\tau}_i = \frac{C'_{\bar{\mu}} - 1}{k} \quad \forall i = 1, \bar{\mu} \quad \text{and} \quad \bar{\tau} = \bar{\tau}^{*_{\bar{\mu}}}. \]

If some \( \bar{\tau}_i \) are unequal to each other, then there exist two of these \( \bar{\tau}_i \)'s (say \( \bar{\tau}_j, \bar{\tau}_k \)) not equal to each other. Consider all the other \( \bar{\tau}_i \)'s fixed, and carry out the optimization

\[
\left\{ \begin{array}{l}
\sum_{i=1 \atop i \neq j, i \neq k}^{p} (\bar{\tau}_i)^a + \inf_{\tau_j \geq 0, \tau_k \geq 0} (\tau_j)^a + (\tau_k)^a \\
\end{array} \right. \quad \text{s.t.} \quad \frac{C'}{\prod_{i=1 \atop i \neq j, i \neq k}^{p} (k\bar{\tau}_i + 1)} = (k\tau_j + 1)(k\tau_k + 1)
\]

Since \( \frac{C'}{\prod_{i=1 \atop i \neq j, i \neq k}^{p} (k\bar{\tau}_i + 1)} > 1 \), application of lemma 1 to this two variable optimization problem suggests that its global optimum is assumed either at \( \tau_j = 0 \) or at \( \tau_k = 0 \) or at \( \tau_j = \tau_k \).

Assembling these two variable values with the rest of the \( \bar{\tau}_i \)'s yields a new global minimum for \( \mu \). The solutions \( \tau_j = 0 \) or \( \tau_k = 0 \) contradict the assumption that the cardinality \( N_0^7 \) was the maximum possible among all global minima of \( \mu \). Then only \( \tau_j = \tau_k \) is possible. If this new value of \( \tau_j, \tau_k \) is equal to the rest of the \( \bar{\tau}_i \)'s, then again the new \( \tau \) will equal \( \tau^{*_{\bar{\mu}}} \). If there exists one \( \bar{\tau}_i \) (say \( \bar{\tau}_l \)) not equal to the new equal value
of \( \tau_j, \tau_k \left( \tau_j = \tau_k \right) \), then consider all the other \( \tau_i \)'s fixed, and carry out the optimization

\[
\begin{bmatrix}
\sum_{i=1, i \neq j}^{n} (\tau_i)^a + \inf_{\tau_j \geq 0, \tau_i \geq 0} 2(\tau_j)^a + (\tau_i)^a \\
\text{s.t.} \\
C = \left( k\tau_j + 1 \right)^2 \left( k\tau_i + 1 \right)
\end{bmatrix}
\]

Since \( \frac{C}{\prod_{i=1, i \neq j}^{n} (k\tau_i + 1)} > 1 \) application of Lemma 1 to this two variable optimization problem again suggests that its global optimum is assumed either at \( \tau_j = \tau_k = 0 \), or at \( \tau_i = 0 \), or at \( \tau_j = \tau_k = \tau_i \). Using the same cardinality argument as above it is established that only \( \tau_j = \tau_k = \tau_i \) is possible. Repeated application of the above argument \( p - 1 \) times yields the conclusion that \( \tau^{*\bar{p}} \) is a global minimum of \( \mu \).

b. From part a. it is clear that \( \inf_{n \in \mathbb{N}} \mu_n = \mu_{\bar{p}} = \inf_{p \in \mathbb{N}} \left( \left( \frac{1}{C^{\frac{1}{p}} - 1} \right)^a \right) \). To identify \( \hat{p} \), define the function \( h: [1, \infty) \to \mathbb{R}; h: x \to h(x) \triangleq x \left( \frac{1}{C^{\frac{1}{x}} - 1} \right)^a \). Its first and second derivatives are:
\( \hat{h} : [1, \infty) \to \mathbb{R} ; \hat{h} : x \to \hat{h}(x) = \left( C_x - 1 \right)^{a-1} \left[ \frac{1}{C_x} - 1 - \frac{a \ln(C)}{x} \right] \)

\( \ddot{h} : [1, \infty) \to \mathbb{R} ; \ddot{h} : x \to \ddot{h}(x) = -(a-1) \left( C_x - 1 \right)^{a-2} \frac{\ln(C)}{x^2} C_x + \frac{1}{x^3} \left[ \frac{a \ln(C)}{x} \right]^2 \)

\( \left( C_x - 1 \right)^{a-2} \frac{a \ln(C)}{x} \left( C_x - 1 \right)^{1/a} \)

It is easy to verify that \( \forall x \in [1, \infty) \; \hat{h}(x) \geq 0 \Leftrightarrow \left( aC_x - 1 \right) \geq 0 \Leftrightarrow \ln(a) + \frac{1}{x} \ln(C) \geq 0 \)

\( \Leftrightarrow -\frac{\ln(C)}{\ln(a)} < x \) and thus \( h \) is strictly convex \( \forall x < -\frac{\ln(C)}{\ln(a)} \) and strictly concave

\( \forall x > -\frac{\ln(C)}{\ln(a)} \), and \( \hat{h} \) is strictly increasing \( \forall x < -\frac{\ln(C)}{\ln(a)} \). In addition it holds

\( \infty > h(1) = (C - 1)^a > 0 \), \( \infty > h \left( -\frac{\ln(C)}{\ln(a)} \right) = -\frac{\ln(C)}{\ln(a)} (a^{-1} - 1)^a > 0 \)

\( \hat{h}(1) = (C - 1)^{a-1} \left[ C - 1 - a \ln(C) C_x \right] \) and \( \hat{h} \left( -\frac{\ln(C)}{\ln(a)} \right) = \left( \frac{1}{a} - 1 \right)^{a-1} \left[ \frac{1}{a} - 1 - \ln \left( \frac{1}{a} \right) \right] > 0 \)

\( \lim_{x \to +\infty} h(x) = \lim_{x \to +\infty} \frac{\left( C_x - 1 \right)^a}{x} = \lim_{x \to +\infty} \frac{-a \left( C_x - 1 \right)^{a-1} \ln(C) C_x^{-2} - x^{-2}}{x} \)

\( = a \ln(C) \lim_{x \to +\infty} \frac{C_x^{-1}}{C_x - 1} = +\infty \)
Thus if $Ca \leq 1$ then $h$ is strictly concave $\forall x \in (1, \infty)$ and given the values of $h(1)$, $\lim_{x \to +\infty} h(x)$ it

then holds that $Ca \leq 1 \Rightarrow \inf_{x \in [1, \infty)} h(x) = h(1) = (C' - 1)^a$.

If $Ca > 1, C' - 1 - a \ln (C') C' > 0$ then $h$ is strictly convex $\forall x \in \left(1, -\frac{\ln (C')}{\ln (a)}\right)$, and strictly concave $\forall x \in \left(-\frac{\ln (C')}{\ln (a)}, \infty\right)$, $h$ is strictly increasing $\forall x < -\frac{\ln (C')}{\ln (a)}$, and $\hat{h}(1) > 0$. Then $h(x) > 0 \forall x \in \left(1, -\frac{\ln (C')}{\ln (a)}\right)$, which implies that $h$ is strictly increasing $\forall x \in \left(1, -\frac{\ln (C')}{\ln (a)}\right)$.

Combined with $\lim_{x \to +\infty} h(x) = +\infty$, this yields:

$$\{Ca > 1 \wedge C' - 1 - a \ln (C') C' > 0\} \Rightarrow \inf_{x \in [1, \infty)} h(x) = h(1) = (C' - 1)^a$$

If $Ca > 1, C' - 1 - a \ln (C') C' < 0$ then $h$ is strictly convex $\forall x \in \left(1, -\frac{\ln (C')}{\ln (a)}\right)$, and strictly concave $\forall x \in \left(-\frac{\ln (C')}{\ln (a)}, \infty\right)$, $h$ is strictly increasing $\forall x < -\frac{\ln (C')}{\ln (a)}$, and $\hat{h}(1) < 0$. Since

$$\hat{h} \left( -\frac{\ln (C')}{\ln (a)} \right) = \left( \frac{1}{a} \right)^{a-1} \left[ \frac{1}{a} - 1 - \ln \left( \frac{1}{a} \right) \right] > 0,$$

then there exists a unique

$$\hat{x} \in \left(1, -\frac{\ln (C')}{\ln (a)}\right); C' \left( 1 - \frac{a \ln (C')}{\hat{x}} \right) - 1 = 0.$$

Combined with $\lim_{x \to +\infty} h(x) = +\infty$, this yields:
\[ \{ C a > 1 \land C' - 1 - a \ln(C) < 0 \} \Rightarrow \inf_{x \in [1,\infty)} h(x) = h(\hat{x}) = \hat{x} \left( \frac{1}{\hat{x}} - 1 \right)^a \]

where \( \exists \text{unique } \hat{x} \in \left( 1, -\frac{\ln(C)}{\ln(a)} \right) : C^{\frac{1}{\hat{x}}} \left( 1 - \frac{a \ln(C)}{\hat{x}} \right) - 1 = 0 \).

