UNIVERSITY OF THE WITWATERSRAND, JOHANNESBURG

Integration and Synthesis of Heat and Mass Exchanger Networks for CO_2 Capture in Power Plants

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A thesis submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, Johannesburg, in fulfilment of the requirements for the degree of Doctor of Philosophy in Chemical Engineering.

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March 2020

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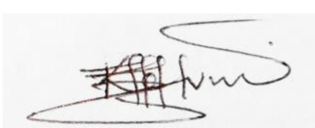

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Dedication

I dedicate this thesis to God Almighty who has preserved me thus far, the Holy Spirit for inspiration while I was preparing manuscripts for publication from this research, and to the loving memory of my late father, Mr. Dennis Aghogho Yoro who passed on 14 years ago when I was at the peak of high school education and at the threshold of starting my academic journey in the field of chemical engineering as an undergraduate. May his soul continue to rest in peace. AMEN!

Abstract

CO_2 capture and storage (CCS) have been identified as a promising technology that could allow for the continual use of coal in power generation, and yet maintain a near-zero emission of CO_2 into the atmosphere. However, the major challenge facing the retrofitting of CO_2 capture systems to existing power plants is that most CCS techniques are material and energy-intensive. This subsequently reduces the operational efficiency of the power plants and also increases the energy penalty, as well as operational cost. To date, the blending of sorbents with inhibitors such as piperazine (PZ) solvents, amine-2-amino-2-methyl-1-propanol (AMP), the use of phase change materials, amine scrubbing and the use of external utilities such as steam and cooling water have been the common strategy to minimize energy consumption during CO_2 capture in power plants.

In this thesis, a technique to minimize the high energy and material requirement during absorptive and adsorptive CO_2 capture in coal-fired power plants was proposed, developed and tested. The principles of heat and mass integration were employed in this study to minimize energy consumption and resource usage during CO_2 capture in power plants. Heat exchanger networks (HENs) were synthesized in this study to address energy minimization while the application of mass exchanger networks (MENs) were introduced to address the excessive consumption of resources and utilities such as cooling water, steam, sorbents etc during CO_2 capture. Furthermore, a systematic method for the synthesis of combined heat and mass exchanger networks (CHAMENs) with regeneration was developed and tested in this thesis to simultaneously minimize the use of energy and mass during CO_2 capture considering sorbent regeneration.

Also, to ensure the cost-effectiveness of the MENs, a technique was presented to target the minimum mass separating agents (sorbent) as well as the capital costs for the heat and mass exchanger networks. The method used was simple and based on insight, rather than relying on a mathematical 'black-box' approach. Graphical tools new to CCS studies, such as the *y*-*x* and the *y*-*y** composite curve plots were introduced to allow the minimum exchanger sizes to be determined before network design. Capital cost targets were traded off against the established operating cost targets to optimize the total cost first with no design being necessary. The total annualized cost (TAC) for the network which includes the cost of mass separating agents, hot

and cold utilities, was minimized using an objective function to reduce process cost. To account for fluctuations in operating parameters during absorptive CO_2 capture, a simultaneous (mathematical programming) approach was used to synthesize optimal heat exchanger networks (HEN) with non-isothermal mixing and fluctuating parameters, while minimum utility cost for the CO_2 absorption process was determined at selected parameter points. The HENs synthesis procedure presented in this thesis took into consideration quantified uncertainties in inlet temperatures and flow rates to address the major shortcomings observed in previously reported methodologies.

Area targeting of heat exchangers was investigated in this study to determine the capital cost of the synthesized multi-period network. Where a simultaneous synthesis technique was used, a multi-period MINLP model was developed to generate a HEN with optimized heat exchanger areas and total annualized costs while the concept of pinch analysis was used for the sequential approach. A linear programming technique was then used to synthesize an effective transport network for captured CO_2 from power plants in different locations using a hypothetical case study. The synthesized CHAMENs network confirmed $ 0.1998 million/yr as the estimated total annualized cost accruable if combined network with regeneration is integrated for CCS as suggested in this research.

The outcome of this study further revealed that about 19.1 % of sorbent used for adsorptive CO_2 capture could be saved by integrating mass exchanger networks in CCS studies. Besides, this study also discovered that about 25-30 % of the energy used during CO_2 separation could be saved by integrating the heat exchanger networks developed and described in this thesis. Conclusively, this study established that the application of heat exchanger network (HEN) and mass exchanger network (MEN) to minimize energy and material consumption during CO_2 capture is unique and effective in CO_2 capture systems where solid and liquid sorbents are used, compared to existing methods. Interestingly, the techniques proposed in this study which are relatively new to CCS can be fully extended to other CO_2 capture techniques after minor modifications. The major shortcoming identified in this study is the generation of some process data, hence scientific assumptions had to be made in such cases.

Acknowledgements

'No man is an island'. As such, a doctoral thesis of this nature wouldn't have been possible without the help, prayers, support, and encouragement from colleagues, friends, family, and other benefactors. In light of this, I will like to use this section to acknowledge everyone who has contributed in one way or the other towards the success of this research. First of all, I thank God Almighty for his blessings, guidance, wisdom, sustenance and protection throughout my doctoral study at the University of Witwatersrand (WITS)**.**

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Publications and Presentations

The following publications and conference presentations emanated from this study. Kindly note that this thesis is a careful compilation of these publications and presentations. Copyright permissions were obtained where such publications were used verbatim in this thesis (see appendix D).

Book chapter contributions:

1. **K.O. Yoro,** M.O. Daramola., CO_2 emission sources, Greenhouse gases and the Global warming effect – Chapter 1, In: the book *'Advances in CO_2 capture'* Elsevier, **2019. Accepted (in press).**

2. **K.O. Yoro**, A.J. Isafiade, M.O. Daramola., Synthesis of Mass Exchanger Networks Using Sequential Techniques., *Transactions on Engineering Technologies: World Congress on Engineering and Computer Science*, **2019 Accepted (in press).**

Peer-reviewed journal articles:

1. **K.O. Yoro**, A.J. Isafiade, M.O. Daramola., A Review on Heat and Mass Integration Techniques for Energy and Material Minimization during CO_2 Capture, *International Journal of Energy and Environmental Engineering*., **2019**, **https://doi.org/10.1007/s40095-019-0304-1**

2. **K.O. Yoro**, A.J. Isafiade, M.O. Daramola., Multi-period Heat Exchanger Network Synthesis with Temperature Intervals and Uncertain Disturbances, *Chemical Engineering Transactions*, **2019**, **https://doi.org/10.3303/CET1976174**

3. **K.O. Yoro**, M.K. Amosa, P.T. Sekoai, J. Mulopo, M.O. Daramola., Diffusion Mechanism and Effect of Mass Transfer Limitation during the Adsorption of CO_2 by polyaspartamide in a Packed-Bed Unit, *Int. Journal of Sustainable Engineering*, **2019**, **https://doi.org/10.1080/19397038.2019.1592261**

4. **K.O. Yoro**, M.K. Amosa, P.T. Sekoai, M.O. Daramola., Modelling and Experimental Investigation of Effects of Moisture and Operating Parameters on the Adsorption of CO_2 onto Polyaspartamide, Int. *Journal of Coal sci. and Tech.*, **2018**, **https://doi.org/10.1007/s40789-018-0224-3**

5. **K.O. Yoro,** M.O. Daramola., Energy recovery during Absorptive CO_2 Capture Using Flexible Heat Exchanger Networks, Energy (Elsevier), EGY-D-20-00496, **Submitted**,

6. **K.O. Yoro,** A.J. Isafiade, M.O. Daramola., Development of a Network for Effective CO_2 Transport in Power plants: A Hypothetical Study, **(Manuscript in preparation)**.

Peer-reviewed international conference proceedings:

1. **K.O. Yoro**, A.J. Isafiade, M.O. Daramola., Synthesis of Optimal Heat Exchanger Networks with Quantified Uncertainties and Non-isothermal Mixing, *IOP*: *Material Science and Engineering*, **2019. Published**.

2. **K.O. Yoro,** N. Chiwaye, A.J. Isafiade, M.O. Daramola., Energy and Material Minimization during CO_2 Capture Using Combined Heat and Mass Integration Technique, *SINTEF Academic Press*, **2019. http://hdl.handle.net/11250/2638104**

3. **K.O. Yoro**, A.J. Isafiade, M.O. Daramola., Multi-period Heat Exchanger Network Synthesis with Temperature Intervals and Uncertain Disturbances. In: Proceedings of the 22nd Conference on Process Integration for Energy Saving and Pollution Reduction (PRES'19), Agios Nikolaos, **Crete, Greece,** 20th – 23rd October **2019**. **https://doi.org/10.3303/CET1976174**

4. **K.O. Yoro**, A.J. Isafiade, M.O. Daramola., Sequential Synthesis of Mass Exchanger Networks for CO_2 Capture. In: Proceedings of the 26th *World Congress on Engineering and Computer Science (WCECS 2018)*, 23 – 25th October, **2018**., University of California, Berkeley – **San Francisco, USA-** ***Best paper award,*** **Published.**

Local conference abstracts and presentations:

1. **K.O. Yoro**, A.J. Isafiade, M.O. Daramola., Synthesis of Heat Exchanger Networks for Multi-period CO_2 Capture Operations, **Oral presentation** *4th National Conference on Global Change*. Bolivia Conference Centre, Polokwane, **Limpopo, South Africa.** 3rd – 6th December **2018**.

2. **K.O. Yoro,** M. Singo, J.L. Mulopo, M.O. Daramola, Modelling and Experimental Study of the CO_2 Adsorption Behaviour of Polyaspartamide as an Adsorbent during Post-Combustion CO_2 Capture., **Poster presentation**, *5th Biennial Carbon and Storage Conference*, **Durban South Africa,** 5th -8th October **2017**.

3. **K.O. Yoro,** A.J. Isafiade, M.O. Daramola, Mass Separating Agent Targeting during CO_2 Capture Using an Improved Mass Integration Technique, **Oral presentation**, Industry-Academia Partnership Programme (IAPP), University of the Western Cape, **Cape Town South Africa**, 4th – 6th February **2019**.

4. **K.O. Yoro,** A.J. Isafiade, M.O. Daramola, A New Technique for Energy and Resource Minimization during CO_2 Capture in Coal-fired Power Plants, **Oral presentation**, 10th WITS Cross Faculty Postgraduate Symposium, 3rd - 4th September **2019- *Best oral presentation award (3rd place)***

5. **K.O. Yoro**, A.J. Isafiade, M.O. Daramola, Synthesis of heat and mass Exchange Networks for CO_2 Capture from Power plants, **Poster presentation**, University of the Witwatersrand research day presentation, 28th September **2017**.

6. **K.O. Yoro**, A.J. Isafiade, M.O. Daramola, Energy and Material Minimization during Industrial CO_2 Capture Using Combined Heat and Mass Integration Techniques, **Poster presentation**, WITS-CHMT school research day, 29th August **2019.**

Awards won on merit:

1. Sequential Synthesis of Mass Exchanger Networks for CO_2 Capture, 26^{th} World Congress on Engineering and Computer Science (WCECS 2018), 23 – 25th October **2018**, University of California, Berkeley – San Francisco, USA. (**Best paper award- Merit (Student)**)

2. A New Technique for Energy and Resource Minimization during CO_2 Capture in Coal-fired Power Plants. 10^{th} Wits Cross-Faculty Postgraduate Symposium, 3^{rd} - 4^{th} September **2019,** Johannesburg, South Africa. (**Best oral presentation award (3^{rd} prize)**)

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List of Abbreviations

CAPEX = Capital Expenditure ($/yr)

CCS = Carbon/CO_2 Capture and Storage

CCSU = Carbon Capture Storage and Utilization

CHAMENs = Combined Heat and Mass Exchanger Networks

CO_2 = Carbon dioxide / Carbon (iv) oxide

COG = Coke-oven-gas

EMAT= Estimated minimum approach temperature (^oC)

GAMS = General Algebraic Modelling System

HE = Heat exchanger

HEN = Heat exchanger network

HENS = Heat exchanger network synthesis

HENs = Heat exchanger networks

HRAT = Heat Recovery Approach Temperature

IN = Inlet

LMTD = Log Mean Temperature Difference (^oC)

LP = Linear Programming

MEN = Mass Exchanger Network

MSA = Mass separating agent/lean stream

MINLP = Mixed Integer Nonlinear Programming

MP = Mathematical Programming

OPEX = Operating Expenditure

OUT = Outlet

PT = Pinch Technology

TAC = Total Annualized Cost ($/yr)

Parameters

A = Heat transfer area (m^2)

AC = Annual Cost ($/yr)

B = Exponent in cost equation of heat exchanger

B_{CU} = Area cost of heater exponent ($)

B_e = Exponent of HE area cost

B_{HU} = Exponent of cooler's area cost

C = Unit cost for MSA/lean stream/utility ($)

CF = Fixed cost for heat exchanger ($)

C_{CU} = Hot utility unit cost ($)

C_{CU} = Hot utility unit cost ($)

C_e = Heat exchanger area cost coefficient

CF_{CU} = Unit charge of cooler (fixed)

CF_e = Heat exchanger unit's fixed charge

CF_{HU} = Heater unit's fixed charge

C_{HU} = Unit cost of hot utility ($)

$C_{HU,w}$ = Unit cost of hot water ($)

C_j = Final CO_2 adsorbed by MSA

Cp = Heat capacity (kJ/^oC)

cu = Cold utility

F_{CP} = Heat capacity flow rate of the main stream (kW/°C)

G_i = Mass flow rate of the rich main stream (kg/s)

hu = Hot utility

L = Mass flow rate of the MSA/lean main stream (kg/s)

FC = Annualized capital cost ($/yr)

N = Number of mass exchanger trays

Q = Heat load (kW)

q = Quantity of exchanged heat between hot stream I and cold stream j in stage k

qcu = Heat exchanged between hot stream I and cold utility

T, IN_{CU} = Temperature of cold utility (inlet) (^oC)

T, IN_H = Initial inlet temperature of the hot stream (^oC)

T, IN_{HU} = Inlet temperature of the hot utility (^oC)

T_j^{LB} = Inlet temperature to MSA (^oC)

T_j^{UB} = Outlet temperature from MSA (^oC)

T, OUT_H = Hot Stream final outlet temperature (^oC)

T, OUT_{HU} = Hot utility temperature – Outlet (^oC)

U_{CU} = Overall heat transfer coefficient for a match of the hot stream i and cold utility

U_{HU} = Overall heat transfer coefficient for a match of cold stream j and hot utility

U = Coefficient of transferred heat for each heat exchanger (overall)

x_j^s = Supply mass composition of CO_2 in the MSA

x_j^t = Target mass composition of CO_2 in the MSA

x = Concentration of MSA/lean stream (g/L)

y = Concentration of rich stream (g/L)

z = Binary variable showing the existence of matches for hot and cold streams i and j in k stage

Zcu = Variable showing presence of matches for cold utility (Binary)

Zhu = Variable showing presence of matches for hot utility (Binary).

Indices

i = i^{th} rich stream

j = j^{th} MSA/lean stream

k = Stage index

k^{th} = k^{th} stage in MEN

Symbols

ΔT_{min} = Minimum temperature difference

Δy = Rich stream composition difference

$ = US Dollar

CHAPTER ONE

General Introduction

This chapter presents a brief introduction to the entire thesis. Motivation, research questions, and objectives are clearly outlined. The scope, novelty and benefits of this research to the scientific and engineering community are highlighted.

1.1 Motivation and Background

Power plants fuelled by fossil fuels contribute about 33 – 40 % of the total CO_2 emission with coal-fired power plants being the main contributor (Tian and Yang, 2016). For instance, a typical 500 MW coal-fired power plant is capable of emitting about 2–3 million tons of CO_2 per year (Zhang, 2016). The devastating effects as a result of the high concentration of greenhouse gases such as CO_2 in the atmosphere are raising serious global concerns. This has necessitated the need to search for low-cost and efficient technologies to capture CO_2 thereby reducing its emission into the atmosphere.

CO_2 capture from power plants or any stationary point source offers great potential for a significant reduction in CO_2 emissions (Li et al., 2016; Yoro et al., 2016). However, most of the CO_2 capture methods proposed in the literature are highly material and energy intensive. Researchers have emphasized the need to save material and energy in industrial processes in the past to guarantee the economic advantage of these processes (Ravagnani et al., 2005; Seid and Majozi, 2014a, 2014b). To mitigate global climate change through CO_2 capture, storage, and utilization (CCSU) with minimized energy and material consumption, it is imperative to develop a CO_2 capture system that comprises networks of heat and mass exchangers that will ensure minimum energy and material consumption via process integration concept.

It has been identified that the major energy-exchange units in any chemical industry are the heat exchangers (Chen and Hung, 2005). It has also been reported in literature that integration of mass exchangers in various industrial applications could lead to the minimization of material (mass separating agents and external utilities) consumed (Yoro et al., 2018; Mano et al., 2019). Furthermore, application of heat exchanger networks can also lead to minimized energy consumption (Wu et al., 2015: Pavão et al., 2018). As such, synthesis of heat exchanger networks (HENs) and mass exchanger networks (MENs) have been proposed in this thesis as a systematic way of effectively and efficiently minimizing energy and material consumption during absorptive and adsorptive CO_2 capture from power plants.

Many industries are re-focusing on economically and environmentally benign designs to revamp their design and operational requirements to attain the objective of satisfying both environmental regulations and minimum energy consumptions in chemical processes (Ozonoh et al., 2019). To minimize CO_2 emission from coal-fired power plants through CCS and maintain stable plant efficiency, the old power plants should be retrofitted with CO_2 capture devices with an optimal HEN and MEN configuration. New ones should not be built without CO_2 capture units with an optimal HEN and MEN configuration. Furthermore, this study was also inspired by the need to integrate not just heat exchanger networks (HENs), but also mass exchanger networks (MENs) during CCS operations. Integration does not only introduce the benefit of energy-saving, but it also leads to increased interactions between separate plant units (such as reactors, separators, columns and furnaces). These interactions subsequently result in changes in plant characteristics and behaviours whenever nominal operating conditions such as inlet temperatures, flowrates etc., are altered due to disturbances or changes in the manipulative inputs. In HENs and MENs, these disturbances propagate downstream paths and the whole length of the network causing changes in stream target temperatures as well as set-points, thereby resulting in sub-optimal plant operation. Due to their ability to reduce energy and material consumption as well as CO_2 emission, the interest in synthesizing HENs and MENs have significantly increased. Power plants need to be integrated with CO_2 capture units to satisfy environmental regulations without making the plant more complex with an adverse effect on plant economy.

Currently, pinch analysis (sequential) and mathematical programming-based (simultaneous) methods are the most popular techniques for synthesizing HENs and MENs. These techniques have played very important roles in solving industrial problems for synthesizing HENs and MENs (Linnhoff and Hindmarsh, 1983; Payet et al., 2018). With the recent advancement in computing technology, the mathematical programming method has shown significant potential in solving problems involving HENs and MENs. Pinch analysis, on the other hand, has attracted tremendous attention in setting energy targets for many industrial processes (Majozi et al., 2006; Tan et al., 2014; Priya and Bandyopadhyay, 2017). These energy targets solely rely on the choice of the minimum approach temperature (ΔT_{min}) of the chemical process in the heat exchanger network synthesis. Pinch technology has wide applications in both new and retrofit design cases. So far, the application of pinch technology in retrofit design cases is much higher than in new design applications (Gadalla, 2015; Cheng and Wang, 2016; Anastasovski, 2017). Pinch analysis techniques have also been reported for carbon planning where various energy sinks and sources for CCS were explored (Tan et al., 2009, 2014). However, its application in CO_2 capture studies for concurrent energy and material minimization is still new and has not been fully explored.

Analogies exist between heat and mass exchange networks. Mass transfer from a set of rich streams to a set of lean streams corresponds to heat transfer from a set of hot streams to a set of cold streams during CO_2 capture (Hallale and Fraser, 2000a, 2000b). Adsorption and absorption are widely recommended methods for CO_2 capture and they are highly exothermic processes where a high amount of heat energy is released to the surrounding. Given the aforementioned, it is clear that heat and mass are fundamental utilities of operation in any CO_2 capture process. Hence, heat and mass integration during CO_2 capture requires an in-depth investigation. To minimize energy usage, material consumption and mitigate environmental hazards attributed to the emission of anthropogenic CO_2 into the atmosphere, various integration methods (including mass and heat integration networks) were explored in this study. Industrial heat and mass exchanger networks are important because of their role in recovering material and process heat in a process (Wan-Alwi et al., 2011; Chen and Wang, 2012). Mass exchanger networks can be used for screening mass separating agents as well as satisfying mass transfer demands in a CO_2 capture process while still meeting environmental and economic requirements (Liu et al., 2013).

Design and synthesis of heat and mass exchange networks for heat and mass integration studies in the past always gave rise to discrete optimization problems, which if presented in algebraic form results in mixed-integer optimization problems (Rathjens et al., 2016). Mathematical programming through the use of computer programs in choosing a suitable alternative from a set of available options could be a very good technique to solve the aforementioned problem (Short et al., 2016). Furthermore, there have been considerable advances in mathematical programming techniques in process integration studies in the past four decades. As a result, the solution of mixed-integer nonlinear programming problems with rigorous global optimization of nonlinear programs has become a reality in recent times. In addition, there have been new trends towards logic-based formulations that can facilitate the modelling and solution of these problems. Finally, the availability of modelling systems that can facilitate the formulation of optimization problems has also recorded tremendous progress through mathematical programming, as well as the development of several solution strategies in process synthesis. Mathematical programming can also be used to investigate and determine the most efficient and cost-effective way to allocate scarce resources in an industrial process.

Pinch analysis, based on thermodynamic principles provides a systematic approach for material and energy saving in many chemical processes by identifying optimal energy/mass utilization strategy (McBrien et al., 2016). Pinch analysis technique has a wide range of applications in many industrial processes (Fernández-Polanco and Tatsumi, 2016; Mehdizadeh-Fard et al., 2017), in finance (Geldermann et al., 2007; Roychaudhuri and Bandyopadhyay, 2018) and supply chain management (Tan et al., 2015; Foo, 2016). The basic concept of pinch analysis in heat integration is to match the available internal heat sources with the appropriate heat sinks to maximize energy recovery and to minimize the need for external utilities. In an attempt to maintain cost-effective networks during the design and integration of individual network in a chemical process due to the interaction which exists amongst process parameters, it is essential to apply pinch analysis techniques during process integration and design (Klemeš and Kravanja, 2013; Diamante et al., 2014). Although the composite curves obtained through pinch analysis can be used to set energy targets, they are however tedious when applied to large problems and each step of the synthesis process is dependent on previous steps hence it may not involve a simultaneous trade-off in competing costs. Another disadvantage of the pinch approach is that its application will be difficult when considering issues such as multiple objectives and time-dependent scenarios. As a result, this study aims to apply the principles of pinch analysis in combination with mixed-integer nonlinear programming (MINLP) for selected CO_2 capture techniques to determine optimal material and energy-saving during CO_2 capture. CO_2 capture is a heat and mass exchange process because heat and mass exchange occur preferentially between sorbent and adsorbates in a typical CO_2 capture process. Heat energy is released in high quantities during CO_2 separation and high amount of heat energy is also required during sorbent regeneration in a CO_2 capture process (Wurzbacher et al., 2016; Yoro and Sekoai, 2016). The recent emphasis on material minimization has also necessitated the need for the industrial application of mass exchanger networks in this study.

Literature has suggested ways to minimize energy during CO_2 capture using chemical additives and inhibitors such as piperazine and 2-amino-2-methyl-1-propanol (AMP) solutions (Oexman et al., 2008). However, additives are expensive and this makes CCS an expensive technology. Secondly, additives have only been used in gas-liquid separation processes to minimize the energy requirement without considering the minimization of materials consumed. Against this background, this study was aimed at integrating and synthesizing heat and mass exchanger networks to minimize high energy requirement and excessive material consumption simultaneously during CO_2 capture from power plants. The technique introduced in this study can be used for minimization of energy and material in all CO_2 capture methods and also in multi-period scenarios. The study employed the principle of pinch analysis and mathematical programming to minimize the consumption of energy and material during CO_2 capture. Since heat and mass exchange occur simultaneously during CO_2 capture, the outcomes documented in this thesis further explored the possibility of synthesizing a combined network (that considers a simultaneous heat and mass exchange) for CO_2 capture to determine their energy and material-saving potentials.

1.2 Problem statement

Retrofitting power plants with CO_2 capture units result in a sharp decline in plant efficiency and an increase in loss of material and energy. Research reports have surfaced in the open literature on the application of heat and mass exchange networks for minimization of material and energy consumption in many industrial applications (El-Halwagi and Manousiouthakis, 1990; Isafiade and Short, 2016; Isafiade et al., 2016). Considerable research efforts have also been dedicated to the application of pinch technology in designing networks that link CO_2 emission sources to the sink sources (Diamante et al., 2013; He et al., 2014). As far as could be ascertained, no report in open literature has adequately discussed the synthesis of a network (considering both heat and mass exchange) for CO_2 capture to optimize the system towards attaining minimum consumption of energy and material with optimal total annualized cost (TAC) using both sequential (pinch analysis) and simultaneous (mathematical programming) techniques. Furthermore, the application of pinch analysis for minimizing material usage and energy consumption with its cost implications in selected CO_2 capture techniques such as adsorption and absorption has not been given adequate attention in the past. Additionally, the use of mathematical programming methodologies to determine the most cost-effective way to transport captured CO_2 from various power plants in CO_2 capture networks to a central point of utilization or storage cannot be traced to any literature report. Therefore, the research efforts as documented in this thesis sought to address the aforementioned gaps in this field. Synthesis and optimization of CO_2 capture network need to be investigated because the outcome could be beneficial in synthesizing HENs and MENs. Reports on the integration of HENs and MENs in CO_2 capture studies using process synthesis techniques as contained in this thesis will contribute immensely towards the advancement and implementation of CCS technology in power plants if properly harnessed.

1.3 Hypotheses and research questions

In this study, the following hypotheses were made;

- Heat recovery between different streams going in and out of a process could minimize energy requirement and the quantity of external utilities (cooling water and steam) consumed during absorptive and adsorptive CO_2 capture.

- Pinch analysis and mathematical programming concepts could be used to set utility targets for the process streams and provide a clearer understanding of the interactions amongst various units in a typical CO_2 capture process.

- The principles of linear mathematical programming may be used to develop a network for effective transport of captured CO_2 from power plants to storage sites. While fluctuations in process parameters within certain ranges due to variations in environmental conditions and other disturbances during CO_2 capture could be handled by synthesizing a multi-period HEN.

- The synthesis of HENs and MENs (separately or combined) plays a pivotal role in minimizing the high energy and material requirement in a typical CO_2 capture process because of the integral relationship between heat and mass during CO_2 capture.

To prove the aforementioned hypotheses, the following research questions were posed and investigated in this study.

1. Can the application of process integration techniques embodying heat and mass exchange network synthesis via sequential (pinch technology) and simultaneous techniques (mathematical programming) produce a CO_2 capture network with minimal energy penalty and material usage?

2. What energy and material-saving scheme in (1) will produce minimum energy penalty and material usage using selected CO_2 capture methods such as absorption and adsorption technology?

3. Can mathematical programming techniques be used to design and synthesize an effective transport network for captured CO_2 from different point sources to a central point of storage or utilization?

4. What is the cost implication of using the heat and mass exchanger networks synthesized in this study (both separately and combined) for selected CO_2 capture methods such as absorption and adsorption?

1.4 Aim and objectives

The main aim of this study was to introduce process synthesis and thermodynamically-driven methodologies via the application of heat and mass exchanger networks to maximize energy recovery and minimize material usage during CO_2 capture from power plants. The study was also aimed at achieving optimal operation at constant set-point target temperatures in the presence of uncertainties and disturbances.

To achieve this goal, the following specific objectives were set out:

1. To carry out a preliminary investigation towards the generation of useful data that will ensure the feasibility of synthesizing heat and mass exchanger networks for CO_2 capture.

2. To synthesize an optimal heat and mass exchanger network for CO_2 capture from power plants using sequential (pinch analysis) and simultaneous (mathematical programming) techniques.

3. To identify the energy-saving scheme needed to achieve a reduced energy penalty and material usage during CO_2 capture in a typical coal-fired power plant.

4. To determine the capital and total annual operating costs for combined heat and mass exchange networks by considering sorbent and energy minimization during CO_2 capture as a case study.

5. To develop a cost-effective transport network for captured CO_2 from different power plants to a central storage site or utilization point.

1.5 Scope of research and justification of the study

The scope of the research reported in this thesis spans across CO_2 capture as well as the introduction of heat and mass integration principles to this field. It is worth emphasizing that CO_2 transport, storage, and utilization do not fall directly within the scope of the research reported here. Hence, they are only discussed briefly in the last chapter of this thesis to provide a platform for other researchers to expand on the study. The content of this thesis covers the application of conceptual, graphical, as well as analytical techniques in pinch technology, as well as mathematical programming to identify optimal energy and material minimization strategy during CO_2 capture. This was done by matching available internal heat source with appropriate heat sinks. This study further covers the application of modern mathematical programming techniques to synthesize a combined heat and mass exchange networks (CHAMENs) for CO_2 capture. This research conceptualized the possibility of developing a simple transport network for captured CO_2 from power plants to storage or utilization sites. In a nutshell, the scope of this research covers the field of absorptive and adsorptive CO_2 capture as well as process synthesis and integration.

Although literature is rich in different methodologies to minimize the consumption of energy and material in some selected industrial processes, only a few studies have considered using process heat and process mass separating agents (MSAs) through heat and mass exchanger networks for this purpose. The recent studies of Onishi et al. (2018), Klemeš and Varbanov (2018), Kang and Liu (2018a, 2018b), Velázquez-Guevara et al. (2018) and Kermani et al. (2018) have shown that it is possible to synthesize and optimize HENs and MENs to suit this purpose but no clear explanation has been provided on how to integrate the synthesized network for heat, mass exchange, and regeneration in a CO_2 capture system. Although CO_2 capture is not restricted to coal-fired plants alone, CO_2 capture from coal power plants was considered in this study because coal is the major source of power generation in South Africa, and coal-fired power plants are the major contributor of CO_2 emission to the atmosphere. Secondly, during the separation of CO_2 from a flue gas stream, heat energy (steam) is used to influence the sorption process and high energy is required during CO_2 stripping and sorbent regeneration. Furthermore, because of the highly exothermic nature of most CO_2 capture processes, a lot of heat is given off in the process and a lot of cooling water will be required to cool down the process. These high energy and material consumption reduces the efficiency of power plants and also makes CCS expensive to implement in many developing countries. To improve the efficiency of power plants retrofitted with CCS systems and reduce the cost of the technology, this study introduced the application of process synthesis techniques through heat and mass integration as a cheaper alternative to the existing energy and material saving methods during CO_2 capture.

The integration of heat and mass exchanger networks using process integration principles have not been fully harnessed for energy and material minimization during CO_2 capture in power plants. The methodologies proposed in this study can be instrumental in saving the cost of energy, and material during the capture of CO_2 from power plants without compromising energy efficiency and environmental friendliness of the process. Also, it could pave the way to enhancing good practice, policy, and decision-making in energy exploration and exploitation studies. Figure 1.1 depicts the steps taken in this study to achieve the set goals.

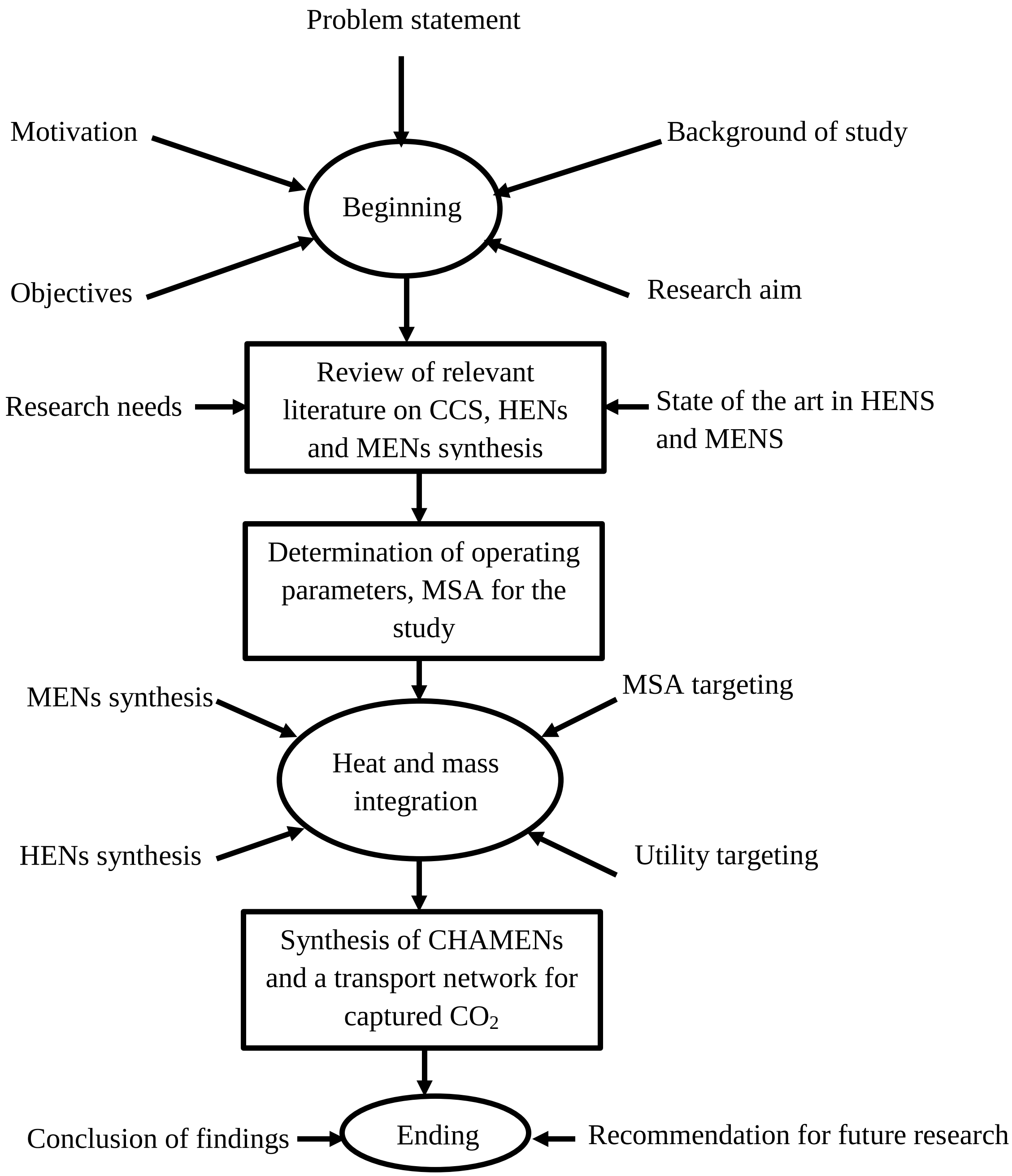


Figure 1.1: A flow chart for the major steps involved in this research.

1.6 Novel contributions of this study

Most research reported in the area of CO_2 capture, storage, and utilization (CCSU) focused more on the synthesis, characterization, and performance evaluation of materials for CO_2 capture.

Only a few studies considered addressing the high material and energy requirement during CO_2 capture. So far, amongst the suggestions presented for energy and material minimization in CCS studies, none considered the application of process heat via heat and mass integration techniques. In this thesis, new ideas to tackle the challenge of energy and material minimization during CO_2 capture using process synthesis approaches were suggested, developed and tested. Other novelties and significant contribution to the existing body of knowledge in this field include the following:

- ❖ A critical review of the literature revealed that the most common method used to minimize high energy usage during CO_2 capture has been the blending of additives and inhibitors with CO_2 capture sorbents, amine scrubbing, sorbent blending, and the use of phase change materials etc. as a way to tackle energy and material consumption during CO_2 capture. The aforementioned techniques are expensive and only tackled energy and not material minimization. But this study introduces a new approach through heat and mass exchanger network synthesis that will not only address energy minimization in CO_2 capture systems but also tackle material (sorbent and utility) wastage. As far as could be ascertained, this approach has not been reported before in this field.

- ❖ Apart from just heat and mass exchanger network (HEN and MEN) synthesis problems, this study further implemented the outcome of the synthesized HEN and MEN in a super-critical coal-fired power plant with CO_2 capture alongside its operating and capital costs.

- ❖ Unlike previous reports on heat and mass integration, this study considered sizing (height targeting) of the heat and mass exchangers required for the CO_2 capture case studies, height targeting as well as the network design using both simultaneous and sequential techniques.

- ❖ Development of an optimal transport network to convey captured CO_2 from a central power plant to different storage sites or utilization points via linear programming techniques is presented for the first time in this thesis to ensure effective transport of CO_2 with minimized material wastage.

- ❖ The number of literature investigating the operation of HEN for energy minimization during CO_2 capture is scanty compared to those that report HEN design. For the first time, HENs operation was investigated in this study to control the effect of disturbances and uncertainties in the network while achieving optimum operation with minimum utility consumption and changing target temperatures during CO_2 capture.

- ❖ Finally, this study identified an improved process integration technique to handle a simultaneous heat and mass exchanger network at fluctuating operational conditions and also a mixed integer nonlinear model with non-isothermal mixing assumptions unlike the common ones with isothermal mixing assumptions. This contribution is new in the field of CCS and has not been considered before now.

To provide quick access to information documented in this thesis, a few findings from this study have been communicated to the scientific community through referred peer-reviewed journal articles, book chapter contributions, and conference presentations (see Appendix A for copies of these contributions).

1.7 Thesis layout

Chapter One: This chapter presents a general introduction to the purpose of the completed work. The motivations, objectives, justification of study as well as the novelty and contributions to existing knowledge in this field are itemized. A list of scientific journal articles, book chapter contribution and peer-reviewed conference proceedings that emanated from this research work are also listed in this chapter.

Chapter Two: An exhaustive review of pertinent literature on heat and mass integration in relation to CO_2 capture were explored and explained in this chapter. The chapter examined various methodologies for the synthesis of heat exchanger networks (HENs) and mass exchanger networks (MENs). Emphases were made on the analysis of these methods alongside their advantages and disadvantages as well as applications in CO_2 capture studies. Recent progress on heat and mass exchanger networks for energy and material minimization with CO_2 capture was also reviewed. The research need/gap in this field was identified in this chapter and reported in subsequent chapters. The main emphasis in this chapter was placed on the application of heat and mass integration techniques for energy and material minimization during CO_2 capture. This chapter was published verbatim as a review article in the international journal of energy and environmental engineering (Springer Berlin Heidelberg). The full-length paper is attached in Appendix A.

Chapter Three: This chapter presents the general methodology of the research. The methodologies used in this thesis are described and briefly discussed here. A preliminary investigation on the behaviour and the applications of the mass separating agent (adsorbent) considered in this study for CO_2 capture was also reported in this chapter. The feasibility of synthesizing heat and mass exchanger networks to optimize a CO_2 separation process was determined and the heat and mass exchanger units were also described in this chapter. This chapter provides the basis for the research reported in this thesis. Two journal papers were published from this chapter in International journal of Sustainable engineering (Taylor & Francis) and International journal of coal science technology (Springer). The full-length papers are attached in Appendix A. The preliminary investigation was carried out to achieve the first objective of this research.

Chapter Four: Here, the synthesis and application of mass exchanger networks for minimization and targeting of mass separating agents (MSA) were discussed. A sequential approach that comprises the combination of composition intervals with other thermodynamic principles was proposed in this chapter and applied to a case study involving CO_2 adsorption. The chapter further provides information on the minimum quantity of external MSA required for the packed bed adsorption of CO_2 and the most constrained region (pinch point) of the mass exchanger network design in this research were also determined. Height targeting and sizing of the absorption column were also discussed here to achieve the second objective of this research. The content of this chapter has been published as a conference paper in IAENG WCECS 2018 proceedings and a book chapter contribution (Published by springer nature). The accepted contributions have been included in Appendix A of this thesis.

Chapter Five: Sequential synthesis of heat exchanger networks for CO_2 absorption was contextualized in this chapter for energy minimization considering temperature intervals and uncertain disturbances. Minimum utility cost for the CO_2 absorption process was sequentially determined at selected parameter points and a new procedure for the optimization of heat exchanger networks for absorptive CO_2 capture was presented. The third objective of this research was achieved here. A research paper has been published in a reputable journal (Chemical engineering transactions) from this chapter and the full paper is attached in Appendix A of this thesis.

Chapter Six: In this chapter, a simultaneous (mathematical programming) approach was used to synthesize an optimal heat exchanger network (HEN) for CO_2 capture with non-isothermal mixing process uncertainties. Consideration of fluctuating operating parameters in the synthesized HEN was introduced in this chapter. The fourth objective of this research was achieved in this chapter. Interesting research findings from this chapter have been peer-reviewed and accepted for publication in IOP materials and Engineering. The full-length paper has been included in Appendix A of this thesis.

Chapter Seven: This chapter discussed the synthesis and optimization of a combined heat and mass exchanger network for concurrent energy and material minimization during adsorptive CO_2 capture. A combination of both sequential and simultaneous techniques to synthesize a combined heat and mass exchanger network (CHAMEN) was proposed and tested in this chapter. The chapter also presents a transport network for effective transportation of captured CO_2 from power plants to the storage site using a simple linear programming approach. A hypothetical case study was well-thought-out in this chapter to test the possibility of developing a network for CO_2 transport in South African power plants to achieve the fifth objective of this research. Major findings from the study reported in this chapter have been communicated to the scientific community through oral presentations at the 10^{th} Trondheim Conference on Carbon Capture, Storage and Transport held in Norway, and also a manuscript was accepted from this chapter for publication in SINTEF Academic Press (see Appendix A).

Chapter Eight: This chapter documented a general summary of the findings from this research. Overall conclusions from preceding chapters and a summary of major contributions made to new knowledge were also presented in this chapter alongside recommendations for future research.

Kindly note that all references cited in this thesis are provided at the end of chapter eight. Relevant mathematical programs, GAMS models, full-length research outputs in the form of publications as well as copyright clearance and award certificates that emanated from this research are provided in the appendix section of this thesis.

CHAPTER TWO

Review of Literature

This chapter provides information on the state-of-the-art review of heat and mass exchanger networks using both sequential and simultaneous methods. Optimal process integration strategies to minimize energy and material usage during CO_2 capture were identified from previous studies and also discussed. The knowledge gaps in this field were identified and discussed in this chapter. Ideas that could constitute significant contributions to science were first suggested here before they were explored in subsequent relevant chapters of this thesis. Alternative strategy for energy and resource saving that applies to most CO_2 capture methods were carefully discussed in this chapter. To disseminate the findings of this research and contribute to the body of knowledge, this piece of scientific information was published in form of a review article in the International journal of energy and environmental engineering (see appendix A1 for a copy).

2.1 General perspective on CCS and its energy demands

Carbon capture and storage (CCS) is a promising technology that aims at reducing CO_2 emissions from large point sources such as fossil fuel-fired power plants (Yoro and Sekoai, 2016; Yoro et al., 2019a, 2019b). However, the high energy demands and excessive material usage associated with CO_2 compression and separation processes have been a serious challenge currently facing the full implementation of CO_2 capture and storage technologies (Yoro et al., 2017). There is a need to save energy and minimize material usage during CO_2 capture to ensure the economic advantage of the capture technology (Seid and Majozi, 2014a, 2014b). This is because the cost of energy and materials for CO_2 capture has increased and this trend is expected to continue with an increase of about 13.4 % by the year 2040 due to consistent high energy demand from many industrialized nations globally (Song et al., 2017; Sadare et al., 2018). The challenge of energy and excessive use of materials in process industries can be tackled to a large extent by minimizing the consumption of energy and mass (Sekoai and Yoro, 2016). In the context of this research, energy refers to the heat required during sorbent regeneration while material (mass) refers to the mass separating agents (sorbents) and extra utilities such as cooling water and steam which ought to be minimized during CO_2 capture using heat and mass exchanger networks.

Heat and mass exchanger network retrofitting is envisaged as a promising option for reducing energy and material consumption which could lead to enhanced economic and environmental sustainability. The main aim of heat exchanger networks (HENs) and mass exchanger networks (MENs) retrofitting is to decrease the external energy demand and extra material consumption by increasing heat and mass exchange simultaneously among process streams in an existing process plant (El-Halwagi and Manousiouthakis, 1989; Klemeš and Kravanja, 2013). HENs and MENs retrofitting can be performed using pinch analysis and/or mathematical programming. Over the past decades, systematic methods based on simultaneous mathematical programming and sequential techniques have been applied to achieve improved energy and material minimization in chemical process industries (Klemeš and Kravanja, 2013).

The literature is rich in various process integration methods to minimize excessive heat-energy consumption and material usage in different industrial processes. For example, El-Halwagi and Manousiouthakis (1989) suggested the synthesis of mass and heat exchanger networks for effective material and heat minimization in industrial processes. Considering the need for energy minimization and effective material usage in energy-intensive industrial processes, some authors focused on distillation processes (Osuolale and Zhang, 2016; Cui et al., 2017), bioethanol production process (Ahmetović et al., 2010), calcium looping systems (Lara et al., 2013), and COG sweetening (El-Halwagi and Manousiouthakis, 1989). Other reports available on CO_2 capture studies have focused on developing materials for CO_2 capture and storage (Kazi et al., 2017; Jin et al., 2018) without considering how to minimize its associated high energy requirements. Some reports in the literature discussed ways to minimize high energy penalty and material minimization considered the use of solvents such as piperazine and KOH to reduce the energy requirement for CO_2 absorption using monoethanolamine (Cullinane and Rochelle, 2004; Freeman et al., 2010; Zhao et al., 2018). However, it is worthy to note that the techniques available for CO_2 capture do not only involve gas-liquid absorption but also the use of solid materials and membranes. Techniques for minimization of energy and material consumption during CO_2 capture using solid sorbents have not been given much attention in the literature.

Application of HENs and MENs in this field could proffer a solution to energy and material minimization. Major techniques that have been used to synthesize HENs and MENs in the past have been summarized in Figure 2.1 under simultaneous mathematical programming and sequential techniques.