Remembering the definition \( \hat{p} = \arg \min_{p \in \mathbb{R}} \mu_p = \arg \min_{p \in \mathbb{R}} \left( C^{\frac{1}{p}} - 1 \right)^a \), the above leads directly to the conclusion that:

If \( \{ C a \leq 1 \lor \{ C a > 1 \land C' - 1 - a \ln(C) > 0 \} \} : \hat{p} = 1 \)

If \( \{ C a > 1 \land C' - 1 - a \ln(C) < 0 \} : \begin{cases} \text{if } n_u < \text{int} (\hat{x}) : \hat{p} = n_u \\
\text{if } \text{int} (\hat{x}) < n_u < \text{int} (\hat{x}) + 1 : \hat{p} = \min \left( \text{int} (\hat{x}) , n_u \right) \\
\text{if } \text{int} (\hat{x}) + 1 \leq n_u : \hat{p} = \min \left( \text{int} (\hat{x}) , \text{int} (\hat{x}) + 1 \right) \end{cases} \)

\( a > \max \left( \frac{1}{C} , \frac{C' - 1}{\ln(C)'C} \right) \Rightarrow \exists \text{unique } \hat{x} \in \left( 1, -\frac{\ln(C)}{\ln(a)} \right) : C^{\frac{1}{\hat{x}}} \left( 1 - \frac{a \ln(C)}{\hat{x}} \right) - 1 = 0 \)

O.E.A.
4.13. References:


20. Trambouze, P., Piret, E. Continuous Stirred Tank Reactors: Designs

CHAPTER 5

CO₂ Capturing from Power Plant Flue Gases: Energetic Comparison of Amine Absorption with MgO based, Heat Integrated, Pressure-Temperature-Swing Adsorption

5.1. Abstract

In this work, a novel, heat-integrated, pressure-temperature-swing-adsorption (PTSA) process is proposed for the capture of CO₂ from the flue gas of fossil-fueled power plants. The proposed PTSA process utilizes MgO to capture CO₂, in cyclic adsorption/desorption steps involving temperature and pressure swings. The adsorption/desorption temperature and pressure operating conditions are found by globally solving the associated Gibbs free energy minimization problem. The proposed process is heat-integrated, and involves a heat-pump, a refrigeration loop, a flash-separator train with inter-stage compression and cooling, and a heat exchange network. Our energetic analysis suggests that a 12% increase in power output can be attained for 90% CO₂ capture, over an amine process featuring the same CO₂ capture level.

5.2. Introduction & Background

Roughly 80% of all anthropogenic CO₂ emissions are a result of fossil fuel combustion (Carapellucci & Milazzo (2003)). Fossil-fueled power plants are responsible for roughly 40% of total CO₂ emissions, coal-fired plants being the main contributors (Holtz Eakin & Selden (1995)). Atmospheric CO₂ presently represents ~63% of all atmospheric gas contributions to climate change (Hofmann et al. (2006)). The growth rate of CO₂ emissions since 2000 was greater than the CO₂ emission growth rate predicted by the most fossil-fuel intensive emissions scenario developed in the late 1990s by the intergovernmental panel on climate change (IPCC)
(Raupach et al. (2007)). Indeed, the CO₂ growth rate increased from less than 1 ppm/yr in the 1960s to about 2 ppm/yr after about 2000 (Keeling et al. (1980)), thus raising the fear of runaway warming indicated by a lessening ability for terrestrial biosphere and ocean to take up carbon dioxide (Fung et al. (2005), Le Quéré et al. (2007)). To limit the global temperature rise to less than 2°C by 2100, the Intergovernmental Panel on Climate Change (IPCC Fourth Assessment Report (2007)) has estimated that a 50-85% reduction in emissions from present levels this would be required by 2050.

The above suggest that large scale CO₂ capture efforts should focus on fossil-fueled power plants. CO₂ capturing from such power generating facilities can be performed either by first gasifying/reforming their fossil fuel, capturing CO₂ from the gasification/reforming products, and thencombusting the reformed fuel (pre-combustion process); or by firstcombusting the fossil fuel, and then capturing CO₂ from the combustion flue gases (post-combustion process) (Yang et al. (2008), Kanniche et al. (2010)).

This paper will focus on post-combustion capture, the most advantageous and easiest to implement (Lucquiaud & Gibbins (2009), Wang et al (2011)) amongst CO₂ capture technologies. In particular, the post-combustion capture block operates downstream of the power generation section of the plant (Husebye et al. (2011)). As a result, should the CO₂ capture block encounter any problems, power generation can continue uninterrupted albeit at the cost of CO₂ venting to the atmosphere. Pre-combustion CO₂ capture on the other hand requires complicated and costly plant overhauls, including large capital cost expenditures such as required for the commissioning of IGCC (Integrated Gasification Combined Cycle) power plants (Ruben et al. (2007)).

Most post-combustion CO₂ capture technologies can be classified under either CO₂ absorption or CO₂ adsorption technologies (Wong & Bioletti (2002)). Absorption technologies
consist of either physical absorption, where CO$_2$ is physically absorbed into a solvent in the absence of chemical reactions (i.e. Selexol©) (Bucklin & Schendel (1984), Shah & Huurdeman (1990)) or chemical absorption where CO$_2$ is chemically absorbed by a solvent, typically an alkyl amine such as MEA, DEA or MDEA, via chemical reactions of ionic nature (Sharma (1965), Vaidya & Kenig (2007), Sartori & Savage (1980), Versteeg & Van Swaaij (1988), Freguia & Rochelle (2004), Dang & Rochelle (2003)). Similarly, adsorption technologies can be either physical in nature, where CO$_2$ is adsorbed onto a material in the absence of chemical reactions, such as adsorbent 13X and 5A Zeolites (Ho et al. (2008), Merel et al. (2008)) or chemical in nature, where CO$_2$ is adsorbed onto a material such as Calcium Oxide in the presence of chemical reactions (Hoffman & Pennline (2001), (Reddy & Smirniotis (2004), Wu et al. (2008)).

The most widely used CO$_2$ capture technique is chemical absorption using amine solutions (Simmonds et al. (2002), Aaron & Costas (2005)). CO$_2$ absorption using amines can be performed in a tray or packed column (Yeh et al. (2001)) and can be modeled using a rate-based model (Pacheco & Rochelle (1998), Dang & Rochelle (2003)), a mass transfer-based model (Aroonwilas & Tontiwachwuthikul (1998), Mandal et al. (2001)), or a combination of both (Kenig et al. (2003), Aroonwilas & Veawab (2007)). Following the CO$_2$ absorption step, solvent regeneration (CO$_2$ desorption) occurs in a stripper through a highly energetically demanding process featuring a substantial reboiler heat duty (Desideri & Paolucci (1999), Sakwattanapong et al. (2005), Tobiesen & Svendsen (2005, 2006)). Indeed, energy consumption in the stripper can be as much as 15-30% of total plant power output (Jassim & Rochelle (2006)).

The rest of the paper is structured as follows. First, the general steam-cycle without carbon capture is briefly described, and its thermal efficiency is quantified. Energetic data from a real
subcritical pressure coal-fired steam cycle plant with no capture block are employed (DOE/NETL-401/110907 (2007)), and detailed information regarding the operation of the steam-cycle’s main units (turbine train and boiler) is provided. A general steam-cycle with amine carbon capture technology is next introduced to highlight how a cycle’s efficiency is adversely affected when a CO$_2$ capture block is appended. Data for the same subcritical steam cycle modified to accommodate an amine absorption capture block are employed (DOE/NETL-401/110907 (2007)) to validate the capture block’s effect in reducing net plant power output. Next, the alternative, adsorption based, CO$_2$ capture method proposed in this work is presented. The method is first motivated by a Gibbs free energy global minimization study, of the simultaneous phase/reaction equilibrium of the MgO/MgCO$_3$/N$_2$/O$_2$/CO/CO$_2$/H$_2$O/Mg(OH)$_2$ system. Operating conditions for both the desorber and adsorber units are identified in this study. Then, a novel, heat-integrated, Pressure Temperature Swing Adsorption (PTSA) CO$_2$ capture process is presented. The general process, consisting of 5 blocks, is broadly depicted by indicating the general functionality of each block. In the ensuing subsections, a more elaborate presentation detailing each consecutive block’s inner workings is provided via the tabulation of all the streams’ properties. A comprehensive energetic comparison of the amine-based and sorbent-based capture blocks is consequently carried out, that clearly identifies the energetic superiority of the proposed MgO-based CO$_2$ capture process. Finally, conclusions are drawn.
5.3. Steam-cycle with no Carbon Capture

A basic schematic of a traditional power plant is shown in figure 1. The two main units are a boiler, where a heat input $Q_{\text{Boiler}}$ supplied by burning coal is used to generate superheated steam and a steam cycle, which expands this superheated steam through a multi-stage turbine down to a lower pressure (vacuum) and temperature, thus producing work $W_{\text{Gen}}$ in the process. The cycle is closed by adjoining a condenser to the turbine outlet to liquefy the steam, and a pump to bring the water back to the pressure of the boiler. The flue gas generated in the boiler is

Figure 5.1: Traditional steam-cycle power plant schematic
in turn used to pre-heat one of the two incoming air streams to increase the efficiency of the boiler unit. The thermal efficiency of a steam-cycle is defined as (Smith & Van Ness & Abbott (2005)):

$$\eta = \frac{W_{Gen}}{Q_{Boiler}}$$

(5.1)

Where $Q_{Boiler}$, $W_{Gen}$, and $\eta$ denote the boiler heat input rate, the turbine power generation rate, and the steam cycle efficiency respectively.

From (5.1) it is obvious that the efficiency of a cycle increases proportionally with the work generated (decreases inverse proportionally with the heat supplied) for a fixed heat input (work output) value. Adding a carbon capture technology, amine- or sorbent-based, will affect either one or both of these two parameters (heat input, work output) in different ways. It will be shown that the sorbent-based technique reduces the thermal efficiency over that of the no-capture process to a lesser extent than the amine-based one, resulting in an energetically favorable, efficient, and economically desirable design.

In the case study under consideration, the no-capture coal-fired subcritical pressure steam-cycle plant steam generator power output is 463,500 kW. Accounting for auxiliary power losses, the net power output is 433,778 kW. The cycle’s thermal efficiency is 39.78%. Based on (5.1), using the net power output value, the heat of the boiler translates into

$$Q_{Boiler} = 4.228 \times 10^9 \frac{\text{BTU}}{\text{hr}}.$$  

The actual heat rate of the boiler is $3.72 \times 10^9 \frac{\text{BTU}}{\text{hr}}$ due to non-ideal boiler operation and heat losses (88% efficiency). A detailed depiction of the steam cycle for the case of no carbon capture is shown in figure 5.2, which a process flow diagram (PFD) is created in the UniSim software by Honeywell. This PFD and associated simulation was reconstructed
from the supplied Mollier diagram in (DOE/NETL-401/110907 (2007)). The conditions of every stream in figure 5.2 are displayed in table 5.1.

The boiler generates 392 kg/s of superheated steam at 175 bars and 811 K. Superheated steam leaves the boiler to the high pressure (HP) turbine where it is expanded to the reheat pressure and temperature of 45 bars and 618 K, respectively. Cold reheat steam exits the HP turbine at the said conditions before it is split into two streams. One stream consisting of 30.8 kg/s of steam is used to perform some heat integration with various sections of the boiler (economizer, feed water pre-heating), while the other stream, consisting of the steam balance (361.2 kg/s), is resupplied to the boiler, via the de-superheating spray, where it is re-heated to 811 K in a two-stage re-heater. Hot reheat steam leaves the finishing reheat section at 40 bars and 811 K and is sent to an intermediate pressure (IP) turbine with an outlet pressure and temperature of 11.7 bars and 650 K respectively. The outlet of the IP turbine is again split into two streams. One stream consisting of 50 kg/s of steam is used to perform some heat integration with various sections of the boiler (air re-heater, de-aerator, feed water pre-heating), while the other stream consisting of the steam balance (311.2 kg/s) is sent to the low pressure (LP) turbine connected to a vacuum condenser, operating at a pressure and temperature of 0.08 bar and 315 K respectively, where it is exhausted with a 5.5% moisture content.

Having discussed the steam cycle leaving the boiler to generate work in the turbine sequence, the path of the flue gas is next explained to account for factors which affect the efficiency of the boiler and eventually the net efficiency of the total cycle. The power plant’s flue gas exits the boiler at atmospheric pressure and 647 K, with a molar composition of 15% CO₂, 10% H₂O, 70% N₂, and 5% O₂. In a Ljungström® tri-sector air pre-heater, the flue gas is used to preheat two incoming air streams, a primary air stream from 306 K to 625 K and a secondary air
stream from 303 K to 597.2 K. The flue gas leaves the air pre-heater at atmospheric pressure and 428 K to undergo desulfurization in the flue gas desulfurization (FGD) unit, before being sent to the stack where it is directly released to the atmosphere in the absence of a proper carbon separation technology. A UniSim PFD of such a tri-sector air pre-heater unit appears in figure 5.3. The two carbon separation technologies under investigation, amine- and sorbent-based, are discussed next.

![UniSim PFD of steam turbine train; No CO₂ capture](image)

**Fig. 5.2**: UniSim PFD of steam turbine train; No CO₂ capture
### Table 5.1 a-b: Description of stream properties shown in fig. 2

<table>
<thead>
<tr>
<th>Stream Name</th>
<th>Superheated Steam / HP inlet</th>
<th>Cold Reheat/HP Outlet</th>
<th>To Heat Integration (1)</th>
<th>Cold Reheat/IP Inlet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (bar)</td>
<td>175</td>
<td>45</td>
<td>45</td>
<td>45</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>811</td>
<td>618</td>
<td>618</td>
<td>618</td>
</tr>
<tr>
<td>Flow Rate (kg/s)</td>
<td>392.00</td>
<td>392.00</td>
<td>30.80</td>
<td>361.20</td>
</tr>
<tr>
<td>% Vapor</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Stream Name</th>
<th>Hot Reheat/IP Inlet</th>
<th>IP Outlet</th>
<th>To Heat Integration (2)</th>
<th>LP Inlet</th>
<th>LP/Condenser Outlet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (bar)</td>
<td>40</td>
<td>11.7</td>
<td>11.7</td>
<td>11.7</td>
<td>0.08</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>811</td>
<td>650</td>
<td>650</td>
<td>650</td>
<td>315</td>
</tr>
<tr>
<td>Flow Rate (kg/s)</td>
<td>361.20</td>
<td>361.20</td>
<td>50.00</td>
<td>311.20</td>
<td>311.20</td>
</tr>
<tr>
<td>% Vapor</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>94.50</td>
</tr>
</tbody>
</table>

**Figure 5.3:** UniSim representation of a Ljungstrom® Tri-sector air pre-heater used in industrial boiler
5.4. Steam-cycle with Amine-Based Capture

As mentioned earlier, a power plant loses efficiency when retrofitted with amine-based carbon capture technology, since some heat generated in the boiler is diverted from work production to solvent regeneration. Indeed, as shown in Figure 5.4, a retrofitted power plant typically includes a let-down (LD) turbine that runs parallel with the low-pressure (LP) turbine. Some of the steam exiting the intermediate pressure (IP) turbine is diverted to this let-down (LD) turbine, where it produces work, and gives rise to an LD turbine exhaust consisting of relatively high-quality steam (490.8K and 3.24 bar) which, in this amine based CO$_2$ capture design, is used to supply the energy required for solvent regeneration. In the no CO$_2$ capture design, this steam would have been further expanded down to the low temperature and vacuum pressure of the condenser (315 K and 0.08 bar) to yield maximum work production. An energetic comparison between the two designs can thus be readily carried out. To this end, the amount and quality of steam needed for solvent regeneration, in the amine based CO$_2$ capture design, depend on the desired percentage of CO$_2$ capture from the flue gas stream, as well as on the regeneration energy of the particular amine solvent being employed (energy/unit CO$_2$ captured).
In this study, a state-of-the-art solvent regeneration energy of 1550 Btu/lb \( \text{CO}_2 \) captured will be considered, although commonly used amines have higher regeneration energies of around 2350 Btu/lb \( \text{CO}_2 \) captured (DOE/NETL-401/110907 (2007)). For this regeneration energy, Table 5.2 illustrates the dependence of the amount of steam extracted at the IP/LP crossover junction, and of the power cycle’s loss of efficiency, on the different levels of carbon capture. This work will focus on the maximum carbon capture obtainable using amine technology (90% \( \text{CO}_2 \) capture) as delineated in Table 5.2. The modified power generation scheme, with inclusion of steam extraction at the LD/LP crossover junction, is shown in via a UniSim PFD in figure 5.5. Power production is greatly reduced compared to the base case; from 463,500 kW to 393,000 kW.

**Figure 5.4:** Steam cycle plant layout with amine-based carbon capture technologies

![Steam cycle plant layout](image-url)
<table>
<thead>
<tr>
<th>CO₂ Capture (%)</th>
<th>Steam Extraction at IP/LP Crossover (kg/s)</th>
<th>Net Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>35</td>
</tr>
<tr>
<td>30</td>
<td>50.83</td>
<td>31.7</td>
</tr>
<tr>
<td>50</td>
<td>84.72</td>
<td>29.3</td>
</tr>
<tr>
<td>70</td>
<td>118.60</td>
<td>26.9</td>
</tr>
<tr>
<td>90</td>
<td>152.50</td>
<td>24.5</td>
</tr>
</tbody>
</table>

**Table 5.2:** Steam extracted at IP/LP crossover and Net Efficiency as function of CO₂ capture % (DOE/NETL-401/110907 (2007))

Fig. 5.5 UniSim PFD of steam turbine train; 90% CO₂ capture using amine absorption

Tables 5.3 a-b denote specific stream information as they appear in figure 5.5, to reflect the adverse effect that amine based CO2 capture has on the power plant’s net power generation, as compared to the baseline power plant which does not include CO2 capture.
Subsequent efforts will be geared towards determining the energetic efficiency of the MgO-based capture process, as compared with the aforementioned amine process, for the same CO$_2$ capture requirement (90%). To this end, a Gibbs free energy minimization problem is first globally solved to yield appropriate adsorption/desorption process conditions. These results are then utilized in the creation of a novel heat-integrated PTSA process, which is, as discussed earlier, integrated with several other auxiliary mechanisms (refrigeration loop, separation train, heat exchange network, and redesigned boiler air pre-heater) to generate an energetically desirable overall design. In the next section, the mathematical formulation of the Gibbs free energy minimization problem is presented and globally solved using the GAMS® package.
5.5. Gibbs Minimization Analysis

To identify appropriate operating conditions for the proposed Pressure-Temperature-Swing-Adsorption (PTSA) CO$_2$ capture process using MgO adsorbent, a simultaneous reaction, phase equilibrium study is carried out. It involves gaseous species CO, CO$_2$, H$_2$O, O$_2$, and N$_2$ accounting for post-combustion air, and solid species MgO, MgCO$_3$, Mg(OH)$_2$. The goal is to identify whether there exist capture conditions so that the equilibrium conversions of the reactions $\text{MgO} + \text{CO} \leftrightarrow \text{MgCO}_3$ and $\text{MgO} + \text{H}_2\text{O} \leftrightarrow \text{Mg(OH)}_2$ are high and low respectively, and release conditions so that the equilibrium conversion of the reaction $\text{MgO} + \text{CO}_2 \leftrightarrow \text{MgCO}_3$ is high.