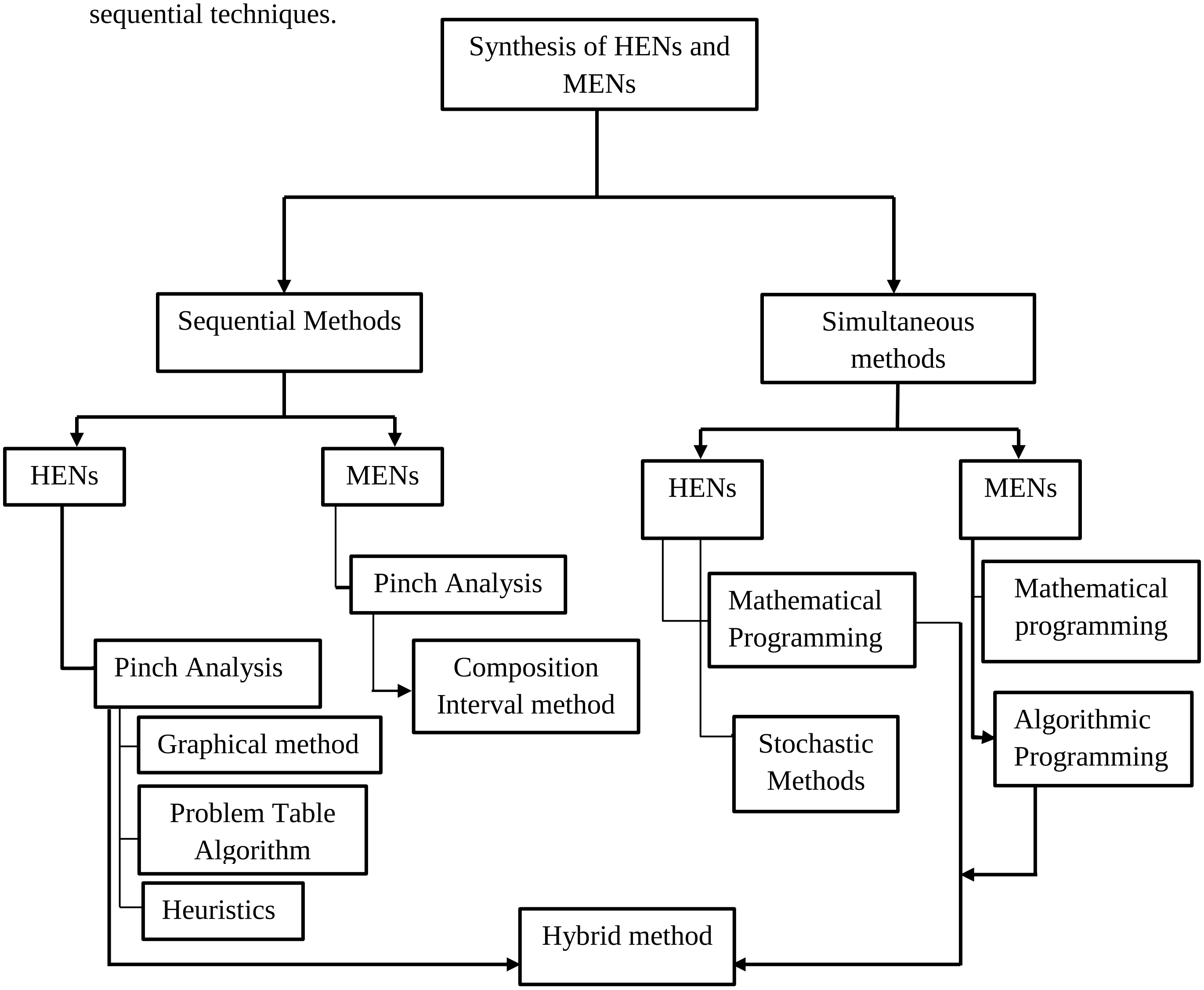


Figure 2.1: Methodological procedures for the systematic synthesis of heat and mass exchanger networks.

This chapter presents exhaustive information on the potential application of HENs and MENs synthesis methodology as an optimal process integration strategy for energy and material minimization during CO_2 capture. This study begins with the presentation of an optimal process development strategy during CO_2 capture followed by the synthesis techniques for HENs and MENs. Synthesis of a combined heat and mass exchange network for minimization of energy and material consumption during CO_2 capture is then discussed because of the integral relationship between heat and mass during CO_2 capture. At the end of this review, a combined technique for the synthesis of heat and mass exchanger networks is suggested as a strategy to fully harness the benefits inherent in simultaneous optimization of the two networks using mathematical programming techniques. Finally, the prospects for energy penalty reduction in various CO_2 capture technologies are highlighted and future research topics suggested. Schematic overview of this review is presented in Figure 2.2.

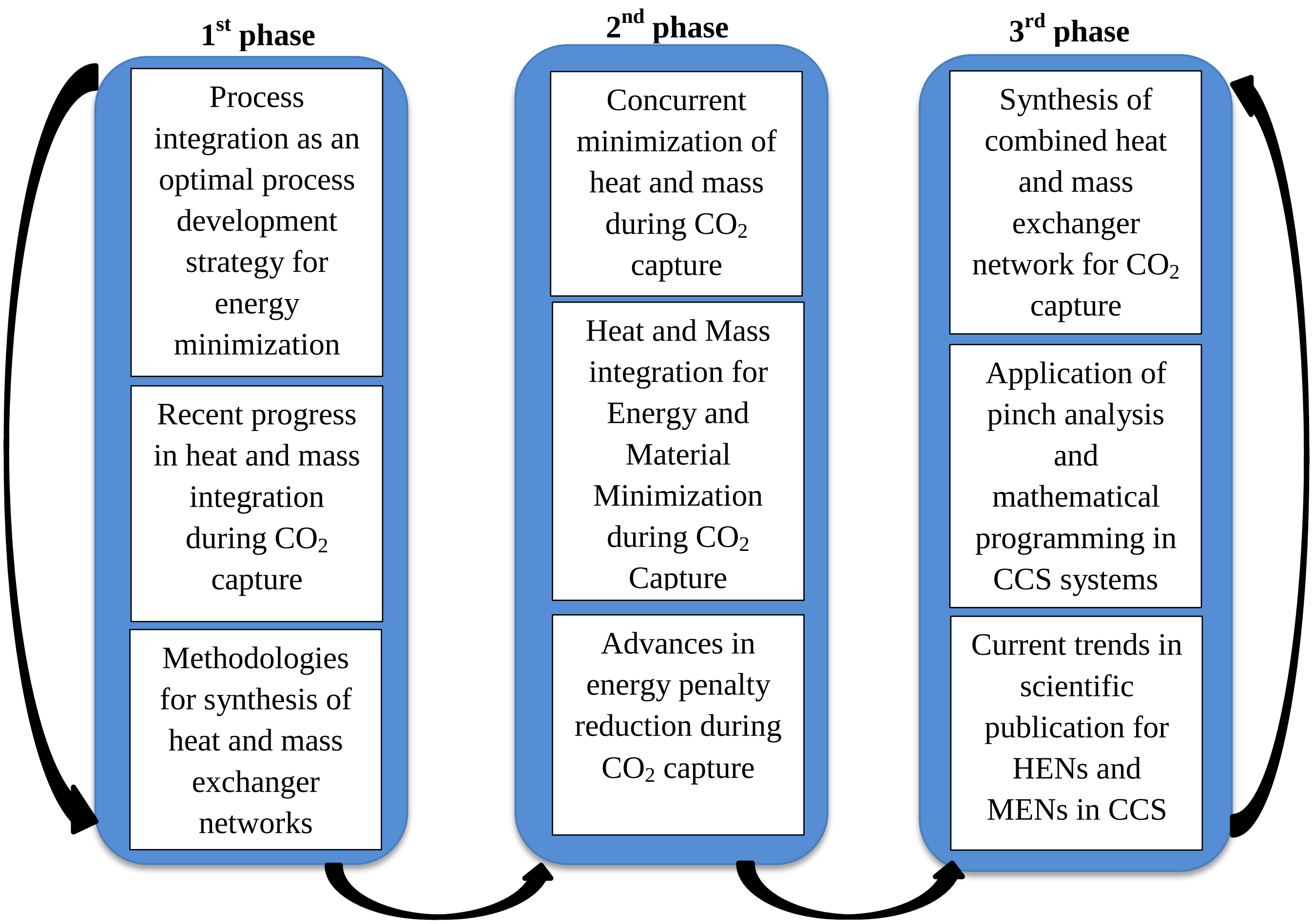


Figure 2.2: A schematic overview of this literature review

2.2 Synthesis methods for heat and mass exchanger networks

The major task in a heat exchanger network synthesis problem is identifying the best pair of process streams to be coupled with the heat exchangers to maximize energy recovery and minimize high consumption (Wechsung et al., 2011). This pairing problem is a theoretically explosive combinatorial problem with nonlinear models describing each unit and its size, resulting in a mixed integer nonlinear programming (MINLP) model. An ideal HEN in CO_2 capture studies should not only be optimal in nominal conditions but also operable in the specified changing environment with allowance for non-isothermal mixing especially when the plant introduces significant changes in the operating conditions. In other words, an optimal HEN is expected to remain operable under varying process conditions without losing stream temperature targets and at the same time, maintain an economically optimal energy integration. Application of heat exchanger networks (HENs) and mass exchanger networks (MENs) in CO_2 capture is an important strategy to minimize energy and utility targets of the capture process. Methodologies for the synthesis of HENs and MENs are broadly classified into two; sequential and simultaneous synthesis methods.

2.2.1 The sequential synthesis method

Sequential synthesis of heat and mass exchanger networks involve the use of pinch concepts and graphical illustrations to decompose a heat or mass exchanger network design problem into sub-problems to minimize energy costs, number of units, investment costs and the amount of material to be consumed (Ahmad et al., 2012). Partitioning the design problem into a series of sub-problems helps to reduce the computational requirements for obtaining an optimal network design. For a typical heat exchanger network design problem, the sequential method can be carried out by dividing the temperature range of the problem into temperature intervals while for a typical mass exchanger network design task, the problem is divided into composition intervals. These intervals are then used for modelling heat and mass exchange while obeying some heuristic and thermodynamic laws. Since a typical CO_2 capture system involves fluctuation of parameters such as stream inlet temperatures, gas flow rates, and heat capacities, due to issues such as changes in environmental conditions, changes in feed quality, process upsets and other disturbances, it is recommended in this research that a multi-period synthesis network approach should be considered for the design of CO_2 capture networks. A schematic of a proposed Pinch Technology-based methodology for synthesizing HENs and MENs for energy and material minimization during CO_2 capture is presented in Figures 2.3 and 2.4 respectively while Table 2.1 compares different techniques for energy and material minimization. The application of pinch-based design techniques in HENs after subdividing the problem into temperature intervals is dependent on a minimum heat recovery approach temperature (HRAT) while in MENs it is dependent on the minimum allowable composition difference 'ε' (Mian et al., 2016). In this study, it is suggested that the locations of bottlenecks for energy savings and material minimization are found for multi-period HENs and MENs before the minimum energy usage is determined. These bottlenecks are known as the energy recovery pinch points.

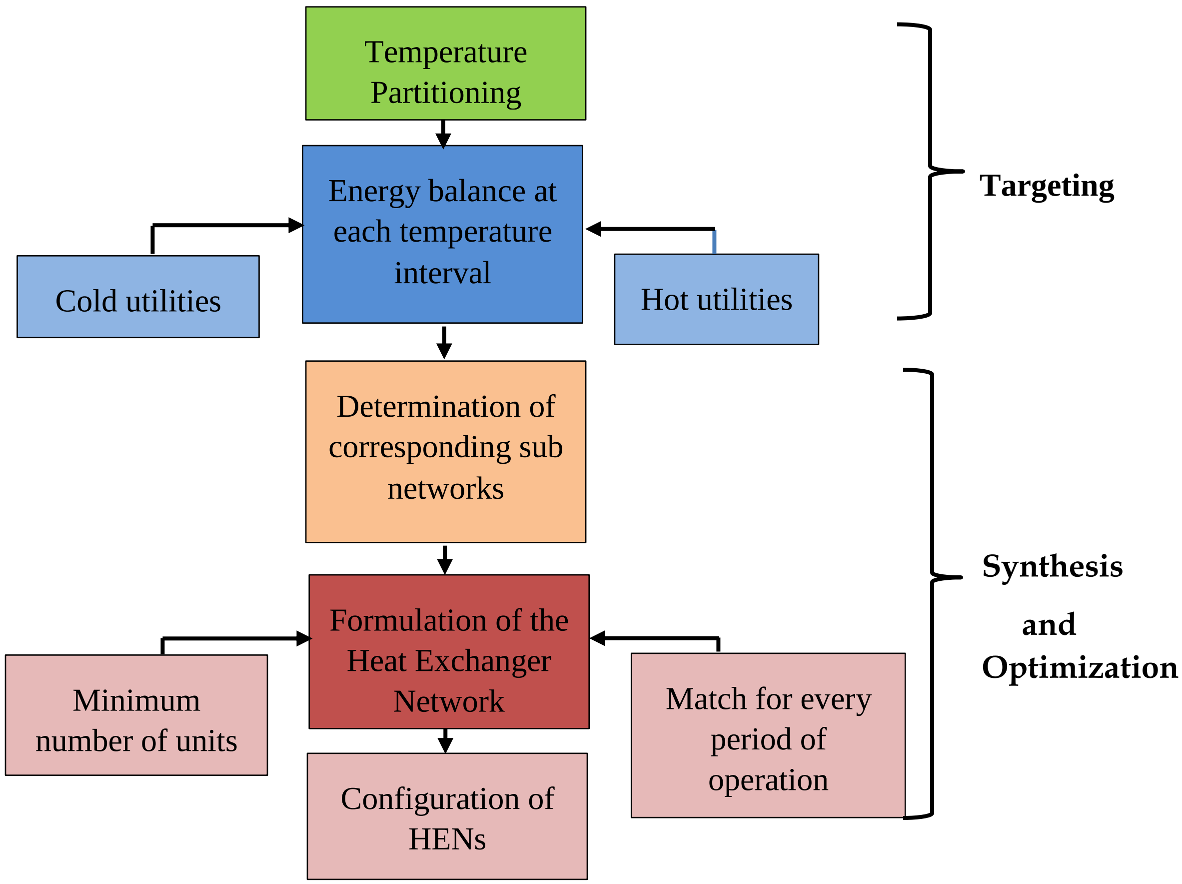


Figure 2.3: A proposed technique for the sequential synthesis of multi-period HENs

The pinch points can be more than one; depending on the number of periods of the network. Besides, there is also a possibility for the existence or non-existence of pinch points. The different pinch points obtained or a calculated global pinch point can then be used to decompose the heat and mass exchanger network into sub-networks. The minimum number of heat/mass exchanger units for the network can be determined using Equations (2.1) and (2.2) respectively depending on whether a pinch point exists or not.

$$NS_{AP} - 1 + NS_{BP} - 1 \quad (2.1)$$

Total number of streams (N) – 1 (2.2)

Where N_{SAP} is the total number of steams above the pinch and NS_{BP} is the total number of streams below the pinch.

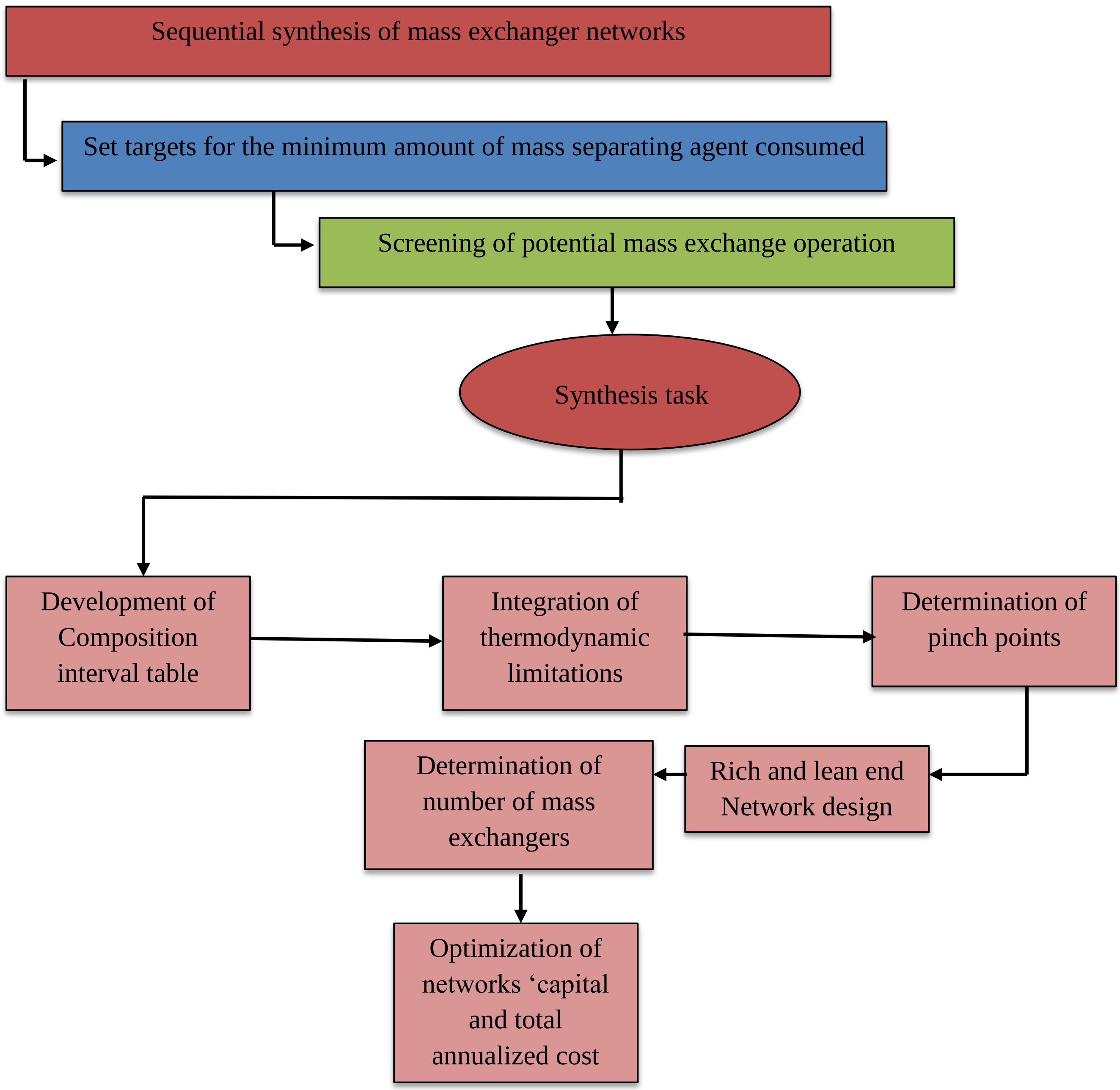


Figure 2.4: Schematic procedure for the sequential synthesis of mass exchanger networks

The main drawback of the sequential technique for HENs and MENs synthesis are the trade-offs between the utilities, the number of units and the area of the heat exchangers which are not usually considered in an integrated approach. Besides, decomposition of the problem into sub-problems based on the pinch analysis and optimization of these sub-problems lead to sub-optimal networks. Therefore, it is imperative to solve the HENs and MENs synthesis problem simultaneously in single-take using other approaches such as mathematical programming techniques which are simultaneous.

2.2.2 The simultaneous synthesis method

Heat and mass exchanger networks are synthesized simultaneously when it is necessary to achieve an optimal network without decomposing the task into sub-problems (Kang and Liu, 2018). The simultaneous technique considers the problem as a whole task and solves directly without splitting it into smaller tasks. The simultaneous synthesis method involves the formulation of mixed-integer nonlinear programs (MINLP) or genetic algorithms (GA) for the heat and mass exchanger problems. The solution obtained is dependent on the simplifying assumptions made to solve the complex models. Simultaneous synthesis of HENs and MENs involve the use of superstructures (in some cases stage-wise superstructures), hyperstructures etc comprising a variety of structural possibilities to optimize and eliminate redundant features (Xia et al., 2018). Trade-offs between capital cost (fixed costs of heat/mass exchanger units and area costs) and operating cost (hot and cold utility costs) are considered in a single optimization framework. A schematic step by step procedure for simultaneous synthesis of a heat exchanger network that can operate with a different set of conditions such as temperatures and heat loads are presented in Figures 2.5.

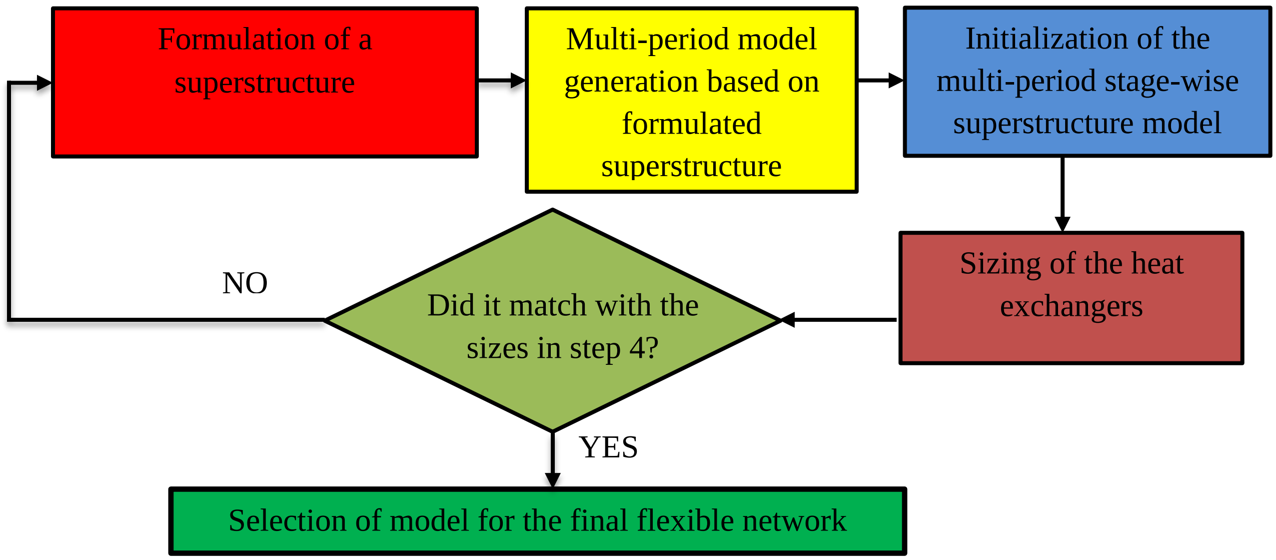


Figure 2.5: Schematic procedure for simultaneous synthesis of HENs

2.3 Overview of process integration as an optimal process development strategy

Process integration has been widely embraced as an integral part of process intensification which can be used in describing specific system-oriented activities related to process design with applications exclusively focused on resource conservation, pollution prevention, and energy management (Dunn and El-Halwagi, 2003; You et al., 2008). Synthesis, analysis, and optimization are the three basic components of any effective process integration methodology. Process integration has a significant effect on many chemical industries through heat-exchanger-network optimization.

The application of process integration in CO_2 capture systems makes it possible to identify the optimal process development strategy for the capture networks as well as identifying the most cost-effective way to complete the CO_2 capture process (Pokoo-Aikins et al., 2010; Cheng and Wang, 2016; McBrien et al., 2016). Amongst the available process integration methodologies, pinch analysis is currently the most commonly used. This could be attributed to the simple nature of its underlying concepts and the spectacular results it has presented in numerous studies in the past. Hence, it forms a major point of discussion in this chapter.

Although pinch analysis has been reported for various energy and resource saving studies in the past, its application in energy and material minimization studies with respect to CO_2 capture system is still new and cannot be traced to any current report in open literature. For example, Kemp (2005) reported the application of pinch analysis for the efficient use and minimization in a dryer where a direct reduction of dryer heat duty was discussed. Harkin et al. (2010) presented a study on the application of composite curves using the concept of pinch analysis to reduce energy penalty during CO_2 capture. The authors did not extend their study to include network design. Despite the huge success of the pinch technique reported by the author for energy minimization, the principles have not been extended to designing a network for CO_2 capture. In scenarios where CO_2 producing plants are co-located within an industrial development zone or geographical area, it is imperative to design an optimal network for energy reduction and efficient resource usage using process network integration as this will offer immense opportunities for energy and resource sharing amongst the plants.

Ooi et al. (2013) reported an investigation on general CCS planning using pinch analysis technique where a novel graphical targeting tool was proposed to address the problem associated with storing captured CO_2 from power generating plants into reservoirs. The limitation here is that the study was constrained to just CO_2 storage without looking critically into simultaneous energy and material minimization during the capture process. In another study, Wan-Alwi et al. (2012) discussed an extended pinch analysis concept to determine the minimum electricity target for systems with hybrid renewable energy sources using power pinch analysis. The authors mainly emphasized the application of pinch analysis to energy usage during power generation in power plants without a direct extension of the concepts in CO_2 capture systems which are unique. Such uniqueness lies in the fact that energy enhances mass transfer, both in absorption and regeneration, in CO_2 capture processes. Extending the power pinch analysis to CO_2 capture networks will be highly beneficial since it integrates hybrid energy sources. However, the power pinch concept will need to be modified to accommodate separation processes which are found in CO_2 capture systems. Graphical pinch location methods to determine the amount of material consumed in industrial processes is presented in Figure 2.6 and Figure 2.7. These figures, which are called the composite curves in Pinch Technology, are analogues of each other. Figure 2.6 is for MENS while Figure 2.7 is for HENS. If the Pinch Technology method is applied in CCS networks, Figure 2.6 would involve targeting the minimum flows of CO_2 absorbents and regenerants, while Figure 2.7 would involve setting targets for the amount of energy required to achieve optimum absorbent/regeneration temperatures, as well as other energy needs of the overall integrated network. Table 2.1 presents a list of strategies that have been used for energy and material minimization in CO_2 capture systems. The table also shows whether the methodology is applied to simultaneous heat and mass exchange. Information on Table 2.1 shows that application of heat and mass integration techniques in CO_2 capture systems can minimize both energy and material simultaneously. According to the literature reports reviewed so far, it is evident that researchers have made significant efforts to develop new strategies for energy minimization in many industrial applications on one hand. On the other hand, methodologies for material usage minimization have also been developed. However, most of the suggested strategies do not involve a concurrent minimization of both energy and mass. This review suggests that energy consumption and material usage can be minimized simultaneously during industrial processes like CO_2 capture using a combined heat and mass integration approach.

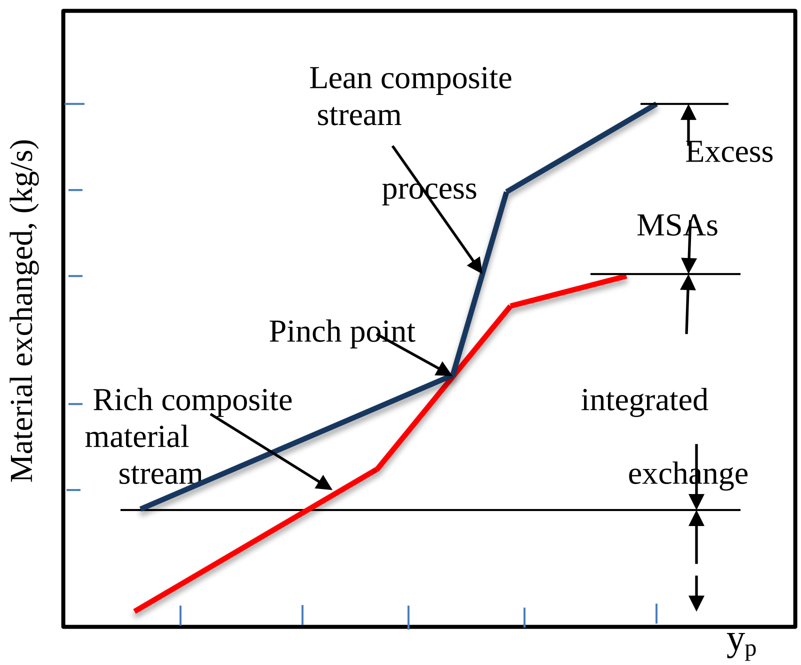


Figure 2.6: Pinch location using a graphical method (modified from El-Halwagi and Manousiouthakis 1989).

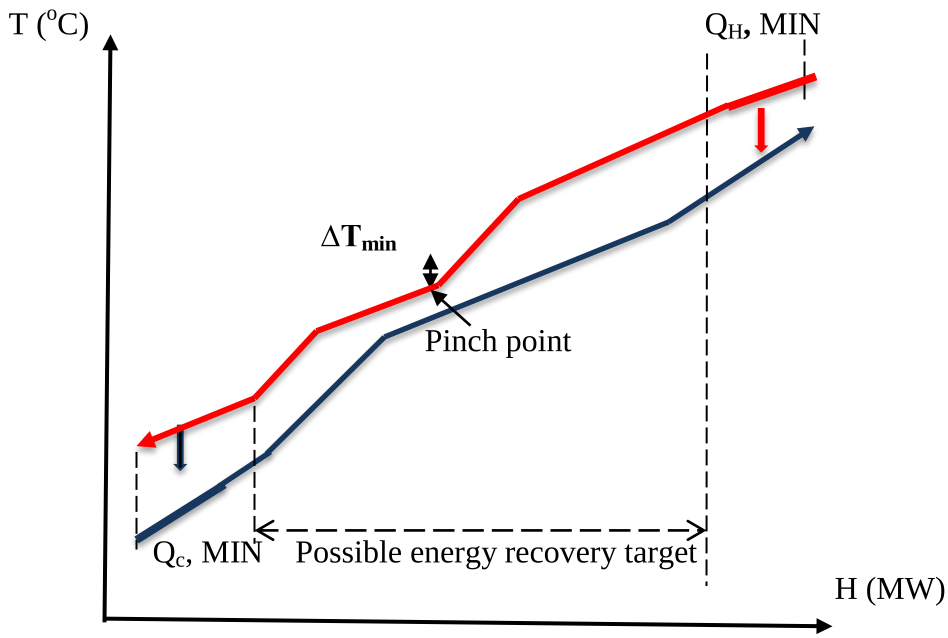


Figure 2.7: Minimum energy targeting using composite curves (Adapted and modified from Manan et al. (2017)).

Table 2.1: Comparison of energy and material minimization techniques

Technique	What can be minimized?	
	Energy consumption	Material usage
Use of additives e.g. piperazine	√	X
Ammonia cycling	√	X
Waste heat utilization	√	X
Fluor Econamine process	√	X
Heat and mass integration	√	√

2.4 State-of-the-art in the application of heat and mass integration techniques

2.4.1 Heat integration

Heat and mass integration are two types of process integration technologies that have been practised for improving energy and material efficiency in the process industries. Heat integration is achieved by integrating a heat exchanger network (HEN) into a process system for energy recovery (Chang et al., 2018; Tarighaleslami et al., 2018). Heat integration is mostly applied in energy systems when examining the potential of improving heat exchange between heat sources and heat sinks to reduce the amount of external heating and cooling utilities which is a way of ensuring energy minimization (Kapil et al., 2012; Mohammad-Rozali et al., 2013). Heat integration during CO_2 capture could be a reliable method for reducing the high energy penalty associated with most CO_2 capture technologies. Researchers have developed new calculation methods for energy and material minimization as well as the design of heat exchanger and coupling of utilities in many energy-intensive processes with minimum temperature difference through heat integration using pinch concepts (Klemeš and Varbanov, 2013; Sturm et al., 2015). However, the application of pinch analysis alone cannot adequately achieve simultaneous energy and material minimization in a process such as CO_2 capture. This is because heat transfer occurs in most of these systems with some inefficiency due to unavoidable stack losses. This makes the heat value of the burnt fuel always greater than that absorbed by the process. As a result, energy and material consumption cost may not be easily evaluated directly from the energy targets indicated in the pinch diagrams. It has also been pointed out in previous research (Lara et al., 2014) that the loss of some important information can occur when process and utility streams are combined into the same grand composite curve (GCC). This loss of information has led to missed opportunities in designing an optimal network for energy and material minimization.

To provide a solution to the aforementioned problem posed by the pinch technique, researchers have come up with different methodologies for a simultaneous energy and material minimization during CO_2 capture. For instance, in the works of Romeo et al. (2011) and Berstad et al. (2012), calcium looping was recommended as the most suitable CO_2 capture technique for effective energy and material minimization. This is because the researchers envisaged that the waste CaO from CO_2 capture in a cement plant can be combined with waste energy from the clinker cooling and CO_2 capture system which can then be used to generate additional power without the utilization of coal. Furthermore, part of the power generated can be used for CO_2 compression. The purge from the CO_2 capture system can also be used as input to the cement plant thus reducing the raw material consumption and fuel usage for the calcination of the saved limestone. By applying this method, the authors confirmed a lower CO_2 avoidance cost with the integrated process than with any other combination method (either with power plants and CO_2 capture system, or cement plants with CO_2 capture systems). As such, the authors proposed that if these three processes are integrated, about 94 % of CO_2 that would have been emitted into the atmosphere can be avoided because of the energetic efficiency augmentation associated with the integrated processes. However, a major drawback of this integrated process is that both systems have to operate simultaneously and this requires a lot of energy consumption although material usage could be minimized. Furthermore, there could be some effects of sulphur and $CaSO_4$ formed during the CO_2 capture process on the cement characteristics and the deactivated CaO in the clinker during production; thus, reducing the quality of cement produced from the integrated cement production plant.

Nemet et al. (2012) reported a new methodology for heat integration with emphasis on optimization of heat exchanger networks' cost over a long period. The authors developed a deterministic and stochastic multi-period mixed-integer nonlinear programming (MINLP) model for the synthesis of heat exchanger networks in which the utility cost coefficients were forecasted for the lifetime of the process. The stochastic approach was applied to the simultaneous consideration of future price projections of HENs while the multi-period approach with future price projections was applied for sustainable design of HENs with higher heat recovery and consequently, with lower utility consumption. The study revealed that utility savings were 18.4 % for hot and 32.6 % for cold utility yielding an increase in the Net Present Value (NPV) by 7.8 %. As much as this proposed methodology was useful for minimizing heat energy usage, it could not be conveniently applied in the case of CO_2 capture because CO_2 capture is a simultaneous heat and mass exchange process which involves the application of both heat and mass exchange networks. Given this, the proposed methodology is not sufficient for energy and material minimization studies because it is limited to only heat exchanger networks.

Nawi et al. (2015) suggested a new algebraic technique for total site carbon integration. This proposed technique is capable of minimizing energy requirement during carbon capture, utilization, and storage. The method was applied to a hypothetical case study to determine potential CO_2 exchange using CO_2 headers at different percentage purity as well as a central pure CO_2 generator. The authors reported a 43 % reduction in CO_2 emission with reduced energy consumption using this novel technique. The proposed targeting technique could be used by carbon planners to conduct further analysis and feasibility studies involving carbon capture storage and utilization. However, the technique did not include analysis of more carbon capture methods as well as a techno-economic study to ascertain its applicability on a large scale. It is envisaged in this review that a combined application of the aforementioned techniques in integrated symbiotic systems might further minimize energy usage and also reduce energy penalty associated with most CO_2 capture technologies

Escudero et al. (2016) applied a pinch analysis approach in combination with Aspen plus simulation to evaluate the heat recovery options and to design an optimized heat exchanger network for a specified power plant. The authors used an Aspen Plus simulation model to simulate the power plant (including all the subsystems and the new networks). In the end, the authors reported a net increase of about 32.5 % in the net efficiency of the power plant. Energy penalty was also reduced from 10.54 to 7.28 efficiency points using this concept. However, CO_2 capture is a simultaneous mass and heat exchange process, the authors did not consider the synthesis of mass exchanger networks to take care of external mass separating agents or utilities in their study. Nevertheless, the synthesis of a hybrid network that considers simultaneous heat and mass exchange for effective design of a CO_2 capture network as proposed in this study is capable of minimizing the external mass separating agents and utilities involved in the design.

Most methodologies for energy and material minimization investigated in the past come with limitations such as computational difficulties, high cost of technology and material wastage. To fill this gap, this study proposes the development of integrated methods for CO_2 capture (including mass and heat integration networks) because the integration of heat and mass exchange networks have resulted in a significant saving of heat energy and mass (materials) in other processes in the past (Wan-Alwi et al., 2011; Chen and Wang, 2012). Industrial heat and mass exchanger networks are important because of their role in recovering material and process heat in a process effectively. Mass exchanger network synthesis via mathematical programming is also an important strategy for screening mass separating agents as well as satisfying mass transfer demands in a CO_2 capture process while ensuring that environmental and economic requirements are met (Liu et al., 2013). The synthesis of a combined heat and mass exchanger network using a hybrid technique comprising both pinch analysis and mathematical programming is recommended for problems involving heat and mass exchanger networks such as CO_2 capture. The suggested hybrid approach in this review is new and to the best of our knowledge, it has not been applied in any CO_2 capture study for energy and material minimization. Figure 2.8a is a composite curve showing a reduction of the internal carbon footprint of a CO_2 emitting power plant while Figure 2.8b denotes the benchmark value for CO_2 emission together with internal and external carbon footprints. Figures 2.8(a) and (b) were adapted from Tjan et al. (2010) and they illustrate how a graphical pinch analysis technique enhances the decision-making by prioritizing strategies for carbon footprint reduction in a single power plant. Table 2.2 gives a summary of the process synthesis techniques, methods and focus area reported till date.

2.4.2 Minimum utility targeting with heat integration

Proper placement or adjustment of heat exchangers on hot and cold streams can be used to recover maximum energy from the process streams and decrease the demand for more hot and cold utility usage in the industries thereby dropping down process costs. Most of the literature in this field is either tailored towards developing a HEN with minimum utility consumption, heat exchanger (HE) areas and numbers of HE units using simultaneous techniques, or they are aimed at synthesizing networks with reasonable trade-offs between annualized capital and operating cost. As far as could be ascertained, integration of HEN in environmental process engineering for effective energy minimization during absorptive CO_2 capture is new and have not been reported before now. Also, apart from the synthesis and optimization of HENs, most studies in the past have not critically looked into its application, operation, and control. But in this thesis, the concept of heat exchanger network synthesis was extended beyond just synthesis and targeting to include its testing for energy minimization during absorptive CO_2 capture. Although the methodology used to synthesize the HEN in this thesis is not entirely new in process system engineering, the inclusion of new assumptions like fluctuating process parameters, new calculation techniques for the energy targets and its application for energy recovery during the absorptive CO_2 capture in power plants is new and forms a contribution to new knowledge in CCS studies.

Minimization of heating and cooling utility consumptions can be achieved through heat integration (Santi et al., 2018). This is attained by taking into account all the hot and cold streams concurrently while focusing on heat recovery between hot and cold streams, instead of heating and cooling with utility streams. Composite curves can be constructed during heat integration to represent the heating and cooling demands of the entire system and also determine the minimum utility requirements of a process. Rodera and Bagajewicz (1999) identified that the critical step during utility targeting with heat integration is to first denote the individual hot and cold streams on a single diagram and then determine the minimum utility duties for the whole system. If the representation is done graphically, it is called a composite curve and if it is done on a table, it is called a temperature interval diagram (TID). In this research, heat integration will be reported using both graphical (composite curve) techniques and the temperature interval method. A simplified procedure for the graphical construction of composite curves is diagrammatically presented in Figure 2.8c. The TID provides all the necessary information to create a heat-exchanger network but avoids the construction of composite curves. However, the graphical method indeed provides useful insights to heat integration that are not available in the tabular form. The TID method uses temperature-interval boundaries determined from the shifted supply and target temperatures of both hot and cold streams for heat integration.

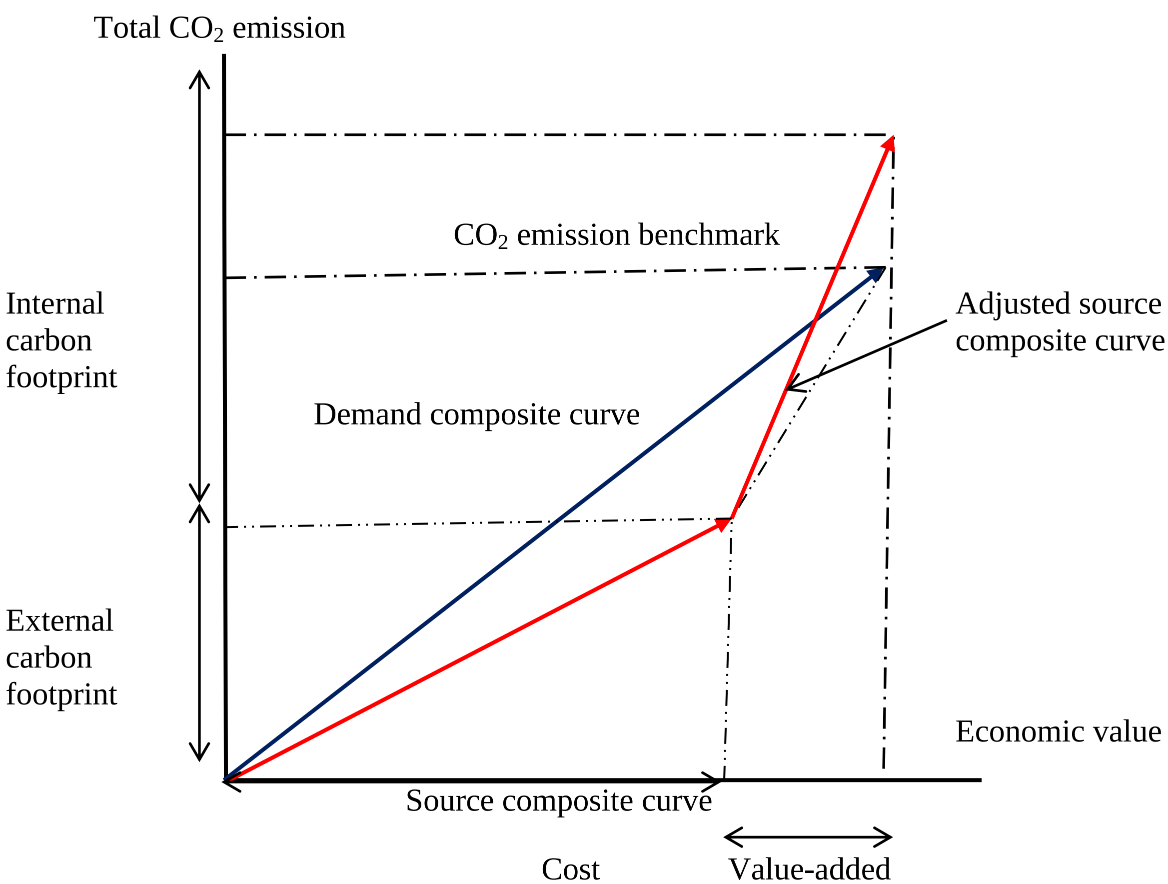


Figure 2.8a: Emission footprint composite curves for reduction of the internal carbon footprint.

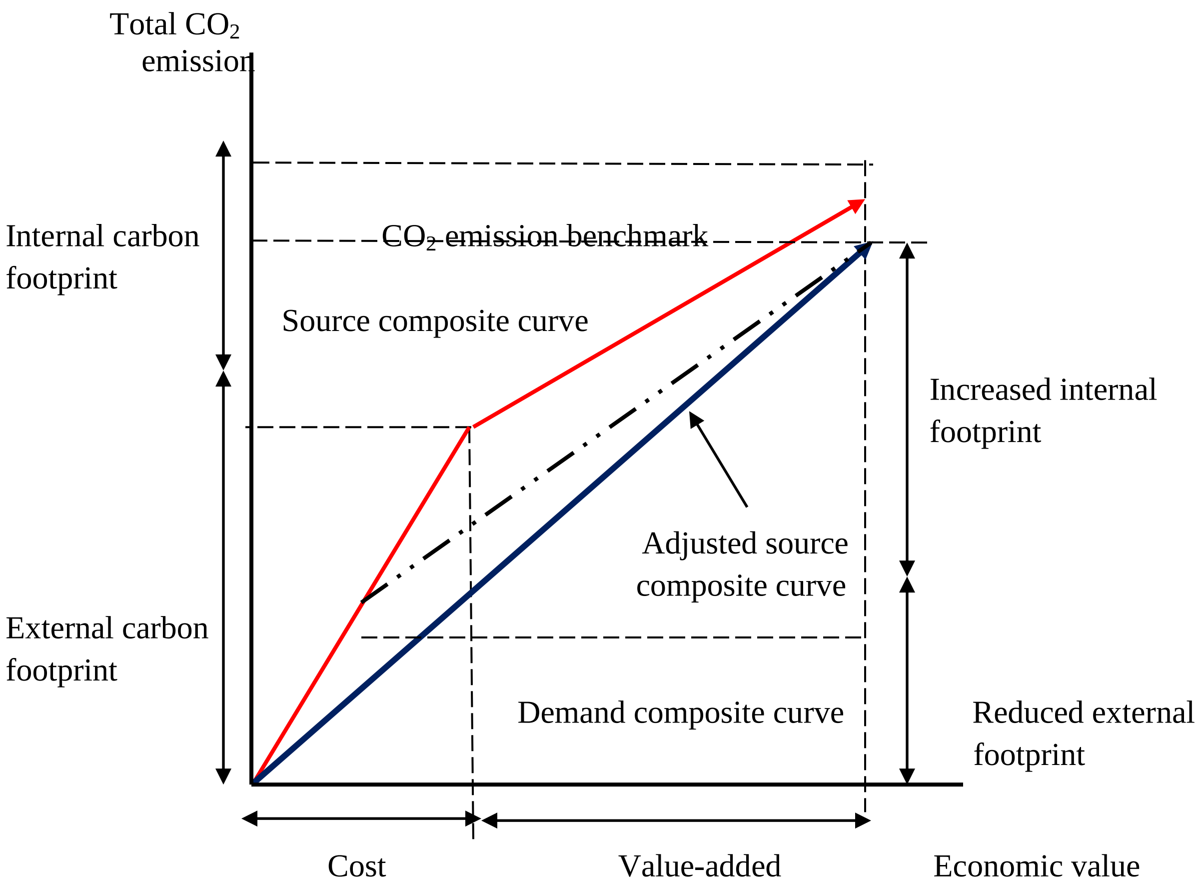


Figure 2.8b: Emission footprint composite curves for benchmark value for carbon intensity: (Adapted and modified from Tjan et al. (2010))

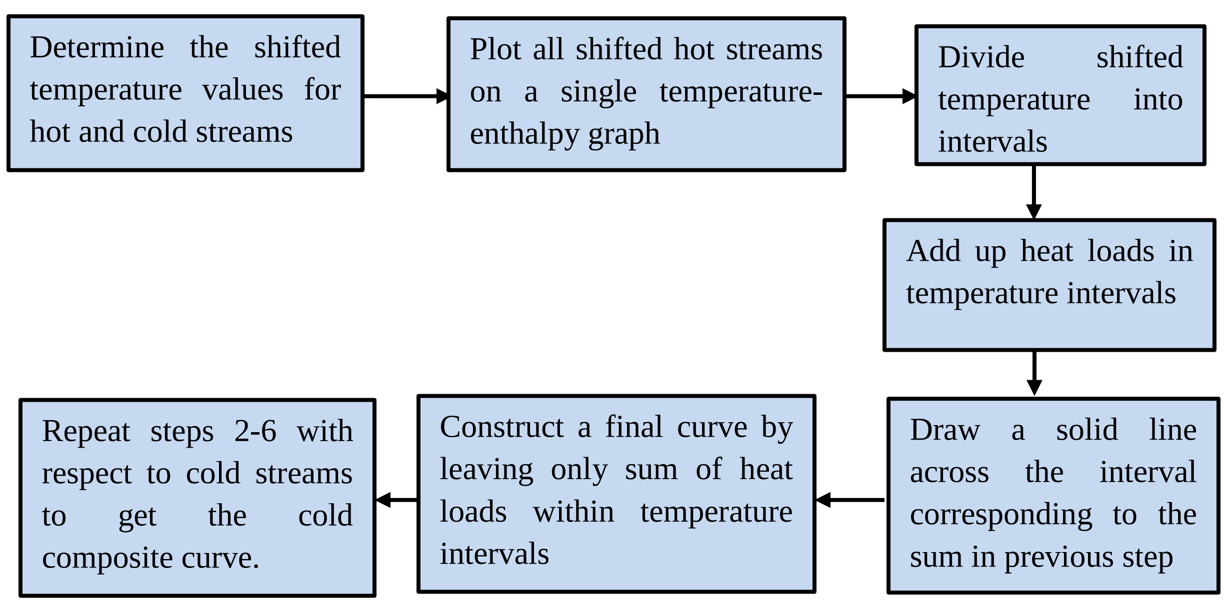


Figure 2.8c: A stepwise procedure for constructing hot and cold composite curves

2.4.3 Mass Integration

Mass integration is a systematic methodology that offers an essential understanding of the global flow of mass within the process. The concept of mass integration can be used to identify performance targets and to optimize the allocation, separation, and generation of streams as well as species in an industrial process (Ong et al., 2017). Within a mass-integration framework, mass-exchange operations are employed in intercepting sources by selectively transferring certain undesirable species from several waste streams (sources) to some mass-separating agents (MSAs). Mass integration problem involves transferring mass (contaminant load) from rich process streams to lean process streams to achieve their target concentration and simultaneously minimize waste generation and the consumption of utilities such as freshwater and external mass separating agents (Li et al., 2018). Detailed reviews on mass integration technology have been reported by Klemeš and Perry (2007) and Klemeš et al. (2007, 2013). Mass integration technology has potential applications in tail gas utilization, catalyst-supporting medium recovery, water management, and CO_2 separation.

Because of the growing concern on the increasing levels of CO_2 concentration in the atmosphere, this study has focused mass integration in CO_2 capture system in power plants to reduce the carbon footprint linked with power generation in coal-fired power plants, El-Halwagi (1997, 2011) suggested that '*interception*' is a key element for mass integration. Effective pollution prevention can be achieved by a combination of stream segregation, interception, recycle from sources to sinks (with or without an interception) and sink/generator manipulation (Vázquez-Ojeda et al., 2013). MEN synthesis can be incorporated into a full mass-integration analysis. During mass integration, used mass streams are employed with adequate treatment to reduce external mass consumption.

2.5 Heat and mass exchanger network synthesis

Heat and mass exchanger network synthesis remains an area of continuous development in process engineering due to the current trend of increasing energy and material costs. Heat and mass exchanger networks use available heat in a process through the exchange that occurs between hot and cold process streams to decrease energy demands, utility costs and capital investment in most industrial processes. Integration of heat and mass exchanger networks for industrial applications can improve the economics of plant operation.

Several advances have been reported for the design of heat and mass exchanger networks using approaches which involve the pinch point and mathematical programming (Grossmann and Guillén-Gosálbez, 2010a). Recently, simultaneous design and optimization methodologies have been proposed (Psaltis et al., 2016). Due to the complex nature of most mathematical equations involved in the synthesis of heat and mass exchanger networks, the application of mathematical programming in process synthesis could be achieved by simplifying various superstructures and model equations through the use of simplified capital cost functions. Mathematical programming has also shown significant potentials in solving HENs and MENs problem with the recent advancement in computing technology. It deals mainly with heat integration, synthesis of heat and mass exchanger networks or synthesis of process schemes and process subsystems. It is remarkable to note that the final effect of the synchronized method is not only the expected reduction in energy consumption but also the reduction in raw material consumption. The scope of process integration through mathematical programming has improved in recent times and it can be applied in process industries to optimize heat and mass exchanger networks for carbon emission reduction and water minimization (Liew et al., 2017).

The foremost role of mathematical programming in the synthesis of HENs and MENs is to improve concepts (and also create new ones) by expressing them in precise forms to obtain ideal and feasible solutions of complex problems (Chen and Grossmann, 2017). Apposite trade-offs between raw materials, operating and investment costs, as well as product income, can be established by applying mathematical programming in overall systems concurrently; thus, attaining accurately integrated details. Mathematical programming techniques in the synthesis of HENs and MENs require the postulation of a superstructure of alternatives (whether it involves a high level aggregated model or a detailed model). The main issues associated with postulating superstructures for HENs and MENs include the major type of representations that can be used, its modelling implications, and the feasible alternatives that must be included to guarantee that the global optimum is not ignored. To analytically generate superstructures that contain all the alternatives of interest in a process such as CO_2 capture, a graphical-theoretical approach with polynomial complexities is proposed in this review to find all interconnections in a process network with nodes for processes and chemicals adequately specified. Apart from the selection of superstructures, the choice of a detailed optimization model is also necessary for effective energy and material minimization. The postulation of superstructures and selection of optimization models will be a very reliable procedure in synthesizing process networks for waste minimization during CO_2 capture.

Mathematical programming in combination with pinch analysis can be used in a hybrid manner to synthesize a combined heat and mass exchanger network that will minimize both energy consumption and excessive material usage simultaneously during CO_2 capture. Pinch analysis techniques should be used to set the energy targets while mathematical programming can then be used to synthesize the networks by building upon the existing SYNHEAT model in General Algebraic Modeling System (GAMS) software. A detailed methodology for this is diagrammatically presented in the next chapter (see chapter three).

Aggregated mixed integer nonlinear programming (MINLP) models can also be used in mathematical programming. This reduces the computational difficulties associated with mathematical programming and improves the synthesis process. The aggregated MILP model suitable for studies of this nature is the transhipment model. The model uses pinch location methods to calculate the minimum amount of energy expended and material consumed during CO_2 capture (Krishna Priya and Bandyopadhyay, 2017). This procedure is easy to embed in any mathematical programming model for process synthesis. It can also perform a simultaneous flowsheet synthesis and heat integration because it has both mathematical programming and pinch analysis integrated into it (Szitkai et al., 2002; Chen and Hung, 2005). Current trends in the application of HENs, MENs and CHAMENs reported in the literature to date are summarized in Table 2.2.

Table 2.2: Current application of HENs, and MENs in literature

Network type	Synthesis technique	Method	Application / Focus	References
HENs and MENs	Simultaneous	Mathematical programming	Pollution prevention	El-Halwagi (1997), Linke and Kokossis (2004)
MENs	Sequential	Carbon storage composite curves (CSCC)	Carbon capture and storage Planning	Ooi et al. (2013)
HENs	Sequential and Simultaneous	Pinch analysis & Mathematical programming	Process Integration	Martín and Mato (2008)
HENs	Sequential	Pinch analysis	Heat exchanger network design	Grossmann and Guillén-Gosálbez (2010a)
HENs	Simultaneous	Mathematical programming	Environmental sustainability	Biegler et al. (2014)
HENs and MENs	Simultaneous	Nonlinear programming	Chemical process optimization	Trespalacios and Grossmann (2014)
HENs	Simultaneous	Nonlinear & general disjunctive programming	Process systems engineering	Bagajewicz et al. (2000)
WENs	Simultaneous	Mathematical programming	Water integration	Jeżowski (2008)
WENs	Simultaneous	Mathematical programming	Water network design	Tan et al. (2014)
HENs	Sequential	Floating pinch method	Utility targeting	Harkin et al. (2010)
HENs	Sequential	Graphical / Pinch Method	Energy-saving and pollution reduction	Onishi et al. (2017); Varbanov et al. (2015)
WHENs	Simultaneous	Mathematical programming	Minimization of overall environmental impact and TAC	Isafiade (2018)
HENs	simultaneous	Mathematical programming	Heat exchanger network retrofit	Hafizan et al. (2019)
HENs	Sequential	Sequential LP, MILP, and NLP models	Minimum utilities demand and pinch point	Akpomiemie and Smith (2018)
HENs	Sequential	Pinch retrofit method	Methods for achieving cost-effective HENs retrofit	Sreepathi and Rangaiah (2014)
HENs	Simultaneous	Reassignment strategies and multi-objective optimization	HENs retrofit	Boix et al. (2012)
HENs & WNs	Simultaneous	Mathematical programming	Energy and water minimization	Kermani et al. (2018)

HENs-WN	Simultaneous	Mathematical programming	Energy and water minimization	Tan et al. (2017)
MENs	Simultaneous	Mixed-integer linear programming	Industrial resource conservation	Lee (2017)
HENs	Simultaneous	Mathematical programming	Carbon sequestration retrofits in the electricity sector	Gharaie et al. (2013)
MENs	Sequential	Multi-objective pinch analysis	Hydrogen and water conservation	Chen and Hung (2005)
MENs	Sequential	Pinch technology	Reduction in pollutant emissions and the use of MSAs	El-Halwagi and Manousiouthakis (1989)
MENs	Simultaneous	Mathematical programming	Waste minimization	Szitkai et al. (2006)
MENs	Simultaneous	Mathematical programming	Pollutant emissions reduction	Isafiade and Fraser (2009a)
MENs	Simultaneous	Mathematical programming	Non-uniform exchanger specifications and MSA regeneration	Linnhoff and Hindmarsh, (1983)
HENs	Sequential	Pinch technology	Utility targeting	Chaturvedi et al. (2017), Foo and Manan (2006)
MENs	Simultaneous	Mathematical modelling	Determination of minimum energy targets	Wan-Alwi and Manan (2010)
MENs	Sequential	Gas cascade analysis technique composition interval method	Minimum utility targeting	Yoro (2017), Short et al. (2018)
Combined MENs and HENs	Sequential	Pinch analysis	Absorption of SO_2 from gas streams	Isafiade and Fraser (2007)
CMAHENs	Sequential	Mass pinch & pseudo-T-H diagram	Minimization of the total annualized cost of CHAMEN	Liu et al. (2013)
MENs	Sequential and Simultaneous	CID and algorithmic programming	Material recovery / Synthesis of cost-effective MEN’s	Yoro et al. (2019b)
MENs	Sequential	Pinch analysis	Water minimization	Ujang et al. (2002)
MENs	Simultaneous	Mathematical programming	Efficient separations and optimal use of MSAs	Isafiade and Short (2016a)
Flexible HENs and MENs	Simultaneous	Mathematical programming	Minimizing total annualized cost (TAC)	Leong et al. (2016)
HENs	Simultaneous	Timesharing schemes	Minimization of utility consumption rate	Short et al. (2018)
HENs	Sequential	Mixed-integer nonlinear programming	Minimizing the TAC (Multicomponent)	Ladislav et al. (2016),

HENs	Sequential	Pinch point analysis	CO_2 transport and Storage	Aspelund and Gundersen (2009)
HENs	Simultaneous	Mathematical programming and heuristics	Minimization of TAC (area, pumping, and utility expenses)	Souza et al. (2016),
HENs	Simultaneous	Mathematical programming	Minimization of Utility and piping cost	Aaltola (2002) Tarighaleslami et al. (2018)
HEN and UEN synthesis	Sequential and Simultaneous	Pinch analysis & Mathematical programming	Cost and exergy derivative analysis	Kravanja and Glavič (1997)
HENs	Simultaneous	Meta-heuristic approach	Multi-period optimization of HEN	Pavão et al. (2018)

2.6 Recent trends in scientific publication for HENs and MENs synthesis methodologies

The end of the query process in Scopus for scientific contributions in this field retrieved a total of 447 peer-reviewed journal publications of interest to HENs and MENs synthesis starting from 1990 when the first contribution related to the synthesis of MENs was presented by El-Halwagi and Manousiouthakis (1990), up until October 2019 which gives an idea on how the interest in this field has grown over time. Figure 2.9 shows the distribution of journal publications using different synthesis techniques by year where PA stands for Pinch Analysis, MP is Mathematical programming and PA-MP is a combined pinch analysis and Mathematical programming approach. Figure 2.10 gives a percentage summary of the applications of these techniques.

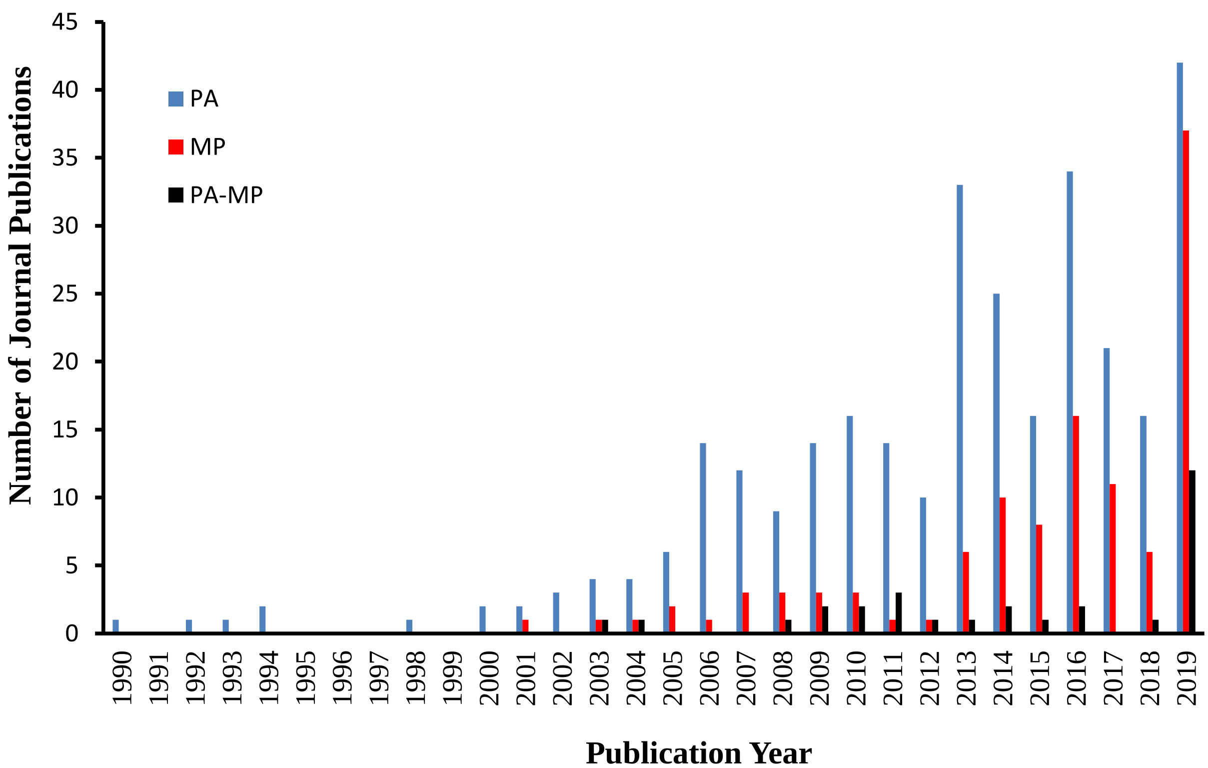


Figure 2.9: Published articles on the use of different synthesis solution methods (Obtained from Scopus, August 1990- October 2019)

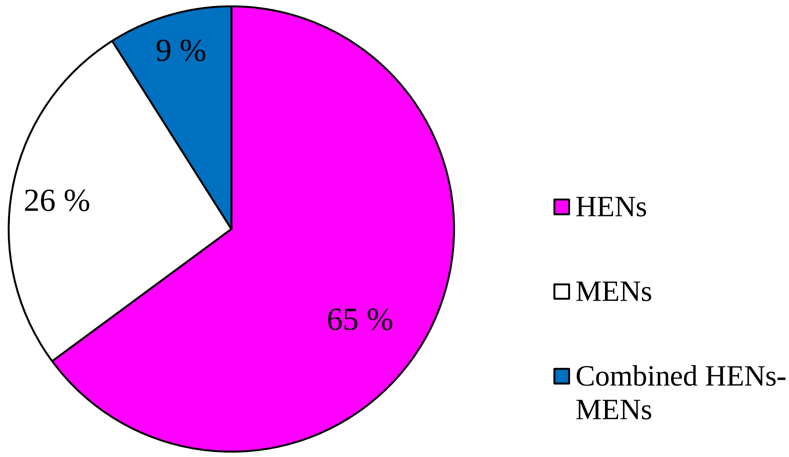


Figure 2.10: Distribution of synthesis methods applied in HENs and MENs by year (Obtained from Scopus August 1990 - October 2019)

Figure 2.9 shows that in 114 contributions, the mathematical programming (MP) method was applied; Pinch analysis (PA) technique was used in 286 contributions while a combination of combined pinch analysis and mathematical programming (PA-MP) was applied in 40 contributions. It is evident that the pinch analysis technique is well researched and has been used the most by researchers in the field of process integration. In addition, mathematical programming techniques in HENs and MENs synthesis was first introduced as early as 1977 but its application for energy and material minimization was not fully considered afterwards. According to the timeframe considered in this review (1990-2019), a full application of mathematical programming for CO_2 capture and energy recovery studies was reported only after 2002 while the combination of pinch analysis and mathematical programming started in 2003; and till date, it is not adequately researched compared to other methods. It is also worthy to note that there has been an increasing number of publications in the application of process synthesis techniques in the last 8 years (2010-2019). Figure 2.10 shows that 65 % of the aforementioned contributions were used in heat exchanger network (HEN) synthesis, 26 % of the reported techniques were applied in mass exchanger network (MEN) synthesis while a combined HEN and MENs synthesis accounted for only 9 %.

The trend observed in this section reveals that a combined pinch-mathematical programming technique for the synthesis of a combined heat and mass exchangers still need more research and more concerted research efforts should be directed towards it. Hence, it forms a major recommendation from this review.

2.7 Pinch analysis and mathematical programming in CO_2 capture systems

2.7.1 Application of pinch analysis in CO_2 capture

Recent studies in sustainable environmental engineering have highlighted the need to improve the efficiency, material, and energy-saving potential of most CO_2 capture methodologies (Harkin et al., 2010; Quader et al., 2015; Liang et al., 2016; Anastasovski, 2017). The amount of CO_2 emitted from industrial processes need to be minimized using CCS techniques with minimum energy expenditure and material usage. With the application of pinch analysis in CO_2 capture systems, appropriate loads on various process streams can be identified and as such, energy consumption and material usage during CO_2 capture can also be minimized (Anantharaman and Gundersen, 2016; Mohd-Nawi et al., 2016). Also, pinch analysis can provide a target for the minimum energy consumption of the entire CO_2 capture process from the process data of a CO_2 capture operation. The energy-saving potential for the process is then obtained using composite curves. The minimum energy-saving requirements set by composite curves depend on the energy and material balance of the CO_2 capture process. Adjusting the energy and material balance of the capture system makes it possible to further reduce its energy requirement (Marques et al., 2017).

Pinch analysis, which is based on thermodynamic principles provides a systematic approach for energy saving with a wide range of applications in many chemical processes (Fernández-Polanco and Tatsumi, 2016; Mehdizadeh-Fard et al., 2017), in finance (Roychaudhuri et al., 2017), in supply chain management (Roychaudhuri et al., 2017) and power sector planning (Bandyopadhyay and Desai, 2016; Akpomiemie and Smith, 2018). The use of pinch analysis in setting energy targets and mass separating agents targets in industrial processes has attracted a lot of attention in the past (Muster-Slawitsch et al., 2014; Chaturvedi et al., 2016; El-Halwagi, 2017); though not directly applied to CO_2 capture studies. Besides, pinch analysis has also recorded wide applications in both new and retrofit design situations. So far, the application of pinch technology in retrofit design is much higher than in new design applications (Li et al., 2016; Tan et al., 2016). Pinch analysis approach was first reported in power plants CCS by Tan and Foo (2007) to address CCS planning problem, particularly for carbon capture planning. The basic concept of pinch analysis in heat integration is to match the available internal heat sources with the appropriate heat sinks to maximize energy recovery and to minimize the need for external utilities (Zheng et al., 2017). To maintain cost-effective mass and heat exchange networks during the design and integration of individual network in CO_2 capture systems resulting from the interaction which exists amongst the process parameters, it is essential to apply pinch analysis techniques during process integration and design (Zheng et al., 2017; Yoro et al., 2019c).

The earliest graphical pinch analysis technique (known as the CCS planning composite curve) developed for carbon capture and storage (CCS) was reported by Tan et al. (2009). The authors used composite curves to determine the minimum extent of CCS retrofit in a given power grid where an average parasitic power loss and carbon removal ratio for the entire sector was assumed. The technique was also extended to identify minimum compensatory power to make up for the parasitic power losses of the carbon capture system. In a subsequent work by Ooi et al. (2014), this technique was extended to multi-period cases; but not without some intrinsic limitations which were attributed to the graphical technique used. To address this limitation, Shenoy and Shenoy (2012) proposed an algebraic targeting technique based on the concept of limiting composite curve earlier suggested by Agrawal and Shenoy (2006) and Hallale (2002) to overcome the intrinsic nature of the graphical targeting technique. The method used an algebraic technique called the composite table algorithm to locate the CCS targets, before displaying the graphical result. However, the main drawback with this technique is that it does not consider parasitic power loss which according to Matsuda et al. (2009), is very significant during CCS implementation in the power sector.

To address the limitation observed by Matsuda et al. (2009) and Sahu et al. (2014) proposed another algebraic targeting technique with a graphical display where non-zero emissions from compensatory power plants may be integrated into CCS planning. The proposed technique was an extension from the synthesis of resource conservation networks (RCNs) based on the targeting techniques of source composite curve and waste composite curve reported by Bandyopadhyay (2006, 2009). The aforementioned reports all revealed that pinch-based planning can be used in multi-region systems where sources and sinks exist in distinct geographic clusters during CO_2 capture, but none has critically addressed how to use pinch techniques to integrate heat and mass exchanger networks in power plants to simultaneously check high energy and material consumption when CO_2 capture devices are retrofitted into power plants. Hence, it is addressed in this research.

In this thesis, Pinch analysis is presented as a more preferred technology for heat exchanger network synthesis especially in retrofitting because of the following reasons;

1. It provides a systematic procedure which guarantees optimum design without relying on luck and guesses.
2. The design is based on thermodynamics and can be applied to all processes and technologies be it continuous or batch, new design or retrofit design.
3. About 15 % or more energy cost reduction is guaranteed where the process has already been optimized by "conventional" methods like pinch technology.
4. Pinch analysis shows us how to make better use of existing equipment and systems, and thus minimizes new equipment requirements in capacity upgrades.

2.7.2 Application of mathematical programming in CO_2 capture

Apart from pinch technology, mathematical programming is another technique that could be used to synthesize optimum heat and mass exchanger networks for effective energy and material minimization (Hallale and Fraser, 2000a; Morton, 2002; Grossmann and Guillén-Gosálbez, 2010b) but it has not been adequately tested in CO_2 capture systems. Design and synthesis of heat and mass exchanger networks give rise to discrete optimization problems which if presented in the algebraic form will result in mixed-integer optimization problems (Rathjens et al., 2016). Mathematical programming through the use of computer programs in choosing a suitable alternative from a set of available options is a very good technique to solve the aforementioned problem (Short et al., 2016). There have been substantial advances in the application of mathematical programming methods for process synthesis in the past. The solutions of mixed-integer nonlinear programming problems as well as the rigorous global optimization of nonlinear programs have also become a reality in recent times. There have also been new trends towards logic-based formulations that can facilitate the modelling and solution of these problems.

Due to the complex nature of most mathematical equations involved in the synthesis of mass and heat exchange networks, the use of mathematical programming in process synthesis has been achieved in the past by simplifying various superstructures and model equations through the use of simplified capital cost functions. Mathematical programming techniques have been adequately reported in the literature for synthesis of heat and mass exchange networks (Salama, 2005; Abbood et al., 2012; Isafiade et al., 2015; Isafiade and Short, 2016b). Some studies in process systems engineering field have also suggested the need to improve the efficiency and energy-saving potential of CO_2 capture systems while reducing the emissions of greenhouse gases and volatile organic compounds (Huang and Karimi, 2014; Sodhro et al., 2018). Most industrial processes throughout the world still use more energy and material than necessary and also emit large volumes of anthropogenic CO_2 into the atmosphere (Meylan et al., 2015; Lee et al., 2017). The amount of CO_2 emitted from these industrial processes need to be mitigated using CCS techniques with minimum energy and material expenditure. Pinch analysis and mathematical programming are useful techniques that can be used in this regard (Linnhoff and Hindmarsh, 1983). The scope of process integration through mathematical programming has improved in recent times and it can be applied in process industries to optimize heat and mass exchange networks for carbon emission minimization and water utilization (Sturm et al., 2015).

In this thesis, it is recognized that availability of modelling systems that can facilitate the formulation of optimization problems have recorded tremendous progress through mathematical programming and pinch technology, as well as the development of several solution strategies in process synthesis. Nonetheless, the research reported in this thesis further suggests that the idea of mathematical programming can be used in conjunction with pinch analysis and extended to different capture methods like membrane separation, adsorptive and absorptive CO_2 capture.

2.8 Energy penalty in CO_2 capture systems

One important issue that needs to be addressed in most CO_2 capture methods is the high energy requirement, because; energy availability is an important global issue. High energy penalty and excessive use of external utilities are other challenges confronting the capture of CO_2 from power plants (Yoro, 2017a). CO_2 compression and sorbent regeneration during CO_2 capture account for about 92 % of the energy penalty associated with most carbon capture and storage technologies (Sanz-Pérez et al., 2016). For instance a typical CO_2 capture system that is based on monoethanolamine (MEA) requires a significant amount of energy at about 3.0 – 4.5 GJ/t CO_2 to regenerate the solvent in the stripper reboiler as well as energy for the stripper feed which is usually provided by cooling of the lean solvent (Escudero et al., 2016b). According to a report by Zenz-House et al. (2009), the energy penalty associated with retrofitting CO_2 capture devices into existing power plants is estimated between 50 and 80 %. Further analysis of the thermodynamic limit indicates that the energy penalty during CO_2 capture can be improved by harnessing the available waste heat and improving the 2nd-law efficiency of temperature-swing adsorption systems (Khalilpour and Abbas, 2011). Furthermore, Zenz-House et al. (2009) postulated that in a real-life situation, it is difficult to attain an energy penalty reduction below 25 % during post-combustion CO_2 capture. The researchers also indicated that to offset the energy penalty incurred during capture and storage, about 80 % CO_2 emissions will require either an additional 390–600 million tonnes of fuel, additional 69–92 gigawatts of CO_2-free-baseload power, or a 15–20 % reduction in overall electricity usage. CO_2 capture units also require power to operate the gas compressors and other auxiliary equipment. Heat energy is also rejected from the stripper and compressor during CO_2 capture and compression. Retrofitting CO_2 capture devices in existing power plants will lead to a deficit of heat in the plant which has generally been proposed to be overcome by supplying heat and extracting steam from the turbine to the stripper reboiler. But according to Heede (2014) and Zhai et al. (2015), the proposed method subsequently reduces energy expenditure but could drop the net efficiency of the power plant by about 30–40 %. Developing a network for heat and mass exchange during CO_2 compression and regeneration using heat and mass integration approaches as reviewed and proposed in this section is a more reliable method that would ensure optimal energy and material usage with stable plant efficiency. Hence it forms the major focus of this review. A breakdown of the associated energy penalty in a typical CO_2 capture process is presented in Figure 2.11.

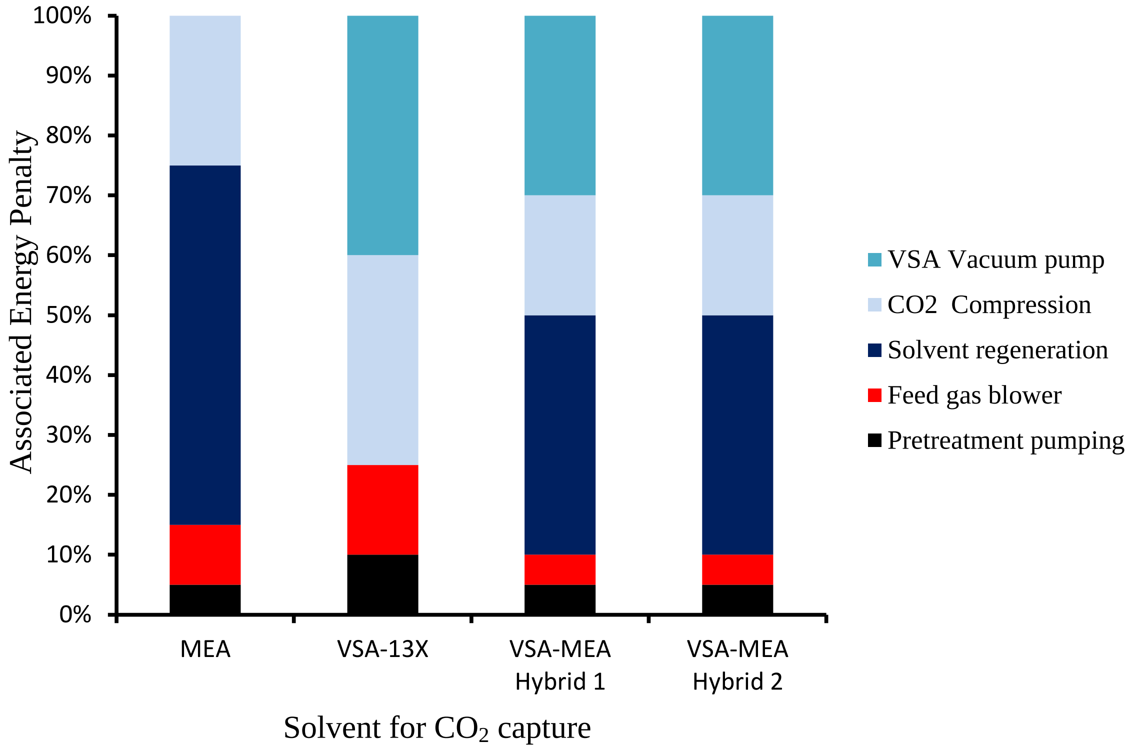


Figure 2.11: Percentage breakdown of total energy requirement during CO_2 capture via absorption.

2.8.1 Advances in energy penalty reduction during CO_2 capture

Energy penalty can be reduced in several ways and this solely depends on the CO_2 capture technology used (Jenni et al., 2013). According to Jassim and Rochelle (2006), a high energy penalty associated with chemical absorption systems during sorbent regeneration can be lowered by varying the solvents used. Yoro and Sekoai (2016) suggested the use of solvents such as piperazine in amine systems during CO_2 capture by chemical absorption to reduce the high energy requirement during sorbent regeneration in absorption systems. Koytsoumpa et al. (2018) suggested the application of the Fluor Econamine Plus process for energy minimization. This technology involves a combination of improved solvent formulation with an improved process design which includes absorber intercooling, split flow arrangements, integrated steam generation and stripping with flash steam to reduce total energy consumption. The authors claimed that about 20 % reduction in energy penalty associated with CO_2 capture was achieved in pilot studies with fluor econamine plus process in original monoethanolamine plants.

Conversely, the major drawback is that the methodology is limited to only absorption technique and does not provide a solution for minimization of extra utilities (mass) during the process.

Sharma and Azzi (2014), as well as Oh et al. (2018), recommended the use of ammonia cycle to generate energy from the available waste heat in a monoethanolamine-based CO_2 capture system retrofitted to a power plant. By applying the ammonia cycle method, the authors observed that energy penalty reduced significantly from 28 to 22 %. However, the major challenge associated with this method is that the ammonia condenser must be operated with a continuous flow of cooling water at 15 °C. If the ammonia condenser is operated with cooling water at a warmer temperature above 15 °C, the said level of efficiency would not be achieved.

Reports published by Alabdulkarem et al. (2012) and Goto et al. (2013) revealed that the utilization of waste-heat streams to increase the overall plant efficiency and reduce energy penalty during CO_2 capture could be a suitable option for energy penalty reduction and maintaining good plant efficiency. In this methodology, the researchers proposed the use of hot water stream for coal pre-drying in the flue gas line before desulphurization; the stripper-condenser and the CO_2 compressor intercoolers can also be used to heat the boiler feed water thereby completely removing the need for the existing boiler feed water heaters. However, the report did not state whether the heat energy saved is better utilized within the power plant itself to improve the overall efficiency. Table 2.3 summarizes the selected CO_2 capture methods, their energy consumption, and net plant efficiency after retrofitting CO_2 capture devices as reported by several authors in the past. It was observed in Table 2.3 that energy consumption increased while net plant efficiency dropped drastically in most studies after retrofitting CO_2 capture devices; hence the need for heat and mass integration.

So far, several researchers have suggested the utilization of waste heat during CO_2 capture to reduce the energy penalty associated with retrofitting CCS devices onto a power plant (Rubin et al., 2007; Supekar and Skerlos, 2015; Hills et al., 2016). However, plant efficiency, optimum energy, and material usage are usually compromised while attempting to capture CO_2 by retrofitting CO_2 capture devices on existing power plants. New methods to reduce energy penalty during CO_2 capture while maintaining stable plant efficiency are highly sought for till date. Synthesis of a combined heat and mass exchange network for this purpose could proffer a lasting solution to the drop in plant efficiency, high energy and material consumption associated with retrofitting CCS devices in power plants. As far as could be ascertained from previous studies, no report in open literature has applied process integration vis-à-vis pinch analysis together with mathematical programming in a combined manner to systemically integrate a CCS system within a power plant for energy penalty and material usage minimization during CO_2 capture; as such, it can form a very interesting topic for future research. Table 2.3 presents some selected CO_2 capture methods reported in the past, as well as their associated energy consumption

Table 2.3: Selected CO_2 capture methods in the literature, their associated energy consumption and plant efficiencies

Type of System	Energy Consumption (kJ/mol)	Plant Efficiency (%)	Reference
Absorption; MEA	1.03	21.39	Bhattacharyya and Miller (2017)
Absorption; MEA	2.32	14.93	Sanpasertparnich et al. (2010)
Absorption; MEA	7.76	14.52	Cau et al. (2016)
Absorption; K_2CO_3/PZ	7.44	20.29	Oexmann and Kather (2009), Oexmann et al. (2008)
Absorption; NH_3	25.48	17.03	Versteeg and Rubin (2011)
Absorption; Generic Solvent	7.62	20.67	Oexmann and Kather (2010)
Adsorption; zeolite 13X	22.57	16.11	Oreggioni et al. (2015)
Membrane; One stage	98.56	8.88	Bounaceur et al. (2006)
Membrane; Two-stage	12.76	4.54	Merkel et al. (2010)
Cryogenic; Stirling coolers	169.84	3.90	Song et al. (2014)

2.8.2 Heat and mass exchanger networks for energy and material minimization during CO_2 capture

Heat exchanger network synthesis is the most commonly studied problem in process synthesis than mass exchanger network synthesis (Furman and Sahinidis, 2002). Hallale and Fraser (2000b) identified the heat exchanger as the major heat transfer unit between process industries in any chemical industry. As such, the synthesis of heat exchanger networks (HENs) has been extensively studied as a systematic way to effectively minimize energy consumption in most industrial processes (Wu et al., 2015). A typical heat exchanger network represents an interaction between hot and cold process streams as well as utilities while a mass exchanger network depicts an interaction between rich and lean streams in a process to meet optimum plant requirement. Figure 2.12 shows a combined heat and mass exchanger network for effective heat energy and resource minimization during CO_2 capture. So far, heat and mass exchanger networks have been effectively synthesized using process integration methodologies such as pinch analysis and mathematical programming, but it has not been applied in the area of CO_2 capture for energy consumption and material minimization. Currently, pinch analysis and mathematical programming-based methods are the most popular methods for synthesizing heat and mass exchanger networks because they play very important roles in solving industrial problems concerning heat and mass exchange.

Absorption and adsorption are well-known technologies for CO_2 capture (Dutcher et al., 2015; Yoro and Sekoai, 2016). However, as earlier highlighted, CO_2 capture using absorption and adsorption techniques are highly exothermic in nature, energy, and material intensive (Quintella et al., 2011). This limitation has made these well-known CO_2 capture technologies to record high process costs. To tackle this challenge and minimize resources in important industrial processes, there is a need to synthesize optimal mass exchanger networks that will minimize material usage. In the field of chemical engineering, process integration is a reliable tool for analyzing process mass and energy flows thereby reducing the use of raw materials, external utilities, waste discharge as well as maximizing the internal heat and mass exchange. The synthesis of mass exchanger networks in this study will help in providing a solution to the problem of excessive use of external utility associated with most absorptive/adsorptive CO_2 capture processes. Mass exchanger network synthesis (MENs) using simultaneous approach (mathematical programming) is well established and adequately reported in the literature (Foo et al., 2004; Liu et al., 2013b; Isafiade et al., 2016). However, it has been observed that the determination of an optimal network using simultaneous techniques is often complex due to the non-convexity of the mathematical representation of the problem.

Most of the current researches in process synthesis focus on the synthesis of heat exchanger networks (Hafizan et al., 2016; Pavão et al., 2017a, 2017b). For example, recently, Romeo et al. (2019) investigated size and energy penalty reduction in combined carbon capture cycles using heat exchanger networks. The few available literature reports on mass exchanger network synthesis mostly discussed single-component problems using simultaneous approaches (Alva-Argáez et al., 1999; Chen and Hung, 2005). Less attention has been dedicated to multi-component mass exchanger network synthesis using sequential techniques. From the literature reports reviewed so far, the major gap identified in the sequential synthesis of multicomponent MENs is the difficulty in systematically choosing between the process and available external mass separating agents (MSA) in a mass exchanger network. Hence, this study applied sequential techniques to address material minimization during the adsorption of CO_2 from a flue gas stream in this chapter. Just like other studies reported in the past, the process MSAs in this study are generated from within the process and readily available onsite while external MSAs need to be bought and brought onsite. The more process MSA consumed by a process means that less external MSA will be required for the process. Hence, considering the cost of MSA, a good mass exchanger network is designed to consume more process MSAs and less external MSAs.

In this chapter, a combined network is suggested for the synthesis of heat and mass exchanger network using heat and mass integration techniques for a concurrent minimization of energy and material consumed during CO_2 capture in power plants and presented in Figure 2.12.

2.9 The future of heat and mass integration in CO_2 capture

Despite the tremendous potentials of heat and mass integration for utility minimization, limited investigations have been reported for the synthesis of heat and mass exchanger networks for energy and material minimization in CO_2 capture studies. This field constitutes an emerging area of research in the scientific community and application of process synthesis techniques to solve problems in environmental studies will be one of the hot research topics in the future. Heat and mass integration techniques proposed in this chapter could be extended in future research to take into account a combined heat and mass exchanger network for CO_2 capture which can also be linked to a regeneration network to account for energy and material loss during sorbent regeneration. This has not been given adequate attention in the past and could constitute a potential research topic in this field. Combination of pinch analysis with mathematical programming in a single methodology is still a more effective technique during heat and mass integration in CO_2 capture systems compared to other methods previously reported in the literature. A hybrid network optimization approach may also be tried for heat and mass exchanger applications in future studies. Life cycle assessment of heat and mass exchangers can be carried out in future studies to investigate its environmental impact using mixed integer linear and non-linear programming mathematical models. To ensure effective utilization of CO_2 with minimized material wastage using the strategies highlighted in this chapter, a section of this thesis will focus on a detailed design of a transport network to transport captured CO_2 from different power plants to a central storage site or utilization point.

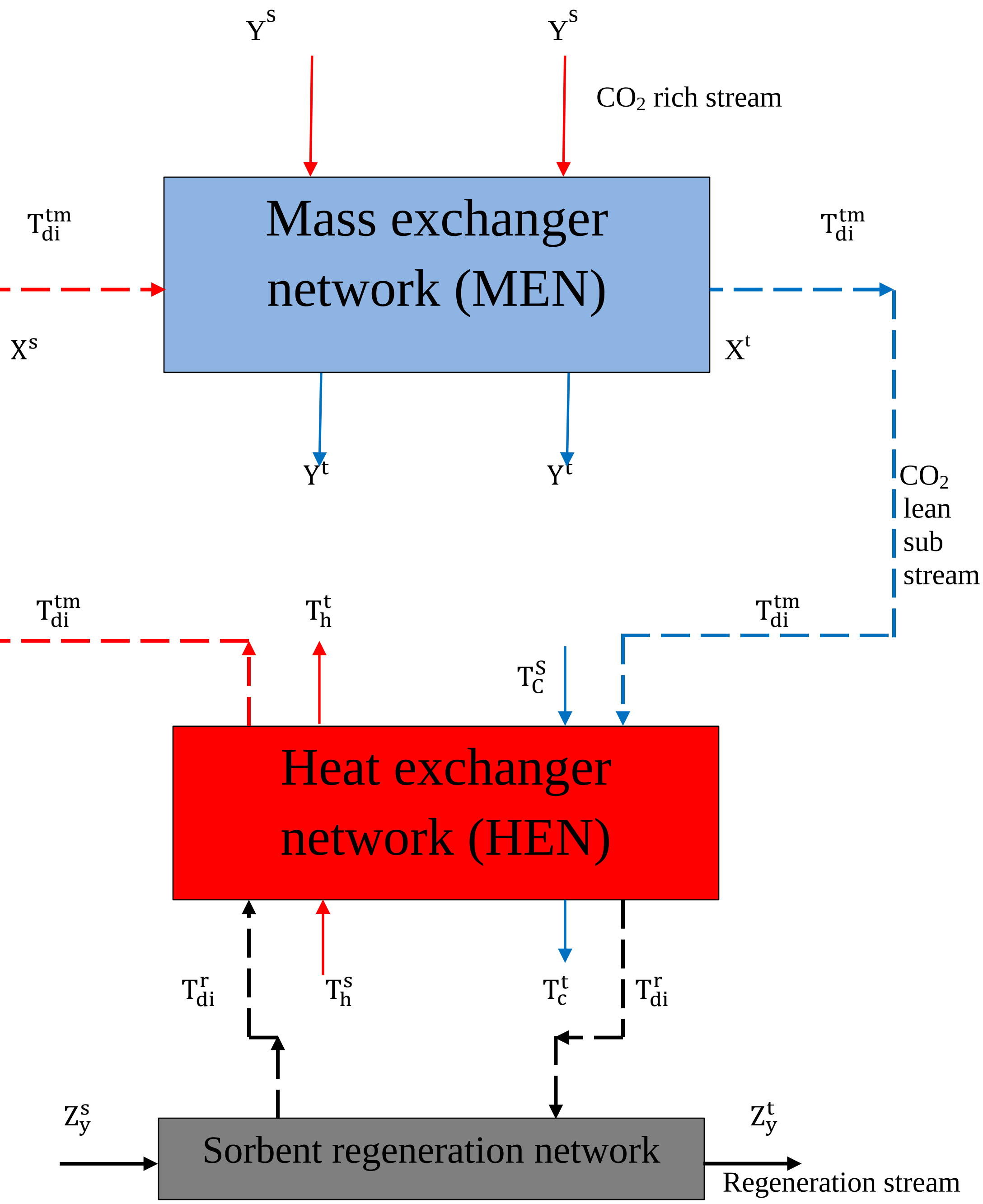


Figure 2.12: A combined heat and mass exchanger network for CO_2 capture. [Modified from Isafiade and Fraser (2009)].

Where Y^s is the supply composition of rich stream, Y^t is the target composition of the rich stream, T_{di}^{tm} is the mass exchange temperature of lean substream, X^s is the supply composition of lean stream, X^t is the target composition of lean stream, T_h^t is the target temperature of the lean stream, T_C^S is the supply temperature of the lean stream, T_{di}^r is the regeneration temperature of the lean substream, Z_y^s is the supply composition of the regenerating stream and Z_y^t is the target composition of the regeneration stream. A schematic procedure for applying heat and mass integration in power plants is presented in Figure 2.13. The procedures start from a design stage and end in optimization which could lead to optimal results. The procedure is stepwise with each stage leading to another.

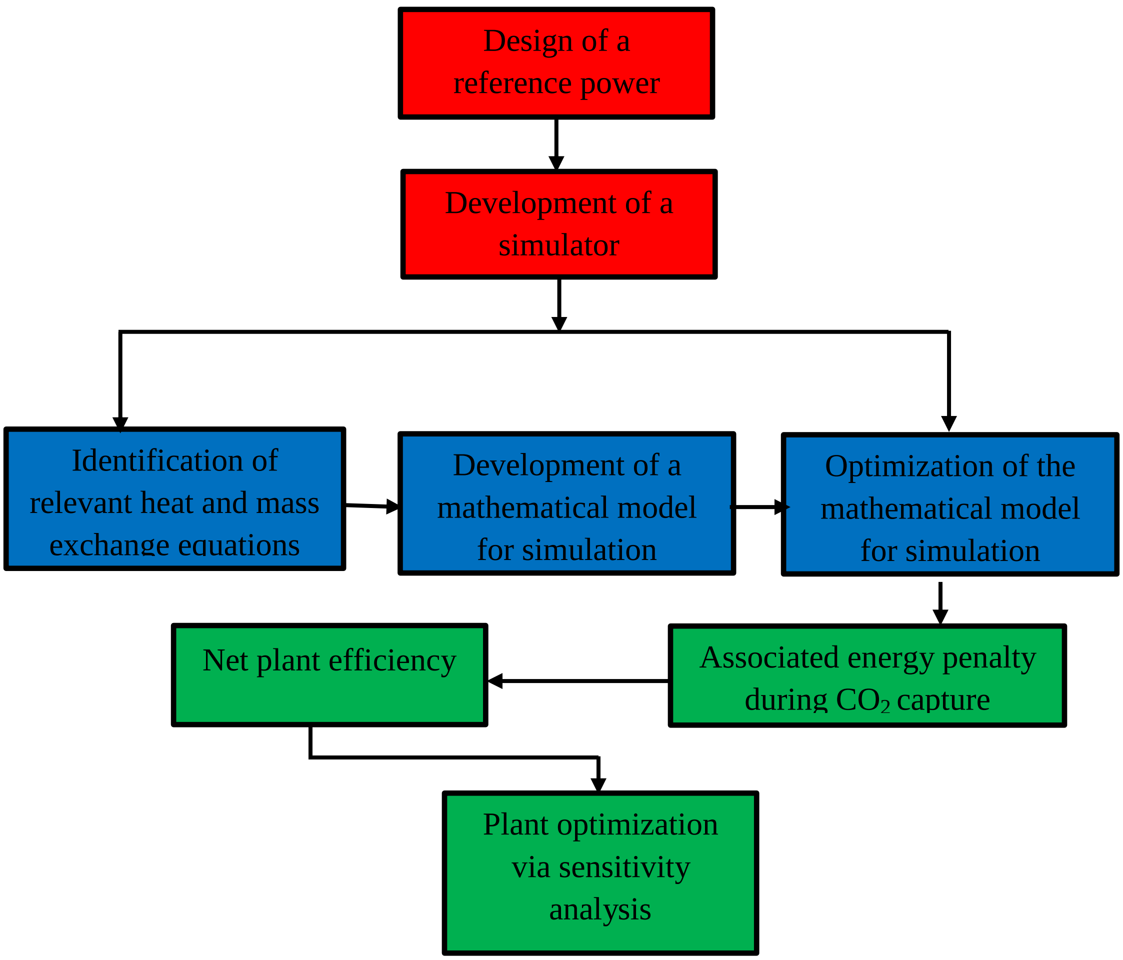


Figure 2.13: Schematic layout of a proposed methodology for heat and mass integration in power plants.

2.10. Concluding remarks

Undoubtedly, the challenge of high energy consumption and excessive material consumption in many industrial applications has fuelled the need to search for sustainable ways to minimize excessive energy and material consumption. High consumption of energy and materials associated with most CO_2 capture methods has hindered its implementation and commercialization on a pilot scale in most developing countries. The implementation of inexpensive strategies like heat and mass integration as suggested in this chapter to check this limitation could boost its process development and large-scale application. This chapter also highlighted that heat and mass integration can proffer a solution to the energy crisis facing the implementation of CCS in the power sector of most developing countries. A short overview of the state-of-the-art in the application of different techniques for the synthesis of heat and mass exchanger networks has also been presented. It has been identified that the use of inhibitors and additives, phase change materials, sorbent blending and amine scrubbing have been the common strategy used to minimize high energy requirement in energy-intensive processes such as absorptive CO_2 capture. However, the use of these additives is only suitable in gas-liquid absorption systems and cannot be fully extended to gas-solid adsorption or membrane systems during CO_2 capture because it is limited in terms of solvent capacity. Other techniques can only account for either energy or material minimization and not both. But this study has identified heat and mass integration techniques as the best alternative to account for energy, material and process cost savings during CO_2 capture.

Application of heat and mass integration techniques through the synthesis of heat and mass exchanger networks as identified in this chapter can play a very crucial role in the improvement of system efficiency in industrial processes. It can also be extended to minimize high energy and material consumption in both liquid and solid sorbents applications; hence it is applicable in all CO_2 capture methods. Finally, since a typical CO_2 capture method involves both heat and mass exchange occurring simultaneously, synthesis of a combined heat and mass integration network has been suggested to concurrently minimize energy and material minimization in CO_2 capture studies in this thesis.

Based on the aforementioned findings and research gaps identified in this review, subsequent chapters of this thesis have demonstrated the promising potentials of integrating heat and mass exchanger networks for CO_2 capture from power plants by:

1. Evaluating the possibility of applying the concept of heat and mass integration during CO_2 capture to minimize its associated high energy penalty and material consumption as a better alternative to existing technologies which are expensive to implement. The use of internally generated heat energy within the process instead of external heat will be fully investigated in subsequent chapters of this thesis for this purpose. The possibility of extending the proposed techniques to other CO_2 capture methods for energy and material minimization will also be explored.

2. Investigating both sequential and simultaneous techniques to synthesize the heat and mass exchanger networks for CCS operations.

3. During CO_2 capture, parameters such as temperature and gas flow rate are not always constant due to environmental factors. Therefore, synthesizing a multi-period heat exchanger network that will be able to operate with fluctuating operating parameters will be discussed in this thesis.