The total Gibbs free energy of the solid-gas system under consideration is a function of pressure, temperature, and of the number of moles of each species in each of the two phases. It is well established in the literature that for fixed pressure, and temperature, this reactive multiphase system is at equilibrium if and only if the system’s total Gibbs free energy is at its minimum value. Thus, for fixed pressure, temperature, and initial number of atoms of all elements present in the system, the number of moles of each species in each of the two phases at equilibrium can be identified by minimizing total Gibbs free energy function subject to material conservation constraints (which ensure that atomic balance is maintained), phase equilibrium constraints (which ensure equality of chemical potentials for each species in all phases in which the species is present), and non-negativity constraints for all moles of each species in each phase. Considering that each of the species considered is only present in one phase, the resulting optimization problem can be formulated as follows (Smith & Van Ness & Abbott (2005)):
\[
\begin{align*}
\text{minimize } & \quad G \left( \left\{ N_i^{(j)}, \mu_i^{(j)} \right\}_{i=1, \ldots, NC, j=G, S} \right) = \sum_{i=1}^{NC} \sum_{j \in \{G, S\}} N_i^{(j)} \mu_i^{(j)} \\
\text{Subject to:} & \\
A \cdot \sum_{j=G}^{S} N_i^{(j)} - B = 0 \quad (5.2) \\
\mu_i^{(j)} &= \Delta G_i^{(j)} (T) + RT \ln \left( \frac{\hat{f}_i^{(j)}}{f_i^{(j, o)}} \right); \quad i = 1, NC; \quad j \in \{G, S\} \quad (5.3) \\
N_i^{(j)} &\geq 0; \quad i = 1, NC; \quad j \in \{G, S\} \quad (5.4)
\end{align*}
\]

where \( G \) is the total Gibbs free energy, \( N_i^{(j)} \) is the number of moles of the \( i \)th component in the \( j \)th phase, \( \mu_i^{(j)} \) is the chemical potential of the \( i \)th component in the \( j \)th phase, \( A \) is the atomic balance matrix, \( N_i^{(j)} \) is the number of moles vector in the \( j \)th phase, \( B \) is the number of initial atom-moles vector, \( \Delta G_i^{(j)} (T) \) is the ideal Gibbs free energy of formation for component \( i \), in phase \( j \) at \( T \), \( \hat{f}_i^{(j)} \) is the fugacity of the \( i \)th component in the \( j \)th phase, \( f_i^{(j, o)} \) is the fugacity of the \( i \)th component in the \( j \)th phase at standard conditions, \( NC \) is the number of components and \( G, S \) are the gas and solid phases respectively.

Substitution of \( \mu_i^{(j)} \), through equation \( (5.3) \), into the objective function, transforms this problem into a nonlinear program with convex objective function and an affine set of constraints (Pena Lopez & Manousiouthakis (2010)). Thus its solution through traditional local minimization techniques is guaranteed to identify the global optimum.

It is important to emphasize that while the above described Gibbs free energy minimization method requires no knowledge of individual reactions taking place in this multiphase system, its results can be readily interpreted in terms of equilibrium conversions for individual reactions in which the considered species may be participating. For the gas species \( O_2 \),
N2, CO, CO2 and H2O, and solid species MgO, MgCO3 and Mg(OH)2 considered here, the obtained results can be interpreted in terms of the possible absorption and desorption reactions (5.5) and (5.6) shown below.

\[
\begin{align*}
MgO + CO_2 & \leftrightarrow MgCO_3 \quad (5.5) \\
MgO + H_2O & \leftrightarrow Mg(OH)_2 \quad (5.6)
\end{align*}
\]

Thus, first conditions can be identified under which CO2 adsorption is carried out, while no H2O adsorption occurs; and then other conditions can be identified under which CO2 desorption, and no H2O adsorption occurs.

The optimization problem is solved using the GAMS® package assuming an inlet flue gas molar composition of 15% CO2, 10% H2O, 70% N2, and 5% O2 (DOE/NETL-401/110907 (2007)). During the desorption step, larger quantities of steam favor the reverse direction of reaction (5.5), however downstream processing of larger steam flow are economically restrictive, therefore a steam to CO2 molar ratio of 5.66 for the desorption operation is specified. The optimal operating conditions for both the adsorption and desorption steps are determined through a pressure-temperature space exploration procedure, and the CO2 and H2O capture levels are calculated via solution of the optimization problem. During the absorption step the conditions sought are to favor the forward direction of reaction (5.5), while the forward direction of reaction (5.6) is undesirable. Therefore during the absorption step it is important to identify conditions which would largely favor reaction (5.5) over (5.6). In other words, it is desired to maximize CO2 capture and minimize H2O capture. Following the outlined procedure, an operating pressure and temperature of 1 atm and 545 K, respectively, are selected for the adsorption process with the potential to absorb 92% CO2 fed and no water (form MgCO3 only,
no Mg(OH)$_2$. Similarly, an operating pressure and temperature of 0.08 atm and 560 K, respectively, are selected for the desorption process to fully desorb CO$_2$ with no simultaneous water adsorption (decompose MgCO$_3$ to MgO and CO$_2$ only, no Mg(OH)$_2$ formation). Gibbs free energy, enthalpy of formation and heat capacity terms are displayed in table 4. Heat capacities can be calculated using (5.7).

\[
\frac{C_p}{R} = A + B \cdot T + C \cdot T^2 + D \cdot T^{-2} \quad (5.7)
\]

<table>
<thead>
<tr>
<th>Components</th>
<th>$\Delta G_f^o$ (J/mol)</th>
<th>$\Delta H_f^o$ (J/mol)</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$ (g)</td>
<td>-393509</td>
<td>-394359</td>
<td>5.457</td>
<td>0.001045</td>
<td>0</td>
<td>-115700</td>
</tr>
<tr>
<td>CO (g)</td>
<td>-110525</td>
<td>-137169</td>
<td>3.376</td>
<td>0.000557</td>
<td>0</td>
<td>-3100</td>
</tr>
<tr>
<td>H$_2$O (g)</td>
<td>-241818</td>
<td>-228572</td>
<td>3.47</td>
<td>0.00145</td>
<td>0</td>
<td>12100</td>
</tr>
<tr>
<td>O$_2$ (g)</td>
<td>0</td>
<td>0</td>
<td>3.639</td>
<td>5.06E-04</td>
<td>0</td>
<td>-22700</td>
</tr>
<tr>
<td>N$_2$ (g)</td>
<td>0</td>
<td>0</td>
<td>3.28</td>
<td>0.000593</td>
<td>0</td>
<td>4000</td>
</tr>
<tr>
<td>MgO (s)</td>
<td>-601700</td>
<td>-568900</td>
<td>5.123</td>
<td>8.75E-04</td>
<td>0</td>
<td>-74480</td>
</tr>
<tr>
<td>MgCO$_3$ (s)</td>
<td>-1111000</td>
<td>-1028000</td>
<td>9.37</td>
<td>6.95E-03</td>
<td>0</td>
<td>-209351</td>
</tr>
<tr>
<td>Mg(OH)$_2$ (s)</td>
<td>-924700</td>
<td>-833700</td>
<td>6.562</td>
<td>7.95E-03</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

**Table 5.4:** Gibbs free energy, enthalpy of formation and heat capacity terms for all considered species (Smith et al. (2005), Dean (1999)).
5.6. Steam-cycle with Sorbent (MgO)-Based Capture:

A modified boiler air-preheater (block 1) is introduced to adjust for the adsorption/desorption bed temperatures, while providing as much air pre-heating duty as possible to maximize boiler efficiency. CO$_2$-laden steam at 0.08 bar and 560K is initially cooled down to atmospheric temperature, and is then sent to a mild refrigeration loop at 278K (vapor-compression cycle - block 3) to facilitate CO$_2$ separation in a series of flashes/compressors/coolers (separation structure – block 5). Pure CO$_2$ is delivered at atmospheric pressure to the chemical transformation plant, while the separated H$_2$O is recycled to replenish the steam desorption loop. A heat-exchanger network is also designed to minimize external energy usage (block 4) to reheat the steam following each desorption cycle. Finally, a CO$_2$/H$_2$O separation section (block 5) is required to separate the two components, and deliver high purity CO$_2$ at atmospheric pressure for subsequent compression/liquefaction. Each block is thoroughly described in the following subsections (5.2-5.6), with specific information relating pressure, temperature, composition, and mass flow rate for every existing stream listed in tabulated form in its appropriate section. The steady-state operation of these processes is possible through the use of multiple beds in the PTSA process whose time-dependent operation is coordinated in such a way that it does not affect the time-independent operation of the remaining process. This coordination is elaborated upon during the description of the PTSA process.

With respect to SO$_2$ and NO$_x$ removal, while it is possible to use a fluidized bed boiler containing limestone to adsorb sulfur as it is released during combustion, a more commonly employed design consists of a flue gas desulfurization (FGD) unit. Prior to entering the FGD unit, oxidation (formation of SO$_3$ from SO$_2$ precursors) and cooling of the flue gas results in the formation, condensation and precipitation of sulfuric acid. The level of cooling of the flue gas
before entering the FGD unit directly affects the amount of sulfuric acid precipitated. The SO$_2$ lean flue gas leaving the FGD unit is then re-heated, using heat recovered from pre-FGD cooling, to a temperature favoring the dispersion of the remaining residual toxic substances and is sent to a stack column. In the present MgO-based capture design, flue gas containing SO$_2$ passes through the sorbent-loaded adsorber; therefore, doping of the nano-particles with Ceria (Cerium 4 Oxide) allows for an elevated sulfur poisoning tolerance and helps preserve the sorbent (Hong & Smirniotis (2009). SO$_2$ and NO$_x$ will then be carried through with the CO$_2$ lean flue gas leaving the MgO adsorber and will be separated downstream.

Fig. 5.6: UniSim PFD of proposed MgO-based, CO$_2$ capture design, decomposed into 5 blocks
5.6.1 Block 1: Modified Boiler Tri-sector Heat Exchanger

In the traditional no CO\textsubscript{2} capture design, the flue gas leaving the power plant’s boiler is used to preheat two incoming air streams (primary and secondary) in the tri-sector heat exchanger shown in figure 5.3, and discussed in sec. 5.2.2 to increase the efficiency of the boiler. As demonstrated in figure 5.7, in the MgO based CO\textsubscript{2} capture design, the “Hot Flue Gas” leaving the boiler is first sent to HX-1, where it is used to heat 0.08 bar steam, from 553K to 560 K, so that the steam can then be sent to whichever bed is currently in desorber mode, as “Steam to Desorber (Inlet)”. The hot flue gas exits HX-1 as “Internal Stream 3”, and enters the modified trisector heat exchanger where it heats the aforementioned primary and secondary air streams, and exits as “Internal Stream 4”. Then, it is first directed to HX-2, where it preheats the secondary air-stream, and is subsequently sent to whichever bed is currently in adsorber mode as “Flue Gas to Adsorber”. After transferring \((0.1500 - 0.0139)/0.1500 = 90.73\%\) of its original CO\textsubscript{2} content to the MgO adsorbent, the flue gas then exits the adsorber as “Flue Gas from Adsorber” and is finally used to preheat again the secondary air stream in HX-3 and exit the system as “Cold Flue Gas”. The detailed conditions of all streams in block1 are listed in Table 5.
In the MgO based CO$_2$ capture design, stream “Sec. Air Stream to AH” is being preheated to a temperature that is below the temperature of that same stream in the no CO$_2$ capture design. In turn, this implies a lower energy input to the boiler in the new design. This energetic deficiency manifests itself through an increase in the required boiler heat duty that is
equivalent to the rate of enthalpy change of $1.274 \times 10^6 \text{ kg} / \text{hr}$ air from 597 K to 560 K, which is equal to $0.476 \times 10^6 \text{ Btu/hr}$. The heat duty of the new boiler is therefore $\dot{Q}_{\text{Boiler}}^{\text{new}} = 3.767 \times 10^9 \text{ BTU/hr}$, which is 1.27% greater than the duty of the traditional boiler $\dot{Q}_{\text{Boiler}} = 3.72 \times 10^9 \text{ BTU/hr}$. Therefore, the efficiency of the new boiler is slightly reduced compared to that of the boiler in a traditional steam-cycle plant, in the absence of carbon capture technology.