4. Suggesting a cost-effective transport network for captured CO_2 from the power plant to specific storage sites.

CHAPTER THREE

Research Methodology and Preliminary Investigation

Methods and procedures employed in investigating the objectives of this study are discussed in this chapter. Firstly, preliminary investigations were carried out experimentally to gain an insight into the effects of operating conditions such as supply and target compositions, concentrations, gas flow rates, the mass of sorbent etc in adsorptive CO_2 capture. The supply and target temperatures, heat capacity flow rates and enthalpies were also determined in the preliminary study and used in the HEN synthesis section of this study. Furthermore, an investigation was carried out on mass transfer influence on the process using a mathematical modelling approach. The outcome of these investigations serve as the basis for subsequent investigations on HENs and MENs and documented in this thesis. Furthermore, a brief overview and outcome of the preliminary investigation are documented in this chapter. It is noteworthy to mention that results of the preliminary investigations have been published in two peer-reviewed journals and referenced in this chapter as Yoro et al. (2019a) and Yoro et al. (2019b). See Appendix A4 and A5 for copies of these publications.

3.1 Introduction

The main aim of MENs synthesis in this research is to decrease extra material consumption by increasing mass exchange simultaneously among process streams in an existing process plant (Singh and Khanam, 2017) while the main aim of synthesizing HENs in this thesis is to minimize energy consumption by utilizing internal process heat instead of introducing external utilities such as steam (Luo et al., 2013). In most CO_2 capture techniques, the MSAs are usually the sorbents used for the capture process (Jovančić and Radetić, 2008) and the utilities are usually cooling water and steam. For this study, the mass separating agents considered were monoethanolamine (MEA) for absorption and polyaspartamide (PAA) for the adsorption. Details of these sorbents (polyaspartamide) including absorption kinetics and mass transfer correlations have been published elsewhere (Yoro et al., 2019a, 2019b; Chitsiga et al., 2016), hence it is not repeated here. Information on the liquid sorbent (MEA) investigated in this study has been widely discussed by other researchers (Singto et al., 2016; Mjalli et al., 2017; Squadrito 2018; Bougie et al., 2019). Based on the knowledge gap highlighted in Chapter two of this thesis, this study was divided into several segments as shown in Figure 3.1. As earlier pointed out at the beginning of this chapter, a detailed description of the techniques introduced and methods of synthesis are presented and discussed in subsequent chapters where they are used. Figure 3.1 illustrates the procedures employed in this study while Figure 3.2 depicts the methodical steps taken. It is also worth stating that despite the many literature reports on HENs and MENs synthesis techniques, a room was made to introduce new concepts and assumptions to the synthesis techniques documented in this thesis.

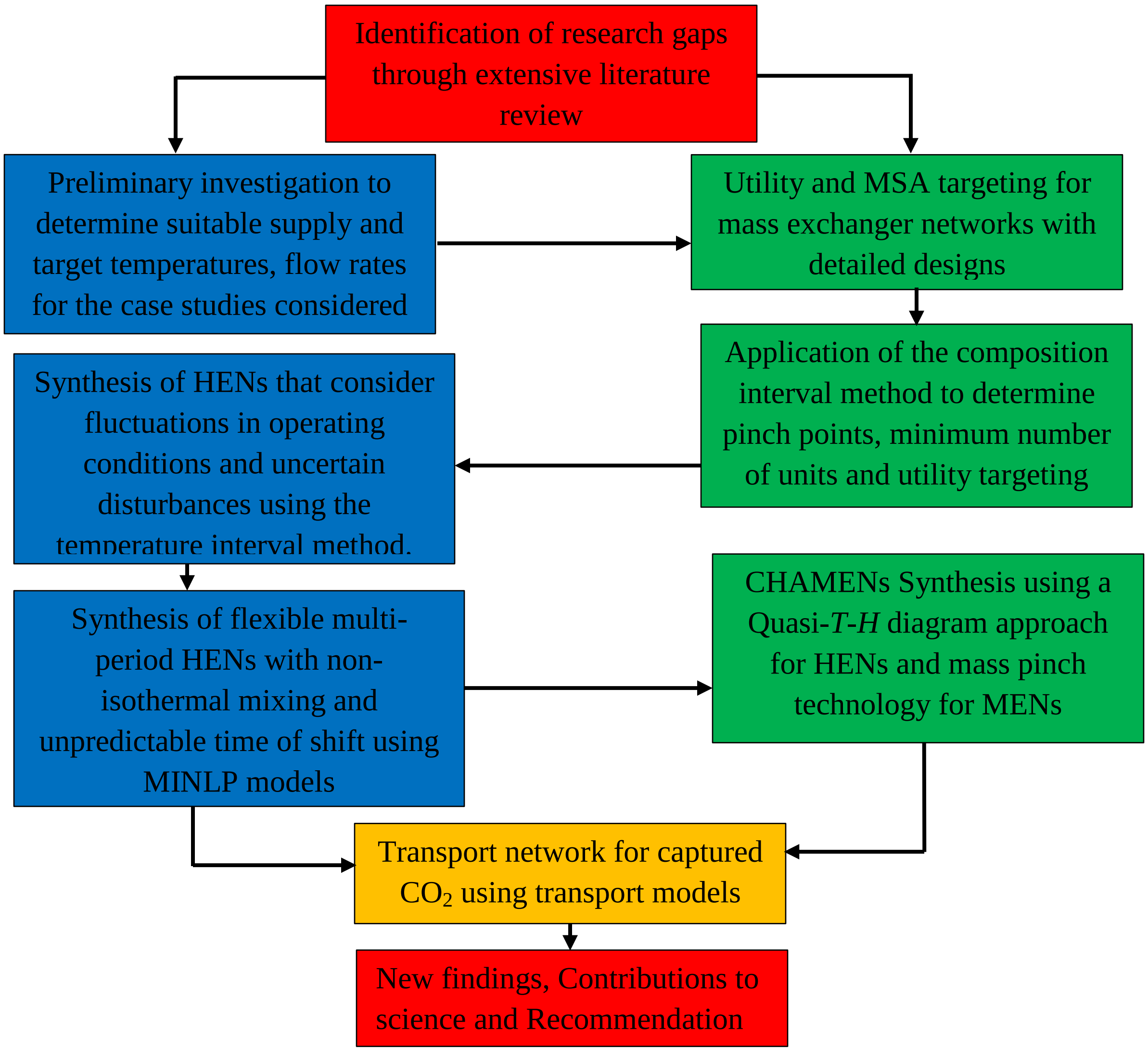


Figure 3.1: A summary of the methodological steps considered in this research

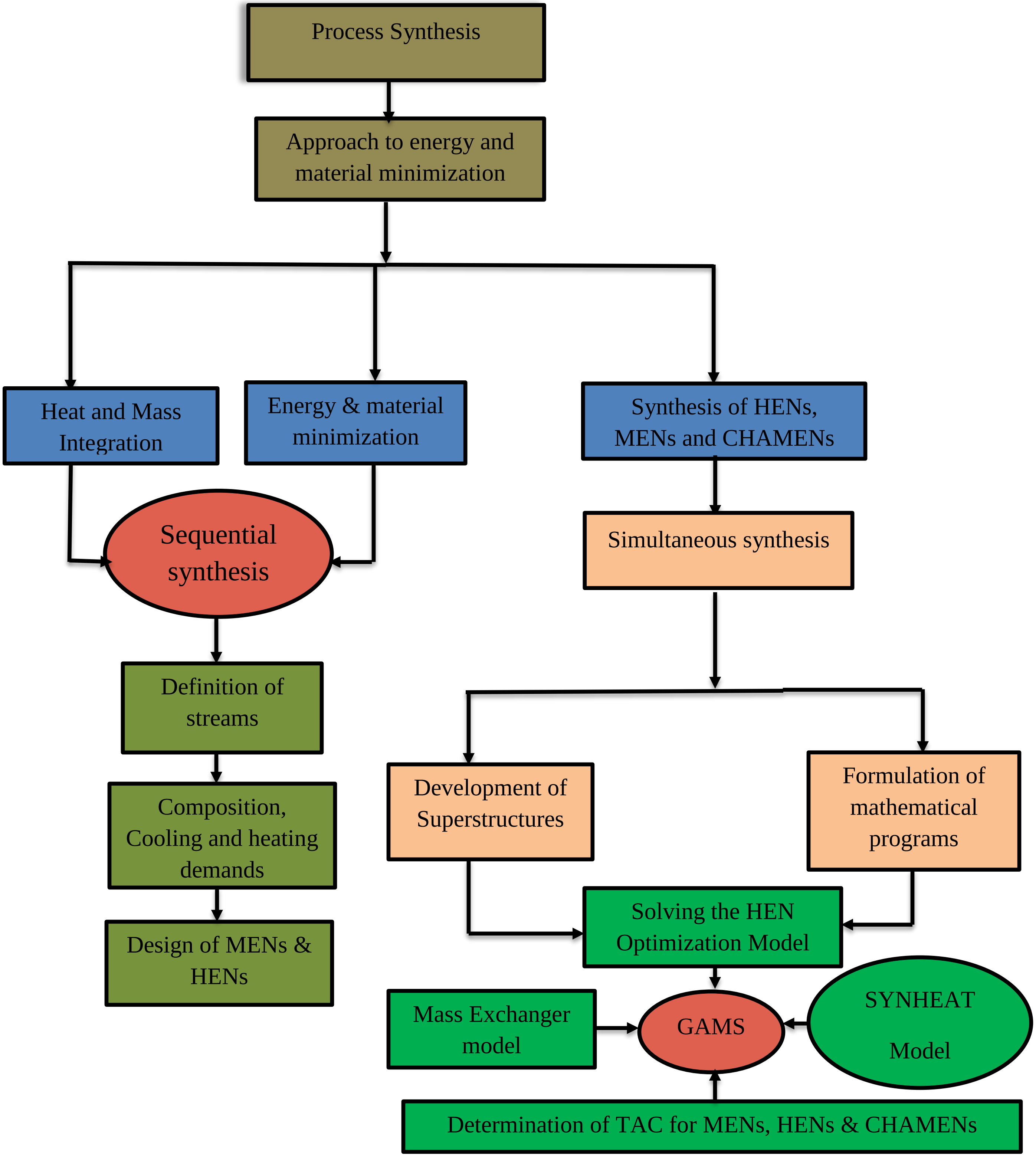


Figure 3.2: Conceptual overview of a proposed methodology for this study.

3.2 Development of heat and mass exchanger networks (HENs and MENs)

According to El-Halwagi and Manousiouthakis (1989), classification of the sorbent-based separation process is dependent on the nature of its mass separating agent (sorbent); this may take the form of liquid or solid sorbents. Distillation, crystallization, and evaporation are typical examples of energy-separating-agent processes while common mass-separating agent processes are absorption, adsorption, desorption, ion exchange etc. Since this thesis focuses mainly on heat and mass separating agent processes, heat and mass exchanger networks were synthesized for energy and resource minimization in absorption and adsorption systems.

The heat and mass exchanger networks generated in this study are based on both sequential and simultaneous techniques. A detailed description of the sequential and simultaneous synthesis methods has been provided in Chapter two while a schematic overview of the methodology for both sequential and simultaneous techniques is presented in Figure 3.2. The temperature and composition interval methods were modified and used for sequential synthesis of HENs and MENs respectively using the concept of pinch technology and thermodynamic principles, while the simultaneous synthesis of both HENs and MENs were done using mathematical programming in GAMS (General algebraic modelling system). The SYNHEAT model in GAMS which was originally developed by Yee and Grossmann (1990) was modified further in this thesis to include new assumptions to synthesize the desired HENs. New concepts such as a modification of objective functions, inclusion of non-isothermal assumptions with an index to represent multi-period scenarios and integrating it to the field of CO_2 capture are the major differences between the HENs model developed in this thesis and ones in previous studies. To minimize the number of units for the heat-exchangers, the heat transferred in each exchanger was maximized by first identifying the total heat available from the hot stream and the heat required by the cold stream. Then, the lesser of the two was chosen to maximize the heat transferred in the unit.

3.3 HENs and MENs optimization with GAMS

The simultaneous optimization of the heat and mass exchanger networks reported in subsequent chapters of this thesis were implemented and solved in the general algebraic modelling system

(GAMS) environment. GAMS is a software package used to solve schemes of equations/models and it was developed by the GAMS Development Corporation (Flores-Tlacuahuac and Grossmann, 2010). This software package contains different solvers for different purposes. The main driving force behind the development of GAMS has been the need for researchers to use mathematical programming in optimization as a framework for solving real-life problems in the field of science and engineering (Bussieck and Meeraus, 2004). Various kinds of economic models can be written down as a system of equations, including systems analysis, non-linear optimisation and equilibrium modelling in GAMS. Environmental issues such as the problem addressed in this thesis can be built in the GAMS models in different ways. To address the peculiar need in respective chapters of this thesis, standard models (objective functions) were developed and then equations for emissions, concentration abatement (in MENs), and economic costs of the networks were introduced and solved. The GAMS design package explored in this research has ideas drawn from interactive database theories. Mathematical programming techniques were used to merge these ideas to suit specific needs in this research as suggested by Rosenthal (2012). A graphic interface of the GAMS package used in this research is shown in Figure 3.3 while detailed explanations on the methodologies used are provided in subsequent chapters of this thesis where they have been used. The GAMS programme written for this research took the standard format of a normal GAMS programme. Modifications were however made in the parametric values, assumptions and commands used to run the program. The general format for a GAMS programme takes the structure depicted in Figure 3.3.

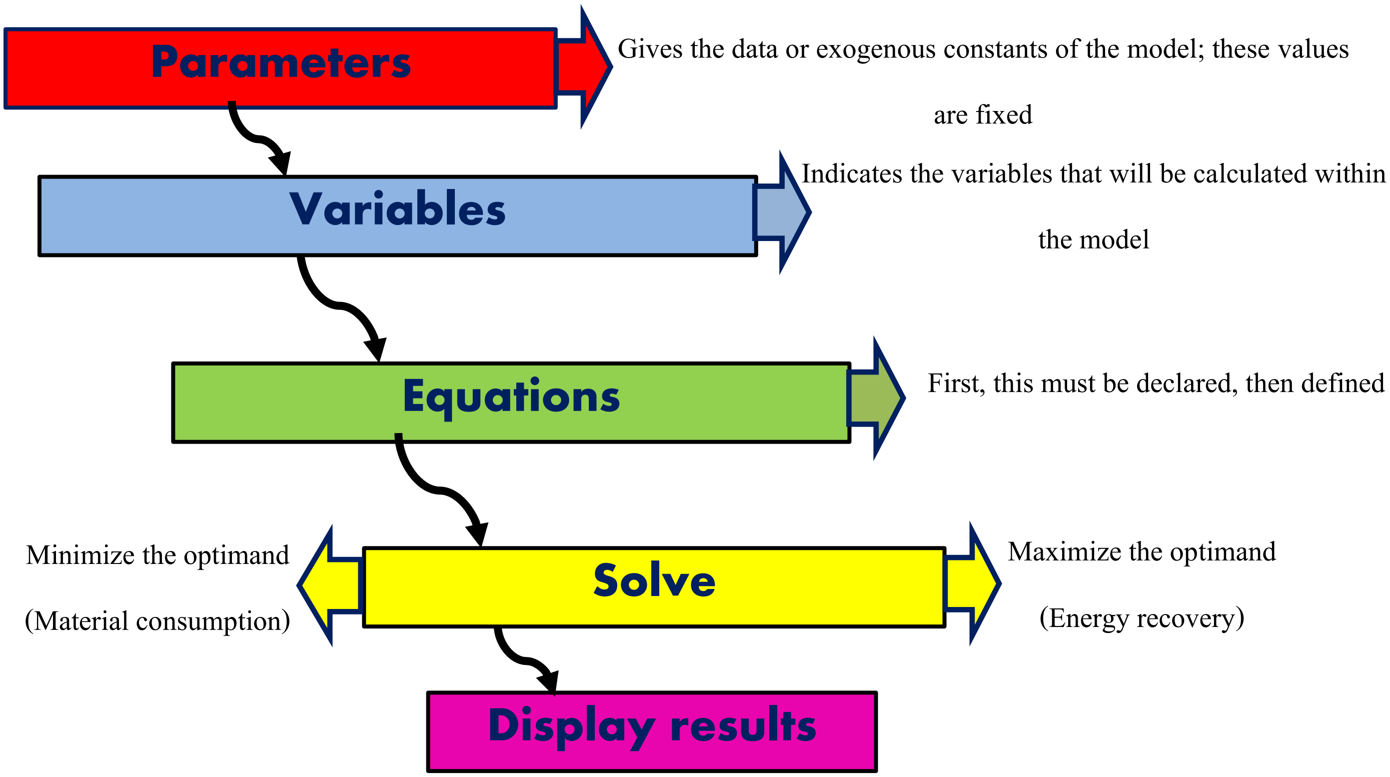


Figure 3.3: Schematic representation of the format for a program in GAMS

3.4 Minimum utility and MSA targeting

Minimum utility and MSA targeting were carried out in this thesis for the HENs to minimize the amount of hot and cold utilities used by the network for CO_2 capture and also account for the energy and materials (e.g sorbents, cold and hot utilities) that could be saved in the process. For the MENs, MSA targeting was done to minimize material consumption and also account for the amount of mass transfer agent (sorbent in this case) that could be saved by integrating the MENs network synthesized in this study in a CO_2 capture problem. Minimum composition difference was set for the MENs while a minimum approach temperature was set for the HENs in this study. For the selected minimum approach temperature (ΔT_{min}) in this study, the hot and cold utility demands were calculated using a transhipment model similar to that of Papoulias and Grossman (1983) using a simultaneous approach. However, the new thing with the transhipment model used in this research is that it was extended to include multi-periods and multiple utilities. The minimum utility target was made constant in the loops of the framework until the ΔT_{min} is adjusted. In the sequential synthesis part of this thesis, the stream data was inserted into a Microsoft Excel file to determine the minimum utility target for the chosen ΔT_{min} and pinch temperature(s) to develop the composite curves of the streams. A flow chart representing how the utility and MSA targeting was done in this study is presented in Figure 3.4.

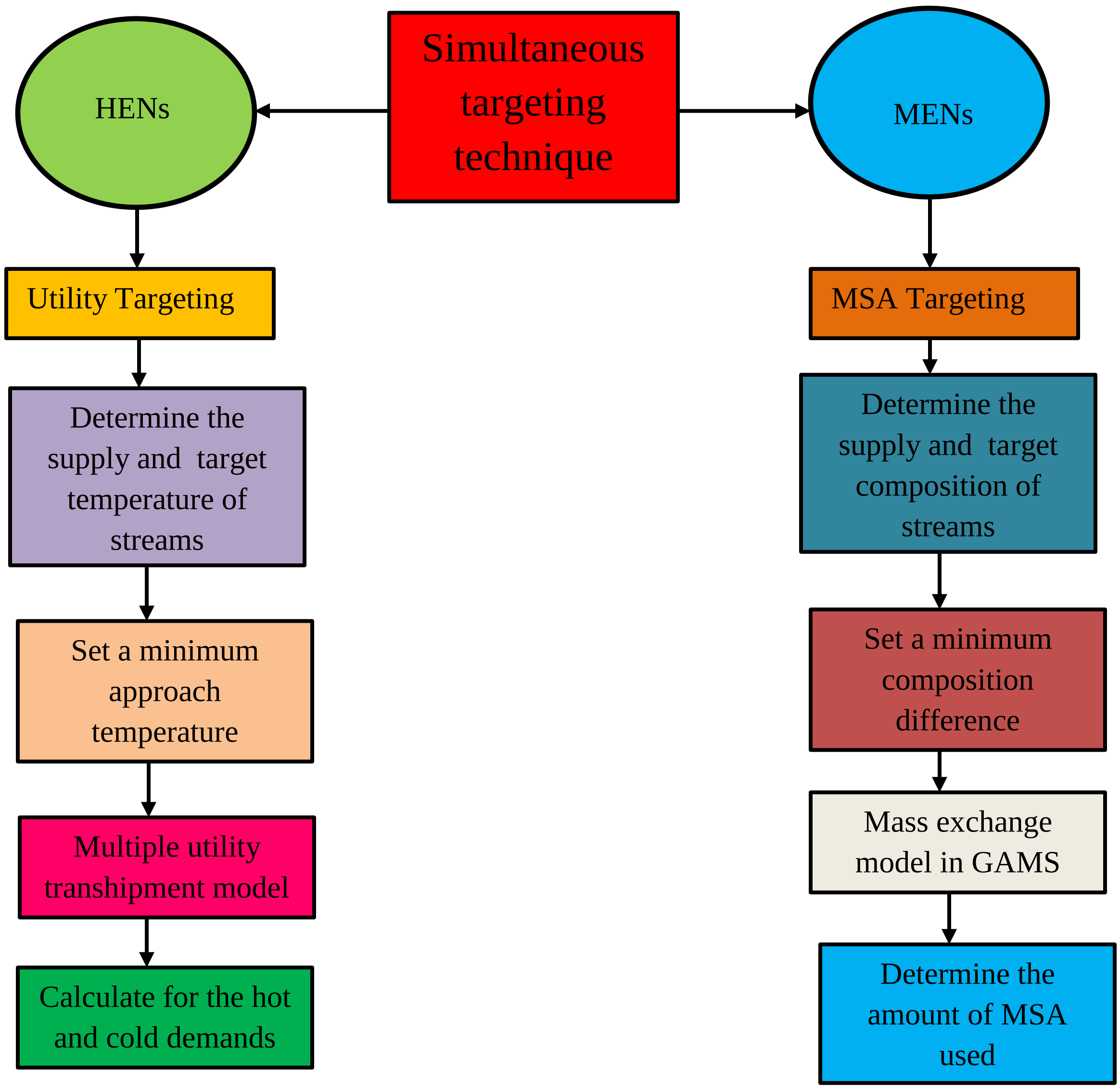


Figure 3.4: Schematic representation of the utility and MSA targeting steps

3.5 Minimum number of units

According to Papoulias and Grossman (1983) and Hallale and Fraser (2000a), an appropriate network of heat and mass exchangers must comprise of a lesser number of heat and mass exchanger units respectively. This means that the lesser the number of heat and mass exchanger units in a network, the better its total annualized cost. The minimum number of units for the networks developed in this study was formulated as a MILP transhipment task based on an improved model of Quirante et al. (2018) in cases where simultaneous techniques were used. The MILP model used in this investigation slightly differs from the model of Papoulias and Grossman, (1983) and Quirante et al. (2018) because the works of the aforementioned researchers did not adequately consider sub-networks, and pinch decomposition with heat transfer across pinch point(s). To allow for heat transfer across pinch point(s), the minimum approach temperature (ΔT_{min}) of the heat exchanger was changed from the set temperature. The energy target that was calculated by the model was used as the input to determine the absolute minimum number of units for the network. The data obtained were programmed as a GAMS code to determine the minimum number of units (U_{min}). Further explanations on this have been provided in the respective chapters where the synthesis was reported (see chapters 5, 6 and 7).

3.6 Evaluation of the synthesized network

The effectiveness and performance of the proposed methodologies and the synthesized network in this thesis were tested and subsequently reported in relevant chapters. For example, the mass exchanger networks (MENs), heat exchanger network (HENs), transport network as well as combined heat and mass exchanger networks (CHAMENs) synthesized in this research for effective, material, heat or combined heat and material minimization during post-combustion CO_2 capture in power plants were tested using real-life examples or case studies. Results obtained were corroborated with previously reported methodologies in the literature and conclusions were made. The methodologies used in this thesis were modifications from previous synthesis techniques. Hence, the need to compare the results with previous methods to validate the strength or weakness of the technique proposed in this study. As suggested by Martín-Cejas (2005), Najafi et al. (2011) and Kim et al. (2009), capital and operating cost functions for the heat, mass and combined networks synthesized in this thesis were determined and compared with what was previously reported by other researchers to establish the strength, superiority and strengthen the confidence of the reader in the synthesis approach proposed and used in this thesis. Synthesis of a regeneration network was considered in this work to account for the energy that could be minimized by the network during sorbent regeneration. This was done by combining both pinch and mathematical programming concepts to generate an optimal CHAMEN with regeneration.

3.7 Preliminary investigation: The mass transfer agent (sorbent) and Operating conditions

This main focus of this thesis is to introduce process synthesis concepts for energy and material saving during CO_2 capture which has not been considered in literature before now. Most studies in the field of CO_2 capture usually stop at the development and performance evaluation of sorbents. Yoro (2017) reported a new material for CO_2 capture alongside its kinetic and parametric behaviours. This study extended, improved and introduced new concepts to the previous work reported in Yoro (2017). Before the research reported in this thesis was carried out, a preliminary study was conducted to establish the basis for this research. The sorbent which is considered in this thesis as the mass separating agent (MSA) was first investigated for its suitability in a study as this. Optimal process conditions such as flow rates, supply and targets temperatures, supply and target compositions obtained from this preliminary investigation were used in this study were determined in this chapter before they were tested in the GAMS model. For a detailed understanding of the behaviour of the MSA (Polyaspartamide) used in this study and its optimal operating conditions, the reader is advised to read Yoro et al. (2019a) and (Yoro et al., 2019b). However, a brief description of the experimentation approach is discussed in Section 3.7.1. Major findings from the preliminary investigation have been summarized in Tables 3.1 - 3.3. The sorption process was greatly influenced by the effect of process parameters. The preliminary study revealed the gas flow rate, biot and Boyd numbers as well as diffusion parameters that were used in the extension of this work. The outcome of the preliminary investigation was also compared with literature and no significant difference was observed.

Table 3.1: mass transfer parameters for adsorptive CO_2 capture with polyaspartamide at specific operating conditions.

Parameters	Run 1	Run 2	Run 3	Reference
Flow rate (mL/s)	1.50	2.00	2.50	Yoro et al. (2019b)
	1.00	2.00	5.00	Lin et al. (2017)
Biot number	17.80	22.45	30.74	Yoro et al. (2019b)
	18.60	23.43	31.80	Lin et al. (2017)
Boyd number	4.15	4.15	4.15	Yoro et al. (2019b)
	5.23	5.23	5.23	Lin et al. (2017)
K_{id} (m/s)	1.24×10^{-4}	1.58×10^{-4}	2.13×10^{-4}	Yoro et al. (2019b)
D_s (m^2/s^2)	0.21×10^{-14}	0.84×10^{-14}	1.30×10^{-14}	Yoro et al. (2019b)

All modelled results used in this research have been corroborated with experiments to ascertain their validity and reported in appropriate journals. It is also worth stating at this point that the sorbents (MSAs) considered in this research are monoethanolamine (MEA) and Polyaspartamide (PAA). The physical properties of the sorbents; MEA have been adequately reported in the literature by other researchers (Reitmeier et al., 1940; Singto et al., 2016; Squadrito 2018; Mjalli et al., 2017) while the characterization and other analysis results on polyaspartamide alongside its properties have been extensively discussed in our previous studies (Ngoy et al., 2014, 2017; Chitsiga et al., 2016; Yoro 2017; Yoro et al., 2017, Yoro et al., 2019a, 2019b). Hence they are not repeated in this work. Both sorption processes were carried out in a packed bed column.

Polyaspartamide is an amine-grafted polymer-based material recently developed for CO_2 capture. The material was obtained when polysuccinimide was reacted with Ethylenediamine (EDA). This material has been adequately studied in the past, and it has proven to be a potential adsorbent for CO_2 capture because of its rich amine content, high thermal stability (473.15 K), high adsorption capacity (365 mg/g) and porosity (Ngoy et al. 2014; Chitsiga et al. 2016; Ngoy et al., 2017). Nuclear Magnetic Resonance analysis was carried out on the adsorbent (polyaspartamide) by Chitsiga et al. (2016) to determine whether the synthesis was qualitatively successful. Among other analyses carried out on this adsorbent were Fourier Transform Infrared Spectroscopy (FTIR) to identify all the functional groups present on the adsorbent's surface, Thermo gravimetric analysis (TGA) to determine the thermal stability of polyaspartamide, Scanning Electron Microscopy (SEM) was carried out to obtain clear images showing the opened pores and cavities in the adsorbent, while the BET analysis was carried out on polyaspartamide to determine its pore size, pore volume and the surface area (Chitsiga et al. 2016). Details on its preparation, characterization and cost have been extensively discussed in our previous works (Ngoy et al., 2014; Chitsiga et al., 2016; Ngoy et al., 2017; Yoro 2017; Yoro et al., 2019a, 2019b). Hence, it is not repeated in this thesis.

3.7.1 Brief experimental approach for the collection of process data

To obtain the experimental values that were considered in the synthesis aspect, continuous gas-solid adsorption experiments were conducted in a laboratory-scale packed bed adsorption column (dimension of the packing is 8.5 mm in diameter and 125 mm in length). The packed bed is characterised by non-uniform flow distribution, radial mass and momentum transfer processes as well as varying diffusion coefficient. A balanced mixture of 15% CO_2 and 85% N_2 was used to mimic a flue gas source in this study while CO_2 concentrations were read directly from the CO_2 gas analyser; Model: ABB-AO2020 (Frankfurt, Germany). The column was packed with polyaspartamide (0.1 g) and the initial temperature of the adsorption bed was increased to 100 ^oC to remove moisture from the adsorbent. The initial concentration of CO_2 in the gas mixture was read directly from the CO_2 gas analyser; model ABB-AO2020 (Frankfurt, Germany). The gas mixture was then allowed to flow through the reactor bed at specific flow rates after taking note of the initial concentration. The optimal operating conditions were then obtained and used in some chapters of this thesis to synthesize HENs and MENs. A detailed description of the experimental procedure is provided in Yoro (2019a) and extended in Yoro et al. (2019b). The reader is advised to study these publications for the detailed experimental procedure of the capture process as such details do not directly fall within the scope of this chapter. A standard flow diagram showing the various energy-consuming units where heat integration is needed (in dashed lines) and required utilities during CO_2 absorption is presented in Figures 3.5.

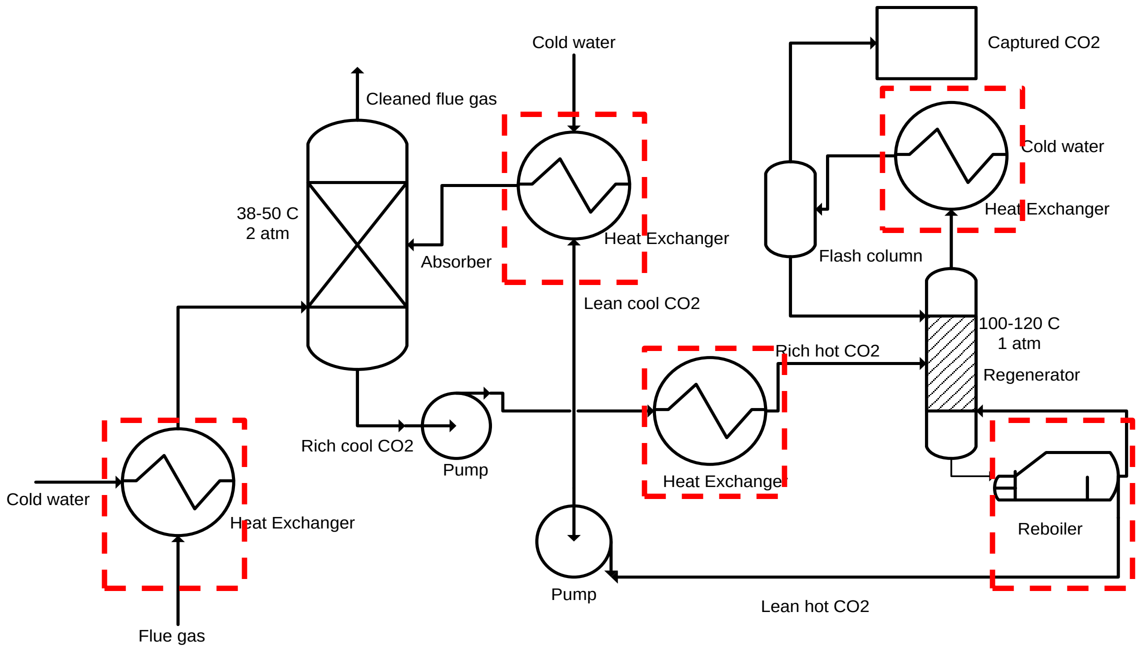


Figure 3.5: General chemical absorption system for CO_2 separation with sorbent regeneration

3.7.2 Determination of minimum MSA used and mass transfer limitation

To determine the effect of mass transfer limitation during the adsorption of CO_2 onto the mass separating agents (MSA) considered for the mass exchanger units in this research, a systematic study of the diffusion mechanism was carried out in a packed-bed adsorption unit using a differential adsorption bed method and published in Yoro et al. (2019b) (see appendix A). The rate-limiting step where mass transfer limitation is usually dominant was determined using diffusion models. The behaviour of the MSA, based on the intra-particle diffusion rate parameter derived from the plots of CO_2 adsorbed versus the square root of time was also noted. Other parametric details obtained for the material in this preliminary investigation is presented in Table 3.2 and 3.3. In Table 3.2, the optimal gas flow rates for the sorption process that will be used in the synthesis aspect of this thesis was presented. The estimated bed contact time (EBCT) and breakthrough time were also determined in Table 3.2 and used in the MENs synthesis section of this thesis. The adsorption efficiency of the solid mass transfer agent (MSA) used determined and presented in Table 3.3 and used as part of the process variables for the synthesis of MENs. From these data (Table 3.1 - 3.3), process parameters were obtained and used to determine the minimum amount of mass transfer agent (sorbent) that will be used or saved by the mass exchanger network.

Table 3.2: Breakthrough and bed contact times with maximum adsorption capacity

Flow rates (mL/s)	Breakthrough time (s)	Maximum adsorption capacity (mg/g)	EBCT (s)
1.5	400	365	160
2.0	300	305	120
2.5	200	282	96

Table 3.3: Adsorption efficiencies of MSA at selected gas flow rates

Gas flow rate (mL/s)	Pressure (bar)	Temperature (^{o}C)	CO_2 capture efficiency (%)
1.50	2.00	203	92.67
2.00	2.00	218	90.00
2.50	2.00	230	86.67

Detailed information on the mass transfer zone limitation and why it was considered suitable for the research reported in this thesis has been provided in our published works; Yoro et al. (2019a, 2019b) which are included in the appendix section of this thesis. The reader is advised to check the aforementioned references for explanations on the properties and all experimental procedures. Absorption was considered in this thesis because it has been widely accepted as a mature technology for CO_2 capture while adsorption was considered because it is currently gaining increased attention as a reliable CO_2 capture technique in the field of carbon capture and storage.

3.7.3 Determination of process parameters

The use of process operating parameters such as supply and target temperatures, the heat capacity of the gas, heat capacity flow rates of the CO_2 lean stream as well as the composition of CO_2 in the lean stream are very important in process synthesis studies like this because they help in evaluating the performance of the MSAs and eventually the synthesized networks. Since this study seeks to introduce the application of HENs and MENs to minimize high energy penalty and material consumption identified in the previous work of Yoro (2017), process parameters, variables and details obtained for the MSA were used for the HEN and MEN synthesis task in subsequent chapters of this thesis. Furthermore, new process parameters for the gas flow rates, heat capacities etc. were also calculated for in this preliminary investigation to determine the most suitable and optimum process condition to include in this thesis. This section of the preliminary investigation has been concluded and reported in the literature (Yoro et al., 2019a, 2019b).

Table 3.4: Optimal process conditions obtained for this study

Parameters	Optimal range of operating conditions
Temperatures (^oC)	60 - 230
Pressure (bar)	2.0
Gas flow rates (mL/s)	1.5 – 2.0
CO_2 concentration (vol. %)	15.0
Mass of MSA used (g)	0.1

Detailed discussion on how these process parameters were obtained (methodologies) and their optimum values have also been reported in our recently published work Yoro et al. (2019a) which is included in Appendix A. A summary of the process data and operating conditions are presented in Table 3.4 as adapted from Yoro (2017) and Yoro et al. (2019a; 2019b). Finally, since most chapters of this thesis are careful compilations of our published works, a deeper discussion on the respective methodologies used to actualize each research objective is presented in detail where they are needed in subsequent chapters of the thesis.

3.7.3. Process optimization

Process synthesis is a key design activity which focuses on the generation of alternatives for creating new processes or retrofitting existing ones. Process synthesis, integration, and intensification are the three pillars of process design. Current synthesis and integration methods can find optimal design targets and process configurations when all the alternatives are known beforehand (Tian et al., 2018). Also, most research in process synthesis and integration have shown that once a network is synthesized for a particular process and its performance evaluated, it is necessary to further develop its design objectives (Lira-Barragán et al., 2014; Demirel et al., 2018, 2019; Van-Fan et al., 2018; Mitsos et al., 2018; Skiborowski, 2018). For a typical process synthesis task, process optimization is achieved when the continuous iteration and analysis of the process objectives are achieved and a solution is found. In the process synthesis task reported in this thesis, different solutions were obtained which may not be the optimal solution. This, therefore, justifies the need why process optimization should be included in any process integration technique. Process optimization involves a careful selection of the "best" solution from a set of other potential solutions.

In this thesis, an objective function was developed and used to optimize the process by either maximizing or minimizing its variables. The major area where process optimization was used in this thesis was during MSA and utility targeting, as well as minimization of the total annualized cost of the network which includes sizing. Process optimization was carried out in this research using the steps highlighted in Figure 3.5. the steps presented in Figure 3.6 involves first the identification of the need to optimize, implementation of process optimization models and automation of the process.

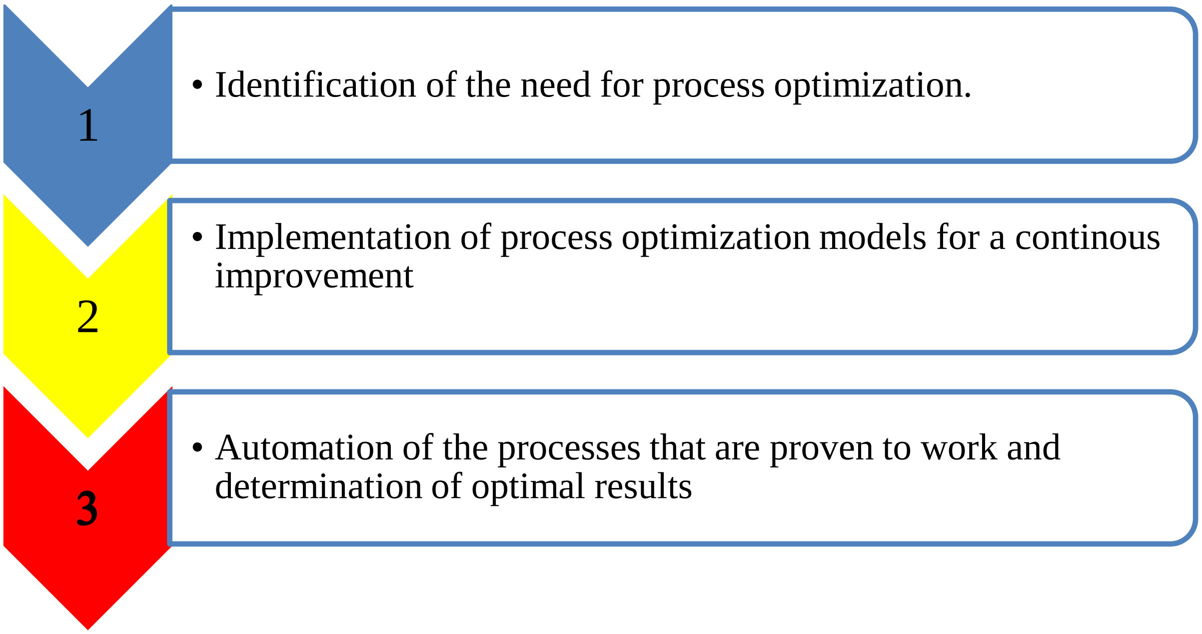


Figure 3.6: Process optimization steps

3.8. Concluding remarks

This chapter has discussed a brief overview of the methodologies and the preliminary study conducted to provide a good starting point for the studies documented in this thesis. The results obtained from this preliminary study forms the basis for the research. The study revealed the behaviour of the MSA (sorbent in this case) and optimum operating conditions to achieve better results. The outcomes from this chapter were used in subsequent chapters to synthesize optimal heat and mass exchanger networks. The general methodologies used in this study to synthesize heat and mass exchanger for effective energy minimization, plant efficiency improvement and material minimization during CO_2 capture in power plants have been summarily described in this chapter. However, as earlier mentioned, specific synthesis methodologies are presented in specific chapters of this thesis. Both sequential and simultaneous synthesis techniques were used in this study. Finally, it is worth emphasizing here that results obtained from the synthesis procedures for both HENs and MENs described in this chapter are not presented here, but are presented and discussed in subsequent chapters of this thesis (See chapters 4 - 8).

CHAPTER FOUR

Sequential Synthesis of Mass Exchanger Networks for CO_2 Capture

This chapter presents process integration techniques towards minimizing material consumption during CO_2 capture using MENs. The development of an optimal network of mass exchangers for cost-effective adsorption of CO_2 from a flue gas stream is reported using a step-by-step technique. Extension of the technique proposed in this study beyond just mass separating agent (MSA) targeting to include sizing (height targeting) of mass exchanger networks and cost targeting with MENs network design is new and forms a major contribution to existing knowledge in the field of environmental sustainability and engineering. This chapter has been peer-reviewed and published as a conference proceeding, and as a contribution to a book chapter in Transactions on Engineering Technologies: World Congress on Engineering and Computer Science (see appendix A3 and A8 for the full-length publications).

4.1 Introduction

Mass exchangers are direct contact mass-transfer units that use mass separating agents (MSAs) to preferentially separate certain components (example; impurities, pollutants and by-products) from a rich stream to a lean stream (Raškovi, 2007; Zhou et al., 2016; Yoro et al., 2018). Popular mass exchange operations include adsorption, stripping, absorption, ion exchange, and solvent extraction. On the other hand, Mass Exchanger Networks (MENs) are integrated mass exchangers used in the chemical industry to decrease waste generated to tolerable levels at the cheapest cost (Liu et al., 2013a). Mass exchange units are important during industrial applications such as CO_2 separation and distillation process (Xu et al., 2014; Wang et al., 2015). There is a need to design and operate mass exchange units in a coordinated and integrated manner. This could be achieved through mass exchanger network synthesis. The study investigated in this chapter presents a systematic approach for the synthesis of mass exchanger networks involving utility and capital cost targeting as well as its network design. The pinch-based approaches use sequential concepts and graphical illustrations to decompose the mass exchanger network design problem into sub-problems to minimize energy and utility costs, number of units and investment costs as well as the amount of material to be consumed in an industrial process (Diban and Foo, 2019). The mathematical programming methodologies are simultaneous in nature. They offer the possibility of synthesizing the network in a single step by formulating the problem as a mixed-integer nonlinear program (Klemeš and Varbanov, 2016; Grossmann and Guillén-Gosálbez, 2010; Guillén-Gosálbez and Grossmann, 2010; Klemeš et al., 2018). In this chapter, the sequential synthesis technique is considered for mass exchanger networks. A typical mass exchanger with flow streams in countercurrent directions is presented in Figure 4.1.

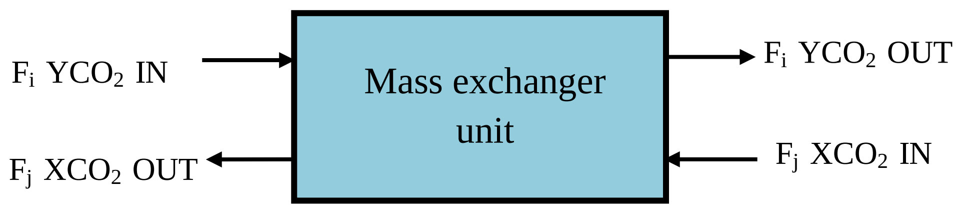


Figure 4.1: A counter-current mass exchanger for CO_2 absorption

For the mass exchanger network in this study, the streams from which the targeted components are removed are designated as rich streams which contain the CO_2 while the streams to which the targeted component (CO_2) is transferred to is referred to as the lean-stream which contains the mass separating agent. It is expected that the lean stream should be partially or completely immiscible with the rich stream. A far as could be ascertained, there has been limited research in mass integration studies under rigorous process modelling conditions for adsorptive CO_2 capture as reported in this study. Synthesis of mass exchange networks covers a substantial part of the mass integration framework.

As a result, this study seeks to apply mass integration techniques to CO_2 capture studies with MSA targeting, material minimization and network design for effective use of materials during the industrial separation of CO_2.

4.2 Advances in mass exchanger network synthesis

Recent reports in the synthesis of mass exchanger networks show that the literature is rich in non-sequentially based methods and approaches for mass exchanger networks synthesis (Foo et al., 2005; Liu et al., 2013c; Foo and Tan, 2016; Patole et al., 2017; Singh and Khanam, 2017; Short et al., 2018; Velázquez-Guevara et al., 2018). The synthesis of separation sequences for mass exchanger networks was first reported by Siirola et al. (1971) using a heuristic approach. This was the first attempt to synthesize mass exchanger networks for separation systems reported by researchers in the early 70's. The authors established that it might not be possible to always apply a heuristic approach to most systems due to thermodynamic limitations. Because of this, Thompson and King (1972) introduced a technique that combined heuristics with algorithmic programming to determine the types of separation processes alongside their sequences. In another study, an evolutionary approach for the synthesis of multicomponent separation sequences involving mass exchanger networks was proposed by Stephanopoulos and Westerberg (1976). This evolutionary approach could be further developed into a combined heuristic and evolutionary strategy for the synthesis of mass exchanger networks. El-Halwagi and Manousiouthakis (1989) proposed a procedure for optimal synthesis of MENs using a sequential method (pinch analysis). The authors suggested that, by using a composition interval method, a composition pinch point could be set on the mass transfer composite curves and the minimum allowable composition difference 'ε' can be ascertained. The minimum utility targets (minimum MSA consumed) can be obtained from the mass transfer composite curves before any network design using this approach. Furthermore, the use of P-graph theory to solve problems involving mass exchanger networks (MENs) was introduced by Friedler et al. (1996). The work of Friedler et al. (1996) was further improved by combining the P-graph theory with the non-linear mathematical programs of Cabezas et al. (2018) to determine the network structure and its operating conditions.

It is worthy to note that most of the methods highlighted applied mathematical programming (simultaneous techniques). The main disadvantage of the simultaneous methods is the difficulty faced while setting up and understanding the mathematical formulations involved. In response to this, a pinch-based methodology for the synthesis of mass exchanger networks (MENs) considering the capital cost target was presented by Hallale and Fraser (1998). The authors addressed a special case involving water minimization in which both utility and the capital costs were targeted before network design. Application of the principles of Pinch Technology for mass integration has been adequately reported by El-Halwagi and Manousiouthakis (1989), but the researchers did not discuss its application in low-temperature mass exchange problems like CO_2 adsorption. The two pinch technology-based methods discussed in the past have shown that the principle of pinch technology is essential in providing mass targets for a mass exchange network.

To address the major gaps identified from previous studies, the research reported in this chapter used pinch concepts to synthesize a network of mass exchangers for optimal adsorption of CO_2 from a rich flue gas stream, with polyaspartamide (sorbent) as the mass separating agents that must be minimized during the adsorption of CO_2, while the mass exchange unit is the packed-bed column where the adsorptive CO_2 capture takes place. In the sequential technique proposed here, the overall synthesis problem is decomposed within a sequence of smaller problems that are easier to solve. However, this approach cannot explore the interactions between sub-systems to obtain an improved solution. The sequential procedure in this study can further be used to target optimal loads and levels for multiple utilities by using the process grand composite curve on a direct numerically-based technique. It can also be used to determine the consumption target of each utility by maximizing the use of the cheap utilities (process MSA) and minimizing loads of expensive ones (external MSA) used to remove CO_2 from a CO_2-rich process stream with little operating costs. A thermodynamic analysis of the CO_2 adsorption process was also outlined in this study using the composition interval method. Feasible structures were formulated and the synthesis problem was expressed in a two-stage targeting procedure as an optimization task. Unlike previous studies reported for mass exchanger network synthesis, this chapter considers a trade-off between the process MSA (sorbent) and external MSA (cooling water and steam) to determine the minimum amount of external MSA required for the CO_2 capture process.

The research discussed in this chapter differs from previous studies on mass exchanger networks synthesis in that the minimum mass of CO_2 to be captured by the external mass separating agent

(MSA) is first determined after the network design. Thermodynamic constraints and cost of MSAs (sorbents) are also incorporated into the synthesis task in this study to generate a cost-effective and thermodynamically feasible network. Although this study mainly deals with material minimization during gas-solid adsorption, the principles and techniques can easily be extended to any mass exchanger network with other solid and liquid sorbents as MSAs. Also, it is the purpose of this work to determine the maximum amounts of process and external MSAs (adsorbent) that can be used to remove CO_2 from a CO_2-rich process stream with reduced operating costs.

4.3 Problem statement

The problem addressed here involves preferential adsorption of CO_2 from a CO_2/N_2 mixture using a solid sorbent (polyaspartamide), and is expressed as follows;

'Given is a set of rich gaseous stream *'R'* and a set of solid lean stream *'S'*. The rich streams have flow rate represented as *'F'*, and the lean streams have flow rate represented as *'L'*. Note, in this study, the flow rate for the solid lean stream is not known but it was assumed to be the quotient of the mass of adsorbent and the adsorption time. The rich stream compositions are to be reduced from supply compositions *Ys*to target compositions Y_t, while the lean streams have supply compositions X_i increasing to target compositions X_t. The process MSA is restrained by a definite maximum flow rate expressed in Equation (4.1) as proposed by El-Halwagi and Manousiouthakis (1989)'.

$$L_i \leq L_j \tag{4.1}$$

Where L_j is the mass flow rate of the lean process stream and Li is the mass flow rate of the rich process stream. The task is to synthesize an optimal network of mass exchanger units that can preferentially separate CO_2 from the rich mixture of CO_2 and N_2 using a set of mass separating agents, at a minimum cost by minimizing the total amount of MSA used. The lean streams have been classified as process mass separating agent (MSA). The more process MSA used by the network means there will be little or no need for the use of external MSA. The mass flow rate of the process MSA is already known and obtained by dividing its mass with the total adsorption time from the previous experiment reported by Yoro (2017). According to Yoro and co-workers (Yoro, 2017; Yoro et al., 2017, 2019a, 2019b), the removal of CO_2 is necessary because CO_2 is a greenhouse gas that is harmful to the atmosphere if allowed to be emitted. Hence, its separation is considered in this thesis more cost-effectively and efficiently.

To tackle the problem highlighted in this study, the following major assumptions have been made;

1. The flow direction of the CO_2 in the mass exchanger unit is counter current.
2. Throughout the network, the mass flow rate of each stream is constant.
3. To attain a single equilibrium relation, temperature and pressure of each stream (lean and rich) slightly fluctuate throughout the network.
4. Exchange of mass between rich-rich and lean-lean streams is not allowed.

4.4 The synthesis procedure

The synthesis task for the problem earlier identified in this study is presented as a two-stage task with gas composition difference as the driving force. First, the minimum amount of mass separating agents (Process MSA) for CO_2 adsorption was determined using thermodynamic analysis then, the network configuration. In the next stage of the synthesis task, a composition interval for each feasible pair of the rich-lean stream is used in a generalized procedure to minimize the total annualized cost of the mass exchanger networks (MENs). Flow rates of the external MSA were then determined and potential mass exchange operations screened according to the procedure of Kaguei and Wakao (1992). Rich and lean end network design was formulated, and then minimum utility target networks were generated by merging any rich-end design with any corresponding lean-end design. Other possible results that could be obtained from using the proposed pinch-based method described in this section are summarized in Figure 4.2.

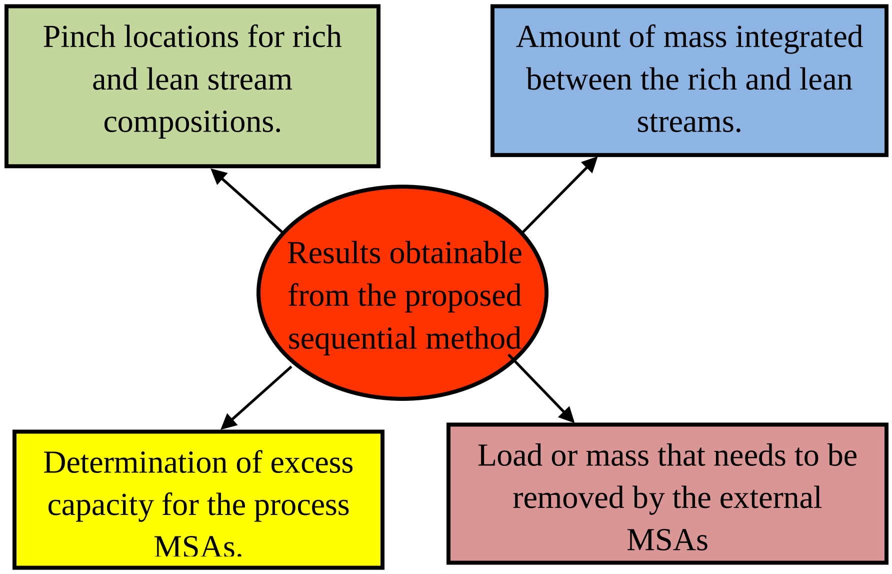


Figure 4.2: A list of likely results from using pinch-based methods proposed in this study.

4.5 The sequential concept for MENS

The concept of pinch analysis was used to formulate a composition interval table which was eventually used to locate pinch bottlenecks (pinch points) at specified minimum allowable composition difference ($\varepsilon = 0.0001$). This value of 'ε' was chosen to avoid infinite sizing of mass exchangers which could make the generated network design expensive.

The maximum possible composition of the solute in the lean phase X_j is in equilibrium with the rich-stream composition, Y_i. However, this will necessitate a need for a considerably large mass exchanger. Hence, a minimum driving force between the operating and the equilibrium lines ($\varepsilon = 0.0001$) known as the minimum composition difference was assigned as suggested by EI-Halwagi, (1997). The minimum composition difference "ε" considered in the mass exchanger network synthesis task in this chapter is analogous to the minimum approach temperature ΔTmin in a typical heat exchanger network task. The minimum composition difference also ensures a feasible transfer of mass in the network. The driving force for mass transfer is represented by the distance between the operating line and the equilibrium line. The closer together these lines are the more stages that will be needed. If these lines touch or cross one another, an infinite number of stages will be required. The main intention for specifying the minimum composition difference in this task is to ensure that the aforementioned situations do not occur in any of the mass exchangers in this study.

The minimum utility requirement of the capture process was also determined using the same approach. Equilibrium equation for the transferable component (CO_2) is in a linear relationship between the process MSAs and the rich stream concentration as expressed in Equation (4.2).

$$Y = mX^{*} + b \tag{4.2}$$

X^{*} is the maximum equilibrium composition of the lean stream theoretically attainable. The minimum allowable composition difference 'ε' was introduced in the equilibrium relation expressed in Equation (4.2) to avoid infinite sizing of mass exchangers as earlier mentioned and the new equilibrium equation is presented in Equation (4.3).

$$Y = m(X^{*} + \varepsilon) + b \tag{4.3}$$

The corresponding composition scales of components in the lean and rich streams were determined from Equation (4.3) as first proposed by El-Halwagi and Manousiouthakis (1989). In the composition interval table presented in this study (see Table 4.1), composition intervals correspond to the supply or target composition of components in each stream. The material balance on CO_2 that is moved from stream i to stream j was obtained using Equation (4.4).

$$F_i\,(Y_{CO2}\,\text{IN} - Y_{CO2}\,\text{OUT}) = L_j\,(X_{CO2}\,\text{OUT} - X_{CO2}\,\text{IN}) \tag{4.4}$$

Where F_i is the flow rate of the rich stream, Lj is the lean stream flow rate, Y_{CO2}^{in} and Y_{CO2}^{out} are the inlet and outlet mass fractions of CO_2 in the rich stream, X_{CO2}^{out} and X_{CO2}^{in} are the outlet and inlet mass fraction of CO_2 in the lean stream respectively as obtained from our previous work on CO_2 adsorption (Yoro 2017). The following points were noted while synthesizing the mass exchanger networks in this chapter;

1. The type of mass-exchange operation that should be used (e.g., absorption, adsorption).
2. Mass separating agent that should be selected (e.g. solvents, adsorbents).
3. The optimal flow rate of each MSA

4. How these MSA's should be matched with the rich streams (i.e. stream parings) and the optimal system configuration.

For this study, Table 4.2 represents the composition mass flows of CO_2 available for capture. It is assumed that each lean process stream leaves the network at a specified outlet composition constrained by Equation (4.1). The composition interval table comprises 3 columns labelled A, B and C excluding the stream representations. Column A and B represent the input and output flow of CO_2 in the streams while column C represents the excess mass of CO_2 available for capture in each interval. The process stream is represented with an arrow on the composition interval table. The rich process streams are denoted as R1 and R2 while lean process streams are S1 and S2. The target composition of the rich stream or the constrained outlet composition of the lean stream is represented by the arrowhead while the tail corresponds to the supply composition of respective streams.

Table 4.1: Rich and lean streams of data

Rich Streams	**F (kmol/h)**	**Y_{in} (kmol/kmol)**	**Y_{out} (kmol/kmol)**	**Density (kg/m^3)**
R1	1.51	0.15	0.06	1.98
R2	1.23	0.15	0.08	1.98
Lean Streams	**K (kmol/h)**	**X_{in} (kmol/kmol)**	**X_{out} (kmol/kmol)**	**Density (kg/m^3)**
S1	1.33	0.10	0.05	1.25
S2	∞	0.10	0.07	1.25

Table 4.2: Composition interval data for adsorptive CO_2 capture

Intervals	**Rich stream**		**Lean stream**	**A**	**B**		**C**
	Y		**X**	**Input (kg/s)**	**Output (kg/s)**		**Excess (kg/s)**
	0.150	R1	0.130				
1				0.000	0.070		0.070
	0.147	R2	0.110	0.070	0.085		0.015
2							
	0.144		0.080	0.085	0.098		0.013
3							
	0.142		0.060	0.098	0.100		0.002
4							
	0.140		0.050	0.100	0.170		0.070
5					S1		
	0.139		0.040	0.170	0.188		0.018
6							
	0.139		0.000	0.188	-	S2	

4.6 Minimum number of units and MSA targeting

According to El-Halwagi and Manousiouthakis (1989), targeting the minimum number of mass exchanger units in a network indirectly minimizes the capital cost of the network because the cost of each mass exchanger is usually a concave function of the unit size. Nonetheless, it is worth pointing out in this study that minimizing the number of units alone is not always sufficient to minimize the capital cost of the network, because the sizes of the mass exchangers are also important.

A detailed procedure for targeting the minimum number of units during the synthesis of mass exchanger networks have been explained in the work of Foo et al. (2005). However, the work of Foo et al. (2005) considered batch operations. But here, continuous adsorption of CO_2 is considered. Furthermore, targeting the number of units for the MENs is briefly discussed in this chapter to include new non-batch concepts to the works of Foo et al. (2004, 2005) such as sizing of mass exchangers and MSA targeting. Just as is the case with heat exchanger networks, fewer units of mass exchangers in a network minimize its complexity and improve its total annualized cost (TAC). Besides, fewer units of mass exchangers also lead to reduced pipework, foundation, maintenance and instrumentation. A minimum number of units for the MENs network 'U' in this study was determined by linking it to the total number of streams in a network, according to Equation (4.5).

$$U = NR_s + NS_L - NS_N \tag{4.5}$$

Where NR_S is the number of rich streams, NS_L is the number of lean streams and NS_N is the number of independent sub-networks into which the original network can be subdivided. It is worth stating that owing to the presence of the pinch composition which divides the problem into two distinct sub-networks, Equation (4.5) was applied independently above and below the pinch. If the case to be considered have different time intervals (i.e. Batch process), process rich or lean streams may exist in more than one-time interval. To reduce the number of units, in such cases, mass exchangers connecting the same pair of rich and lean streams are normally re-used in each time interval. Given this, this study recommends that the targeting technique should consider the opportunities to reuse these exchangers. This recommendation was tested for CO_2 capture studies in the case study discussed (continuous adsorption of CO_2). The value of the minimum approach composition chosen in the case study prevents the infinite sizing of the mass exchangers during design and also reduces the overall design cost of the CO_2 capture process. Since the example considered in this chapter is continuous, Equation (4.5) was used to determine the minimum number of units. But if it were a batch process with time intervals involved as reported by Foo et al. (2005), Equation (4.6) could be used with a time-dependent composition interval table to calculate the minimum number of units for the mass exchangers.

$$U_k = NR_{S,k} + NS_{L,k} - NS_{N,k} \tag{4.6}$$

The streams exist in short time intervals in a batch process. Hence, it is necessary that if the same pair of streams exist in more than one-time interval, the numbers of "additional exchangers", U_{AE}

could be developed from Equation (4.6) and used as presented in Equation (4.7);

$$U_{AE} = N_{TI} - 1 \tag{4.7}$$

Where N_{TI} is the number of time intervals if both streams co-exist. Hence, for a mass exchanger network with 'j' additional exchanger, the minimum number of units is given by Equation (4.8).

$$U = \sum U_k - \sum U_{AE}, j \tag{4.8}$$

Since the minimum allowable composition difference 'ε' is an optimizable parameter in this work, it is possible to transfer CO_2 from a rich stream Y to a lean stream X using Equation (4.9).

$$X_{CO2,\,j} = Y_{CO2,\,I} - b_{CO2} - \varepsilon_{CO2} \tag{4.9}$$

Kindly note that Equations (4.6) to (4.8) are just further extensions for batch systems where time interval is involved. It can only be used in cases involving batch systems like that of Foo et al. (2005). For this study, all other equations listed were used apart from the aforementioned equations.

4.7 Sizing of mass exchanger units

Previous sections of this thesis discussed mass exchanger networks at the targeting and design level (Hallale and Fraser, 2000a, 2000c). This section is dedicated to discussing the techniques proposed for the sizing of individual mass exchangers during a CO_2 adsorption task. The proposed technique will be extended to the overall problem for capital cost targeting. Various important design equations and guidelines are presented and used in developing the targets. At the targeting stage, the stream matches and flow rates through exchangers might be unknown. Hence, it will not be justifiable to use detailed design techniques. All procedures presented in this chapter were tested using case study 4.1;

Case study 4.1:

This example considers two rich and two lean streams. It was adapted and modified from the work of Yoro (2017) which involved the preferential adsorption of CO_2 onto polyaspartamide (the MSA) from two gas streams (rich). The gas compositions (mass fractions) used by Yoro

(2017) were slightly modified in this study by making appropriate molar and mass flow rate conversions where necessary. The problem data for this example is presented in Tables 4.1 and 4.2. Supply composition (mass fraction) of CO_2 in the gas mixture is 15 wt. % for both rich streams.

Mass separating agents (process and external MSAs) were considered with a minimum approach composition specified as 0.0001. Although absorption technique is the most widely used technique and also regarded as the most mature technology for CO_2 capture, the adsorption of CO_2 was considered in this example because the adsorption technique is also fast becoming a popular technique to capture CO_2 from a mixture of gases using solid sorbents (Hedin et al., 2013; Li et al., 2013). By using a composition interval table, it is expected that the minimum amount of MSA required for the sorption process, composition pinch points, minimum number of units, and the optimal network design for the sorption process will all be determined.

The solution to case study 4.1:

To solve this problem, a composition interval table (CIT) for both rich and lean stream is first developed and presented in Table 4.2. Excess capacity of the external MSAs needed for the capture process was obtained from the composition interval table while the molar flow rates of the lean and rich streams are shown in Table 4.2. The CIT developed was used to calculate the minimum mass flow rates of the MSA (adsorbent) required for the adsorption of CO_2 from a flue gas stream.

The literature has confirmed that it is thermodynamically infeasible to transfer a negative output of mass between intervals in a composition interval table (El-Halwagi and Manousiouthakis 1989; Bertran et al., 2017). Negative mass flows in the columns (if any) must be modified by increasing the input to the first interval. In the data presented in Table 4.2, no negative mass was recorded. This means that the case study is thermodynamically feasible without any further modification. Since the thermodynamic constraints are guaranteed to be satisfied with the data in Tables 4.1 and 4.2, it is possible to transfer CO_2 from rich to lean streams in the network. In column C, it is noted that the excess CO_2 removal capacity is 0.070 kg/s. Based on the guaranteed thermodynamic constraints in the case study, this excess can be used to remove CO_2

from the rich streams. The last value in column C (0.018 kg/s) is the minimum mass of CO_2 that is capturable by the mass separating agent (polyaspartamide) from which the minimum flow is determined. This also implies that from the data presented in Yoro (2017), about 21.6 kg of polyaspartamide could be used to capture CO_2 per gramme of adsorbent thereby resulting to about 33.5% savings of adsorbent (Polyaspartamide) using this method. In a similar study, Hallale and Fraser (2000) presented a super targeting technique on MENs and established that the flow of mass separating agents (sorbents) used will be at a minimum value when ε= 0.0001. However, this was applicable to just the problem the researchers considered.

For this study, the value of ε was still assumed as 0.0001 to ascertain if the claim of Hallale and Fraser (2000) can be extended to other problems. It was observed in this study that, when ε_{CO2} is increased, the operating cost of the capture process increases as well. Considering the assumptions highlighted in this study, Equation (4.5) was used to create the corresponding composition scales for CO_2 in the lean process streams. Data on Table 4.2 represent the composition mass flows of CO_2 available for capture while the intervals correspond to the head and tail of the arrow. It was assumed here that each lean process stream leaves the network at a specified outlet composition throughout this study to maintain steady gas compositions. For the case study in this chapter, the minimum utility network of mass exchangers required using Equation (4.5) is;

$U = (2+1) - (1-1) = 3$

Table 4.3: Minimum number of the unit target obtained for MENs compared with literature

Targets	References		
	Hallale (1998)	Ndwandwe (2003)	This study
Units above the pinch	2	2	3
Units below the pinch	3	3	0
Total mass exchangers (units)	5	5	3

The technique used in this study involved composition intervals and a minimum composition difference ε = 0.0001 applied in an adsorptive CO_2 capture study. The reports by Hallale (1998) and Ndwandwe (2003) also involved composition intervals with a minimum allowable composition difference ε = 0.0001 but applied to water minimization studies. Similar results were obtained by both Hallale (1998) and Ndwandwe (2003). This confirms that the value of ε is dependent on the case study considered. In gas related studies (e.g. this study), the minimum allowable composition difference resulted in a higher number of mass exchanger units required above the pinch with a lesser total number of units while in water minimization case studies, using a minimum approach composition interval of ε = 0.0001 will result in lesser number of units above the pinch and more units of mass exchangers in the network.

Table 4.4: Minimum MSA targeting obtained and compared with literature

	References		
	This study	Hallale (1998)	Ndwandwe (2003)
MSA (kmol/hr)	2160	1593	1590
Pinch (kmol CO_2/kmol H_2O)	0.0139	0.000502	0.000503

From the results presented in Table 4.3, three (3) mass exchangers are required for the network synthesis task in this work. Since a minimum-utility network involves one unit more than the target minimum number of units, it is suggested in this study that there is a need to develop a method that will systematically reduce the number of units. Additional important information that could be obtained from the composition interval table presented here is the pinch point composition (a point at which the mass flow of CO_2 available for capture vanishes). From the information provided in Table 4.2, the pinch point exists between interval 5 and 6 with a minimum mass flow of 0.170 kg/s CO_2. This interval represents the most constrained region of the mass exchanger network design because all matches between the rich and lean streams will be subject to a minimum allowable composition difference at the pinch point.

Table 4.4 shows the results obtained using techniques reported in this study and extending the techniques reported by other researchers in this study. When these different techniques were used for material minimization in this chapter, it was observed that although the proposed technique in this study will require a slightly higher amount of MSA than the techniques of Hallale (1998) and Ndwandwe (2003). At this point, it is worth stating that it is better to use the technique proposed here for gas-solid adsorption studies, although El-Halwagi and Manousiothakis, (1989) considered both solid and liquid MSAs as well as fluctuating gas composition. Again, the techniques proposed by Hallale (1998) and Ndwandwe (2003) are good and were originally developed for water minimization studies (absorption). This study attempted extending and applying it to adsorption studies.

4.8.1 Height targeting for the mass exchanger network (MEN)

Hallale and Fraser (2000a, 2000c) identified that continuous contact mass exchangers such as the packed bed column considered in this study usually have its rich and lean phase in direct and continuous contact with no phase separation. Hence, this was noted during height targeting in this study. Also, it was inferred in this study that in sizing continuous-contact mass exchangers, the height of packing and diameter are very important parameters that must not be ignored. Hence they were included in this work. To carry out height targeting in mass exchanger network studies with adsorption columns, a y-y* composite curve is usually used. As a result, a y-y* composite curve similar to the one presented in Figure 4.3 was generated and used to determine the height targets of the mass exchangers in this study. It can also be used to graphically determine the number of stages in the case of stagewise columns as proposed by Hallale (1998). In this study, the heights of the mass exchangers were determined algebraically from the graphical illustration. This makes the technique reported herein slightly different from that of Hallale (1998). The minimum height targeting was first carried out assuming a constant overall coefficient with a constant mass transfer area before considering the height target of mass exchangers with stream dependent mass transfer coefficient and a non-uniform as well as the uniform cross-sectional area of mass exchangers according to Equations 4.10 and 4.11

respectively. Equations 4.10 – 4.15 were adapted from Hallale and Fraser (2000a).and slightly modified in some cases to suit this study.

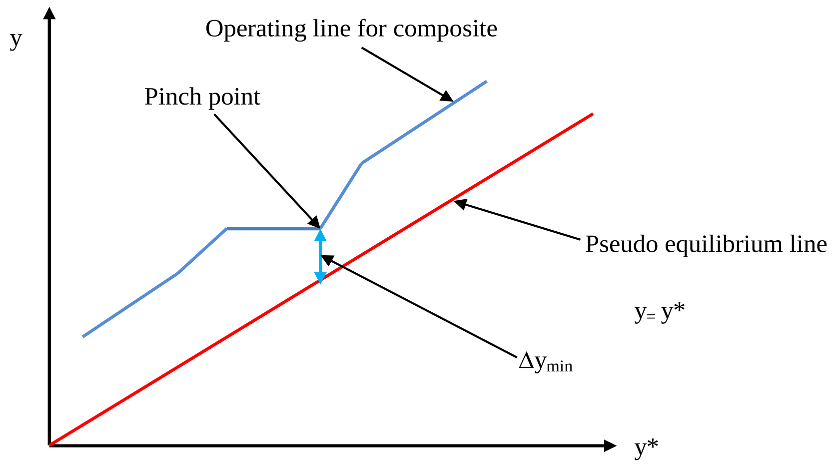


Figure 4.3: A y-y* composite curve for the MENs [Adapted from Hallale (1998)]

$$H_{min}= \frac{1}{K_y aS} \sum_k^{intervals} \frac{W_k}{\Delta y_{tm,k}} \quad (4.10)$$

$$H_{min} = \sum_k^{intervals} \frac{1}{S\Delta y_{tm,k}} \{\sum_i^{rich\ streams} \frac{W_i}{k_y a_i} + \sum_j^{lean\ stresams} \frac{w_j m_j}{k_x a_j}\}_k \quad (4.11)$$

A graphical data for approximate column diameter (D) based on the gas density (ρ) and flow rate (V) was used to estimate the diameters of the packed columns in this chapter as defined by Equation (4.12) as reported by Coulson and Richardson (1979).

$$D = 1.09\rho_v^{-0.25} V_m^{0.5} \quad (4.12)$$

Where the diameter of the mass exchanger is determined by selecting a superficial velocity, information provided in Coulson and Richardson (1979) were used interchangeably with Equation (4.12). The superficial velocity is intended to guarantee appropriate contact while evading hydrodynamic problems such as flooding, sweeping, or entrainment. The cross-sectional area of the column could be determined by dividing the volumetric flowrate by the superficial velocity which in turn gives the diameter of the mass exchanger.

Sizing in continuous-contact mass exchangers requires the use of column diameters. However, diameters cannot be determined before network design for mass exchanger network problems especially when multiple MSAs are involved. To proffer solution to this challenge, a methodology based on exchanger mass which was first proposed by Hallale (1998) was adopted and modified in this thesis by first determining the mass targets with constant lumped coefficient before the mass target with a stream-dependent lumped coefficient. The lumped coefficient (*Kw)* for continuous-contact exchangers is represented by Equation (4.13).

$$K_w = \frac{K_y\, a(2Jf - P_i)}{4P_i \rho_m (1+ f_i)(1+ f_e)(1+f_c)} \qquad (4.13)$$

Where *J* is the welded joint factor, f represents the design stress for the construction material at design temperature, P_i is the internal design pressure, ρ_m is the density of the construction material, f_i is the fractional allowance for any inactive height, f_e is the fractional allowance for extras, $K_y\, a$ is the equilibrium constant and f_c is the fractional allowance for corrosion.

When the lumped coefficient for continuous-contact exchangers is constant in the network, the rigorous minimum mass is expressed as Equation (4.14) where K_{Wi} is the lumped coefficient for continuous-contact mass exchangers for a CO_2 rich stream i.

$$M_{min} = \sum_k^{interval} \frac{1}{\Delta y_{lm,k}} \left(\sum_i^{Rich\ streams} \frac{W_i}{K_{Wi}} \right) k \qquad (4.14)$$

The y-y* composite curve for the MENs synthesized in this study is presented in Figure 4.4. Although the height target for the rich stream below the pinch was included in this work (as shown in Table 4.5) but excluded in previous reports, the total height target obtained was just slightly higher than previously reported height targets.

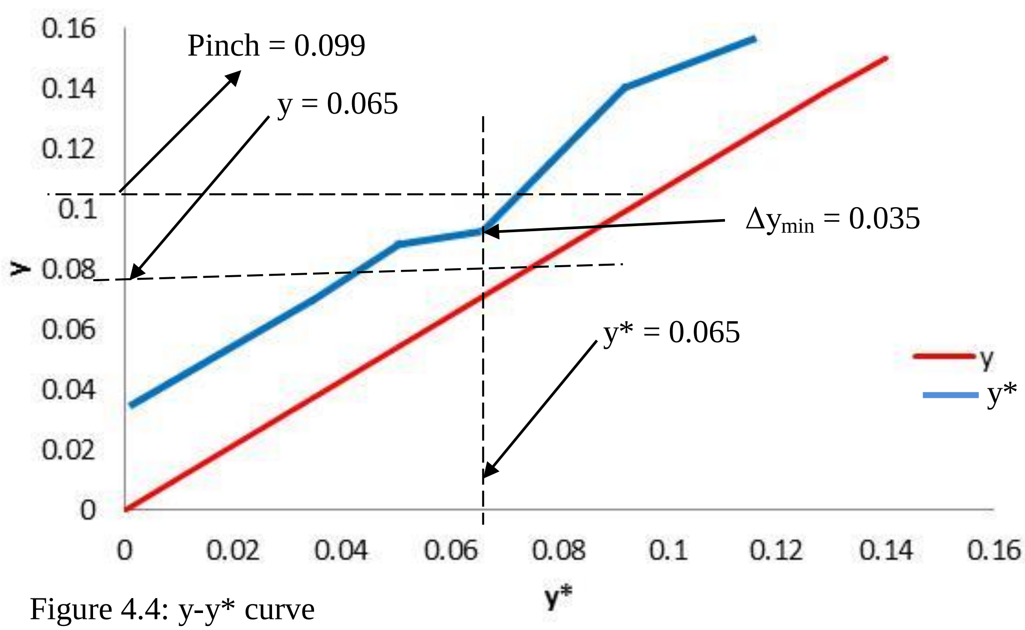


Figure 4.4: y-y* curve

Table 4.5: Height targets obtained compared with literature

Targets	References		
	This study	Hallale (1998)	Ndwandwe (2003)
Above the pinch			
R1	7.44	8.64	8.22
R2	3.11	2.29	2.18
Below the pinch			
R1	7.18	8.40	8.84
R2	2.29	Not reported	Not reported
Total height (m)	20.02	19.33	19.24

From Table 4.5, Hallale (1998) and Ndwandwe (2003) used the same height targeting technique but obtained slightly different results because it was applied in different scenarios (continuous contact and stagewise columns). The slight modification introduced to their work by this study and its application in a packed bed adsorption column accounts for the significant difference in the result obtained. This confirms that column type and area of application should also be considered during height targeting in MENS studies.

4.8.2 Cost targets for the MENs

In the previous sections of this chapter, it was reported that the minimum number of units, minimum number of stages (in case of stage-wise exchangers) or minimum height (in case of a continuous-contact exchanger), as well as calculations for column and tray spacing (in a case involving tray columns) or stage volumes (for staged vessels), can be combined to give an estimate of the installed cost for each mass exchanger in the network (El-Halwagi and Manousiouthakis, 1989; Hallale, 1998; Hallale and Fraser, 1998, Castro et al., 1999; Hallale and Fraser 2000a, 2000b, 2000c; Fraser and Shenoy, 2004;). In view of this, the capital cost for the mass exchanger network obtained in this research was estimated by adding up installed costs for every mass exchanger in the network based on minimum height targeting.

As mentioned previously, the sizing of continuous-contact mass exchangers depends on both the height and the diameter of the exchanger. However, it will be very challenging to determine the cost target of the MENs using this conventional method. Instead of reporting the capital cost of mass exchangers as a function of just height and diameter in this thesis, the capital cost target was reported based on the shell mass which is comparable to the equation for estimating the capital cost in heat exchanger networks. The capital cost target for the MENs network in this study was determined according to Equation (4.15) as adapted from Hallale and Fraser (2000a).

$$\text{Capital cost (based on shell mass)} = N_{units}\left[a+b\left(\frac{M_{min}}{N_{units}}\right)^{c}\right] \tag{4.15}$$

Where N_{units} is the number of mass exchanger units, a, b and c are constants which depend on the specifications of the mass exchanger (adsorption column). Note: the exponent c is usually less than 1, hence a 0.8 value was chosen.

In this chapter, both the operating cost (MSA cost) and the capital cost were predicted as targets. The annual cost of MSA used for the case study investigated in this chapter was determined by multiplying the MSA target flowrate by their costs. To determine the total annualized cost (TAC) targets for the network, the capital cost target was annualized and added to the MSA cost target. Results obtained are presented in Tables 4.3 - 4.6. Table 4.7 shows that some amount of material will be saved with the synthesized network compared to a previous CO_2 adsorption study without mass exchanger network integration. The results show that the network generated using the sequential technique proposed in this study gave better results compared to previously reported techniques in terms of operating, capital and total annualized costs. Kindly note that the technique of Hallale (1998) and Ndwandwe (2003) were adapted and parameters in this study were applied to their technique to obtain results in a CO_2 adsorption study to form a fair basis of comparison with this study as presented in Table 4.6.

Table 4.6: Result summary for cost targeting of MENs

Target	References		
	This study	Hallale (1998)	Ndwandwe (2003)
Operating cost ($/yr.)	74000	77000	79000
Capital cost ($)	1882000	1964000	1996000
Total annualized cost ($)	681000	710000	790085

In Table 4.6, the approach used in this study was carried out and compared with the procedures of Hallale (1998) and Ndwandwe (2003) used with the adsorption parameters in this study since the researchers also considered multiple rich streams but in stage-wise exchangers. It was observed that although the same basis of comparison (multiple rich stream problems) was used, packed bed adsorption beds give better results in terms of the network's capital cost and total annualized cost than stage-wise exchangers.

Table 4.7: Amount of sorbent consumed with & without mass integration

References	Mass of material used (kg)	Technique
This study	1.7	With the integration of MENs
Yoro (2017)	2.1	Without the integration of MENs

Table 4.7 compares this study (where MEN was used) to ensure resource minimization with another CO_2 adsorption study (Yoro 2017) where no mass integration was used. The results reveal that the integration of mass exchanger network during the adsorption of CO_2 from a flue gas stream could result in a significant saving in the quantity of adsorbent used (about 19 % material saving) compared to when mass exchanger network integration is not introduced as seen in the work of Yoro (2017).

4.9 The mass exchanger network design for minimum utility targets

Network design in mass exchanger networks (MENs) is analogous to that of heat exchangers networks (EI-Halwagi and Manousiouthakis, 1989). Network design was carried out in this study using grid diagrams and drawing rich process streams running from left to right and lean streams the opposite way. Stream flowrates and equilibrium constants are shown and mass fractions of compositions are shown above each stream. Mass exchangers are denoted as a pair of fused circles with the mass transferred shown beneath.

Network merging technique was used to generate a network of mass exchangers that require minimum external utility (sorbents) from a composition interval table. The approach used for the design of mass exchanger networks in this chapter is based on an insight from the work of Foo et al. (2004) as well as El-Halwagi and Manousiouthakis (1989). Although the work of Foo et al. (2004) was based on a batch process (with time intervals), the technique was modified in this work to consider a continuous process without time interval. From the composition interval data on Table 4.1, the possibility of generating a network of mass exchangers that use minimum external MSA by merging any rich-end design with a corresponding lean-end design was tested. Figure 4.5 shows a network for minimum utility targets obtained by combining rich and lean-end designs. Figure 4.5 was obtained sequentially, but according to El-Halwagi and Manousiouthakis (1989), when a larger number of streams are involved in minimum utility mass exchanger networks, it will be easier to use a simultaneous approach. The minimum utility network in this study involved an extra unit (mass exchanger) more than the target number of units because of the existence of a pinch which decomposed the task into two distinct problems. A rich end network design was first developed as shown in Figure 4.5 and a lean-end design network is shown in Figure 4.6.

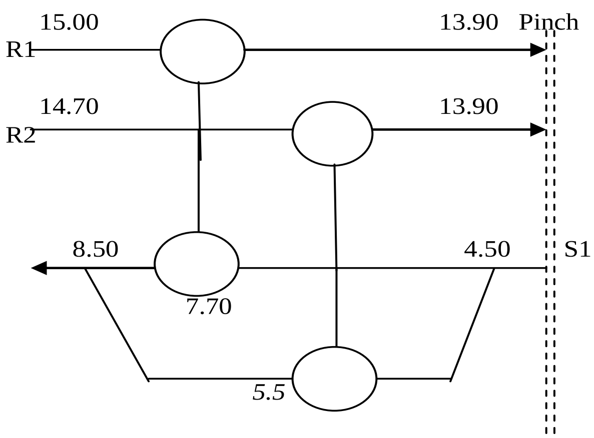


Figure 4.5: A rich-end network design

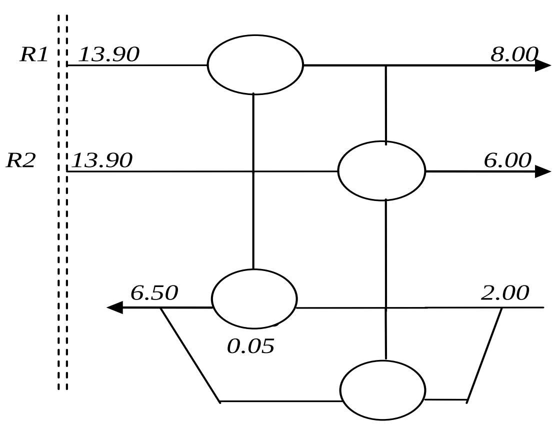


Figure 4.6: A lean-end network design

Minimum utility targets were obtained from the composition interval data in Table 4.1 by combining the rich-end design in Figure 4.5 with a lean-end design in Figure 4.6 (see Figure 4.7). But according to Linnhoff et al. (1979), after merging a rich end with lean end design for a heat exchanger network, the minimum-utility pinched network subsequently generated will have one more than the target minimum number of exchanger units. Due to the existence of a pinch which decomposes the task into two distinct sub tasks, the minimum number of units compatible with a minimum-utility design would be obtained by applying the general mathematical expression for a minimum number of mass exchangers compatible with a minimum-utility design which is presented in Equation (4.5). The global target was attained sequentially with the methodology presented in this chapter, while also ordering the units for process sinks according to the number of waste streams/process sources absorbed. The research content discussed in this chapter has shown that minimum utility targets can be achieved for a CO_2 capture task by simply combining rich and lean-end designs.

The sequential approach presented in this study is straightforward and could be extended to determine the CO_2 avoided, CO_2 capturable and the minimum amount of MSA required for the CO_2 capture process in a detailed study. Nonetheless, it is worth stating here that when larger numbers of streams are involved in minimum utility mass exchanger networks, a simultaneous approach is preferred.

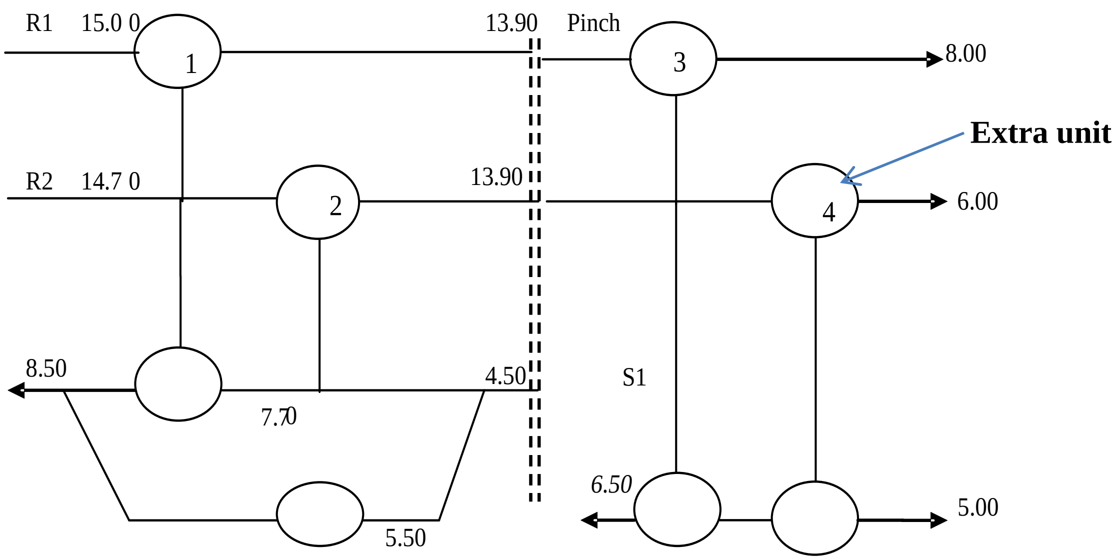


Figure 4.7: A minimum-utility network for the adsorption of CO_2 from a CO_2/N_2 gas mixture.

4.10 Discussion of results

The results confirm the importance of integrating mass exchanger networks in CO_2 capture operations. The utility network (Figure 4.7) developed from merging of lean-end and rich-end designs signify that merging of sub-networks can lead to a minimum utility network with good material recovery. The significant saving of adsorbent by this network using the combined composition interval and y-y* composite curve technique reported in this chapter and compared with other techniques (as shown in Table 4.7) means that if lean and rich-end design networks are merged for an adsorptive CO_2 capture system, about 19.1% of sorbent consumed during the CO_2 adsorption process could be saved. The lower operating and capital costs obtained in this study compared to previous studies means that the approach used in this study is more cost-effective and less expensive to implement. It is also worth stating that all results obtained using the proposed technique in this study were comparable to other similar techniques. The results did not show superiority over all other techniques reported in the past. This means that to get better results in future studies, some of the assumptions made in this study for the mass exchangers could be relaxed, and the introduction of variables like the equilibrium constant and the minimum allowable composition difference in future work could be modified. The pinch points obtained in this study signify the points where the design bottlenecks for the network is located. For this study, the pinch point was at 13.90 as shown in Figure 4.7. This means that the design bottlenecks for the mass exchanger networks exist when the concentration is tending away from the initial concentration. The y-y* composite curve presented in this study for height targeting proved that $y = y^*$ (0.065 = 0.065) for this study (see Figure 4.4). This validates the correctness of the curve and was obtained from the difference between the pinch value and the Δy_{min}. Finally, the total annualized cost, operating costs and capital costs for the synthesized network was a little lower than the one reported using other techniques (see Table 4.6). This means that synthesizing mass exchanger networks for energy minimization using the proposed technique is cheaper and more economical if applied to a CO_2 adsorption problem than the techniques of Hallale (1998) and Ndwandwe (2003).

4.11. Concluding remarks

In this chapter, it has been shown that minimum utility targets for a CO_2 capture system can be attained by combining rich and lean-end designs. A systematic procedure (the use of composition intervals with the y-y* composite curve) has been presented to size the mass exchanger network for resource minimization in most industrial processes. This could be modelled further into a non-linear program to optimize the total annualized cost for the CO_2 capture process in a simultaneous approach. It was also established in this study that the minimum quantity of process MSA required for the packed bed CO_2 adsorption process involving 3 mass exchangers is 1.7 kg polyaspartamide, this is a better result compared to the previous study of Yoro (2017) where mass exchanger networks were not introduced and about 2.1 kg of sorbent was consumed. Furthermore, the most constrained region (pinch point) of the mass exchanger network design in this study was between the 5th and 6th interval. Although this chapter focused mainly on packed bed adsorption columns, the concepts can be applied to stage-wise adsorption and absorption systems with or without time intervals (batch or continuous processes). This work was extended beyond just utility targeting to include cost targeting, height targeting which includes mass exchanger sizing and network design for the MENs. Results obtained were compared with selected studies reported in the past, and the methodology proposed here gave slightly better results. However, the limitation of the sequential procedure proposed in this study is that it cannot consider forbidden stream matches or disallowed mass flows. Future work could consider studying a network with detailed mass exchanger design alongside its capital and operating costs targets. This study suggests that a simultaneous based approach should be considered in future research to corroborate the sequentially-based findings in this thesis. Future studies can also consider looking into the cost per unit of MSA, cost per unit height and other detailed cost function not extensively discussed in this study.

CHAPTER FIVE

Sequential Synthesis of Multi-period Heat Exchanger Networks with Temperature Intervals during CO_2 Capture

This chapter reports the outcome of synthesizing heat exchanger networks (HENs) using sequential techniques. The chapter carefully documents the synthesis of multi-period heat exchanger network considering temperature intervals and uncertain disturbances during absorptive CO_2 capture. The consideration of fluctuating process parameters during CO_2 absorption in the synthesis methodology proposed in this study is new and constitutes new knowledge in this chapter. This chapter has been peer-reviewed and published in the journal of Chemical Engineering Transactions. The full-length paper is attached in Appendix A2.

5.1 Introduction

High energy consumption is a major challenge currently threatening many industrial processes (Vooradi et al., 2019). This has made industrial processes such as absorptive CO_2 capture expensive, energy-intensive and difficult to implement in power plants. Consumption of energy resources especially in industrial applications like CO_2 capture is not uniform; neither are its costs or needs. Absorptive CO_2 capture is generally known to be energy-intensive (Yoro et al., 2019a); this high energy requirement ought to be minimized to ensure its economic advantage. Optimization of heat integration processes within CO_2 capture systems could be instrumental in minimizing energy the high energy requirement; this is because heat integration has the potential of leading to reduced energy consumption and an improved heat transfer with adequate material usage in separation systems.

With the current increase in energy demand in the chemical industries and its obvious high cost, there is a need to make the chemical process in many industrial applications more cost-effective. Heat exchanger optimization could play a part in bridging the gap between energy demand and cost in most industrial processes. Heat exchangers are widely used in many process industries for modifying the temperatures of process streams. A heat exchanger is simply a piece of equipment used in heating up or cooling down streams and the energy exchanged with other process streams (Janaun et al., 2016; Okechukwu and Azeez, 2018), while an assembly of such interconnected heat exchangers in a plant is known as a heat exchanger network (Nielsen and Pedersen, 2018). This means that a heat exchanger network comprises one or more heat exchangers that jointly satisfy an energy conservation task. Synthesis of heat exchanger networks (HEN) can be used to determine the least amount of hot and cold utilities required for a process and also the recovery of process heat in many industrial applications while reducing investment and operating costs (Yeo et al., 2018).

In a typical heat exchanger network, each stream is characterized by supply and target temperature which provides and receives some amounts of heat especially when there is no phase change. Heat energy ceded by a single hot stream is expressed in Equation 5.1 while the heat needed by a single cold stream is determined from equation 5.2;

$$Q_{hot} = F_{hot}Cp_{hot}\,(Thot_{supply} - Thot_{target}) \qquad (5.1)$$

$$Q_{cold} = F_{cold}Cp_{cold}\,(Tcold_{target} - Tcold_{supply}) \qquad (5.2)$$

A minimum temperature difference “ΔT_{min}” between the hot and cold stream is usually required for heat exchange in the HENs. Such a difference is given together with the two sets of streams as input to the problem. ΔT_{min} is a design parameter which is chosen according to a trade-off between the heat integrated and the required heat exchanger area. Thus, it does not require any mathematical formulation.

Previous research reports have shown that the application of Heat Exchanger Networks (HENs) has the potential of minimizing energy demands in many industrial processes due to its good energy recovery advantage (Smith et al., 2010; Escobar and Trierweiler, 2013; Sreepathi and Rangaiah, 2015; Chaturvedi, 2017; Toimil and Gómez, 2017; Yu et al., 2017; Gu et al., 2018). As a result, the application of heat exchanger network for energy and utility minimization during absorptive CO_2 capture in power plants is considered in this study. Several synthesis procedures for heat exchanger networks have been published in the literature (Kang et al., 2016; Rathjens and Fieg, 2019; Xiao et al., 2019).

5.2 Advances in the application of HENs in energy minimization studies

A few studies in the literature have suggested the integration of CO_2 capture plants with power generation plants to minimize energy consumption (Jia et al., 2018; Lim et al., 2018), none has considered a detailed process synthesis approach for effective heat recovery and energy minimization with a keen interest in absorptive CO_2 capture while taking into consideration the heat exchanger loads and area costs. The introduction of heat integration concepts for energy minimization during absorptive CO_2 capture constitutes one of the novelties in this work. It is worthy to note that analysis and optimization of heat integration processes in CO_2 capture systems are very important for energy minimization especially during absorptive CO_2 capture because heat integration leads to reduced energy consumption and improved heat transfer with adequate material usage (Yoro et al., 2019b). But this topic has not been given full attention in CO_2 capture studies. Heat exchanger network synthesis is very pivotal utility targeting and energy minimization in energy-intensive industrial processes (Chaturvedi, 2017). Hence, it is considered in this research.

Different strategies have been proposed for energy minimization in energy-intensive processes like absorptive CO_2 capture in recent times (Yoro et al., 2019c). For instance, Escudero et al. (2016) developed a heat integration methodology based on Pinch Analysis to assess heat recovery options which were used to minimize the high energy penalty in oxy-fuel power plants. Despite this helpful contribution in the area of energy minimization, the methodology has not been adequately extended in post-combustion power plants Yoro and Sekoai (2016). Other researchers considered the use of phase change materials to minimize energy consumption. However, the use of phase change materials in CO_2 capture systems is faced with a lot of limitations such as; low thermal conductivity in their solid phase, difficulty in preventing unsuitable melting and phase separation during sorbent recycling which can lead to a significant loss in latent heat enthalpy, and low volumetric latent heat during stripping. No study has considered a detailed process synthesis approach for effective heat recovery and energy minimization with a keen interest in absorptive CO_2 capture while considering the heat exchanger loads and area costs. In addition, it was observed that most of the energy minimization strategies suggested for absorptive CO_2 capture in the past involve the use of extra mass separating agents, external utilities, or inhibitors which are quite expensive (Yoro et al., 2019b). Although the suggested techniques have helped in minimizing energy usage to an extent in previous reports, it has also increased the cost of operation.