5.6.2. Block 2: Adsorber-Desorber Circuit

5.6.2.1. General Description of Proposed PTSA and its Time-Dependent Operation

In its simplest form, PTSA can be implemented using a two-bed adsorber/desorber system, although multiple beds may be needed for its optimal realization. The proposed PTSA employs a standard steam vapor-compression heat-pump circuit operating between 51.5 bars, and 77.5 bars, and can be operated in four phases which are described as follows. At the beginning of phase 1 (phase 3), the bed pressure and temperature are 0.08 bar and 560K (1 bar and 545K). No flue gas is fed into the bed during phase 1 (phase 3) and heat is subtracted (added) from (to) the bed to (from) the evaporator (condenser), or to (from) any other heat sink given that the cooling (heating) duty is small, to bring the bed temperature to 545K (560K) in preparation for phase 2 (phase 4). At the beginning of phase 2 (phase 4), bed pressurization (de-pressurization) takes place. Then flue gas (steam) at 545K and 1 bar (560K and 0.08 bar) is fed to the bed to accomplish isothermal CO$_2$ adsorption (desorption). During this process, the exothermic heat of adsorption (endothermic heat of desorption) is removed from the bed to the evaporator (added to the bed from the condenser).
5.6.2.2. Design Characteristics of Adsorber/Desorber Beds and Heat-Pump Circuit

The absorber-desorber circuit and its interconnection to the rest of the proposed flowsheet is captured in block 2 and illustrated in Figure 5.9. The main feature of block 2 is a heat pump circuit, with water as working fluid, which is used to transfer heat from one bed operating in the cooling and adsorption phases 1 and 2, to another bed operating at the same time in the heating and desorption phases 3 and 4. Continuous operation of the heat-pump circuit can be attained if the following hold true:
1. The duration of a bed’s cooling and adsorption operation phases 1 and 2, must equal the duration of the bed’s heating and desorption operation phase 3 and 4. This ensures that for each bed in phase 1-2, there exists a corresponding bed in phase 3-4.

2. The heat added to a bed during phases 3-4 minus the heat removed from the corresponding bed during phases 1-2 is equal to the heat pump circuit’s compressor work consumed during that same time.

To quantify the aforementioned relations, the following parameters are introduced.

Let the ratio of moles of MgO in a bed over the duration \( \Delta t_{\text{Cooling}} \) (hr) of the cooling operation, and the ratio of moles of MgCO\(_3\) in a bed over the duration \( \Delta t_{\text{Heating}} \) (hr) of the heating operation be denoted by \( \alpha_{\text{Cooling}} \left( \frac{\text{mol MgO}}{\text{hr}} \right) \), and \( \alpha_{\text{Heating}} \left( \frac{\text{mol MgCO}_3}{\text{hr}} \right) \) respectively.

Let also \( \beta_{\text{Adsorber}} \left( \frac{\text{mol MgO}}{\text{hr}} \right) \) be the ratio of moles of MgO in a bed over the duration \( \Delta t_{\text{Adsorption}} \) (hr) of the adsorption operation, \( \beta_{\text{Desorber}} \left( \frac{\text{mol MgCO}_3}{\text{hr}} \right) \) be the ratio of moles of MgCO\(_3\) in a bed over the duration \( \Delta t_{\text{Desorption}} \) (hr) of the desorption operation, \( \dot{n}_{\text{CO}_2} \left( \frac{\text{mol}}{\text{hr}} \right) \) be the molar flowrate of CO\(_2\) in the hot flue gas stream, \( X_{\text{CO}_2} \) be the percentage of CO\(_2\) that is captured, \( C_{p}^{\text{MgCO}_3} \left( \frac{\text{J}}{\text{mol} \cdot \text{K}} \right), C_{p}^{\text{MgO}} \left( \frac{\text{J}}{\text{mol} \cdot \text{K}} \right), \) and \( C_{p}^{\text{CO}_2} \left( \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) \) be the heat capacities of MgCO\(_3\), MgO, CO\(_2\), \( \Delta C_{p} \left( \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) = C_{p}^{\text{MgCO}_3} - C_{p}^{\text{MgO}} - C_{p}^{\text{CO}_2} \) be the difference in heat capacities between products and reactants for the forward reaction (5.6), and \( \Delta H_{\text{rxn}}^{\circ} \left( \frac{\text{J}}{\text{mol}} \right) = -64,741 \) at standard conditions.
for the forward reaction (5.6). The following equations (5.8)–(5.12) can then be used to quantify the duration $\Delta t_{\text{Adsorption}} (hr)$ of the adsorption operation, and the heat rate exchanged during each of the aforementioned four phases.

$$\Delta t_{\text{Adsorption}} (hr) = \Delta t_{\text{Heating}} (hr) + \Delta t_{\text{Desorption}} (hr) - \Delta t_{\text{Cooling}} (hr) \quad (5.8)$$

\[
\begin{align*}
\dot{Q}_{\text{Cooling}} \left(\frac{J}{hr}\right) &= \alpha_{\text{Cooling}} \left( \int_{T^r=560K}^{T=545K} C_{MgO}^p dT \right) \\
&= \alpha_{\text{Cooling}} \left( -668.74 \frac{J}{\text{mol MgO}} \right) \quad (5.9)
\end{align*}
\]

\[
\begin{align*}
\dot{Q}_{\text{Adsorter}} \left(\frac{J}{hr}\right) &= \dot{n}_{CO_2} X_{CO_2} \left( \Delta H^o_{\text{run}} + \int_{T^r=298K}^{T=545K} \Delta C_p dT \right) \\
&= \beta_{\text{Adsorter}} \left( \Delta H^o_{\text{run}} + \int_{T^r=298K}^{T=545K} \Delta C_p dT \right) = -5.17 \times 10^{11} \frac{J}{hr} \quad (5.10)
\end{align*}
\]

\[
\begin{align*}
\dot{Q}_{\text{Heating}} \left(\frac{J}{hr}\right) &= \alpha_{\text{Heating}} \left( \int_{T^r=545K}^{T=560K} C_{MgCO_3}^p dT \right) \\
&= \alpha_{\text{Heating}} \left( 1,561.9 \frac{J}{\text{mol MgCO}_3} \right) \quad (5.11)
\end{align*}
\]

\[
\begin{align*}
\dot{Q}_{\text{Desorption}} \left(\frac{J}{hr}\right) &= \beta_{\text{Desorption}} \left( -\Delta H^o_{\text{run}} - \int_{T^r=298K}^{T=560K} \Delta C_p dT \right) \\
&= \beta_{\text{Desorption}} \left( 62,926.5 \frac{J}{\text{mol MgCO}_3} \right) \quad (5.12)
\end{align*}
\]

Equations (5.9)–(5.12) above consider that the fully regenerated (fully utilized) bed consists only of MgO (MgCO$_3$) respectively, an assumption justifiable by the equilibrium calculations of section 4.

It is clear from equation (5.10) above that $\beta_{\text{Adsorter}} = 8,183,616 \frac{\text{mol MgO}}{\text{hr}}$. To ensure that a constant heat rate is supplied to and removed from the heat pump apparatus at all times, the heat
rate during the cooling operation is chosen to be identical to the heat rate during the adsorption operation, and the heat rate during the heating operation is chosen to be identical to the heat rate during the desorption operation. In turn this yields equations (5.13) – (5.14), which must govern the duration of various operation steps.

\[
\dot{Q}_{\text{Cooling}} \left( \frac{J}{hr} \right) = \dot{Q}_{\text{Adsorber}} \left( \frac{J}{hr} \right) \quad (5.13)
\]

\[
\Rightarrow \alpha_{\text{Cooling}} \left( \frac{\text{mol MgO}}{\Delta t_{\text{Cooling}}} \right) = \frac{\Delta H^o_{\text{rxn}} + \int_{T^*=298K}^{T^{545K}} \Delta C_p dT}{\tilde{n}_{\text{CO}_2} X_{\text{CO}_2}} \int_{T^*=545K}^{T^{560K}} C_{MgO}^p dT
\]

\[
\Rightarrow \alpha_{\text{Cooling}} \left( \frac{\text{mol MgO}}{hr} \right) = 94.46 \beta_{\text{Adsorber}} \left( \frac{\text{mol MgO}}{hr} \right) \quad (5.14)
\]