Since the early ’90s, substantial contributions in heat exchanger network synthesis have focused more on the synthesis of single period HEN using simultaneous approaches (Yee and Grossmann, 1990; Kang and Liu, 2017). Very few information is available in the literature on the sequential synthesis of multi-period HEN, especially those with uncertain disturbances in sub-periods which is the focus and most important contribution in this chapter. In addition, the application of HEN for energy and area targeting in absorptive CO_2 capture is new and has not been adequately reported. It is also worthy to note that mixed-integer linear and nonlinear programming models have consistently been solved in a sequence to target energy consumption, the number of heat transfer units and capital cost in most HEN synthesis studies in the past (Tan and Foo, 2018). As far as could be ascertained, no methodology has effectively considered temperature intervals and uncertain disturbances in a sequential manner for HENs synthesis in CO_2 capture studies. Though the aforementioned decomposition-based approaches used for HEN synthesis in the past were helpful, the major limitation associated with the approach is that the interactions between the capital and operating cost of multi-period HEN were often overlooked. Furthermore, it has been observed that the consequence of parametric variations in sub-periods within the HEN structure has also been neglected (Isafiade and Odejobi, 2016; Isafiade, 2018). Also, limitations of the heat transfer area have continuously been ignored in previously reported methodologies, though it is expected that both the structure and heat transfer area should be taken as design variables for the flexibility analysis of the HEN.

In addition, the early works of Mathisen and co-workers (Mathisen et al., 1992; Mathisen et al., 1994), Aguilera and Marchetti (1998), Glemmestad et al. (1999), Lersbamrungsuk et al. (2008), Jäschke and Skogestad (2011), Sun et al. (2013), Salihu (2015) and very recently, Klemeš and

Varbanov (2018) as well as Chen et al. (2019) have all suggested different ways to achieving an optimal HEN operation with control. Their contributions presented different model-based control variables (CVs) selection procedures for achieving an economically optimal operation in the presence of uncertainties and disturbances. However, the key challenge reported by the authors was the difficulty in choosing candidate control variables for a plant-wide implementation in a multi-period scenario. Although the scope of this study does not cover the implementation of candidate control variables, it will be a good research for the future.

In addition, where a process model is not available, the selection of a control variable is impossible. This means that energy minimization using the HEN approach discussed by the aforementioned researchers is only feasible using simultaneous techniques where process models can be programmed to select control variables. Furthermore, several standard synthesis techniques for HEN in the past have employed mathematical programming approach (Ryu and Maravelias, 2019). It has also been observed that most studies in the past have assumed that process parameters such as flow rates, inlet and outlet temperatures of process streams are fixed; thus assuming that heat exchangers have only one period of operation. However, this is not true; because in reality, process variables vary within certain ranges due to changes in environmental conditions and other disturbances which may upset the system. In most cases, these changes are multi-period in nature, which then confirms the need to synthesize a HEN that is capable of handling multi-period scenarios.

As a result, this chapter attempts to minimize energy consumption during absorptive CO_2 capture via optimization of heat integration within the process. Sequential synthesis method proposed in this chapter divides the HENs problem into a multiple of sub-problems to reduce its computational requirements and complexities. The four most common sub-problems successively handled in this chapter were;

1. The minimum utility usage (Qc_{min} and Qh_{min}).
2. The minimum number of exchanger units (U_{min}).
3. The minimum area of the network (A).

4. The amount of energy saved.

In this chapter, a sequential procedure is proposed and discussed for the synthesis of heat exchanger network during multi-period operations with specified uncertainties in flow rates and variations in the inlet as well as outlet temperatures of process streams. The synthesis task in this study was sequentially decomposed into three stages. Temperature interval method was used to determine the loads and minimum utilities required by the network in the first stage. Determination of the minimum number of units was considered in the second stage while the third stage was dedicated to the derivation of a network configuration and sizing of heat exchangers to determine the capital cost using area targeting techniques. Furthermore, the hot and cold streams were integrated into the source and sink of a similar problem involving heat and mass integration through direct recycling and the overall target was obtained in a stepwise manner. It was understood from the previous works of El-Halwagi (2006) and Kemp (2011) that the target for maximum heat exchanged can be achieved only if no heat is exchanged across the thermal pinch temperatures, determined through graphical or algebraic methods. Hence, in this study, there was no heat transfer across the pinch but above or below the pinch. The thermal pinch points in this study were used to divide the temperature interval into regions where the designs for the heat exchange networks are independent of one another. Furthermore, no external cold utility was provided over the pinch points and no external hot utility was provided below the pinch points.

Finally, the efficacy of the proposed methodology was tested and compared with an example from the literature that considered similar process data using a simultaneous approach. The proposed procedure considers the effect of parametric fluctuations in sub-periods on the structure of the multi-period HENs to address the major shortcomings observed in previous studies. Area targeting of heat exchangers was also investigated in this study to determine the capital cost of the synthesized network. The results such as the minimum utility requirement and costs, heat transfer area, cost of heat transfer area and the number of units of the heat exchanger networks were determined at selected parameters for absorptive CO_2 capture. The sequential approach developed in this study is straightforward, unique and can be extended to minimize energy in other CO_2 capture methods (e.g. adsorption and membrane separation) as well as other range of industrial processes.

5.3 Energy and Utility Targeting

Energy targeting is key in identifying potential energy savings in any process plant without necessarily carrying out the pinch design (Liew et al., 2018). This is possible through simple material and energy balance across the plant to evaluate the total energy that can be recovered from the process and the amount of additional external heating and cooling utilities needed in the overall process. Energy targeting is a fundamental step in energy integration studies because it defines the minimum amount of energy consumptions in the overall process (Smith, 2005; Sadri and Soltani, 2019). Identifying the sources of heat (hot streams) and sink (cold streams) from material and energy balance stream is primarily the first step in energy targeting. The hot and cold streams can then be converted into hot and cold composite curves and represented on a temperature-enthalpy (T-H) plot. During energy targeting, the driving force for heat transfer between the two curves is usually represented by the ΔT_{min}. A higher value of ΔT_{min} means a lesser amount of process energy recovery is required and vice versa. If the hot and cold composite curves touch each other (ΔT_{min} = 0), infinite heat transfer area is required and the design becomes infeasible. Increasing the value of ΔT_{min} decreases the heat transfer area requirement and increases utility consumption. On the other hand, decreasing the value of ΔT_{min} decreases the utility requirement and increases the heat transfer area, thus signifying the desirability for trade-off optimization to achieve an optimal HEN design. The intersection of ΔT_{min} on the cold and hot composite curves refers to as the 'pinch point'. It is a point where the curves constrict the most. The QH min and $QC\ min$ are the extra heating and cooling utilities that must be supplied to balance the heating and cooling requirements of the HEN design.

5.4 The Problem Statement

The problem in this study is presented as follows:

- ***Constraints:*** "Given are the operational conditions of a set of process streams which include their supply and target temperatures at periods 1 to 3 with heat capacity flow rates heat transfer coefficients and heat capacity flow rates quantified as exact values. Hot and cold utilities are available in all periods of operation.

- ***Objective:*** The task is to synthesize a heat exchanger network (HEN) which is optimally operable for a set of three periods with the least area cost and a minimum number of units and also to determine the amount of energy that could be saved by integrating the synthesized HEN in a CO_2 capture study. The optimal HEN is expected to be defined by the stream matches, the number of units, operating temperature of the heat exchangers, area of heat exchangers and the network configuration.

5.5 Procedure for the Synthesis of multi-period HENs

Targeting, synthesis and optimization are the three main stages used in the synthesis of the heat exchanger network in this study. At the targeting stage, the best theoretical performance of the heat exchanger network was estimated. All targets considered in this work (example, heat transfer area, heat exchanger loads, and the number of units for the HENs) were first recognized before the design because such targets provide the boundaries for the design problem. At the synthesis stage, hot and cold streams were matched and the resulting heat exchanger networks were obtained. The heat capacity flow rate at each period was used as a criterion for selecting the matches based on existing thermodynamic rules. Heat transfer area was minimized and then an initial network was synthesized to minimize the total cost evolved by following some heuristic rules. In the final stage, the synthesized HEN was optimized (See Figure 5.1 for the schematic procedures).

A modified methodical procedure is presented in this chapter for the synthesis of a multi-period heat exchanger network (HEN) using modified data originally obtained from Isafiade et al. (2015) which discussed a simultaneous approach with a minimum approach temperature of 10

°C. The information obtained from Isafiade et al. (2015) was modified to suit a typical CO_2 capture scenario by reducing the temperature range and dividing it into three periods to mimic fluctuating process parameters.

To create a true counter-current profile between the supply temperature (T_s) of the hot stream (H) and the target temperature (T_t) of the cold stream (C) in this study, a minimum approach temperature (ΔT_{min}) of 20 °C was considered and the HEN was synthesized sequentially.

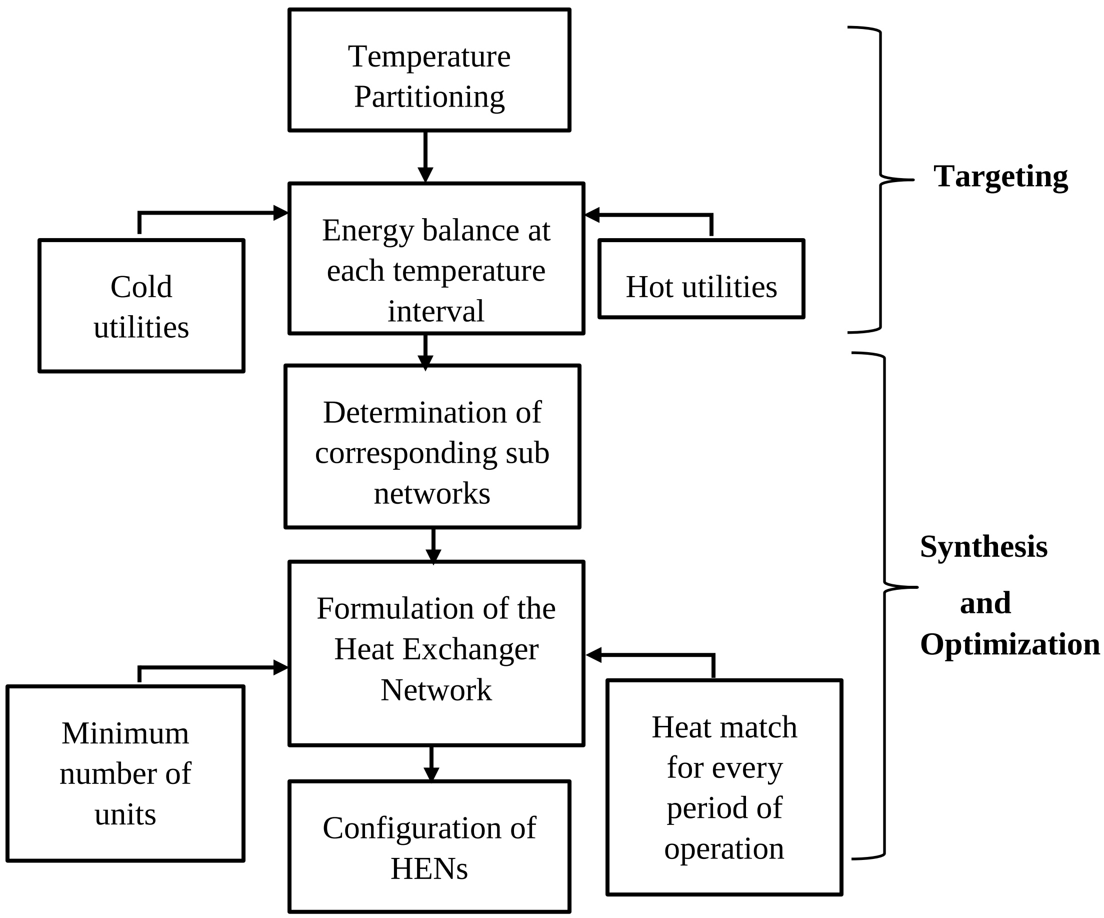


Figure 5.1: Procedure for sequential synthesis of multi-period HENs

Additionally, process data from Isafiade et al. (2015) were modified in this study to accommodate the minimum approach temperature considered in this study; this forms the first step in using the temperature interval method. To account for uncertain disturbances in the multi-period HEN in this study, every period had different values of process parameters. It was assumed that gas flow rates and temperature are not constant for each period of operation; therefore, heat capacity is not constant as well. The temperature range was divided into temperature intervals for periods 1 to 3 using the inlet temperatures of the process streams as shown in Figure 5.2.

Important process data such as the specific heat capacity of CO_2 were determined from the supply and target temperatures in each period (see Table 5.1). As earlier mentioned, all targets (e.g. heat transfer area, heat exchanger loads and the number of units for the HEN) considered in this study were first determined to provide the boundaries for the design problem. The heat capacity flow rate at each period was used as the criterion for selecting the matches based on existing thermodynamic rules. Heat transfer area was minimized and an initial network was synthesized showing reduced total cost by following some heuristic rules. In the final stage, the synthesized HEN was optimized. Hot utility (HU) and cold utility (CU) introduced in the first period alongside their costs are presented in Table 5.2 while the minimum utility requirement (MUR) at each period in the network is shown in Table 5.3.

The temperature interval diagram in Figure 5.2 was obtained using information from Tables 5.1 and 5.2. Periods 1 to 3 were specified in Table 5.1 to show that in a multi-period network, operating parameters fluctuate from period to period. Hot and cold utility streams were included in Figure 5.2 to subsequently generate a balanced Composite Curve for both the hot and cold sides. The resultant balanced composite curve was used to size the heat exchangers and coolers in the network using an area targeting techniques. The utility loads were determined at each period using enthalpy calculations while temperature intervals from periods 1 to 3 were used to determine the minimum utility requirement (MUR) of the network as shown in Figure 5.2. The Total annualized cost (TAC), which is a sum of annual operating and the annualised capital cost was calculated by summing the costs of hot and cold utilities required by the network on an annual basis.

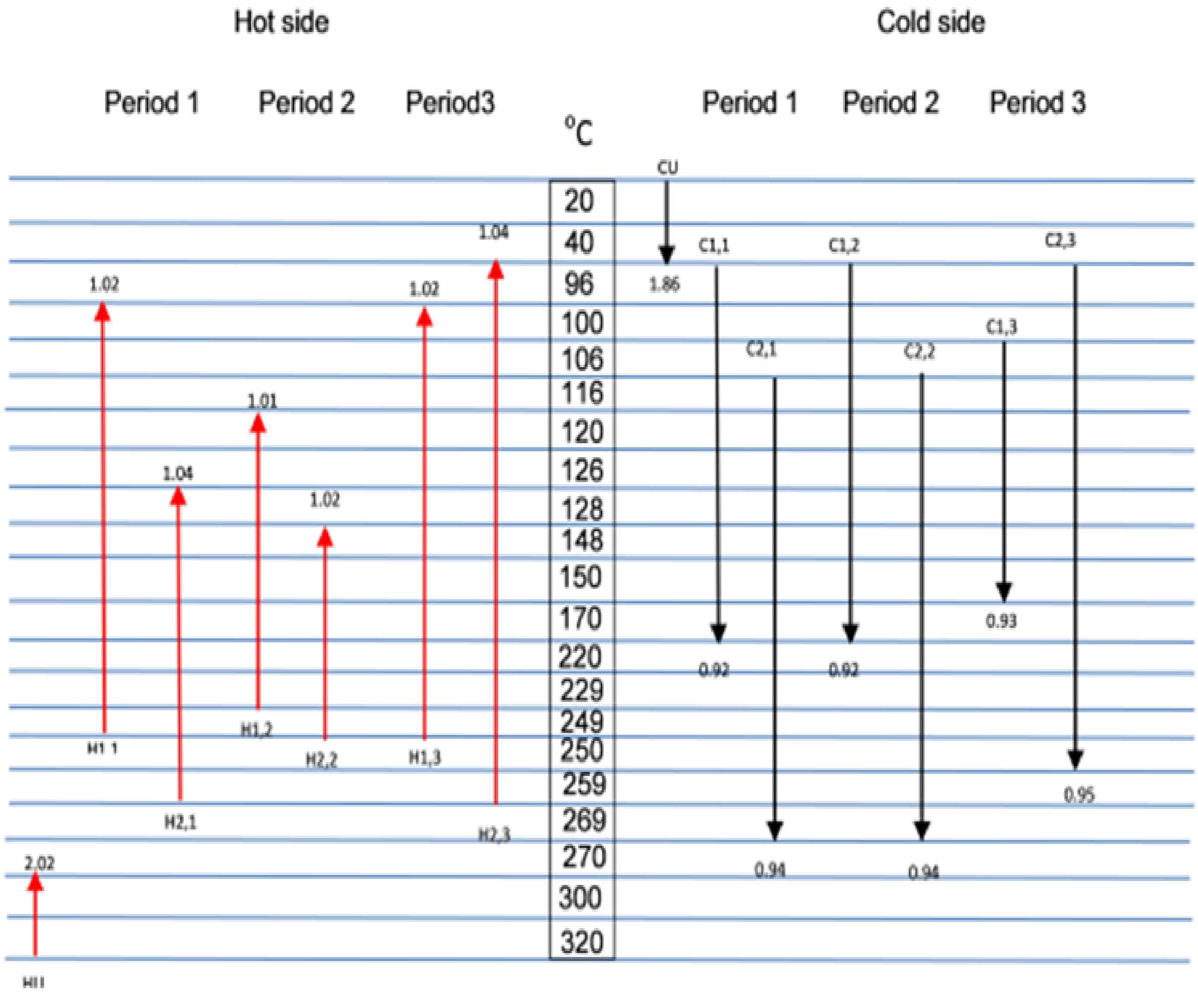


Figure 5.2: Temperature intervals for hot, cold, and utility streams

A cascade showing the transfer of energy between each temperature interval is presented in Figure 5.3. Information obtained from Figure 5.3 shows that the hot utility (steam) introduced into the network in period 1, 2 and 3 are 2.20 kW, 60.40 kW and 0.69 kW while the cold utility is 42.37 kW and 13.38 kW. However, since the case study in this chapter is a multi-period problem scenario, the heat exchanger load introduced at each period is the same and can satisfy energy demands in any of the periods. The pinch temperatures for hot and cold streams differ from one period to another as depicted in Figure 5.4. To determine the minimum number of units and design the network, pinch decomposition and matching of the hot and cold streams were carried out as presented in Figure 5.4. This means that there exist multiple pinch temperatures; hence a global pinch is adopted. The number of units heat exchangers in the network in Figure 5.5 was determined from Equation (5.3) while the area could be was calculated from Equation (5.4). For this study, liquid water is in the shell while CO_2 is inside the tube of the shell and tube heat exchangers.

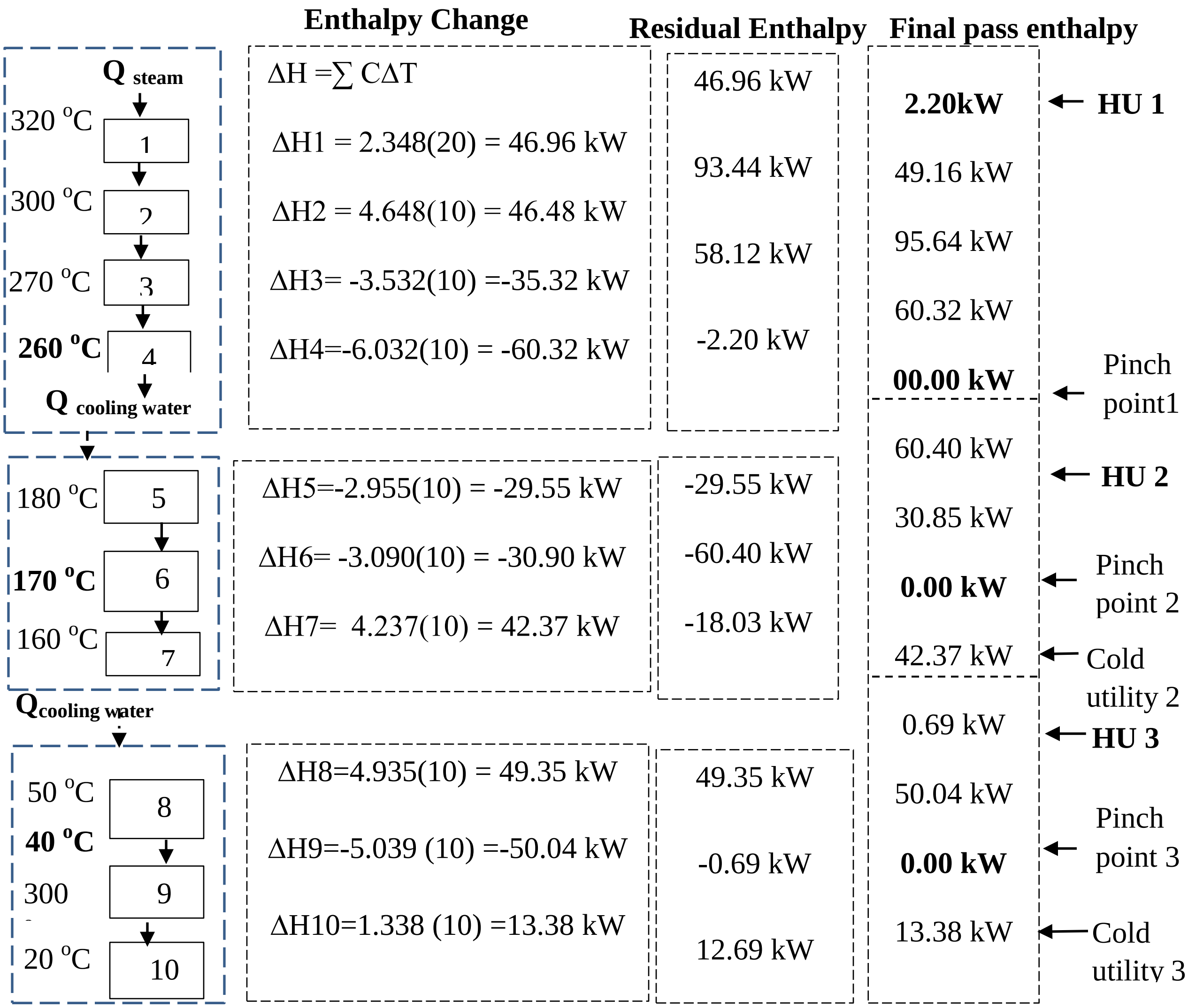


Figure 5.3: Energy transfer between temperature intervals.

$$N = (S_{AP} - 1) + (S_{BP} - 1) \qquad (5.3)$$

A generalized methodology for the synthesis of HEN in this work was modified from the work of Smith et al. (2010) and shown in Figure 5.4. However, it is worth pointing out here that to remain within the scope of this study, offline and online aspect of the HEN optimization is not extensively discussed.

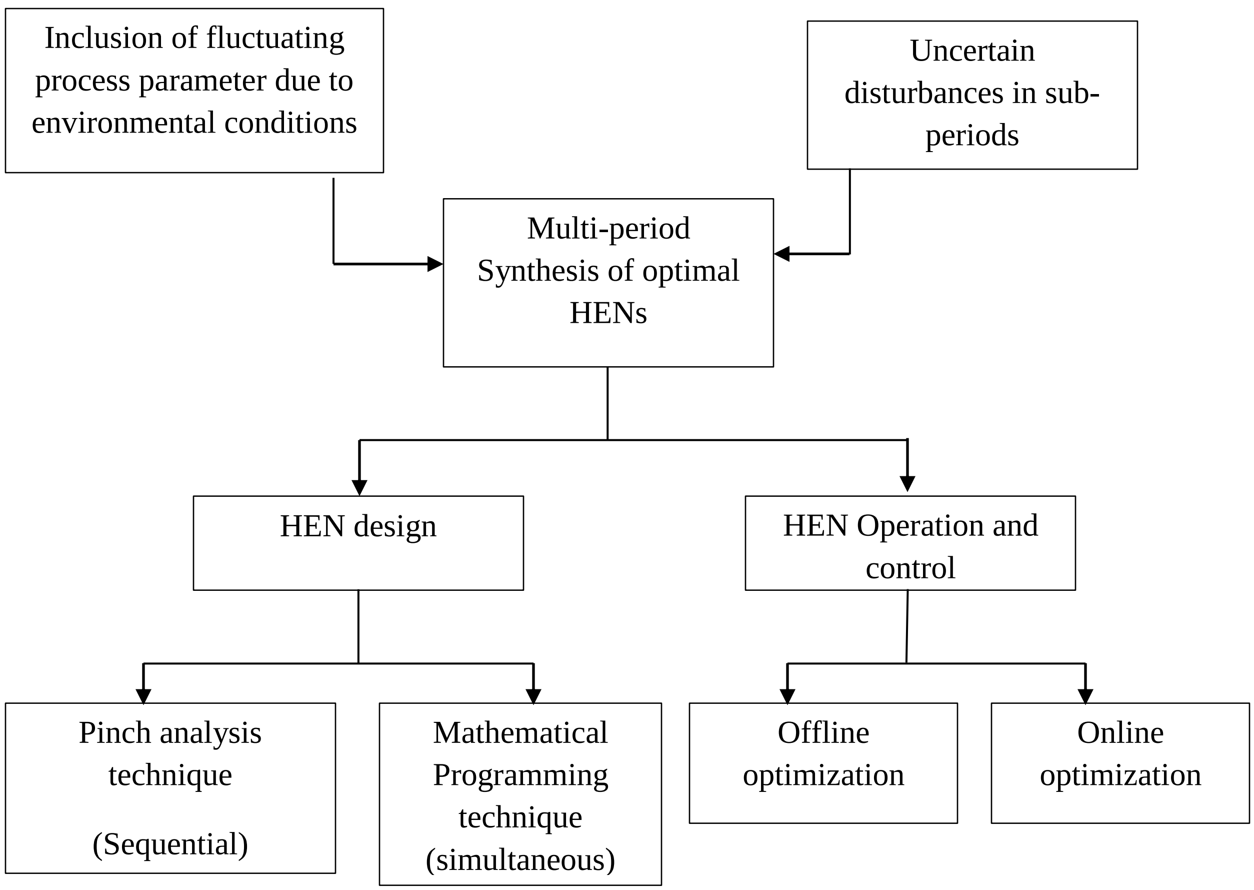


Figure 5.4: A general HEN synthesis and operation methodology

Table 5.1: Process stream data (Modified from Isafiade et al., 2015)

Stream	T_S (°C)	T_t (°C)	F (kW/°C)	Cp (kJ/kg°C)
Period 1				
H1	249	100	10.55	1.02
H2	269	128	12.66	1.04
C1	96	170	9.14	0.92
C2	116	270	15.00	0.94
Period 2				
H1	229	120	7.03	1.01
H2	249	148	8.44	1.02
C1	96	170	9.14	0.92
C2	116	270	15.00	0.94
Period 3				
H1	249	100	10.55	1.02
H2	269	128	12.66	1.04
C1	106	150	16.10	0.93
C2	96	250	10.00	0.95

Table 5.2: Utility data (modified from Isafiade et al. 2015)

Stream	T_S (°C)	T_t (°C)	Cost ($/kW.h)
HU	320	320	28800
CU	20	40	630

Table 5.3: Energy savings

Technique used	Energy consumed (MJ)	References
Heat integration	22.93	This study
Sorbent blending	32.74	Bachelor and Toochinda (2012)
Use of external utilities	30.56	Bougie and Iliuta (2011)

Hot and cold utility targets in the periods form the minimum utility requirement (MUR) of the network presented in Table 5.3. Also obtainable in Table 5.4 are the Pinch temperatures for each Period. From these Pinch temperatures, a global Pinch temperature for the network (170 °C) could be selected and used for subsequent designs. But in this study, the different Pinch Point temperatures were maintained in each period.

The heat transfer area *A* for a corresponding heat exchanger load *Q*, hot stream inlet and outlet temperatures, cold stream inlet and outlet temperatures, and the heat transfer coefficient *U* was assumed from a thermodynamic data table using Equation (5.4) while the capital cost was determined using Equation (5.5). The equations (5.1) – (5.5) were adapted from Yoro et al. (2019f).

$$A = \frac{Q}{U.LMTD} \quad (5.4)$$

$$\text{Capital cost} = 1000 \text{ (number of shells/stream)} + 500A^{0.6} \text{ \$/y} \quad (5.5)$$

N is the minimum number of units, S_{AP} is the number of streams above the pinch, S_{BP} is the number of streams below the pinch, A is the heat exchanger area, and LMTD is the log mean temperature difference. Pinch decomposition and matching of hot and cold streams were carried out to determine the minimum number of units using Equation 5.3 while the optimal network design showing energy load in each period is presented in Figure 5.5.

Table 5.4: Minimum utility, pinch temperature and number of units

Period	Pinch (°C)	MUR (kW)		Number of heat exchangers
		Hot	Cold	Units
1	170	483.13	648.59	3
2	116	482.82	665.60	2
3	106	240.54	483.74	2
	Total Units of Heat Exchangers:			**7**

Table 5.4 presents the minimum utility requirement for the network at different periods and pinch temperatures. It was observed that 2 units of heat exchangers were required at periods 2 and 3 and 3 heat exchangers at period 1. This means that for the 3 periods in this network, a total of 7 heat exchangers is required. If a global pinch temperature is adopted, the same number of heat exchangers will be expected.

5.6. Area targeting, optimization and HEN Design

Area targeting is a vital component that determines the capital cost in HENs. It also plays an important role in capital energy trade-off which determines the optimum ΔT_{min}. Area targeting for the HEN in this study was carried out graphically using balanced composite curves considering streams with a common heat transfer coefficient (see Figure 5.5). The area of the heat exchangers in each period was calculated from the respective LMTD's according to Equation 5.4 and shown in Table 5.5. Deviations from standard literature values observed with the reported results in Table 5.4 could be attributed to the higher value of ΔT_{min} considered in this study. This means that an increase in ΔT_{min} decreases the area targets of the network, but with an increased energy cost. The heat exchanger in period 1 (see Figure 5.5) can serve in the three periods which explains why the synthesized HEN is a multi-period network. No heat exchanger (cooler) was needed by some streams in period 2 (as depicted in Figure 5.5) because such streams in the period can directly get to their target temperatures without using hot or cold utilities during the absorptive CO_2 capture process.

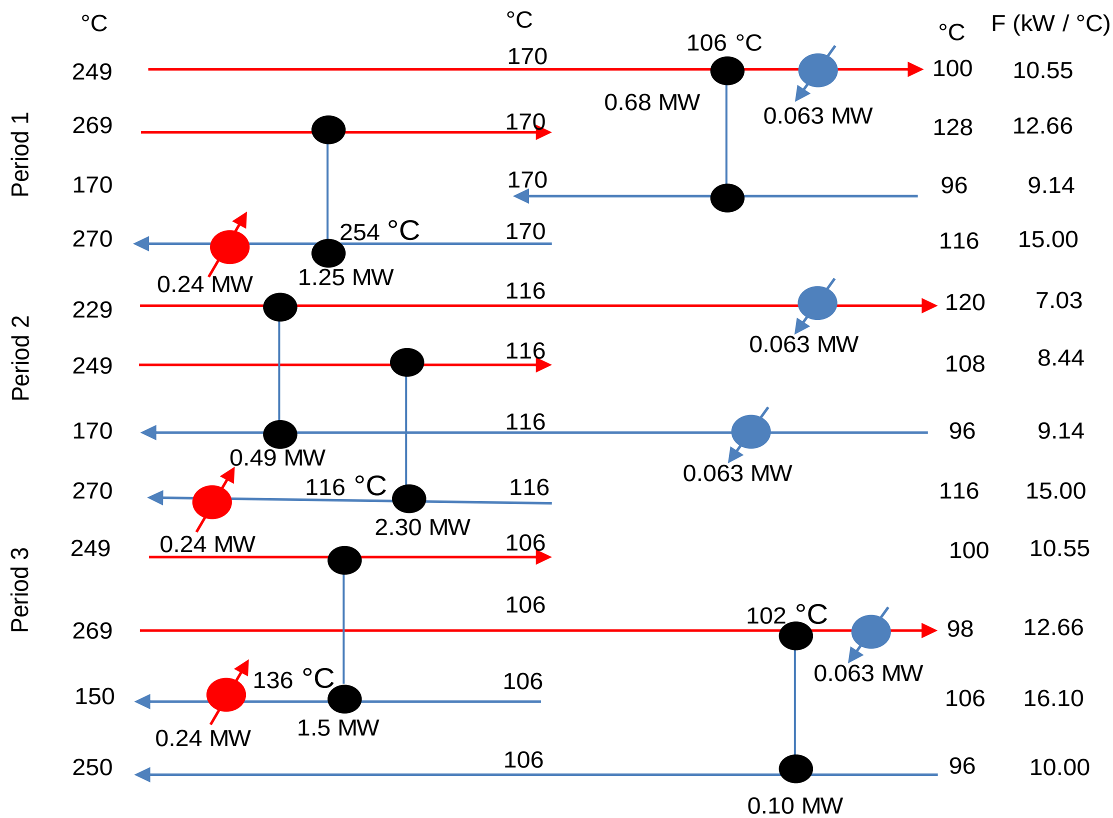
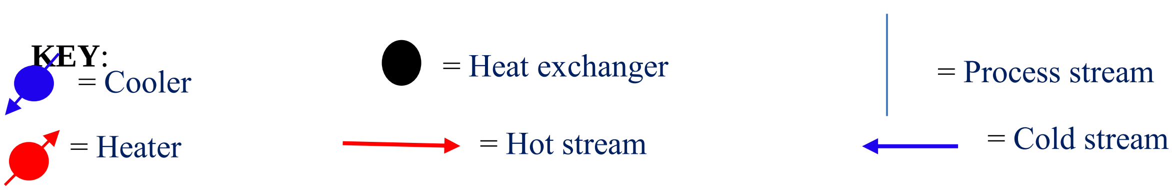


Figure 5.5: Optimal HEN with operational periods and heat loads



The HENs presented in Figure 5.5 shows all feasible stream matches in the network with their energy loads. The different heaters and coolers at each period have the same load and perform the same function for all the stream in a multi-period pattern. The network was synthesized based on the different pinch points obtained at each period. One significant importance of the multi-period network presented in Figure 5.5 is that it is capable of transferring heat within the specified finite set of operating periods, Hence, it can be termed a flexible network. However, its degree of flexibility may be limited to the set of finite operating points for which the network is designed.

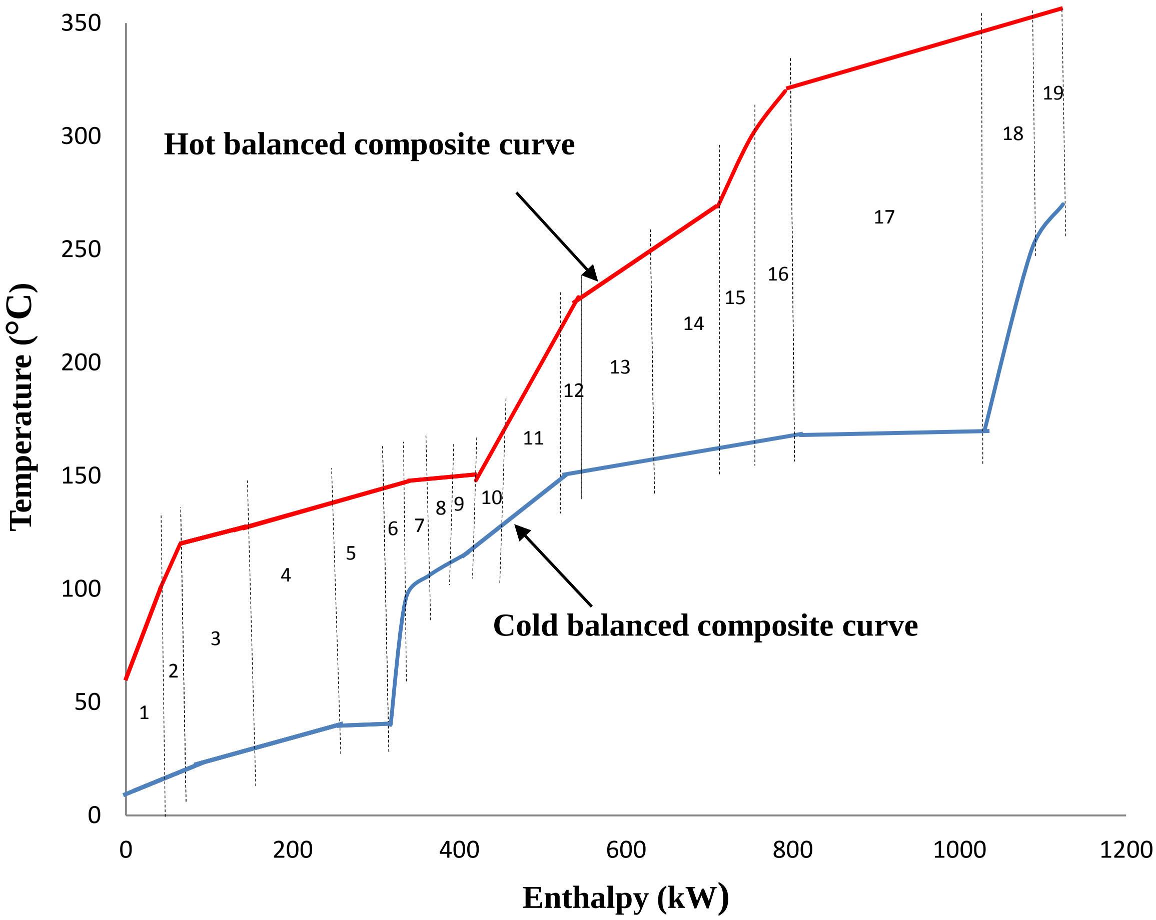


Figure 5.6: Balanced composite curve for the case study

From the balanced Composite Curve shown in Figure 5.6, information about the energy targets and heat transfer area costs of the HENs in this study was deduced. The total annualized cost, capital cost and total heat transfer area for the HENs in this work is presented in Table 5.4 and compared with similar studies reported in the past. Maximum area targets for heat exchangers per stream match at each period is presented in Table 5.5. Since the segments of the hot and cold composite curves are straight lines, unknown temperatures at the vertices were calculated based on the Cp values using linear interpolation technique.

The last step in the sequential HEN design in this study is to optimize the network to achieve a cost-optimal network of heat exchangers with the full likelihood of energy recovery and minimum utility usage. The objective of the HEN optimization task in this study is to minimize the total annualized cost in the entire network, which is defined by the minimum temperature difference "ΔT_{min}". The optimization results are directly influenced by the chosen ΔT_{min} in evaluating the annualized cost. What this means is that the smaller the ΔT_{min} the higher the amount of energy recovery and the larger the heat exchanger area, capital and operating cost of the overall network and vice versa. As suggested by Smith (2005), the degree of freedom for manipulating the HENs capital cost in this study were the loops, utility paths, and splits streams.

The design optimization was formulated as a multivariable optimization subject to;

1. Non-negative heat duty in each match.
2. Positive temperature difference from each exchanger.
3. Stream split, branch flowrates are positive.
4. Total enthalpy change is within a tolerant limit.

Table 5.5: Capital cost, TAC and total heat exchanger area of the resulting HEN compared with literature

Cost parameter / Area		Reference
Capital cost ($/yr.)	16090.62	This study
	Not reported	Isafiade et al. (2015)
Total annualized cost (($/yr.)	29430.00	This study
	62710.46	Isafiade et al. (2015)
Total HEN area (m^2)	1137.79	This study
	2036.65	Isafiade et al. (2015)

The results obtained from the optimization of the capital cost, total heat exchanger area and the total annualized cost of the synthesized network in Figure 5.5 is presented in Table 5.5 and compared with a similar study by Isafiade et al. (2015) that used the similar data, but in a simultaneous technique while this study used a developed sequential approach. From the results, it can be deduced that although simultaneous techniques are currently the most used techniques, it did not yield a better result when applied to a CO_2 adsorption scenario. In this case, the sequential technique used in this study resulted in a superior result in terms of the capital cost, total annualized cost and total area of the HEN. Hence, it safe to say that the effectiveness of a HEN does not solely rely on the synthesis technique used but on the assumptions made during synthesis and its area of application.

Table 5.6: Maximum areas of HEN

Stream match	Heat exchange area (m^2)		
	P1	P2	P3
HU_1-C_2	35.45	22.40	44.80
H_2-C_2	33.75	20.66	42.50
H_1-C_1	36.15	28.44	34.20
CU_1-H_1	36.40	30.55	34.40

The maximum areas obtainable for the utility and process streams for periods 1 to 3 (P1-P3) in the balanced composite curve shown in Figure 5.6 is presented in Table 5.6. It is noteworthy to point out that Equation (5.4) and Figure 5.6 can serve the same purpose. However, to get more accurate results, the balanced composite curve should be used because it eliminates the possibility of assuming values for the heat transfer coefficient 'U' in Equation (5.4). Although the heat exchanger in period 1 could be used as a representative exchanger for the multi-period network, some cases might require bigger heat exchanger areas compared to period 1 as shown in Table 5.6.

5.7 Discussion of results

According to the results presented in this study, lower heat exchanger areas for the network suggest that a more optimal network will be obtained. Lower heat exchanger areas lead to lower total annualized cost (TAC) for a network. Therefore, results in Table 5.5 means that the HEN synthesis technique suggested here is more cost-effective for absorptive CO_2 capture than most techniques earlier proposed in the literature (e.g sorbent blending, use of extra external utilities and phase change solvents). The ability of one heater and cooler to cool and heat the process as shown in Figure 5.6 means that the synthesized network is multi-period in nature and the one heater and cooler can serve in any period in the network. Some streams in Figure 5.6 that do not have heaters or coolers simply mean that heaters and coolers are not needed to get such streams to their target temperatures. This could be because the supply and target temperatures are much closer or because the fluids flowing in such streams are capable of getting to their target temperatures without further heating or cooling (since the CO_2 absorption process is operated on a low-temperature level). However, this is not common in most industrial processes. Also, streams which were excluded from the network are infeasible streams which means no matching can be done on such streams. Furthermore, this network requires a total of 7 heat exchangers compared to other studies. This explains why the HENs in this study resulted in lower capital and total annualized cost. The energy consumed by each technique explains how energy-intensive and expensive such a technique would be. The results obtained and presented in Table 5.3 shows that sorbent blending which is the most prevalent technique for energy minimization still requires more energy than the use of external cooling and heating utilities and heat integration technique proposed in this work. When compared to a sorbent blending study reported by Bachelor and Toochinda (2012) and use of external utilities reported by Bougie and Illiuta (2011) as presented in Table 5.3, about 30 % and 25 % (directly calculated from Table 5.3) of the energy consumed could be saved respectively if the heat integration approach proposed in this study is implemented. Finally, the 3 different pinch temperatures shown in Table 5.4 confirms that although it is possible to have and use multiple pinch points in a network as used in this study, a global pinch point could still be adopted to do the HEN synthesis and design.

5.8. Concluding remarks

This study has presented a simplified 3-step sequential procedure based on pinch technology to minimize the high energy requirement associated with absorptive CO_2 capture. The technique considered temperature intervals, heat exchanger area sizing and uncertain disturbances in flow rates, number of units of heat exchangers at each period. The uncertain disturbances considered in this work means that process variables are not fixed but allowed to fluctuate even within the periods. A new heuristic rule was established and the network topologies obtained using the proposed approach testifies to the applicability of HENs for energy minimization during absorptive CO_2 capture. The new heuristic rule states that the use of feasible matches as initializing matches would result in a multi-period network with a minimum number of heat exchanger units thereby paving a way for remarkable energy saving. This study has also established that the use of process heat through heat integration is a reliable strategy to improve energy efficiency during absorptive CO_2 capture compared to other techniques because of its effective heat recovery advantage. The proposed technique used in this study resulted in an optimal HEN that is flexible with heat transfer devices that can accept changes in operating conditions. Finally, the synthesized HEN yielded encouraging results for absorptive CO_2 capture in terms of capital cost ($16,090.62 /y), utility cost ($29,430.00 /y), heat exchanger areas (1137.79 m^2) and the minimum number of units of heat exchangers (7 units) when compared with literature (see Tables 5.3 - 5.5). The results obtained are improvements over previous studies that considered other energy-saving methods (Table 5.3) or simultaneous techniques with a lesser minimum approach temperature (Table 5.5). Interestingly, the application of the proposed technique in this study could be extended to other CO_2 capture techniques/systems to optimally minimize their energy consumption. Future research can extend this work further by looking into the life cycle assessment of the multi-period process discussed in this study.

CHAPTER SIX

Simultaneous Synthesis of Multi-period Heat Exchanger Networks for CO_2 Capture

This chapter presents a simultaneous (mathematical programming) approach for the synthesis of flexible HENs with non-isothermal mixing assumptions. The major contribution of this chapter is the inclusion of non-isothermal variables in the non-linear model, as well as consideration of quantified uncertainties in inlet temperature and flow rate to mimic a typical CO_2 absorption scenario using monoethanolamine as the solvent. A multi-period MINLP model proposed in this study was used to generate a HEN with optimized heat exchanger area and total annualized costs attributed to utility duties. A framework for generating the flexible HEN over a specified range of variation in flow rates and stream temperature was suggested in this study and presented in this chapter. It is worth stating that this chapter has been peer-reviewed and accepted for publication in IOP: Journal of Physics. See Appendix A6 for the full-length paper.

6.1. Introduction

Most simultaneous HENs synthesis techniques reported in the past considered a single period mode of operation (Linnhoff and Hindmarsh, 1983; Papoulias and Grossmann, 1983a, 1983b; Floudas et al., 1986) while some were based on a superstructure approach (Yee and Grossmann, 1990; Ciric and Floudas, 1991). Sequential synthesis of HENs involves the decomposition of the given problem into smaller tasks through temperature interval partitioning (see chapter five for details). However, in a sequentially-based synthesis technique, targets are set based on existing thermodynamics rules such that it either involves minimization of utility costs, the total number of heat exchangers or the heat transfer area of the network. On the other hand, simultaneous methodologies for HENs synthesis apply mathematical programming concepts through unconventional mathematical solvers to optimize an objective function that studies diverse competing variables at the same time. Yee and Grossmann (1990) proposed a technique based on the application of superstructures with mixed-integer nonlinear programs to minimize an objective function that considered fixed area, and utility costs. Today, many studies on the synthesis of flexible HENs develop their multi-period designs from the model of Yee and Grossmann (1990). However, it was observed in this study that the superstructure of Yee and Grossmann (1990) was developed based on an isothermal mixing assumption. But in most environmental scenarios like CO_2 capture, non-isothermal mixing behaviours may prevail. As a result, this study explores an alternative approach from previous studies by introducing a superstructure with non-isothermal mixing and multi-period considerations with application in absorptive CO_2 capture as an original contribution to the existing knowledge in the field of CO_2 capture and energy utilization.

Heat exchanger networks synthesis (HENS) was first reported in the literature by Broeck, (1944); and since then, it has gained ground in the field of process synthesis and energy minimization studies. A comprehensive review on heat exchanger network synthesis emphasizing its application in maximizing energy usage and minimizing its consumption in most industrial processes have been documented in open literature by Furman and Sahinidis (2002) as well as Yoro et al. (2019c). The importance of HENs in this work is ascribed to its role in controlling the energy cost of a process (Friedler, 2010). The target of every HEN synthesis task is to generate a network design that optimally minimizes investment cost in units and the operating cost for utility consumption.

Before now, some researchers suggested several methods to handle problems in multi-period operations with multiple utilities (Isafiade and Short, 2016; Kang et al., 2016; Miranda et al., 2016). However, most of the methodologies presented by the researchers used the theory of optimizing a condensed framework from a set of feasible matches to advance the generation of results and decrease the intricacy of the resultant network. The main shortcoming identified with this idea is that the resultant HENs always assume that the split streams at each period mix isothermally thereby preventing the superstructure and split streams from exchanging heat in a series formation. Again, there were no clear benchmarks for defining likely matches with an exception that such matches have to exist in the best set of a basic superstructure resolution network. In addition, more time may be required in developing a set of basic superstructure solution network from which the condensed superstructure is generated.

In this chapter, the outcome of investigating parametric flexibility in the synthesis of HENs using a modified SYNHEAT model similar to that of Yee and Grossmann (1990) is presented. In this study, the isothermal mixing assumption of Yee and Grossmann (1990) was relaxed by considering non-isothermal mixing assumptions. Although Björk and Westerlund (2002) were the first set of researchers to suggest the exclusion of the isothermal mixing assumption of Yee and Grossman model, the authors did not consider uncertain disturbances (for example process perturbation) with fluctuations in operating parameters in their methodology. The consideration of uncertain disturbances and fluctuating parameters in the synthesis of HENs with non-isothermal mixing, for energy minimization during absorptive CO_2 capture, is reported in this thesis for the first time. The model of Yee and Grossmann (1990) was adopted in this study because of its simplicity and concurrent inclusion of trade-offs amongst the cost of utility, the number of units and heat transfer area cost. Uncertain parameters were described by a set of discrete operating points in this study. Another contribution to knowledge in this chapter is that the proposed model considers variable stream flow rates and temperatures to mimic a typical CO_2 absorption scenario. The HEN in this study was synthesized in a unique step, and all fluctuating variables were optimized simultaneously.

6.2. State-of-the-art in the simultaneous synthesis of multi-period HENs

Different simultaneous methods for HENs synthesis in multi-period scenarios have been reported in the literature before now, but not without some limitations. For instance, Isafiade and Fraser (2010) and Isafiade et al. (2015) reported the modification of a multi-period stage-wise superstructure (SWS) model to handle tasks with multiple utility options. The researchers suggested a new method where the model could be solved several times and the common matches of the multiperiod HENs used to initialize a reduced superstructure before it was solved as an MINLP model. The major weakness observed in this approach is that the result attained is constrained to a pre-determined fixed period. Hence, the approach in this study considered variable periods. Recently, Azeez et al. (2019) attempted investigating the effect of super targeting and non-isothermal stream mixing in a heat exchanger network using a modified pinch analysis approach. Although the researchers obtained significant results to an extent, their methodology was limited to pinch technology (sequential) alone and does not consider the entire heat exchanger network holistically (simultaneous case) as reported herein.

Conventionally, HEN syntheses have been consistently reported with operating parameters assumed to be fixed at nominal conditions (Aaltola, 2002; Isafiade et al., 2015). However, in a plant environment, there are significant uncertainties attributed to fluctuations in the plant operating parameters as well as other perturbations which distraught the system. In view of this, it is expected that a good HEN design should have the ability to maintain feasible steady-state operation under uncertain conditions.

Escobar et al. (2013) published a report on the sequential synthesis of flexible HENs with operability consideration. In that work, the authors were able to successfully develop a framework that incorporated both flexibility and controllability aspects in HENs. Nonetheless, the main limitation of their study was the application of only steady-state linear models to achieve controllability which resulted in substantial aberrations from the non-linear model which subsequently limits its applicability. Hence, this chapter seeks to address the simultaneous synthesis of multi-period HENs with the inclusion of non-linear steady-state models.

Ahmad et al. (2012) proposed a stochastic-based optimization method for the synthesis of flexible and multi-period HENs. However, their methodology did not consider the effect of uncertain parameters. Jiang and Chang (2015) used a timesharing method through a common area allocation algorithm to identify the descriptive period depending on the period with the longest time interval. Despite the encouraging results obtained by these researchers, their methodology could not be extended to scenarios like absorptive CO_2 capture where operating variables fluctuate.

In another contribution, Kang et al. (2015) developed a technique with a stepwise generalization method to generate multi-period HENs that include features of sub-periods. In this technique, the authors identified the characteristic period using a method similar to that of Jiang and Chang (2015); while Escobar et al. (2014) suggested a novel Lagrangian disintegration methodology. However, their contribution was able to handle single period problems. Also, El-Temtamy and

Gabr (2012) modified the MINLP models of Floudas and Grossmann (1987) by introducing a method where the models could be solved iteratively in a random manner to handle uncertain flow rates and temperatures. However, the method was based on an automated sequential approach for HENs where each step depended on solutions from previous steps which makes it non-simultaneous but sequential in nature. Furthermore, Li and Landa-Silva (2011) suggested a method to synthesize flexible HENs in which the level of network flexibility was determined for a non-convex huge heat exchanger task using a simulated annealing algorithm. To account for the degree of change of fluctuating parameters in their proposed methodology, the authors suggested a direction matrix approach for this prediction. However, their methodology did not adequately consider temperature and gas flow rate fluctuations with non-isothermal conditions.

Although some of the aforementioned reports in literature involved multi-period scenarios, it is worthy to note that fluctuations in process parameters are unpredictable in most industrial operations, and these fluctuations take place around a nominal point which ought to be included in solving energy minimization problems during absorptive CO_2 capture (Jande et al., 2014). The main focus in this chapter is to develop a simultaneous strategy for the synthesis of flexible multi-period heat exchanger networks (HENs) that considers quantified uncertainties, and non-isothermal mixing. The main advantage of the simultaneous approach proposed in this study is its capability to handle the balance between capital and operating costs of the HENs. As described by Gu et al. (2019) and Payet et al. (2018), flexible HENs in this study refer to HENs that can handle a range of steady-state operating conditions which a particular process design can manage.

6.3 Objective function

As earlier highlighted, the objective function in this study is analogous to that of Yee and Grossmann (1990), but with the exclusion of the isothermal mixing assumption. The MINLP optimization model in this study includes the costs of hot and cold utility (energy cost), fixed and area costs cost of heat exchangers and cost of some augmentation device. The objective function aims to minimize the total annualized cost of the synthesized network. The objective function for this study is presented in Equation (6.1).

$$\min TAC \sum_{i\in HP} CCUqcu_i + \sum_{j\in CP} CHUqhu_j + \sum_{k\in CP}\sum_{i\in CP}\sum_{j\in CP} \left\{ CF_{e,ij}z_{ijk} + \left[C_{e,ij} \frac{q\,ijk}{(Ue,ijLMTD\,ijk)} \right]^{B_{e,Ij}} \right\}_{P=1} + \sum_{i\in HP}$$

$$\left\{ CF_{CU,i}zcu_i + C_{CU,i} \left[\frac{q\,cui}{(U_{CU},iLMTD\,cu,i)} \right]^{B_{CU,}} \right\}_{P=2} + \sum_{j\in CP} \left\{ CF_{HU,j}zcu_j + C_{HU,j} \left[\frac{qhu_j}{U_{HU,j}LMTD_{HU,j}} \right]^{B_{HU,}} \right\}_{P=3} \quad (6.1)$$

For Equation (6.1), the following assumptions (Equations 6.2 – 6.7) were made ;

$$Ue_{,ij} = \frac{h_{H,i}\, h_{C,j}}{h_{H,i} + h_{c,j}} \quad (6.2)$$

$$U_{CU,i} = \frac{h_{H\,i}\, h_{CU}}{h_{H,i} + h_{CU}} \quad (6.3)$$

$$U_{HU,j} = \frac{h_{HU}\, h_{c,j}}{h_{CU} + h_{C,j}} \quad (6.4)$$

$$LMTD_{ijk} = \left[(dt_{ijk})(dt_{ijk+1})\left(\frac{dt_{ijk} + dt_{ijk+1}}{2}\right) \right]^{1/3} \quad (6.5)$$

$$LMTD_{CU,i} = \left[(dtcu_i)(T,OUT_{H,i} - T,IN_{CU})\left(\frac{dtcu_i + T,OUT_{H,i} - T,IN_{CU}}{2}\right) \right]^{1/3} \quad (6.6)$$

$$LMTD_{HU,j} = \left[(dthu_j)(T,IN_{HU} - T,OUT_{C,j})\left(\frac{dthu_j + T,IN_{HU} - T,OUT_{C,j}}{2}\right) \right]^{1/3} \quad (6.7)$$

Estimation of the log mean temperature difference in this study is fairly comparable to the one suggested by Chen (1987). This estimation of the log mean temperature difference was done in this study using the assumptions in Equations (6.5) to (6.7) as proposed by Liang et al. (2016) to avoid singularities while calculating the log mean temperature difference.

6.4 GAMS model description for the synthesis of multi-period HENs

The model in this study includes the assigned of continuous variables to temperatures and heat loads at each period modelled in GAMS. The GAMS program is provided in Appendix E of this thesis. The model was then solved to minimize the annualized cost of the equipment with the annual cost of utilities. The model provides matches that take place for every period, areas of each exchanger and resultant heat exchanger loads. To formulate the mixed integer nonlinear programming model for total annual cost embedding utility cost, fixed charges for exchanger units and area. The following delineations were used in this study:

(i) Indices:

i = hot process or utility stream,

j = cold process or utility stream,

k = index for stage 1

KN = index for stage 2

p = operation period;

(ii) Sets:

HP = set of a hot process stream *i*,

CP = set of a cold process stream *j*,

HU = hot utility,

CU = cold utility,

ST = set of a stage in the superstructure, *k* = 1,…, NOK,

PR = set of an operation period, *p*= 1,…, NOP;

(iii) Parameters:

TIN = inlet temperature of stream,

TOUT = outlet temperature of stream,

F = heat capacity flow rate,

U = overall heat transfer coefficient,

CCU = per unit cost for cold utility

CHU = per unit cost for hot utility

CF = fixed charge for heat exchanger unit

C = area cost coefficient for heat exchanger

B = exponent for area cost

AF = annualization factor

NOK = number of stages

NOP = number of periods

DOP = duration of period

QUP = an upper bound on heat exchange

DTUP = an upper bound on the temperature difference

HUUP = an upper bound on total hot utility available

ε = minimum approach temperature of the heat exchanger

(iv) Positive variables:

$t_{i,k,p}$ = temperature of the hot stream *i* at the hot end of stage *k* in period *p*

$t_{j,k,p}$ = temperature of cold stream *j* at the hot end of stage *k* in period *p*

$dt_{i,j,k,p}$ = temperature difference for match (*i*,*j*) at temperature location *k* in period *p*

$dt^{hu} i\ k\ p,$ = temperature difference for the match of cold stream *j* and hot utility in Period *p*

$dt^{cu}\ j\ k\ p,$ = temperature difference for a match of the hot stream *i* and cold utility in Period *p*

$q_{i\,j\,k\,p}$, = heat exchanged between hot stream *i* and cold stream *j* in period *p*

$q^{hu}\ j\ p,$ = heat exchanged between cold stream *j* and hot utility in period *p*

$q^{cu}\ i\ p,$ = heat exchanged between hot stream *i* and cold utility in period *p*

(v) Binary variables:

$z_{i\,j\,k},$, = existence of match (*i*,*j*) in stage *k*,

$z^{hu}j$ = existence of match between cold stream *j* and hot utility,

$z^{cu}i$ = existence of match between hot stream *i* and cold utility;

(vi) Variables:

TAC = total annual costs for the network.

To avoid the inclusion and modelling of bypasses in the MINLP model presented in this study, the objective function considered the area of one match to be the mean value of areas in different periods. However, the model might under-estimate the cost of total area and over-estimate the cost of heat exchanger area. The actual technique for calculating the cost of HEN area in literature is to sum up the costs related to the maximum match areas; where the calculation of the maximum area and the actual cost of the area is done through an objective function, by introducing non-linearities with discontinuous derivatives. However, this could make the model difficult to solve and less robust. As a result, the real total annualized cost in this study was calculated in a separate part of the model after the HENs optimization. In this study, the total annualized cost (TAC) for the network is defined as the summation of the following components: the unit cost for all matches; mean area cost for matches, mean area cost for cold utility matches, mean area cost for hot utility matches, weighted cold utility cost and weighted hot utility cost. The model is expressed as a mathematical formulation in Equation 6.1.

6.5. Mathematical Formulation

The mathematical formulation in this study considered the modification of a stage-wise superstructure that considers all possible matches between hot and cold streams divided into an already known number of stages (k = 2) with a non-isothermal mixing assumption as shown in Figure 6.1.

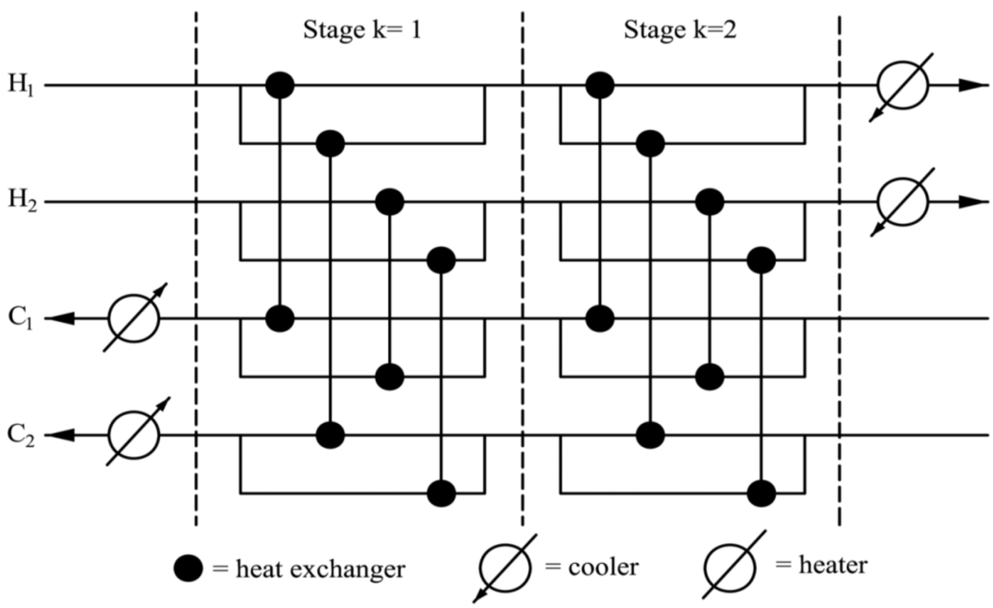


Figure 6.1: The stage-wise superstructure used in this study [Modified from Yee and Grossmann (1990)].

A mathematical formulation was used in this study to simultaneously optimize all costs (heat exchanger area cost, energy cost, and other fixed charges) related to the heat exchanger network. Due to the complex mathematical formulation of the optimization model, selection of matches and number of heat exchanger units were also optimized alongside according to the method of Chen (1987) concerning selected matches, which ensured proper calculation of fixed charges of the HEN.

Heat balance for the exchanger in respective stages was calculated using Equations (6.8) and (6.9). Isothermal mixing assumption of the Yee and Gossman model was replaced with the non-isothermal assumption in this study by introducing nonlinear and nonconvex constraints in Equations (6.8) - (6.13).

$$(tp_{H\,i,j,k,IN} - tp_{H\,i,j,k\,OUT})Fp_{H,i,j,k} = q_{ijk}\,,\ I \in HP,\ j \in CP,\ k \in KN, \tag{6.8}$$

$$(tp_{C\,i,j,k,OUT} - tp_{C\,i,j,k\,IN})Fp_{C,i,j,k} = q_{ijk}\,,\ I \in HP,\ j \in CP,\ k \in KN \tag{6.9}$$

tp_H is the temperature of the splitting stream (hot) while tp_C is the splitting stream temperature (cold), Fp_H is the splitting stream (hot) heat capacity flow rate and Fp_C is the cold splitting stream heat capacity flow rate in each stage.

Each splitter had a heat balance which was determined using Equations (6.10) and (6.11);

$$F_{H,i}\,.\,t_{j,k} = \sum_{j=1}^{CN} Fp_{H,i,j,k}\,.\,tp_{H,i,j,k,OUT},\ j \in CP,\ k \in KN \tag{6.10}$$

$$F_{C,j}\,.\,t_{Cj,k} = \sum_{i=1}^{HN} Fp_{C,i,j,k}\,.\,tp_{C,i,j,k,OUT},\ i \in HP,\ k \in KN \tag{6.11}$$

For each splitter in the network, the mass balance was calculated using Equations (6.12) and (6.13);

$$F_{H,i} = \sum_{j=1}^{CN} Fp_{H,i,j,k} \qquad (i = 1, 2,\dots HN;\ k = 1, 2,\dots, KN) \tag{6.12}$$

$$F_{C,j} = \sum_{i=1}^{HN} Fp_{C,i,j,k} \qquad (j = 1, 2,\ldots CN;\ k = 1, 2,\ldots, KN) \tag{6.13}$$

The overall heat balance for each stream can be calculated using Equations (6.14) and (6.15);

$$(T,IN_{H,i} - T,OUT_{H,i})F_{H,i} = \sum_{k \in KN} \sum_{j \in CP} q_{ijk} + qcu_i , \qquad i \in HP \tag{6.14}$$

$$(T,IN_{C,i} - T,OUT_{C,i})F_{C,i} = \sum_{k \in KN} \sum_{i \in HP} q_{ijk} + qhu_i , \qquad j \in CP \tag{6.15}$$

$T,IN_{H,}$ is the inlet temperature of the hot stream, $T,IN_{C,}$ is the cold stream inlet temperature, HP is the set of hot process streams, CP represents sets of cold process streams and KN is the set of stages for the superstructure.

Heat balance for each stream per stage of the superstructure is determined from Equations (6.16) and (6.17);

$$(t_{H,i,k} - t_{H,i,k+1})F_{H,i} = \sum_{i \in CP} q_{ijk}, \quad i \in HP,\ k \in KN \tag{6.16}$$

$$(t_{C,j,k} - t_{C,j,k+1})F_{C,j} = \sum_{i \in HP} q_{ijk}, \quad j \in CP,\ k \in KN \tag{6.17}$$

Hot and cold utility loads can be determined from Equations (6.18) and (6.19) respectively;

$$(t_{H,i,N,k+1} - T,OUT_{H,i})\ F_{H,i} = qcu_i, \qquad i \in HP \tag{6.18}$$

$$(T,OUT_{c,j} - t_{C,j,1})\ F_{C,j} = qhu_j, \qquad j \in CP \tag{6.19}$$

Minimum approach temperature was calculated from Equation (6.20) ;

$$dt_{ijk} \leq \varepsilon,\ i \in HP,\ j \in CP,\ k \in KN \tag{6.20}$$

Inlet temperature for the superstructure is assigned using Equations (6.21) and (6.22);

$$t_{H,i,1} = T,IN_{H,i,}\ \ i \in HP \tag{6.21}$$

$t_{C\,j,N,K+1} = T, IN_{C,j,}\ \ j \in CP$ (6.22)

The heat exchanger area network structure was determined by building a set of binary variables that represent the existence of each match of the heat exchanger. The binary variables were randomly generated to define likely matches between streams in the two stages. Stream splitting initialization was carried out by initializing all heat capacity flow rates according to the mass balance using Equations (6.23) and (6.24);

$$Fp_{H,i,j,k} = F_{H,i} - \sum_{jt=1}^{j-1} Fp_{H,i,jt,k\,(j=N_C)} \quad (6.23)$$

$$Fp_{C,i,j,k} = F_{C,i} - \sum_{it=1}^{i-1} Fp_{C,it,j,k\,(i=N_H)} \quad (6.24)$$

In the temperature initialization stage, the outlet temperature of the cold splitting stream is isolated as an independent variable according to Equation (6.25) to make the outlet temperature of the splitting streams unequal.

$$tp_{C,i,j,k\,OUT} = T, IN_{H,j} + rand(tp_{H,i,j,k\,IN} – EMAT - T, IN_{C,j}) \text{ if } z_{i,j,k} =1 \quad (6.25)$$

Heat load values were generated randomly with the heat capacity flow rates. Violation of the constraints for minimum approach temperature at both ends of the heat exchanger was avoided in this study by setting a maximum limit of the heat load for the heat exchanger according to Equation (6.26). Equations (6.8) – (6.27) were adapted and modified from Liang et al. (2015)

$$q\ max_{ijk} = \min\ (Fp_{H,ijk}(tp_{H,ijk,IN} - T, OUT_{H,i}), (Fp_{C,ijk}(tp_{C,ijk,OUT} - T, IN_{C,j})) \quad (6.26)$$

$$i \in HP,\ j \in CP,\ k \in KN$$

The annual cost of the heat exchangers is calculated according to Equation (6.27);

$$AC\ (\$) = 10000 + 350A \quad (6.27)$$

6.6 Problem statement, case study, and results

The problem addressed in this study is stated as follows;

"Given are the stream data, the specified range for the uncertainties (e.g. inlet temperatures and heat capacity flow rates) and a minimum approach temperature ΔT_{min}". The task is to simultaneously synthesize a flexible heat exchanger network that is capable of operating non-isothermally under a specified range of disturbance (uncertainties) and unpredictability with a minimized Total Annualized Cost (TAC). Case study 1 was adapted from a CO_2 adsorption experiment and solved according to the proposed methodology in this study.

Case study 1:

This problem considers synthesizing a HEN to minimize energy usage during the absorption of CO_2 from a flue gas stream. The absorption process involves two stages in the superstructure (k=1, 2) with 4 hot and 4 cold streams for period 1 and 2 hot streams, 2 cold streams for period 2. Steam and cooling water are used in the process as hot and cold utilities respectively. The cost of hot utility (steam) is $60/kW.yr while cold utility (cold water) is pegged at $6/kW.yr as described in Isafiade et al. (2015). The process data for this example is presented in Table 6.1 while Table 6.2 presents the result obtained in this work and corroborated with the literature.

Table 6.1: Problem data for the example. (Modified from Yoro 2017)

Stream	T, IN (^oC)	T, OUT (^oC)	F($kW/^oC$)	h ($kW/m^2\ ^oC$)
H1,1	180	90	100	0.60
H2,1	160	100	140	0.50
H3,1	160	50	80	0.20
H4,1	140	40	400	0.30
C1,1	100	160	100	0.40
C2,1	70	140	60	0.70
C3,1	80	120	250	0.60
C4,1	90	130	200	0.20
Steam	170	170	-	0.60
Cold water	20	30	-	0.60
H1,2	150	110	130	0.57
H2,2	120	90	160	0.42
C1,2	60	80	110	0.35
C2,2	40	60	110	0.44

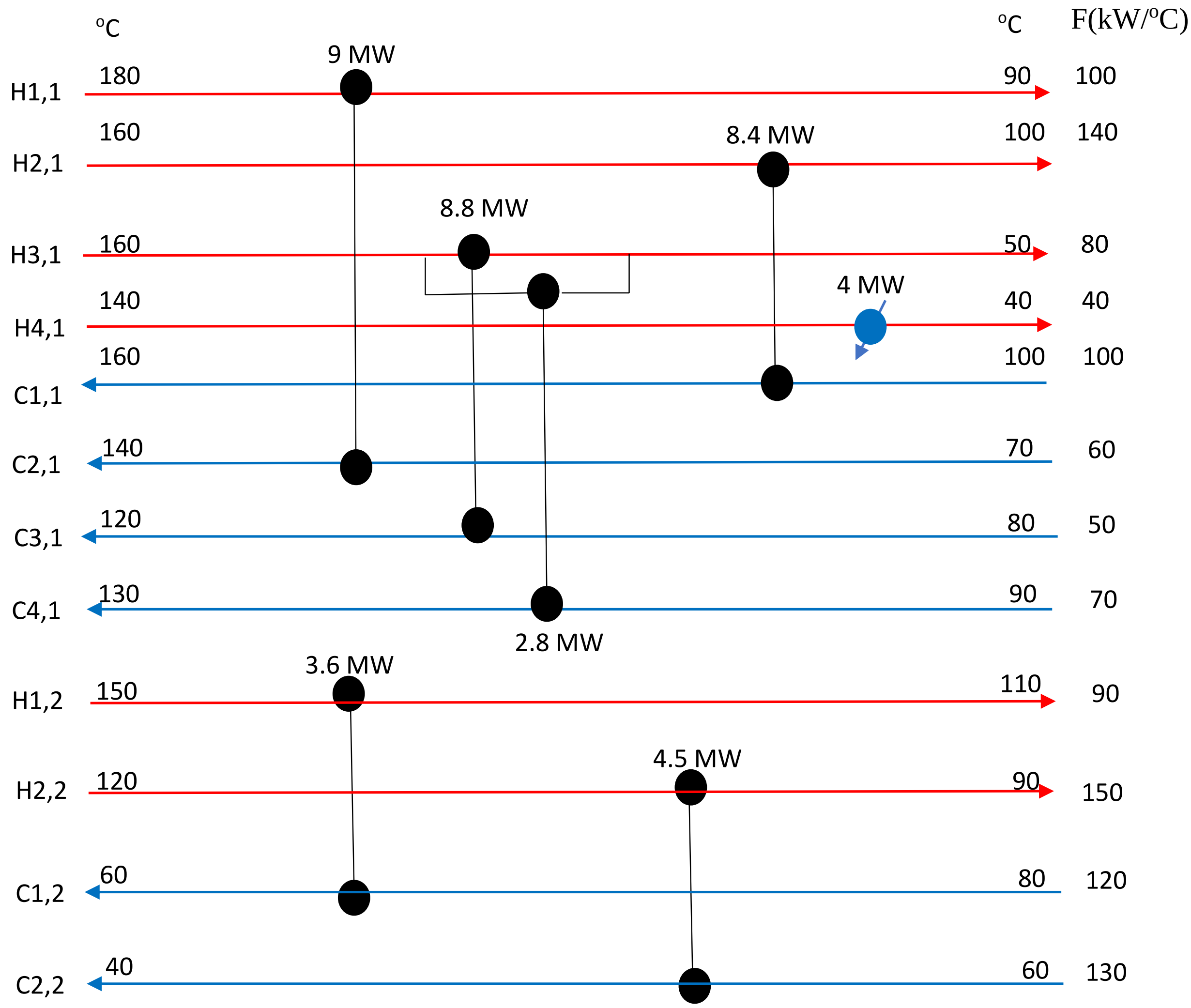


Figure 6.2: The HEN structure for case study 1.

Table 6.2: Results obtained from the synthesized HENs

	Azeez et al. (2019)	Liang et al. (2016)	This study
Total HE area (m^2)	118.00	125.46	100.46
Area cost of HEN ($)	not reported	not reported	13,661
Total annualized cost ($/yr.)	176,330	292,560	136,100
Number of heat exchanger units	6	11	7

Table 6.3: Amount of energy used using HENs (Simultaneous) with recent studies

Energy requirement	Liang et al. (2016)	Singh et al. (2013)	This study
Hot utility load (MW)	24.58	58.94	22.77
Cold utility load (MW)	32.30	74.38	34.55
Total energy (MW)	56.88	133.32	57.32

Table 6.4: Number of units and the annual cost of HENs compared with literature

No. of Units	qcu (MW)	qhu (MW)	Annual cost ($\$x10^6$)	References
11	32.30	24.58	2.926	Liang et al. (2016)
12	32.81	25.09	2.936	Lewin (1998)
13	33.03	25.31	2.960	Linhoff and Ahmad (1990)
7	28.10	18.10	0.136	Khorasany & Fesanghary (2009)
7	34.55	22.77	1.190	This study

6.7 Discussion of results

The HENs network generated in this study is presented in Figure 6.2 while the results obtained are summarized in Tables 6.2 to 6.4 and compared with different methodologies reported by other researchers. It is worth emphasizing that the process parameter and constants from this study were incorporated in the techniques of Azeez et al. (2019) and Liang et al. (2016) with minor amendments to suit the need of this study, to provide a fair basis for comparison with this work. The results in Table 6.2 shows that the non-simultaneous methodology presented by Azeez et al. (2019) gave closer results with the one obtained in this study than that of Liang et al. (2016). This could be attributed to the fact that Azeez et al. (2019) made non-isothermal considerations in their pinch-based technique. However, since their work was sequential in nature and each step depended on the previous one, the HEN was not handled holistically, hence the discrepancy with the results reported in this study. Nonetheless, this study has also shown that when considering multi-period cases for CO_2 absorption, with non-isothermal considerations and fluctuating parameters, simultaneous synthesis techniques yield better results.

Optimal results were achieved in a reasonable computation time of 306 seconds which is slightly faster than the computation time reported by Liang et al. (2016). This signifies that the proposed MINLP model in this study is more reliable for an absorptive CO_2 capture study, and the inclusion of non-linearity due to the non-isothermal assumption introduced in this work has no significant effect on the behaviour of the mixed integer nonlinear program. When compared with the methodologies used in previous studies, it was observed that the quantity of internal hot and cold utilities used by the network synthesized in this study alongside other variables are slightly higher than some of the values obtained from previous reports with exception to the ones reported by Khorasany and Fesanghary (2009) (See Table 6.4). The slight discrepancies observed in the results presented in Table 6.4 are attributed to the different techniques used by the researchers. For example, Liang et al. (2016) used a simultaneous stage-wise synthesis model using initialization techniques in combination with an innovative two-level algorithm while Lewin (1998) used a more generalized method that considered stochastic optimization.

Although the technique proposed in this study and the approach reported by Khorasany and Fesanghary (2009) resulted in a network with the lower number of heat exchangers, the technique presented by Khorasany and Fesanghary (2009) yielded more superior results in terms of the network's annualized cost, HENs area, hot and cold utility demand. This is because the authors used a hybrid methodology that was solved using a two-level algorithmic approach. This implies that if the technique used in this study is solved using a hybrid dualistic-optimization algorithm approach, better results than the ones reported herein may be obtained.

The moderate potential match of hot/cold streams in Figure 6.2 suggests a lesser number of heat exchanger units in the network which will eventually yield a better solution than a network with many heat exchanger units. This explains why the technique used in this study gave better results than most techniques presented in Table 6.4 in terms of the number of units. The HEN structure in Figure 6.2 has 2 stages and stream splitting occurs in both stages. The number of stages and branches of each of the split stream in the network is very important because it determines the optimality of the HENs network. The results also signify that area cost for the HEN is proportional to the total area. This means that the higher the area of the synthesized network, the higher its area cost. A smaller number of heat exchanger areas result in cheaper HENs.

Finally, if the synthesized HEN in this study is integrated into a CCS plant operating at the conditions listed in Table 6.1, less quantity of energy will be required compared to using the techniques of Liang et al. (2016), by using additives and inhibitors or using capacitive deionization as reported by Singh et al. (2013) in Table 6.3. From the results presented in Table 6.3, it is has been found that about 6.3 % energy savings will be recorded if the HENs synthesized in this study is used instead of the HENs synthesized in Liang et al. (2016), while as high as 59.6 % energy savings will be achieved in the power plants if HEN is integrated in the power plants to minimize energy consumption instead of the use of inhibitors and additives that were suggested by Singh et al. (2013). Therefore, the results obtained in this study established that the integration of heat exchanger networks in power plants during absorptive CO_2 capture could save more energy than the blending of sorbents and amine scrubbing suggested by Singh et al. (2013), (see Table 6.3 and 6.4). Besides the fact that the integration of HENs lead to remarkable energy saving, the technique used in synthesizing the HENs also determines the quantity of energy that can be saved.

6.8. Concluding remarks

For the first time, a model (MINLP) for the optimal synthesis of heat exchanger networks (HENs) that involve uncertain source-stream temperatures, fluctuating flow rates, and non-isothermal mixing has been proposed, developed and tested for energy minimization during absorptive CO_2 capture. It is worth stating that although the non-isothermal mixing assumption included in this model introduced non-linear terms in the constraints, no important HEN configuration was completely lost. The HEN generated in this study had a total area of 100.46 m^2 and required 7 units of heat exchangers with a total annualized cost of about \$136,100/yr. The results from this study established that the proposed non-isothermal mixing model can produce a feasible network for indeterminate supply temperatures and flow rates in a relatively more efficient way with fair results. Also, the MINLP can be used for process optimization which could lead to effective energy saving as recorded in this study. It was also discovered that although the body of knowledge is rich with different techniques to minimize energy in industrial processes, the technique proposed and tested in this study gave encouraging results that need to be further explored.

According to the results presented in Table 6.2, the total annualized cost for the HENs network using the proposed MINLP model proposed in this study with non-isothermal assumptions, a total heat exchanger area of 100.46 m^2, Area cost of $10,502 and total annualized cost (TAC) of $136,100/yr. is required compared to values obtained using different methodologies reported by other researchers. Finally, the low TAC value in the results presented in Table 6.2 further establishes that the HEN generated using the proposed technique in this study is more cost-effective and can handle non-isothermal conditions as well as fluctuating operating parameters. For future studies that may involve increased variables with more nonlinear constraints, an initialization strategy with a dualistic (two-level) optimization algorithm could be used to find a solution to the simultaneous HENs problem.

CHAPTER SEVEN

Energy and Material Minimization during CO_2 Capture Using a Combined Heat and Mass Integration Technique with CO_2 Transport

The study presented in this chapter is reported in two areas; first, the synthesis of a combined heat and mass exchanger network (CHAMEN) with regeneration to concurrently minimize energy and mass (material) during adsorptive CO_2 capture without neglecting sorbent (polyaspartamide) regeneration. Secondly, the determination of an optimal cost of transporting captured CO_2 from a power plant to selected storage sites in South Africa. The major contribution in this chapter is the development of an innovative approach that integrates a mathematical programming technique for the heat exchanger networks (HENs) synthesis with a sequentially-based composition interval technique for mass exchanger networks (MENs) synthesis considering regeneration. The content of this chapter has been peer-reviewed and published as a contribution to the proceedings of the 10th Trondheim Conference on Carbon Capture, Storage and Transport (TCCS-10). The full publication is attached in Appendix A7.

7.1 Introduction

Heat and mass exchange occur concurrently during CO_2 capture (Yoro et al., 2019c). Therefore, the application of a combined heat and mass exchanger network (CHAMEN) is envisaged as a very good option to reducing energy and material consumption simultaneously during CO_2 capture (Yoro et al., 2019a). The excessive use of important but expensive resources during CO_2 capture ought to be minimized to make CO_2 capture and transport an affordable technology in developing countries especially in sub-Saharan Africa (Yoro and Sekoai, 2016; Yoro et al., 2017). The application of heat and mass exchanger networks or a combination of both in CO_2 capture studies could be a technique for integrating processes with a potential of providing a meaningful improvement over the synthesis of the individual heat and mass exchanger networks (Shenoy, 1995; Dunn and El-Halwagi, 2003; Isafiade and Fraser, 2007). Since the use of heat and mass is typically intertwined in most CO_2 capture methodologies, it is important to account for such interactions in this study. Furthermore, heat and mass exchanger network synthesis has been a key area of research that has significantly contributed to industrial energy efficiency improvements and material minimization since the past four decades (Zamora and Grossmann, 1998; Henao and Maravelias, 2011).

Until now, researchers have reported the synthesis of heat and mass exchanger networks separately without combining them with a regeneration network (Wechsung et al., 2011; Azeez et al., 2013; Ghazouani et al., 2015). Furthermore, the majority of HENs synthesis techniques reported in open literature applied pure mathematical programming approaches based on the stage-wise superstructure model proposed by Yee and Grossmann (1990). The superstructure-based SYNHEAT model allows for a large number of likely stream matches into a superstructure, while fully considering stream splitting and isothermal mixing (Zamora and Grossmann, 1998; Huang et al., 2012;). According to Furman and Sahinidis (2002), the superstructure-based method is very effective when used to determine potential networks. However, its complex non-linear formulation makes it challenging to solve with current solvers. Also, most superstructure-based formulations do not consider some important details for heat exchanger design, such as fluctuating heat transfer coefficients, pumping costs, number of baffles, tube passes, and number of shells. Besides, the formulation of Yee and Grossman (1990) cannot be extended to consider the aforementioned details for heat exchanger design because its already complex combinatorial nature with increased non-linearity will not yield optimal solutions. Other reports in this field that did not apply the super-structure based approach used pinch analysis-based concepts (Furman and Sahinidis, 2002).

As far as could be ascertained in the literature, most CHAMEN synthesis techniques reported so far applied mathematical programming or pinch analysis techniques separately. No methodology has effectively combined a pinch technology-based technique with a mathematical programming technique to synthesize a combined heat and mass exchanger network while considering sorbent regeneration. This study presents an overview of combined heat and mass exchanger networks synthesis (CHAMENS) with energy and resource minimization while considering sorbent regeneration. It also discusses a hybrid simultaneous-sequentially based methodology to design and operate CHAMENs with a focus on applying it to reduce the high energy requirement associated with sorbent-based CO_2 capture methods. This hybrid technique is new and its application in the field of CO_2 capture has not been reported before now. The method proposed in this study is based on an innovative approach that integrates a mathematical programming technique for the heat exchanger networks (HENs) synthesis and a sequentially-based composition interval technique for mass exchanger networks (MENs) synthesis with regeneration. A combined optimization approach was used to minimize the total annualized cost of the synthesized CHAMEN while an example was solved to test the efficacy of the proposed method.

7.2 Advances in the synthesis of CHAMENs

Many researchers in the past synthesized HENs and MENs separately without combining them with a regeneration network and without using combined techniques (Azeez et al., 2013; Gabriel and El-Halwagi, 2005; Ghazouani et al., 2015; Noureldin, 2012; Tan et al., 2014; Wechsung et al., 2011). Again, majority of the HENs synthesis techniques reported in the literature use mathematical programming approach based on a stage-wise superstructure model originally proposed by Yee and Grossmann (1990) or sequential techniques based on pinch technology (Manan et al., 2004; Statyukha et al., 2008). As far as could be ascertained, no methodology has effectively combined both sequentially-based techniques with simultaneous techniques to synthesize a combined heat and mass exchanger network with sorbent regeneration for energy and material minimization during CO_2 capture.

Srinivas and El-Halwagi (1994) were the first group of researchers to present the synthesis of combined heat and mass exchanger networks. The researchers developed a technique that focused on optimizing individual mass-exchange temperatures in a constant-temperature unit. Srinivas and El-Halwagi (1994) used their proposed technique to simultaneously isolate a certain pollutant from a set of rich streams to a physical and reactive lean stream (mass-separating agents) and also accomplish a specific heat transfer task in a cost-effective way. Nonetheless, the technique is only effective with reactive mass exchangers without making an allowance for the heat exchangers and the regenerating units.

Papalexandri and Pistikopoulos (1994) suggested a hyperstructure-based mixed integer nonlinear programme based mathematical model to tackle the problem of combined heat and mass integration. However, the major drawback with their methodology is that the model formulation for the hyperstructure was observed to be extremely nonlinear and non-convex. This led to the introduction of many binary variables to the problem; hence, it became challenging to find a real explanation close to the optimum one.

Prakotpol and Srinophakun (2004) developed a genetic algorithm in MATLAB to solve a wastewater minimization problem. The researchers formulated an optimization model for both single and multiple contaminants as an MINLP. Although the algorithm proposed was useful for the synthesis problem, it had similar limitations as the hyperstructure-based MINLP model of Papalexandri and Pistikopoulos (1994). Soywiset et al. (2013) then presented a simultaneous technique for heat and mass exchanger network synthesis using an ASPEN process simulator. The authors applied their technique to the synthesis of HENs and MENs separately and also CHAMENs. However, they concluded that CHAMEN synthesis was not suitable for all processes. This simply means that by using their proposed methodology, synthesizing HENs and MENs separately possibly offers a reduced total annualized cost than combining them in a network.

Liu et al. (2013) suggested a new methodology for the simultaneous generation of CHAMENs with multi-dimensional optimization problems. The methodology was a blend of the mass pinch technology for mass exchanger network (MEN) synthesis and a quasi T-H diagram technique for the heat exchanger network (HEN) synthesis which are both sequential in nature. The authors also introduced a lean by-pass stream in a combined network structure to decrease its associated costs. The researchers suggested a new mathematical model and a cross-genetic algorithm annealing-based method achieve a synchronized minimization for the total cost of the MEN and the HEN separately. However, the technique was ineffective when tested for a combined heat and mass exchanger network with multi-period nature.

In addition, Isafiade and Fraser (2007) suggested a methodology based on pinch technology where the sub-HEN and sub-MEN were combined via heat and mass pinch approach to investigate the effect of mass exchange temperature on the annual operating cost and also the effect of annualized capital cost on CHAMENs. Further findings from the study of Isafiade and Fraser (2007) suggests that; depending on the methodology, assumptions, and process in consideration, synthesizing a combined heat and mass exchanger network yields better results than an individual synthesis in contrast to the claims of Soywiset et al. (2013). However, in this study, the blend technique introduced is quite different from the one reported by Liu et al. (2013), because this study adopted a simultaneous-sequential based approach to achieve optimal results.

Since most of the heat and mass exchange operations in a typical CO_2 capture process are multi-period in nature and also are affected by heating and cooling, synthesizing HEN and MEN as two independent processes will not result to an optimal minimization of energy and mass (Isafiade et al., 2015; Liu et al., 2015; Velázquez-Guevara et al., 2018; Yoro et al., 2019b). Most synthesis methodologies reported in the past did not consider a concurrent interaction between heat and mass exchange in their methodologies. Another problem identified in previous studies is that most energy conservation tasks in the area of environmental sustainability suggested non-process synthesis techniques for energy and material minimization during CO_2 capture despite its high cost. But in this study, the use of internal process heat and mass via heat and mass integration is proposed since energy and mass conservation is an effective sustainable approach for resource minimization in industrial processes. This approach could be a promising and less expensive technique to simultaneously minimize energy and material consumption during CO_2 capture from large point sources like power plants.

Against this background, the study documented in this chapter aims to synthesize combined heat and mass exchanger network with regeneration that can minimize the excessive consumption of energy and mass (material) concurrently, while decreasing the levels of CO_2 emission to the atmosphere. The study introduces a new CHAMEN synthesis technique that combines both sequential and simultaneous based principles. This study also discusses multi-period formulations for the first time in a combined heat and mass exchanger network (CHAMEN) with sorbent regeneration. This study also confirms whether the combination of sequential and simultaneous concepts in a single methodology for CHAMENs can yield results with better total annualized cost (TAC). Finally, the development of a transport network for captured CO_2 from power plants to various storage sites was discussed.

7.3 Synthesis of combined heat and mass exchanger network

Several approaches for the synthesis of both reactive and non-reactive CHAMENs have been reported in the literature (Srinivas and El-Halwagi, 1994; Yeomans and Grossmann, 1999; Isafiade and Fraser, 2007; Isafiade and Short, 2016; Yoro et al., 2019d). The major challenge observed with the various methodologies reported so far lies in the combinatorial approach alongside the simultaneous optimization approach between the sub-MEN and sub-HEN. To provide a solution to this challenge, Srinivas and El-Halwagi (1994) proposed a MEN–HEN combination technique, in which the heat exchanged finds a pre- and post-MEN with the lean streams flowing through the MEN at fixed stream temperatures. Although the technique yielded results, it is only applicable to single-period CHAMENs where parameters are fixed and do not fluctuate. It cannot be extended to multi-period scenarios where stream temperatures, flow rates and gas composition fluctuate as seen in a typical CO_2 separation study where sorbent regeneration is paramount. As a result, the methodology of Srinivas and El-Halwagi (1994) was modified in this study to specifically address a CHAMEN synthesis problem with regeneration and fluctuating process parameters. The thermodynamic feasibility of the heat exchanged in this work was ensured by using a lower value of the minimum approach temperature (ΔT_{min}). To improve on the work of Srivinas and El-Halwagi (1994), this study went beyond just optimizing outlet gas composition to introduce a more rigorous optimization-based method for the synthesis of CHAMENs which is a significant contribution to the existing knowledge in this field. Coupling of sub-networks and simultaneous integration, as well as optimization of CHAMEN, is the new concepts introduced in this study for global optimization.

In addition, the body of knowledge in this field is rich in different approaches for the synthesis of both reactive and non-reactive CHAMENs (Srivinas and El-Halwagi 1994; Yeomans and

Grossmann, 2009; Isafiade and Fraser, 2007; Azeez et al., 2013; Liu et al., 2013; Yoro et al., 2019e; Yoro et al., 2019f). However, due to the interaction of heat and mass during adsorptive CO_2 capture, this study reports the synthesis of CHAMENs for adsorptive CO_2 capture alongside the regeneration network. As far as could be ascertained, this has not been reported before now. Furthermore, to improve on the work of Srivinas and El-Halwagi (1994), this study was extended beyond optimizing just the outlet gas composition to introduce a more rigorous optimization-based method for the synthesis of CHAMENs to include the coupling of sub-networks and simultaneous integration, as well as the optimization of CHAMENs.

The following assumptions were made for the exchangers in this study;

1) Individual rich and lean stream have a constant mass flow rate through the network.

2) The mass exchangers operate at a quasi-isothermal condition.

3) Mass exchange temperatures are generated only from the temperatures of the lean streams.

4) Equilibrium relations are assumed to be monotonic functions of the temperature of the sorbent and compositions.

7.4 Problem statement

The combined heat and mass-exchanger network (CHAMEN) synthesis scenario in this study is presented as follows;

'Given are some rich streams 'NR' and some lean streams 'NS' (physical MSAs). The task is to synthesize a cost-effective network of combined heat and mass exchangers that can satisfactorily transfer a certain undesirable pollutant (CO_2) from rich flue gas streams to the MSA (in this case, the sorbent). The flow rate of each rich stream, G_i; it's supply (inlet) composition, y_{si}; and the target/outlet composition, y_{ti} are known and specified in the problem. The supply and target compositions of the MSA (sorbent) during absorptive CO_2 capture are given as x_{sj} and x_{tj} respectively. Furthermore, hot and cold process and utility streams are available to optimize mass exchange temperatures'.

Important problem data for this study such as gas flow rate, concentration and temperature intervals were adapted from the preliminary study discussed in chapter 3 and the study of Yoro (2017).

7.5 Methodology

A systematic combination of both pinch technology and mathematical programming concepts is employed in this study to synthesize a CHAMEN. The step-wise procedure presented in Figure 7.1 was used to set the formulation for the synthesis of a combined heat and mass exchanger network (CHAMEN) in this study.

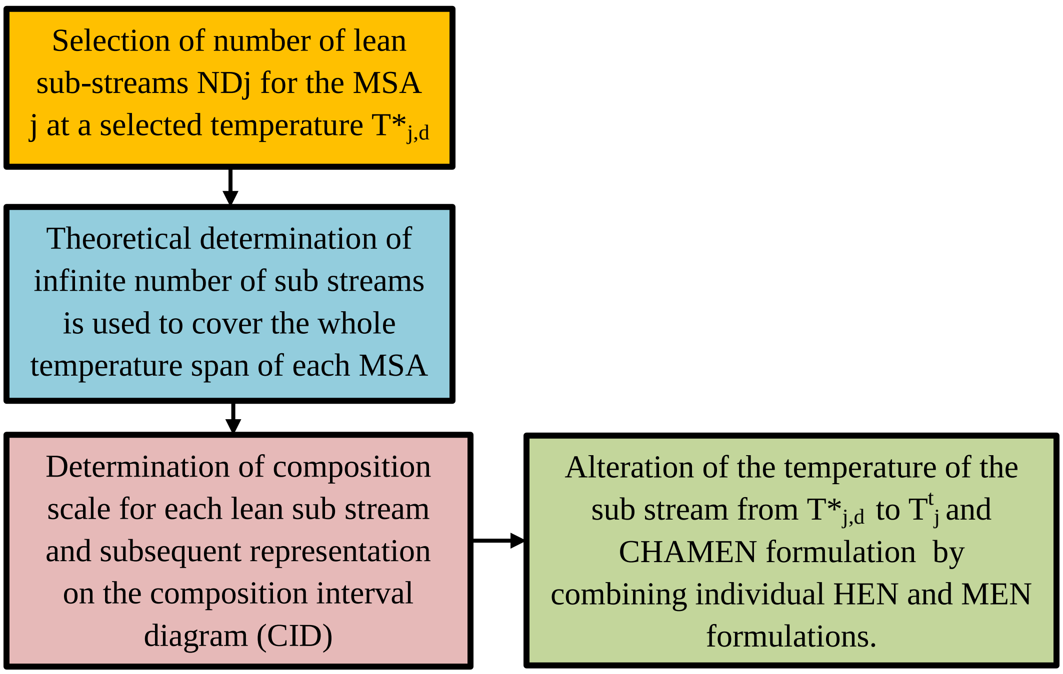


Figure 7.1: Procedure for the CHAMEN formulation

The adsorbent (polyaspartamide) for CO_2 capture suffices as the mass transfer agent (MSA) in this study and its cost is determined from Equation (7.1) as described by Hallale (2000b)

$$\text{Cost of MSA } = \sum_{j=1}^{N_s} C_j \sum_{dj=1}^{ND_j} L_j, dj \quad (7.1)$$

Material balance around the composition interval is determined using;

$$\delta_k - \delta_{k-1} + \sum_j k \sum_{dj\ through\ interval\ K} w^{s}_{j,k} = W^{R}_{k} \quad (7.2)$$

Where k = 1,2 …N_{int}, $L_j, dj \geq 0$, j = 1,2,… N_s

$$\sum_{dj=1}^{ND_j} L_j, dj \leq L^{C}_{j} \qquad j = 1, 2,\ldots N_s \quad (7.3)$$

Mass residual constraints for the case studies considered in this study are stated as;

$$\delta_0 = \delta_{N,int} = 0 \quad (7.4)$$

$$\delta_k \geq 0,\ k = 1, 2 \ldots N_{int} - 1 \quad (7.5)$$

Equations (7.1) - (7.5) were developed in this study according to the description in Hallale (2000a,2000b) and used together with the HEN-targeting equations presented by El-Halwagi (2017) representing the constraints of the CHAMEN synthesis formulation. The equilibrium relation for CO_2 scrubbing in water depends on temperature according to Equation (7.6) which was adapted and modified from Liu et al. (2013) to suit this study;

$$y = x_1(0.053T_1 - 14.5) \quad (7.6)$$

Where y refers to the mass fraction of CO_2 in the flue gas stream, T_1 is the temperature of the water in degree Celsius and x_1 is the mass fraction of CO_2 in the water after scrubbing.