Similarly,

\[
\dot{Q}_{\text{Heating}} \left( \frac{J}{hr} \right) = \dot{Q}_{\text{Desorber}} \left( \frac{J}{hr} \right) \quad (5.15)
\]

\[
\Rightarrow \alpha_{\text{Heating}} \left( \frac{\text{mol MgCO}_3}{hr} \right) = \frac{\beta_{\text{Desorber}} \left( -\Delta H^o_{\text{rxn}} + \int_{T^*=298K}^{T^{560K}} \Delta C_p dT \right)}{\int_{T^*=545K}^{T^{560K}} C_{MgCO}_3^p dT}
\]

\[
\Rightarrow \alpha_{\text{Heating}} \left( \frac{\text{mol MgCO}_3}{hr} \right) = 40.28 \cdot \beta_{\text{Desorber}} \left( \frac{\text{mol MgCO}_3}{hr} \right) \quad (5.16)
\]
From (5.14) and (5.16), it holds that
\[
\frac{\Delta t_{\text{Adsorter}} (hr)}{\Delta t_{\text{Cooling}} (hr)} = \frac{\alpha_{\text{Cooling}} \left( \frac{\text{mol MgO}}{\text{hr}} \right)}{\beta_{\text{Adsorter}} \left( \frac{\text{mol MgO}}{\text{hr}} \right)} = 94.46\text{ and}
\]
\[
\frac{\Delta t_{\text{Desorber}} (hr)}{\Delta t_{\text{Heating}} (hr)} = \frac{\alpha_{\text{Heating}} \left( \frac{\text{mol MgCO}_3}{\text{hr}} \right)}{\beta_{\text{Desorber}} \left( \frac{\text{mol MgCO}_3}{\text{hr}} \right)} = 40.28.
\]

Equation (5.8) can be rewritten as:
\[
\Delta t_{\text{Adsorption}} (hr) \left( 1 + \frac{\Delta t_{\text{Cooling}} (hr)}{\Delta t_{\text{Adsorption}} (hr)} \right) = \Delta t_{\text{Desorption}} (hr) \left( 1 + \frac{\Delta t_{\text{Heating}} (hr)}{\Delta t_{\text{Desorption}} (hr)} \right)
\]
(5.17)

Using (5.17), (5.14) and (5.16), \[
\frac{\Delta t_{\text{Adsorter}} (hr)}{\Delta t_{\text{Desorter}} (hr)} = 1.014
\]

Specifying the following information will determine all the stream properties of the heat pump circuit, including the work of compressor 1 \( W_{\text{comp},1} \), and the flow rate of the working fluid, water \( m_{\text{HP}} \):

1- The evaporator (condenser) operates 540K (565K) the temperatures the adsorber (desorber) bed.

2- The outlet of the evaporator (condenser) consists of saturated vapor (liquid).

3- Compressor efficiency is set at 90%.

Using the above information concerning the temperature and state of the streams exiting the evaporator and condenser units, and the adsorber heat load, the work of the heat-pump

244
compressor as well as the mass flow of working fluid in the circuit is determined to be

\[ W_{\text{comp},1} = 9.275 \text{kW} \left( 3.33 \times 10^{10} \frac{\text{J}}{\text{hr}} \right), \quad \text{and} \quad \dot{m}_{\text{HP}} = 3.39 \times 10^8 \frac{\text{kg}}{\text{hr}}. \]

Since the heat load is such that \( \dot{Q}_{\text{Cooling}} \left( \frac{\text{J}}{\text{hr}} \right) = \dot{Q}_{\text{Adsorber}} \left( \frac{\text{J}}{\text{hr}} \right) \), the heat rate that the heat pump must remove from the adsorber during the cooling and adsorption phases is known. Then, a heat balance analysis of the heat pump apparatus, equation (5.18), yields the desorber load

\[ \dot{Q}_{\text{Heating}} \left( \frac{\text{J}}{\text{hr}} \right) = \dot{Q}_{\text{Desorber}} \left( \frac{\text{J}}{\text{hr}} \right) \]

during the heating and desorption phases. Indeed:

\[
\dot{Q}_{\text{Desorber}} \left( \frac{\text{J}}{\text{hr}} \right) = \dot{Q}_{\text{Heating}} \left( \frac{\text{J}}{\text{hr}} \right) = 5.50 \times 10^{11} \frac{\text{J}}{\text{hr}}
\]

Then \( \beta_{\text{Desorber}} \) and \( \alpha_{\text{Heating}} \) can be evaluated as:

\[
\beta_{\text{Desorber}} = \frac{\dot{Q}_{\text{Desorber}} \left( \frac{\text{J}}{\text{hr}} \right) + W_{\text{comp},1} \left( \frac{\text{J}}{\text{hr}} \right)}{-\Delta H_{\text{rxn}}^o - \int_{T=298K}^{T=560K} \Delta C_p \,dT} = 8.74 \times 10^6 \frac{\text{molMgCO}_3}{\text{hr}} \quad (5.19)
\]

\[
\alpha_{\text{Heating}} = 3.52 \times 10^9 \frac{\text{molMgO}}{\text{hr}} \quad (5.20)
\]

The detailed conditions of all streams in block 2 are listed in Table 5.6.
<table>
<thead>
<tr>
<th>Stream Name</th>
<th>Temperature (K)</th>
<th>Pressure (Bar)</th>
<th>Flow rate (kg/h)</th>
<th>Mole Frac. CO₂</th>
<th>Mole Frac. H₂O</th>
<th>Mole Frac. Air</th>
<th>Vapor Phase Frac.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flue Gas from Adsorber</td>
<td>545</td>
<td>1</td>
<td>1.812e+006</td>
<td>0.0133</td>
<td>0.1161</td>
<td>0.8712</td>
<td>1</td>
</tr>
<tr>
<td>Flue Gas to Adsorber</td>
<td>545</td>
<td>1</td>
<td>1.447e+006</td>
<td>0.15</td>
<td>0.1</td>
<td>0.75</td>
<td>1</td>
</tr>
<tr>
<td>Steam to Desorber (Inlet)</td>
<td>560</td>
<td>0.08</td>
<td>8.468e+005</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Steam from Desorber (Outlet) w/ CO₂</td>
<td>560</td>
<td>0.08</td>
<td>1.212e+006</td>
<td>0.150194</td>
<td>0.849806</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>To HX-4(1)</td>
<td>560</td>
<td>0.08</td>
<td>1.212e+006</td>
<td>0.150194</td>
<td>0.849806</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>To Evaporator (Heat Pump)</td>
<td>540</td>
<td>51.48</td>
<td>5.424e+005</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0.0793</td>
</tr>
<tr>
<td>To Compressor (Heat Pump)</td>
<td>540</td>
<td>51.48</td>
<td>5.424e+005</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1 (Sat.)</td>
</tr>
<tr>
<td>To Condenser (Heat Pump)</td>
<td>565</td>
<td>77.56</td>
<td>5.424e+005</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>To Valve (Heat Pump)</td>
<td>565</td>
<td>77.56</td>
<td>5.424e+005</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0 (Sat.)</td>
</tr>
<tr>
<td>CO₂ Adsorbed</td>
<td>545</td>
<td>1</td>
<td>3.654e+005</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Dummy 1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Cold MgCO₃</td>
<td>545</td>
<td>1</td>
<td>3.654e+005</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Hot MgCO₃</td>
<td>560</td>
<td>0.08</td>
<td>3.654e+005</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

**Table 5.6: Stream conditions of block 2**
5.6.3. Block 3: Vapor-Compression Refrigeration Circuit

The vapor-liquid equilibrium based separation of the CO₂/H₂O desorber outlet mixture, is facilitated by decreasing its temperature to 278K. To accomplish this task, a simple vapor-compression refrigeration cycle operating between 273K and 293K is constructed. This cycle utilizes R134a as the refrigerant. The work requirement of the vapor compression refrigeration circuit corresponds to the work of the compressor 2\(W_{\text{comp},2} = 3300\text{kW}\), and the condenser heat duty is provided by an air fan operating at room temperature.

![Diagram](image)

**Fig. 5.10:** A UniSim PFD of vapor-compression refrigeration circuit (block 3)
<table>
<thead>
<tr>
<th>Stream Name</th>
<th>Temperature (K)</th>
<th>Pressure (Bar)</th>
<th>Flow rate (kg/h)</th>
<th>Mole Frac. CO₂</th>
<th>Mole Frac. H₂O</th>
<th>Mole Frac. R134a</th>
<th>Vapor Phase Frac.</th>
</tr>
</thead>
<tbody>
<tr>
<td>To Flash 1</td>
<td>278</td>
<td>0.08</td>
<td>1.212e+006</td>
<td>0.150194</td>
<td>0.849806</td>
<td>0</td>
<td>0.1679</td>
</tr>
<tr>
<td>To Evaporator</td>
<td>293</td>
<td>0.08</td>
<td>1.212e+006</td>
<td>0.150194</td>
<td>0.849806</td>
<td>0</td>
<td>0.2104</td>
</tr>
<tr>
<td>To HX-4(1)</td>
<td>560</td>
<td>0.08</td>
<td>1.212e+006</td>
<td>0.150194</td>
<td>0.849806</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>To Evaporator (Vapor Compression)</td>
<td>273.85</td>
<td>3</td>
<td>9.210e+005</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0.1143</td>
</tr>
<tr>
<td>To Compressor (Vapor Compression)</td>
<td>273.85</td>
<td>3</td>
<td>9.210e+005</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1 (Sat.)</td>
</tr>
<tr>
<td>To Condenser (Vapor Compression)</td>
<td>293</td>
<td>5.23</td>
<td>9.210e+005</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>To Valve (Vapor Compression)</td>
<td>290</td>
<td>5.23</td>
<td>9.210e+005</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0 (Sat.)</td>
</tr>
</tbody>
</table>

Table 5.7: Stream specifications of block 3
5.6.4. Block 4: Heat Exchange Network Structure

The following heat exchange network has one cold utility inlet (stream “Cold Utility 1 (Inlet)”) consisting of water at 293 K, and one low temperature, hot utility inlet (stream “Steam In”) consisting of steam exiting the modified LP turbine at 0.1 bars and 94.5% vapor fraction. Since steam is being extracted at a pressure above the vacuum pressure of the condenser in the existing traditional power generation scheme (0.0825 bars) as discussed in section 2.2, a certain drop in power generation, equivalent to the enthalpy difference of steam between 0.1 bars and 0.0825 bars, with the same moisture content, must be accounted for. This power generation loss can be evaluated to be 2,777 kW.

![Fig. 5.11: A UniSim PFD of the heat exchange network structure (block 4)](image-url)
CO₂–laden steam exits the desorber bed and enters HX-4 (stream “To HX-4 (1)”), where it is cooled by returning steam stripped of CO₂ (stream “To HX-4 (2)”). Stream “To HX-4 (1)” is cooled in the process from 565K to 374K, and exits HX-4 as stream “To HX-6”. Stream “To HX-6” is then sent to HX-6 where it is further cooled down to atmospheric temperature, using a cold water utility (stream “Cold Utility 1 (inlet)”), and exits as stream “To Evaporator”. Stream “To Evaporator” is sent to the Evaporator unit of the vapor compression refrigeration circuit where additional cooling duty is furnished before exiting as stream “To Flash 1”. Stream “To Flash 1” is at a temperature of 278K to favor maximum CO₂-H₂O separation in flash 1, as will be subsequently described in the next section.

Liquid water depleted of CO₂ leaving flashes 1, 2 and 3, as streams “To MIX (1)”, “To MIX (2)”, and “To MIX (3)”, respectively, is mixed along with stream “Make-Up H₂O” in unit “MIX”. The resulting liquid stream (stream “to HX-7”) is heated in HX-7 from 291K to 314.8K with 99.15% of the material vaporized. To provide this heating/vaporization energy, stream “Steam In”, which represents the modified LP turbine exhaust at 0.1 bar, 319K and 94.5% vapor fraction is completely condensed, and exits HX-7 as saturated liquid stream “Steam Out”. Stream “to HX-7” exits HX-7 as stream “To HX-8(2)” and is further heated by the compressor 1 outlet of the flash-compression sequence, stream “To-HX-8 (1)”. Stream “To HX-8(2)” exits HX-8 as stream “To HX-4 (2)”, while stream “To HX-8(1) exits HX-8 as stream “To HX-9”. Finally, as described in the first paragraph of this section (5.5), returning steam stripped of CO₂ (stream “To HX-4 (2)”), is used to cool the CO₂-loaded steam exiting the desorber bed (stream “To HX-5 (1)”). Stream “To HX-4 (2)” is heated in the process from 322K to 553K, and exits HX-4 as stream “Steam to HX-1”. High temperature heat input is provided in HX-1 as described in section 5.2.
<table>
<thead>
<tr>
<th>Stream Name</th>
<th>Temperature (K)</th>
<th>Pressure (Bar)</th>
<th>Flow rate (kg/h)</th>
<th>Mole Frac. CO₂</th>
<th>Mole Frac. H₂O</th>
<th>Vapor Phase Frac.</th>
</tr>
</thead>
<tbody>
<tr>
<td>To HX-4(1)</td>
<td>560</td>
<td>0.08</td>
<td>1.212e+006</td>
<td>0.150194</td>
<td>0.849806</td>
<td>0</td>
</tr>
<tr>
<td>Steam to HX-1</td>
<td>553</td>
<td>0.08</td>
<td>8.468e+005</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>To HX-4(2)</td>
<td>322</td>
<td>0.08</td>
<td>8.468e+005</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>To HX-6</td>
<td>371.5</td>
<td>0.08</td>
<td>1.212e+006</td>
<td>0.150194</td>
<td>0.849806</td>
<td>1</td>
</tr>
<tr>
<td>To HX-5(1)</td>
<td>278</td>
<td>0.08</td>
<td>8.291e+005</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>To HX-5(2)</td>
<td>291</td>
<td>1</td>
<td>1.621e+008</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>To MIX(1)</td>
<td>291</td>
<td>0.08</td>
<td>9.809e+005</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>To HX-8(2)</td>
<td>314.8</td>
<td>0.08</td>
<td>8.468e+005</td>
<td>0</td>
<td>1</td>
<td>0.9915</td>
</tr>
<tr>
<td>To HX-8(1)</td>
<td>425</td>
<td>0.4977</td>
<td>3.832e+005</td>
<td>0.894072</td>
<td>0.105928</td>
<td>1</td>
</tr>
<tr>
<td>To HX-9</td>
<td>348</td>
<td>0.4977</td>
<td>3.832e+005</td>
<td>0.894072</td>
<td>0.105928</td>
<td>1</td>
</tr>
<tr>
<td>To HX-7</td>
<td>291</td>
<td>0.08</td>
<td>8.468e+005</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>To MIX(1)</td>
<td>291</td>
<td>0.08</td>
<td>8.291e+005</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>To MIX(2)</td>
<td>291</td>
<td>1</td>
<td>3528</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>To MIX(3)</td>
<td>291</td>
<td>0.4977</td>
<td>1.135e+004</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>To Evaporator</td>
<td>298</td>
<td>0.08</td>
<td>1.212e+006</td>
<td>0.150194</td>
<td>0.849806</td>
<td>0.2104</td>
</tr>
<tr>
<td>Cold Utility 1 (Inlet)</td>
<td>293</td>
<td>1</td>
<td>1.621e+008</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Cold Utility 1 (Outlet)</td>
<td>288</td>
<td>1</td>
<td>1.621e+008</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Make-up H₂O</td>
<td>293</td>
<td>1</td>
<td>3133</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Steam In</td>
<td>319</td>
<td>0.1</td>
<td>1.116e+006</td>
<td>0</td>
<td>1</td>
<td>0.9450</td>
</tr>
<tr>
<td>Steam Out</td>
<td>319</td>
<td>0.1</td>
<td>1.116e+006</td>
<td>0</td>
<td>1</td>
<td>0 (Sat.)</td>
</tr>
</tbody>
</table>

**Table 5.8: Stream specifications of block 4**
5.6.5. **Separation Block Structure:**

After being cooled by the evaporator of the refrigeration circuit, CO₂-loaded steam (stream “To Flash 1”) enters the first flash unit (“Flash 1”), where most of the vapor-liquid separation occurs. Liquid stream (stream “To HX-5 (1)”) consisting of 99.999+% water leaves the bottom of the flash and is sent to HX-5, before being sent to the mixer unit (“MIX”). The vapor stream (stream “To Compressor 2”) consisting of 89.40% CO₂ with the balance water leaves the top of the flash and is sent to the first compressor in the sequence (“Compressor2”), where it is compressed to 0.4977 bar before being sent to HX-8 (stream “To HX-8 (1)”) where it is cooled by the returning steam leaving HX-7 (stream “To HX-8 (2)”). Stream “To HX-8(1)” exits HX-8 as stream to HX-9 and is sent to HX-9 where it is further cooled using a cold water utility (stream “Cold Utility 2”). Stream “To HX-9” exits HX-9 as stream “To Flash 2” and is sent to unit “Flash 2” where additional flash separation occurs to increase the recovery of CO₂. Liquid stream (stream “To MIX (3)”) consisting of 99.97+% water leaves the bottom of the flash and is sent to the mixer unit (“MIX”). The vapor stream (stream “To Compressor 3”) consisting of 95.91% CO₂ with the balance water leaves the top of the flash and is sent to the second...
compressor in the sequence (“Compressor3”), where it is compressed to 1 bar before being sent to HX-10 where it is cooled using another cold water utility (stream “Cold Utility 3”). Stream “To HX-10” exits HX-10 as stream “To Flash 3” and is sent to unit “Flash 3” where the last flash separation operation occurs to maximize recovery of CO₂. Liquid stream (stream “To MIX (2)”) consisting of 99.94+% water leaves the bottom of the flash and is also sent to the mixer unit (“MIX”). The vapor stream (stream “CO₂ Atm P, T”) consisting of 97.94+% CO₂ is sent to the final liquefaction and sequestration process, which is identical to the one used in the amine process. The work of compressors 3 and 4, \( W_{\text{comp,3}} \) and \( W_{\text{comp,4}} \) is 14,860 kW and 4,857 kW respectively.

<table>
<thead>
<tr>
<th>Stream Name</th>
<th>Temperature (K)</th>
<th>Pressure (Bar)</th>
<th>Flow rate (kg/h)</th>
<th>Mole Frac. CO₂</th>
<th>Mole Frac. H₂O</th>
<th>Vapor Phase Frac.</th>
</tr>
</thead>
<tbody>
<tr>
<td>To Flash 1</td>
<td>278</td>
<td>0.08</td>
<td>1.212e+006</td>
<td>0.150194</td>
<td>0.849806</td>
<td>0.1679</td>
</tr>
<tr>
<td>To HX-5(1)</td>
<td>278</td>
<td>0.08</td>
<td>8.291e+005</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>To Compressor 2</td>
<td>278</td>
<td>0.08</td>
<td>3.832e+005</td>
<td>0.894072</td>
<td>0.105928</td>
<td>1</td>
</tr>
<tr>
<td>To HX-8(1)</td>
<td>425</td>
<td>0.4977</td>
<td>3.832e+005</td>
<td>0.894072</td>
<td>0.105928</td>
<td>1</td>
</tr>
<tr>
<td>To HX-9</td>
<td>348</td>
<td>0.4977</td>
<td>3.832e+005</td>
<td>0.894072</td>
<td>0.105928</td>
<td>1</td>
</tr>
<tr>
<td>To HX-8(2)</td>
<td>315</td>
<td>0.08</td>
<td>8.468e+005</td>
<td>0</td>
<td>1</td>
<td>0.9915</td>
</tr>
<tr>
<td>To HX-4(2)</td>
<td>322</td>
<td>0.08</td>
<td>8.468e+005</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>To Flash 2</td>
<td>291</td>
<td>0.4977</td>
<td>3.832e+005</td>
<td>0.894072</td>
<td>0.105928</td>
<td>0.9322</td>
</tr>
<tr>
<td>Cold Utility 2 (Inlet)</td>
<td>288</td>
<td>1</td>
<td>6.240e+005</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Cold Utility 2 (Outlet)</td>
<td>289</td>
<td>1</td>
<td>6.240e+005</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>To Flash 2</td>
<td>291</td>
<td>0.4977</td>
<td>4.163e+005</td>
<td>0.894072</td>
<td>0.105928</td>
<td>0.9322</td>
</tr>
<tr>
<td>To MIX(3)</td>
<td>291</td>
<td>0.4977</td>
<td>1.135e+004</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>To MIX(2)</td>
<td>291</td>
<td>1</td>
<td>3247</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>To Compressor 3</td>
<td>291</td>
<td>0.4977</td>
<td>3.718e+005</td>
<td>0.959118</td>
<td>0.040882</td>
<td>1</td>
</tr>
<tr>
<td>To HX-10</td>
<td>343.5</td>
<td>1</td>
<td>3.718e+005</td>
<td>0.959118</td>
<td>0.040882</td>
<td>1</td>
</tr>
<tr>
<td>Cold Utility 3 (Inlet)</td>
<td>288</td>
<td>1</td>
<td>5.959e+006</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Cold Utility 3 (Outlet)</td>
<td>289</td>
<td>1</td>
<td>5.959e+006</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>To Flash 3</td>
<td>291</td>
<td>1</td>
<td>3.718e+005</td>
<td>0.959118</td>
<td>0.040882</td>
<td>0.9792</td>
</tr>
<tr>
<td>CO₂ Atm P,T</td>
<td>291</td>
<td>1</td>
<td>3.686e+005</td>
<td>0.979482</td>
<td>0.020518</td>
<td>1</td>
</tr>
</tbody>
</table>