An objective function was developed in this study to minimize the cost of mass separating agents (MSAs) as well as the heating and cooling utilities. The objective function discussed in this study is a linear programming formulation whose solution determines the optimal flow rate and temperature of each sub-stream as well as its heating/cooling duty. The general methodology used to synthesize the optimal CHAMEN in this study to achieve an improved total annualized cost (TAC) is presented in Figure 7.2.

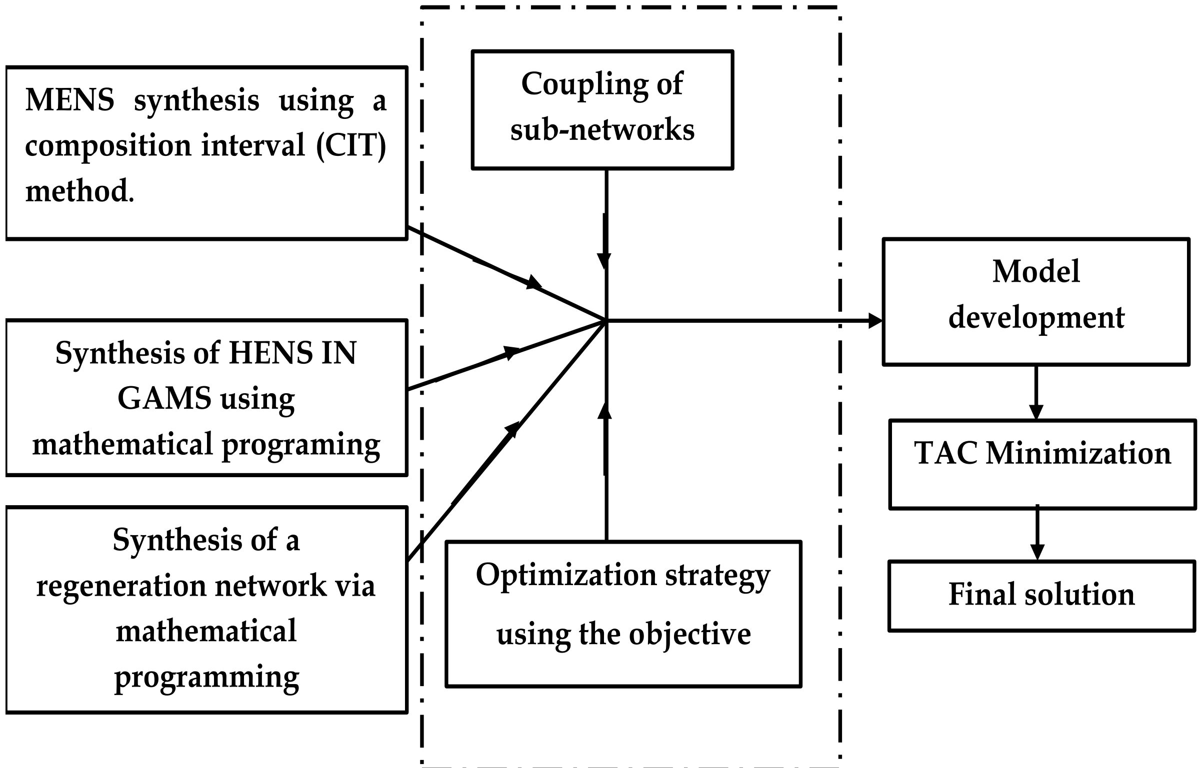


Figure 7.2: Methodology for CHAMEN + regeneration network synthesis.

7.6 Case study for CHAMEN synthesis

The efficacy of the proposed methodology for synthesizing the CHAMEN with regeneration proposed in this study is tested in this section using a CO_2 adsorption case study from the work of Yoro (2017). The case study has a mass exchanger network (MEN) with mass separating agents (which is the sorbent in this case) integrated with a heat exchanger network (HEN) with the possibility of optimally regenerating the MSAs.

The task: ***Adsorption of CO_2 with two MSAs and two cold and hot external utilities***

In this problem, steam and cooling water are the hot and cold utilities added to the process to heat up and cool down the mass separating agents (MSAs) for effective adsorption of CO_2. The task is to synthesize a CHAMEN that can adequately transfer CO_2 in the waste streams to the MSA and the energy and material saved determined based on the stream data presented in Table

7.1-7.3. The physical meaning of all the symbols used in Table 7.1-7.3 and others used elsewhere in this study are already provided in the nomenclature section of this thesis.

Table 7.1**:** Waste stream data for CO_2 separation. Adapted and Modified from Yoro (2017)

Stream	Flow rate Gi (kg/s)	CO_2 supply composition y_i^s	CO_2 target composition y_i^t
R_1	1.5	0.15	0.05

Table 7.2**:** Lean stream data. Modified from Yoro (2017)

Stream	x_j^s	x_j^t	m_j	ε_j	C_j	T_j^{LB} (°C)	T_j^{UB} (°C)
S_1	0.01	0.07	0.10	0.001	0.05	35	50
S_2	0.02	0.09	0.20	0.001	0.01	48	48

Table 7.3**:** Cold and hot utility stream data. (Modified from Yoro et al., 2019f)

Stream	Supply temp (°C)	Target temp (°C)	Cost ($/kW.yr)
C1	15	25	10
C2	28	35	30
H1	130	70	120
H2	120	80	150

Two cooling utilities (cold water) and two hot utilities (steam) are available as shown in Table 3. For this case study, the specific heat capacity is fixed at 4.2 $kJ \cdot kg^{-1} \cdot {}^{\circ}C^{-1}$ (specific heat capacity of water at room temperature) while the minimum approach temperature ΔT_{min} was assumed at 10 °C. The cost of heat exchanger area (A) is expressed in Equation (7.7) as described in Shenoy (2005);

$$\text{Area cost} = 30000 + 750A^{0.81} \tag{7.7}$$

The objective function for the mathematical model is presented as Equation (7.8) and was solved in GAMS (General algebraic modelling system). The GAMS codes (program) is provided in appendix E. The objective function comprises the total annual cost (TAC) of the CHAMEN presented as a combination of the costs associated with the sub-MEN and the sub-HEN. The objective function of the model gives more information on the capital costs of the coolers, heaters and the number of heat exchanger units for all process streams.

$$TAC = \text{Min} \sum_{i}\sum_{j}\sum_{k} N_{i,j,k} \,.\, K_{stage} + H_Y \sum_{j} L_j \,.\, C_j^l + \sum_{v} CF_{cu,v} + \sum_{w} CF_{hu,w} + \sum_{u}\sum_{v}\sum_{w} CF_{u,v,w} +$$

$$\sum_{v} C_{cu,v} \,.\, A_{cu,v}^{Bcu,v} + \sum_{w} Chu_{,w} \,.\, A_{hu,w}^{Bhu,w} + \sum_{u}\sum_{v}\sum_{w} Cv_{w,u} \,.\, A_{v,w,u}^{Bv,w,u} + \sum_{v} C^{cu} .$$

$$q_{cu,v} + \sum_{w} C^{hu} . \, q_{hu,w} \tag{7.8}$$

Hot and cold streams for the networks were determined via optimization using Equation (7.9);

$T_j^s < T_j^*$, $T_j^* < T_j^t$ = hot stream, j ϵ N_i

$T_j^s > T_j^*$, $T_j^* > T_j^t$ = cold stream, j ϵ N_i (7.9)

Equations (7.1) - (7.9) were coupled with non-negativity constraints to form a linear program that can be modelled in GAMS.

Table 7.4**:** Composition interval diagram for CO_2 absorption case study

Interval	Waste stream	X_1, 1 at 35 ^oC	X_1, 1 at 70 ^oC	Composition
	y 0.15 R1			0.09
1	0.13	-	-	0.08
2	0.12	-	-	0.07
3	0.10	-	0.13	0.06
4	0.09	0.13	0.09	0.05
5	0.08	0.11	0.07	0.04
6	0.07	0.09	0.05	0.03
7	0.06	0.05	0.00	0.03
8	0.05	0.00	-	0.02

Table 7.5**:** Temperature interval table

Interval	Hot streams			Target temperature (^oC)
	S_1, 1,	S_1, 2	T (^oC)	
1			35	130
2			28	120
3	HU_1		25	80 CU_1
4			15	70

7.7 Regeneration

Since the example considered in this study involves CO_2 adsorption using a solid sorbent, there is a need to consider the amounts of energy that could be saved during the regeneration of sorbents in the CHAMEN. As a result, a regeneration network was integrated into the CHAMEN in this study. The main MSA target composition during regeneration was determined from the interaction with the stripping column. A complex mathematical problem was solved in GAMS using the DICOPT solver as ΔT_{min} changes and results obtained are presented in Table 7.6. The superstructure showing expected flows in the combined heat, mass exchanger with regeneration network is shown in Figure 7.3 while the synthesized CHAMEN alongside its regeneration is presented in Figure 7.4. To substantiate our claims in this study, the minimum TAC obtained in this study using the proposed technique was compared with other CHAMEN synthesis techniques reported in the past and presented in Table 7.7, while the percentage energy and material saving during adsorptive CO_2 capture using different energy and material saving techniques reported in the past are presented in Table 7.8 and compared with the results from this study. The technique proposed in this study resulted in a more superior value of TAC when compared to previously reported techniques as shown in Table 7.7. The TAC value obtained in this study is closer to that reported by Isafiade et al. (2015). However, the slight difference observed was because the methodology in Isafiade et al. (2015) considered only a simultaneous approach without regeneration, while this study used a combined sequential and simultaneous approach with due consideration to sorbent regeneration.

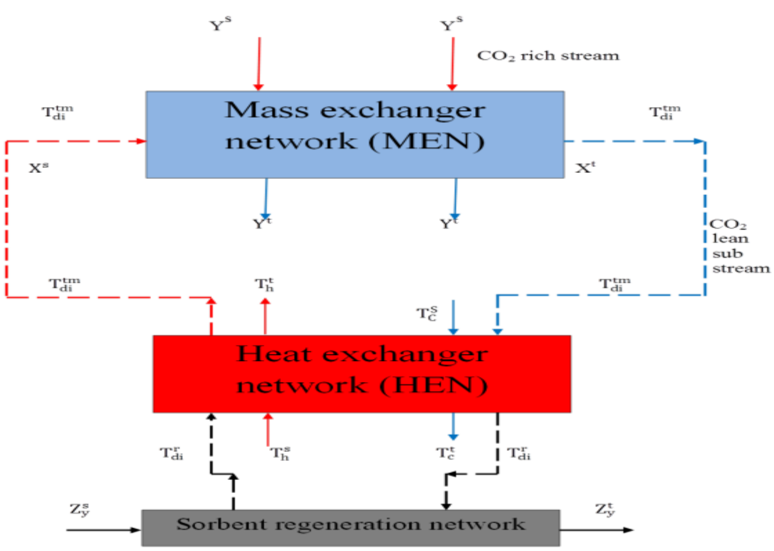


Figure 7.3: The CHAMEN + regeneration superstructure. Adapted from: Yoro et al. (2019a).

Table 7.6: TAC obtained at different target compositions and $\Delta T_{min.}$

Compositions x^s	x^t	ΔT_{min} (°C)	TAC for CHAMEN + Regeneration ($million/yr.)
0.15	0.03	10	0.0708
0.15	0.05	12	0.0756
0.15	0.07	15	0.0800
0.15	0.10	20	0.0863

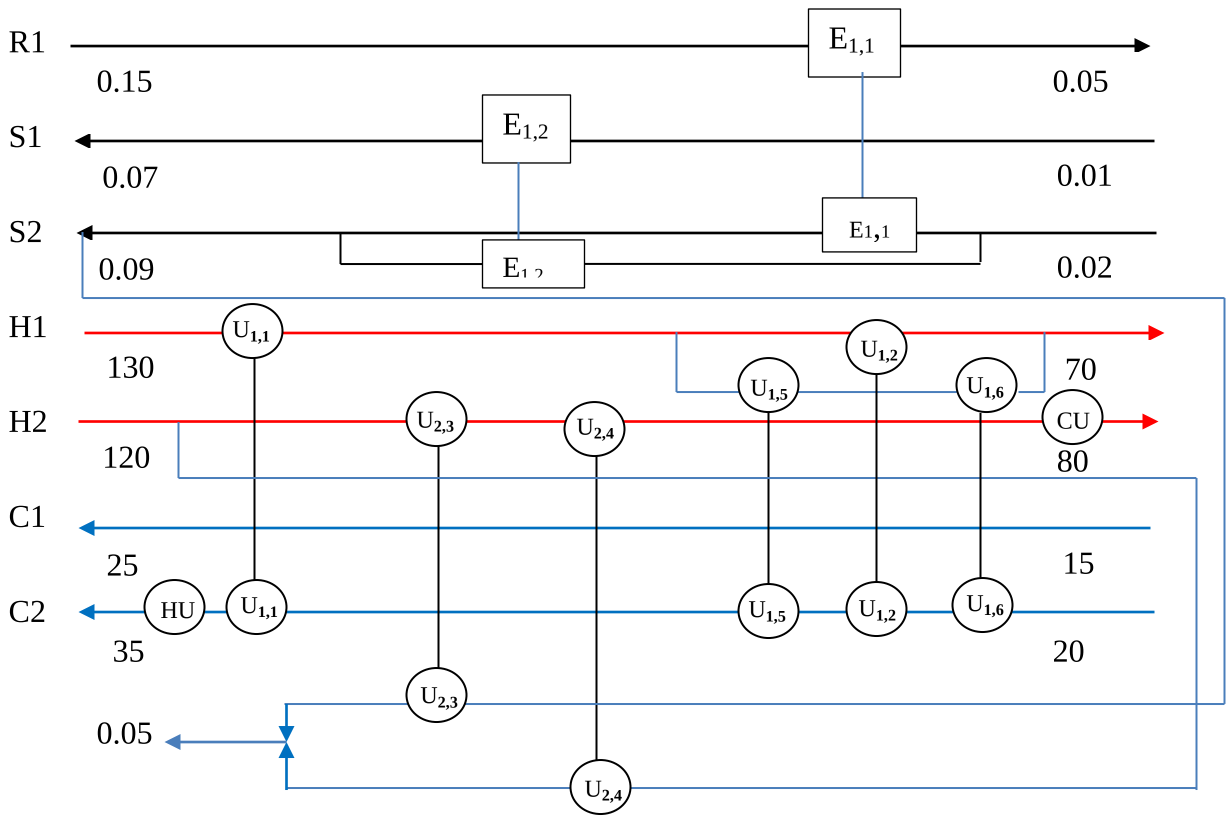


Figure 7.4: CHAMEN with regeneration for this case study

Table 7.7: Minimum total annualized cost compared with literature

Network type	Minimum TAC for CHAMEN (million $/yr.)	Reference
CHAMEN	0.1998	This study
CHAMEN	0.3402	Liu et al. (2015)
CHAMEN	0.1973	Isafiade et al. (2007)
CHAMEN	2.6731	Soywiset et al. (2013)

Table 7.8: Energy and material saved during CO_2 capture using different energy and material saving techniques.

Technique	% Energy saved	% Sorbent/material saved	Reference
CHAMEN + Regeneration	30	19.1	This study
Use of phase change materials	40	Not reported	Shavalieva et al. (2019)
Sorbent grafting (solid)	17	9.0	Bachelor and Toochinda (2012)
Use of external utilities	12	0	Bougie and Iliuta (2011)

7.8 Transport Network for CO_2 Capture

This section discusses a hypothetical case study for CO_2 transport from the capture site to its storage locations. Transporting captured CO_2 from power plants to different storage locations is a huge challenge, especially during the early phases of the development of large-scale CO_2 capture (Neele et al., 2017). In most cases, between the CO_2 capture and utilization phase, the captured CO_2 finds its way back to the atmosphere because of the poor handling during transportation and storage stage. CO_2 transport by ship is an attractive option because of its inherent flexibility in the combination of CO_2 from several sources at different flow rates to one or more storage locations. The technical design of CO_2 shipping infrastructure is subject to the process conditions (requirements) at the well head of the respective storage site.

Transport of CO_2 by ship from port to port has already been practised for a long period with a relatively small volume of CO_2 i.e. up to 1500 m^3 (Weihs et al., 2014; Kjärstad et al., 2016). Nevertheless, this form of transport is only feasible in coastal regions and not arid nations like South Africa. In both coastal and non-coastal nations, when CO_2 is captured, the next step is to convey it to a storage site. The current method of transporting captured CO_2 in coastal regions is via the use of ship vessels while non-coastal countries transport CO_2 using pipelines. Research has shown that CO_2 transport by ship is the least expensive transportation option not only for most of the individual sources but also for most of the potential cluster combinations during the ramp-up of the CCS transport and storage infrastructure (Decarre et al., 2010; Kujanpää et al., 2011; Roussanaly et al., 2013). It has also been confirmed from current literature in this field that the cost of CO_2 transport by water only surges discreetly with increasing transport distance (Awoyomi et al., 2019; Vierth et al., 2019).

The use of pipelines to transport captured CO_2 to storage/utilization sites have been in use for decades, and large volume of gases has been transported through this medium (Essandoh-Yeddu and Gülen, 2009; McCoy, 2009). Pipelines can transport CO_2 in two states: gaseous and liquid. However, this hypothetical study focuses mainly on the transport of CO_2 in its gaseous state where a compressor "pushes" the gas through the pipeline. In some cases, a pipeline can have intermittent compressors at different locations to keep the gas moving. A CO_2 pipeline typically originates at the source of capture and travels directly to the storage site (although, in some cases, it might travel as far as it can in the pipe) then transition to a tanker or ship to finish off its journey. It all depends on where the source, pipeline and storage sites are located.

Figure 7.5: Pipeline transportation of CO_2. [Adapted from Sintef, (2015)]

In South Africa, the major CO_2-emitting power plants are located in the provinces of Gauteng, Mpumalanga and Free State (Yoro and Sekoai, 2016). These regions form South Africa's coal mining areas. Hence, most coal-fired powered plants are situated in these provinces; while storage sites extend from the Karoo Basin, which covers the Eastern Cape, Northern Cape, and Free State to the Orange basin which covers KwaZulu-Natal and the Mpumalanga provinces of South Africa. So far, there is no existing transport network for captured CO_2 from power plants from a certain location to available storage sites as previously highlighted in this study. Hence, the captured CO_2 could find their way back into the atmosphere in the process of being transported to its storage or utilization site. To avoid this as well as ensuring its proper transport and storage, there is a need to develop a network for transporting CO_2 after capture from different power plants to a specific storage site. In response to this need, this section presents a hypothetical study involving transport network for captured CO_2 within different plants in South Africa to a storage site using simple linear mathematical programming techniques. The distance between the power plant and storage sites were obtained from google maps while the amount of CO_2 that could be transported was logically assumed. The cost implications of the proposed network are determined from a linear GAMS model The hypothetical example treated in this chapter is presented as follows;

Case study: Transportation network for captured CO_2

CO_2 is captured from the 1180 MW Grootvlei power plant located in the Mpumalanga province of South Africa. The task is to develop a transport network from this power plant to storage sites located in the Karoo Basin in the Free State, Northern as well as the Eastern Cape Provinces and the orange basin storage site in the KwaZulu-Natal province as presented in Figure 7.6. The cost of the transport considering the distance from the power plant to storage sites will also be determined using linear programming techniques. For this case study, the power plant and storage sites are presented as the sets in GAMS while the parameters refer to the volume of captured CO_2 transported and distance the pipeline must cover from the plant to storage site. The objective function is defined as the cost of transporting the CO_2 from Grootvlei station to any of the storage sites. The linear program is written and run in the GAMS environment. The GAMS codes are available in the Appendix E section of this thesis.

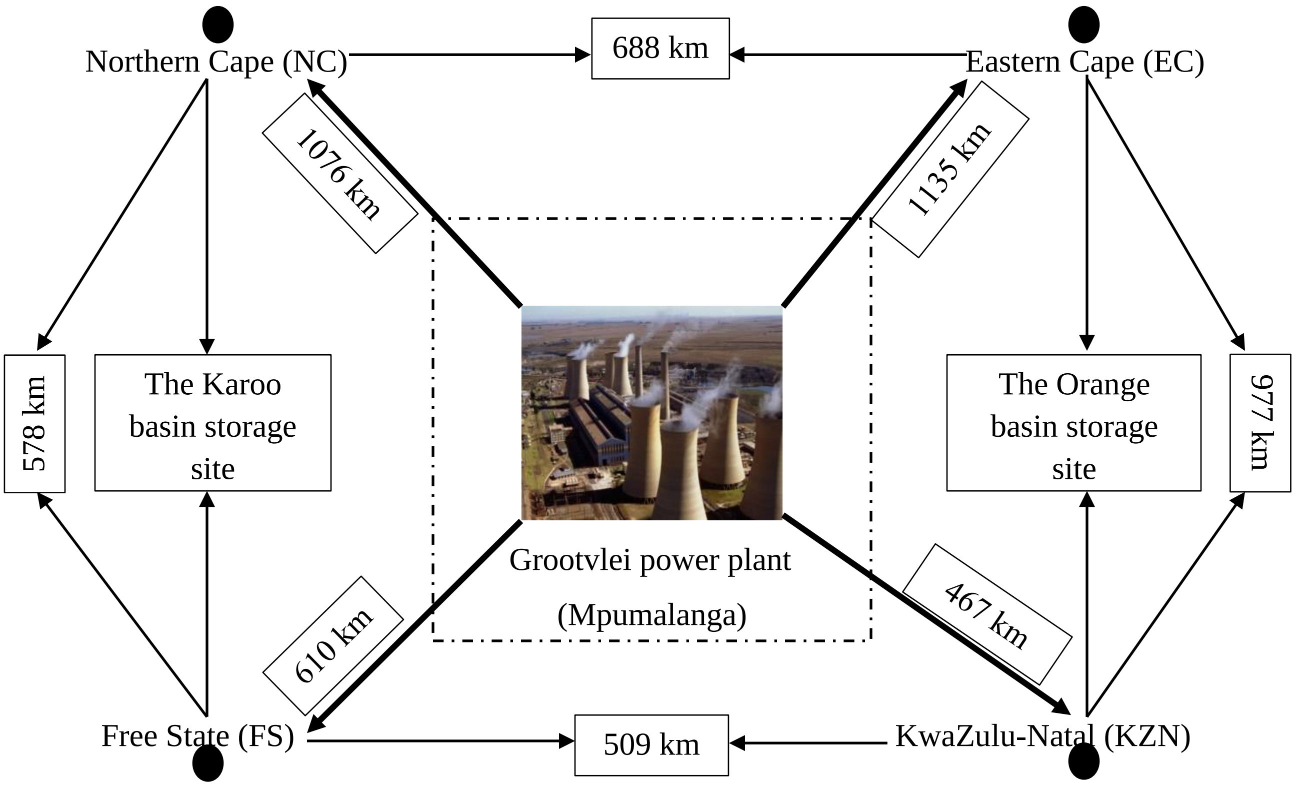


Figure 7.6: Transport routes for CO_2 storage from the capture site in South Africa (Grootvlei Power plant picture obtained from **www.eskom.co.za**)

The distances expressed in Figure 7.6 were noted and imputed in the linear program in GAMS.

In about 0.062 seconds of compilation time, the results presented in Table 7. 9 were obtained;

Table 7.9: Summary of results for the case study

Location	CO_2 to be transported (ton/yr)	Distance (km)	Optimal operating Cost ($/ton)
Free State	10000	610	1850
Northern Cape	12000	1076	3200
Eastern Cape	10500	1135	2850
KwaZulu-Natal	10000	467	1280

The GAMS program for this transportation problem is presented in Appendix E. It is worth emphasizing here that this section of CO_2 transport is a hypothetical study, hence its major limitation is that the distances might be unrealistic for CO_2 transport in a gaseous phase. In such cases, it is recommended that CO_2 be transported in a dense or supercritical phase

7.9 Results and discussion

This study attempted using the composition interval method (for MENS), with temperature interval diagram (for HENS) and linear programming to explore the possibility of synthesizing a combined heat and mass exchanger network with a provision for sorbent regeneration. The composition interval diagram presented in this work was used to ensure the thermodynamic feasibility of the mass exchanged during the CO_2 capture process while the temperature intervals catered for the heat exchanged and potential energy saving. The number of intervals represents the number of process streams (both hot and cold) considered in the capture process. The all-positive values in the composition interval diagram (CID) presented in Table 7.4 established that within any interval, it is thermodynamically feasible to transfer mass from the waste streams to the mass separating agents (sorbents). The solution from the combined network also confirms that the lean stream (sorbent) is actively involved in the adsorption process and a by-pass stream with unequal supply and target temperature is expected. The CHAMENs further illustrates that the incorporation of by-pass streams and the combination of simultaneous with sequential-based synthesis technique yields results with significant improvements over previously reported methodologies that used just a mathematical programming or a sequential approach.

Another important result presented in this study is the total annualized cost (TAC) of the combined network. A lower value of TAC for the CHAMEN means better operating and capital cost for the network which also translates to higher energy savings and minimization of material in the CO_2 adsorption process. Furthermore, results in Table 7.6 show that as the target composition of the gas (for mass exchange) and minimum approach temperature (ΔT_{min}) for heat exchange is increased, the TAC also increases. This means that operating at a lower ΔT_{min} could result in a more efficient combined heat and mass exchanger network with regeneration during CO_2 capture.

The parameters included in the objective function formulated in this work were responsible for the significant reduction in the total annualized cost and energy consumption by the resultant CHAMEN. The value of the minimum approach temperature (10 ^{o}C) adopted in this study impacted positively on energy penalty reduction during adsorptive CO_2 capture which subsequently improves the efficiency of the power plant. The inclusion of a sorbent regeneration network in the CHAMEN in this study established that process synthesis techniques can be used to tackle the high energy requirement associated with most CO_2 capture techniques.

The results in Table 7.7 reveal that the combined methodology introduced in this work is better in terms of the total annualized costs than some methodologies reported in literature. This makes the combined network generated in this study more ideal for application in CO_2 capture studies. The amount of energy and material saved during CO_2 capture reported for different energy and material saving techniques is presented in Table 7.8 and compared with the technique proposed in this study. According to the results in Table 7.8, the integration of CHAMENs with a regeneration network in a CO_2 capture problem could result in 30 and 19 % energy and material saving respectively. Other techniques that reported a slightly higher value could account only for energy saving without material saving. Although the use of phase change materials (solid) as proposed by Shavalieva et al. (2019) is good and resulted in a significantly higher energy saving (40%) as shown in Table 7.8, the technique has not been explored for material saving to date. Amine (MEA) scrubbing is another technique that could result in huge energy savings during CO_2 capture, however, it does not fall within the scope of this chapter because it is liquid-based. Hence, it was not considered for comparison in Table 7.8. From the results presented in Table 7.8, it is evident that the integration of a CHAMEN with regeneration as proposed in this study could potentially facilitate and account for a reduction in energy during CO_2 capture. Kindly note that since this section reports a hypothetical study, no detail parameters like pipeline diameter, CO_2 properties and inlet boundary conditions are provided. Future studies may look into the detailed design to include the aforementioned parameters.

7.10. Concluding remarks

The benefit of combining heat and mass exchanger networks with a sorbent regeneration network for concurrent minimization of both energy and material during CO_2 capture was investigated in this study. It can be inferred from the results obtained in this study that the combination of heat and mass exchanger with a sorbent regeneration network is an effective way of concurrently minimizing both energy and material consumption during CO_2 capture. Results obtained from the case study considered in this work revealed that operating the lean streams at their supply temperatures alone is not the best approach to cut operational cost and simplify CHAMEN network design. Furthermore, it has been shown in this study that it is possible to combine a sequential-based approach (composition interval method) with a simultaneous-based technique (mathematical programming) to achieve optimal results for energy and material saving in a combined heat and mass exchanger network. The combinatorial approach introduced in this study gave insight into how best to combine the heat and mass exchangers with regeneration networks for energy and material minimization. Furthermore, the total annualized cost obtained in this study (TAC=$million 0.1998 /yr.) showed significant improvement over the TAC previously reported which also means a significant reduction in energy requirement when compared with previously reported approaches. The CHAMEN synthesized in this study can be extended to CO_2 capture methodologies such as absorption, membrane, and cryogenic separation to minimize energy and material consumption. Additionally, it was established in this study that although other energy-saving techniques for CO_2 capture (e.g. amine grafting of solid sorbents, blending, and the use of phase change materials etc.) yielded results in terms of energy-saving, if energy and material minimization is to be accounted for concurrently, the application of a combined heat and mass exchanger network would be a better option. Furthermore, it was established in this study that linear mathematical programming techniques can be used to develop a transport network between power plants and respective storage/ utilization locations for effective transport of captured CO_2.

Finally, the transport network section of this chapter revealed that although distance and amount of captured CO_2 to be transported is usually expected to determine the cost, it is not applicable in most cases as considered in this work. Here, the distance to be covered matters most for the pipeline network. Hence, a lower cost was obtained. This means that, if the hypothetical power stations are in full operation and CO_2 is captured from the Grootvlei power plant in Mpumalanga province, it will be safer, quicker and cost-effective to store it in the Karoo basin around KwaZulu-Natal province if the distance is considered; but if the amount of captured CO_2 is considered, storage in the Northern Cape area will be most prefered.

CHAPTER EIGHT

General Conclusions and Recommendations

This chapter presents a deep reflection on the main findings of the research reported in this thesis. It also highlights the contributions of this study to the body of knowledge in this field. Furthermore, the confirmation/rebuttal to the research hypotheses presented in Chapter One of this thesis is presented in this chapter. Recommendations for future research and development in this field are also highlighted.

8.1 General conclusions

The literature has confirmed that climate change is a serious environmental problem that needs urgent scientific attention, while energy consumption and material cost greatly influenced the profitability of most CO_2 capture techniques. On this note, this study was dedicated to addressing two pressing global needs; Affordable & clean energy, as well as climate action. These two needs form part of the seventeen (17) sustainable development goals created by the United Nations General Assembly (UNGA) for sustainable development in 2015. The literature reviewed in this study showed that researchers have put in tremendous efforts to reduce the emission of anthropogenic CO_2 into the atmosphere. Also, different techniques such as adsorption, absorption and membrane separation have been proposed and tested in the literature for CO_2 capture. This study confirms that the combustion of fossil fuels like coal for power generation can continue and yet CO_2 emission is minimized at an optimal cost, which is possible through CO_2 capture and introduction of heat and mass integration in the capture process as discussed in this thesis.

The study documented in this thesis was divided into two parts; a heat exchanger network (HEN) synthesis and mass exchanger network (MEN) synthesis. In each part, the proposed synthesis technique was developed and first tested on a simple HEN and MEN CO_2 adsorption and absorption case studies before extending to a more complex case involving a combined heat and mass exchanger network (CHAMEN) with regeneration for a coal-fired power plant. The research efforts in this thesis also underlined the process barriers (e.g. supply, target and minimum approach temperature, composition difference, heat capacity flow rates etc.) which influence effective heat and mass integration during absorptive and adsorptive CO_2 capture. Furthermore, most chapters in this thesis discussed the potential of synthesizing heat and mass exchanger using both sequential and simultaneous approaches interchangeably.

This study aimed to minimize excessive energy and material consumption during adsorptive and absorptive CO_2 capture. This was achieved by synthesizing and integrating heat and mass exchanger networks using both sequential and simultaneous techniques. The following statements confirm the research hypotheses mentioned in Chapter One of this thesis;

- Heat recovery between different streams going in and out of a CO_2 capture process can decrease the energy requirement and the quantity of external utilities used during absorptive and adsorptive CO_2 capture due to the integral relationship between heat and mass during CO_2 capture,
- The application of HENs and MENs separately or combined can be used to address energy and material minimization during absorptive and adsorptive CO_2 capture.
- Heat and mass integration techniques can be used to set targets (utility and MSA) for industrial process streams to provide a clearer understanding of the interactions amongst various units in a CO_2 capture process.

The aforementioned confirmations have provided direct answers to the research questions posed in the first chapter of this thesis.

The main findings and conclusions drawn from this research are:

- ❖ From the literature review in chapter two, this study identified that the currently available CO_2 capture techniques are highly energy and material intensive; this makes the full implementation CO_2 capture technology expensive. Hence, there is a need to update the body of knowledge with new and cost-effective techniques to tackle this challenge.

- Although the current techniques suggested in the literature were feasible for energy minimization, in most cases, they have not been extended beyond the absorption technology to include material saving.

- The application of process integration techniques embodying pinch technology and mathematical programming can be used to generate a network of heat and mass exchangers for adsorptive and absorptive CO_2 capture. These network of heat and mass exchangers can be used to minimize energy and material consumption most cost-effectively during absorptive and adsorptive CO_2 capture.

- In chapter three, this study confirmed that the use of internal process heat through heat integration can be used to minimize the high energy requirement in most CO_2 capture technologies instead of the use of external utilities. Unlike previously reported methodologies, the approach suggested in this study is not limited to just the absorption technology but can be extended to other CO_2 capture technologies (for example adsorption and membrane separation).

- In chapter four, it was found that the sequential merging of sub-networks (using the principle of pinch technology and the composition interval table) as presented in this thesis could lead to a minimum utility network with good material recovery.

- The composition intervals presented in this study offers a two-feasibility criterion that can be used to identify the essential pinch matches and the stream splitting rationale from the case study problem.

- In chapter five, it was discovered that the energy and material saved during absorptive and adsorptive CO_2 capture using the approach proposed in this study are significantly higher than the energy saved using most techniques reported in the past.

- No synthesis technique (simultaneous or sequential) is categorically superior to the other during energy and material minimization in adsorptive and absorptive CO_2 capture studies as reported in this thesis. However, the assumptions made during synthesis as well as its area of application determines the extent of its superiority.

- ❖ In chapter six, the study reported in this thesis confirmed that no synthesis technique (simultaneous or sequential) is categorically superior to the other during energy and material minimization in adsorptive and absorptive CO_2 capture studies. However, the assumptions made during synthesis as well as its area of application determines the extent of its superiority.

- ❖ Although mathematical programming techniques could be more complex due to its associated non-linearity, it still gives better results than the sequential technique which could be monotonous if large scale problems are considered. The simultaneous synthesis of the heat exchanger networks (using mathematical programming techniques) considered the CO_2 capture system holistically, hence it yielded better results compared to other techniques.

- ❖ In chapter seven, I found out that since a typical CO_2 capture technique involves a simultaneous heat and mass exchange, the synthesis of a combined heat and mass exchanger network with regeneration is more cost-effective for this purpose than synthesizing the heat and mass exchangers separately. The total annualized cost (TAC) obtained in this study showed significant improvement for HENs, MENs and CHAMENs when compared with other techniques in literature.

- ❖ Although most studies in CCS have consistently ignored CO_2 transport after capture, this study has established that mathematical programming techniques (through linear programming) can be used to design an effective transport network for captured CO_2 from a central capture site (power plant) to different storage or utilization sites to cut down on the cost associated with CO_2 transport.

- ❖ Finally, the synthesis of HENs and MENs during absorptive CO_2 capture with fluctuating process parameters as well as the inclusion non-isothermal assumptions as reported in this thesis resulted in a network that can handle processes that operate at different conditions which is typical of the absorptive and adsorptive CO_2 capture process.

8.2 Recommendations for future research

Research involving the application of process synthesis and integration techniques in CO_2 capture studies is still new and has not been fully harnessed. Based on the findings in this study, the following recommendations have been made for future research and development:

- Despite the tremendous potentials of heat and mass integration for utility minimization, limited investigations have been reported for the synthesis of heat and mass exchanger networks for energy and material minimization in other energy-intensive CO_2 capture methods such as membrane and cryogenic separation. This field constitutes an emerging area of research in the scientific community, and the extension of process synthesis techniques to solve problems in these areas will constitute an interesting research topic in future.

- The combination of pinch analysis with mathematical programming in a single methodology is still a more effective technique during heat and mass integration in CO_2 capture systems compared to other methods previously reported in the literature. A hybrid network optimization approach may also be tried for heat and mass exchanger applications in future studies.

- The total annualized cost obtained from the CO_2 transport network developed in this study revealed that the transportation of captured CO_2 from power plants to a storage/utilization site is still expensive. As a result, this report suggests that future studies should consider synthesizing a network for a CO_2 capture system that includes an on-site utilization of captured CO_2 by integrating a CO_2 utilization plant (e.g methanol production plant) with a power plant where CO_2 is captured, and its annualized cost determined.

- ❖ This study considered synthesizing a single period combined heat and mass exchanger network (CHAMEN) for a concurrent minimization of both energy and material during CO_2 capture. Future studies could consider synthesizing a multi-period CHAMEN that can handle multiple variations of process parameters for the same purpose.

- ❖ The capital and operating expenditures (CAPEX & OPEX) for the HENs, MENs and CHAMENs in CO_2 capture studies are very good areas that could be further explored in future studies to determine the possibility of implementing the synthesized network in a large case pilot-based or industrial study.

- ❖ Finally, future research could consider going beyond synthesis and optimization, to reporting the control and operation of the synthesized HENs, MENs and CHAMENs with detailed designs and cost functions using the results discussed in this study as the basis.

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Appendix A- Copies of research output (Publications)

A1

International Journal of Energy and Environmental Engineering (2019) 10:367–387
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ORIGINAL RESEARCH

A review on heat and mass integration techniques for energy and material minimization during CO_2 capture

Kelvin O. Yoro[1] · Patrick T. Sekoai[2] · Adeniyi J. Isafiade[3] · Michael O. Daramola[1]

Received: 24 February 2019 / Accepted: 16 April 2019 / Published online: 26 April 2019

Abstract
One major challenge confronting absorptive CO_2 capture is its high energy requirement, especially during stripping and sorbent regeneration. To proffer solution to this challenge, heat and mass integration which has been identified as a propitious method to minimize energy and material consumption in many industrial applications has been proposed for application during CO_2 capture. However, only a few review articles on this important field are available in open literature especially for carbon capture, storage and utilization studies. In this article, a review of recent progress on heat and mass integration for energy and material minimization during CO_2 capture which brings to light what has been accomplished till date and the future outlook from an industrial point of view is presented. The review elucidates the potential of heat and mass exchanger networks for energy and resource minimization in CO_2 capture tasks. Furthermore, recent developments in research on the use of heat and mass exchanger networks for energy and material minimization are highlighted. Finally, a critical assessment of the current status of research in this area is presented and future research topics are suggested. Information provided in this review could be beneficial to researchers and stakeholders working in the field of energy exploration and exploitation, environmental engineering and resource utilization processes as well as those doing a process synthesis-inclined research.

Keywords CO_2 capture systems · Energy minimization · Energy penalty · Heat and mass exchanger networks · Mathematical programming

Introduction

Carbon capture and storage (CCS) is a promising technology that aims at reducing CO_2 emissions from large point sources such as power plants [1–3]. However, high energy demands and excessive material usage associated with CO_2 compression and separation processes have been the main challenges currently facing the commercialization of most CO_2 capture and storage technologies [4]. There is a need to save energy and minimize material usage during CO_2 capture to ensure the economic advantage of the capture technology [5, 6]. This is because, the cost of energy and materials for CO_2 capture has increased and this trend is expected to continue with an increase of about 13.4% by the year 2040 due to consistent high energy demand from many industrialized nations globally [7]. The challenge of energy and excessive use of materials in process industries can be tackled to a large extent by minimizing the consumption of energy and mass [8]. In the context of this review, energy refers to the heat required during sorbent regeneration, while material (mass) refers to the mass separating agents (sorbents) and external utilities such as cooling water and steam which ought to be minimized during CO_2 capture.

Heat and mass exchanger network retrofitting is envisaged as a promising option for reducing energy and material consumption which could lead to enhanced economic and environmental sustainability. The main aim of heat exchanger networks (HENs) and mass exchanger networks (MENs) retrofitting is to decrease the external energy demand and extra material consumption by increasing heat and mass exchange simultaneously among process streams in an existing process

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A2

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Multi-period Heat Exchanger Network Synthesis with Temperature Intervals and Uncertain Disturbances

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High energy consumption is a major challenge currently threatening many industrial processes. This has made industrial processes such as absorptive CO_2 capture expensive and energy intensive. However, research has shown that the application of Heat Exchanger Networks has the potential of minimizing energy demands in many industrial processes due to its energy recovery advantage. In this study, a sequential procedure is presented for the synthesis of heat exchanger network for multi-period operations with specified uncertainties in flow rates and variations in inlet and outlet temperatures of process streams. The synthesis task in this study was sequentially decomposed into three stages. Temperature interval method was used to determine the loads and minimum utilities required by the network in the first stage. Determination of the minimum number of units was considered in the second stage while the third stage was dedicated to the derivation of a network configuration and sizing of heat exchangers to determine the capital cost using area targeting technique. Efficacy of the proposed methodology was tested using an example from literature. A new heuristic rule was established and the network topologies obtained using the proposed approach testifies to the applicability of HENs for energy minimization during absorptive CO_2 capture.

1. Introduction

Different strategies have been proposed for energy minimization in energy-intensive processes like absorptive CO_2 capture in recent times. For instance, Escudero et al. (2016) developed a heat integration methodology based on Pinch Analysis to assess heat recovery options which were used to minimize the high energy penalty in oxy-fuel power plants. Yoro and Sekoai (2016) proposed the use of promoters and catalysts while the use of additives such as piperazine for energy minimization during absorptive CO_2 capture was suggested in another study by Yoro et al. (2019a). Nevertheless, it has been observed that most of the energy minimization strategies suggested for absorptive CO_2 capture in the literature involve the use of extra mass separating agents, external utilities or inhibitors which are quite expensive (Yoro et al., 2019b). A few studies in the literature have

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Sequential Synthesis of Mass Exchanger Networks for CO_2 Capture

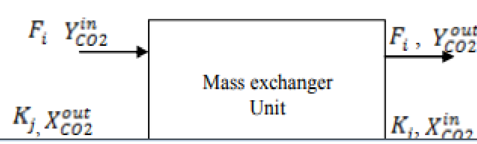
Kelvin O. Yoro, Adeniyi J. Isafiade, Michael O. Daramola, *Member, IAENG*

***Abstract*— Most of the current research in process synthesis focus on heat exchanger network synthesis. Reports on mass exchanger network synthesis mostly discussed single-component problems using simultaneous approaches. However, less attention has been given to mass exchanger network synthesis with multi-component problems using the sequential technique. Till date, it has not been easy to systematically choose between the process and available external mass separating agents (MSA) in mass exchanger network synthesis during the adsorption of CO_2. In this paper, we set out a technique for targeting external mass separating agent and its network design. The technique was applied to a CO_2 adsorption process involving two mass separating agents (process and external MSAs) that overlap. A thermodynamic analysis of the CO_2 adsorption process was outlined in this study using the composition interval method. Feasible structures were formulated and the synthesis task was expressed in a two-stage targeting procedure as an optimization task. Unlike previous studies reported in the past for mass exchanger network synthesis, this contribution considers a trade-off between the process MSA S_1 and external MSA S_2 to determine the minimum amount of external MSA required for the CO_2 capture process. A case study was adapted from open literature to demonstrate the effectiveness of the synthesized mass exchanger network during a typical CO_2 capture process. Outcomes from this study indicate that mass integration via process synthesis is an effective strategy that can minimize the quantity of external utilities required during the adsorption of CO_2 from a rich stream of flue gas.**

***Index Terms*— Adsorption, CO_2 capture, Composition interval method, Mass exchanger networks, Network design**

challenge and address the need to minimize waste in industrial processes, there is a need to synthesize and design optimal mass exchanger networks. In the field of chemical engineering, process integration is a tool for analyzing the process mass and energy flows for reducing the use of raw materials, external utilities and waste discharge as well as maximizing the internal heat and mass exchange. Synthesis of optimal mass exchanger networks for the CO_2 adsorption process could minimize the use of external utilities and provide a lasting solution to the problem of excessive use of external utility associated with most adsorption processes. Synthesis of optimal mass exchanger networks (MENs) using simultaneous approach (mathematical programming) has been rather well established in literature [3]–[5]. Hence, we are considering a sequential approach in this study.

Mass exchangers are direct contact mass-transfer components that utilize mass separating agents (MSAs) to preferentially separate certain components (example; impurities, pollutants and by-products) from a certain rich stream into a lean stream. Mass exchange units are commonly used in separation operations in process industries. Popular mass exchange operations include adsorption, stripping, absorption, ion exchange, and solvent extraction. Fig. 1 shows a typical mass exchanger with flow streams in countercurrent directions.



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Modelling and experimental investigation of effects of moisture and operating parameters during the adsorption of CO_2 onto polyaspartamide

Kelvin O. Yoro[1] · Mutiu K. Amosa[2,3] · Patrick T. Sekoai[1] · Michael O. Daramola[1]

Received: 7 May 2018 / Revised: 17 July 2018 / Accepted: 4 September 2018 / Published online: 17 September 2018

Abstract Parametric effect of moisture and influence of operating variables on the adsorption behaviour of polyaspartamide during CO_2 capture was investigated in this study using experimental and modelling approach. Individual effects of operating conditions (e.g. pressure, temperature and gas flow rates) as well as the effect of moisture on the adsorption capacity of polyaspartamide were methodically investigated using Dubinin–Raduskevich model. Results from the investigations reveal that the presence of moisture in the flue gas had an incremental effect on the adsorption capacity of polyaspartamide; thereby showcasing the potential of polyaspartamide as a suitable hydrophilic material for CO_2 capture in power plants. In addition, pressure, temperature and gas flow rates at 200 kPa, 403 K, and 1.5 mL/s, respectively, significantly influenced the CO_2 adsorption capacity of polyaspartamide. Physisorption and chemisorption both governed the adsorption process while equilibrium studies at different temperatures showed that Langmuir isotherm could adequately describe the adsorption behaviour of the material with best fit with $R^2 > 0.95$.

Keywords Adsorption capacity · CO_2 capture · Moisture · Operating variables · Polyaspartamide

1 Introduction

Coal is one of the world's cheapest and abundant fossil fuel with a wide range of applications in power generation, transport systems and thermal energy production (Chitsiga et al. 2018). However, the use of coal in these important sectors results in the emission of greenhouse gases (especially CO_2) into the atmosphere which is a major cause of power generation or switching to other alternative clean energy sources will make power generation very expensive and unaffordable in most developing countries (Sekoai et al. 2018; Yoro and Sekoai 2016). Research have shown that by applying CO_2 capture and storage techniques, it is possible to continue the use of coal in power generation and yet maintain a near-zero CO_2 emission. Adsorption of CO_2 is a reliable technique that can be used for CO_2 cap-

A5

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Diffusion mechanism and effect of mass transfer limitation during the adsorption of CO_2 by polyaspartamide in a packed-bed unit

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ABSTRACT

A systematic study of the diffusion mechanism and effect of mass transfer limitation during the adsorption of CO_2 onto polyaspartamide is presented using a differential adsorption bed method, carried out in a 100 × 60 × 40 mm packed-bed adsorption unit. The rate-limiting step where