**Table 5.9**: Stream conditions of block 5
5.7. Discussion

The important energetic parameters, which are used in the energetic comparison between amine-based absorption and MgO-based adsorption, are shown in table 5.10. They are total power generated, total power loss due to capture, auxiliary power losses, CO₂ compression power need, boiler heat rate, net power generated, and net plant efficiency. In the case of amine absorption, a power loss of 70,500 kW is attributed to the use of steam towards the operation of the stripper’s re-boiler that is necessary for solvent regeneration. In the case of the MgO sorbent, power loss arises from several origins; namely, compressor operations in the heat pump cycle, vapor compression cycle, and separation blocks (32,292 kW), and steam being used towards water vaporization in the low pressure steam desorption cycle (2,777 kW) instead of being used towards work production. Auxiliary power losses are identical for all three cases at 29,700 kW. CO₂ compression power is only needed by the two CO₂ capture designs, and is identical for both of them at 54,939 kW. Boiler heat rate is slightly higher for the case of MgO sorbents due to the decreased efficiency of the unit as a result of the modified air pre-heater heat exchanger (see block 1). In terms of net plant efficiency (defined as total power generated over boiler heat rate) the MgO sorbent design is 3 percentage points more energetically efficient than amine based absorption (31.28% vs. 28.28%). This increased efficiency manifests itself in an 11.49% increase in net power generation of the MgO sorbent design over the amine-based design (343,792 kW over 308,361 kW).
<table>
<thead>
<tr>
<th>Case</th>
<th>No Capture Technology</th>
<th>90% Capture 2006 Amine Technology</th>
<th>90% Capture MgO Aerosols Sorbent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Power Generated (kW)</td>
<td>463,500</td>
<td>393,000</td>
<td>428,431</td>
</tr>
<tr>
<td>Total Power Loss due to Capture (kW)</td>
<td>N/A</td>
<td>*70,500</td>
<td>**32,292</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>**2,777</td>
</tr>
<tr>
<td>Auxiliary Power Losses (kW)</td>
<td>29,700</td>
<td>29,700</td>
<td>29,700</td>
</tr>
<tr>
<td>CO₂ Compression Power Need (kW)</td>
<td>N/A</td>
<td>54,939</td>
<td>54,939</td>
</tr>
<tr>
<td>Boiler Heat Rate (Btu/hr)</td>
<td>3.72×10⁹</td>
<td>3.72×10⁹</td>
<td>3.767×10⁹</td>
</tr>
<tr>
<td>Net Power Generated (kW)</td>
<td>433,778</td>
<td>308,361</td>
<td>343,792</td>
</tr>
<tr>
<td>Net Plant Efficiency (%)</td>
<td>39.78</td>
<td>28.28</td>
<td>31.28</td>
</tr>
</tbody>
</table>

* Work generated in some part of the plant is used somewhere else for carbon capture  
** Steam used to meet plant heating needs rather than for work generation.

Table 5.10: Comparison of CO₂ capture designs: none, amine-based, and MgO-based

5.8. Conclusions

A novel PTSA process for MgO-based CO₂ capture was developed. The paper first analyzes a general steam-cycle plant to determine the important parameters which affect its efficiency and power output. The effect of CO₂ capture with an amine-based technology on plant power output is then modeled, and the reduction in power generation efficiency is quantified. A Gibbs free energy minimization analysis provides important operational data around which the PTSA circuit is constructed. A detailed description of such a PTSA circuit is then discussed and framed in the context of a fully defined (from a mass and heat balance point of view) capture and separation process consisting of 5 different blocks. Such a process is simulated using the UniSim software to verify its feasibility. This paper therefore generates a framework upon which a rigorous comparison of the two different CO₂ capture processes can be performed. It is shown that an 11.49% increase in net power generation can be achieved by employing the alternate MgO-based CO₂ adsorption instead of the amine process. This favorable energetic comparison of the proposed MgO based design with a state-of-the-art amine absorption process suggests that its
real life implementation be pursued. Our future work will focus on the experimental demonstration of the proposed PTSA process.

5.9. Nomenclature:

\( \eta \): Thermal efficiency of steam cycle

\( \dot{W}_{Gen.} \text{ (kW)} \): Rate of work generated by steam cycle

\( \dot{Q}_{Boiler} \left( \frac{\text{BTU}}{\text{hr}} \right) \): Boiler heat rate

\( \dot{Q}_{Boiler}^{\text{new}} \left( \frac{\text{BTU}}{\text{hr}} \right) \): Modified boiler heat duty

\( G \): Total Gibbs free energy

\( N_i^{(j)} \): Number of moles of the \( i^{\text{th}} \) component in the \( j^{\text{th}} \) phase

\( \mu_i^{(j)} \): Chemical potential of the \( i^{\text{th}} \) component in the \( j^{\text{th}} \) phase

\( A \): Atomic balance matrix

\( \mathbf{N}^{(j)} \): Number of moles vector in the \( j^{\text{th}} \) phase

\( \mathbf{N}^* \): Initial number of moles vector
\( \hat{f}^{(j)}_i \): Fugacity of the \( i \)th component in the \( j \)th phase

\( f^{\alpha(j)}_i \): Fugacity of the \( i \)th component in the \( j \)th phase at standard conditions

\( NC \): Number of components

\( NP \): Number of phases

\( R \): Gas constant

\( T \): Temperature

\( \Delta G^{(j)}_f(T) \): Ideal Gibbs free energy of formation for component \( i \), in phase \( j \) at \( T \)

\( C_p \left( \frac{J}{\text{mol} \cdot \text{K}} \right) \): Heat capacity

\( C_p^{\text{MgCO}_3} \left( \frac{J}{\text{mol} \cdot \text{K}} \right) \): Heat capacity of MgCO\(_3\)

\( C_p^{\text{MgO}} \left( \frac{J}{\text{mol} \cdot \text{K}} \right) \): Heat capacity of MgO

\( C_p^{\text{CO}_2} \left( \frac{J}{\text{mol} \cdot \text{K}} \right) \): Heat capacity of CO\(_2\)

\( A, B, C, D \): Heat capacity polynomial coefficients

\( \Delta G_f^\circ \left( \frac{J}{\text{mol}} \right) \): Gibbs free energy of formation
\( \Delta H_f^o \left( \frac{J}{mol} \right) \): Enthalpy of formation

\( \Delta H_{\text{rxn}}^o \left( \frac{J}{mol} \right) \): Heat of reaction

\( \dot{n}_{\text{CO}_2} \left( \frac{\text{mol}}{\text{hr}} \right) \): Moles of \( \text{CO}_2 \) in flue gas stream

\( X_{\text{CO}_2} \): Percentage of \( \text{CO}_2 \) that is captured

\( \dot{n}_{\text{HP}} \left( \frac{\text{mol}}{\text{hr}} \right) \): Mass flow rate of heat pump working fluid

\( \alpha_{\text{Cooling}} \left( \frac{\text{mol MgO}}{\Delta t_{\text{Cooling}}} \right) \): PTSA cooling cycle parameter

\( \alpha_{\text{Heating}} \left( \frac{\text{mol MgCO}_3}{\Delta t_{\text{Heating}}} \right) \): PTSA heating cycle parameter

\( \beta_{\text{Desorber}} \left( \frac{\text{mol MgCO}_3}{\Delta t_{\text{Desorption}}} \right) \): PTSA desorption cycle parameter

\( \beta_{\text{Adsorber}} \left( \frac{\text{mol MgO}}{\Delta t_{\text{Adsorption}}} \right) \): PTSA desorption cycle parameter

\( \Delta t_{\text{Cooling}} \): Time duration of cooling cycle

\( \Delta t_{\text{Heating}} \): Time duration of heating cycle

\( \Delta t_{\text{Adsorption}} \): Time duration of adsorption cycle
\( \Delta t_{\text{Desorption}} \): Time duration of desorption cycle

\( \dot{Q}_{\text{Adsorber}} \left( \frac{J}{\text{hr}} \right) \): Heat released by the adsorber

\( \dot{Q}_{\text{Desorber}} \left( \frac{J}{\text{hr}} \right) \): Heat absorbed by the desorber

\( W_{\text{comp.1}} \) (kW): Work of compressor1 (PTSA cycle)

\( W_{\text{comp.2}} \) (kW): Work of compressor2 (vapor-compression cycle)

\( W_{\text{comp.3}} \) (kW): Work of compressor3 (first compressor in separation structure)

\( W_{\text{comp.4}} \) (kW): Work of compressor4 (Second compressor in separation structure)
5.10. References:


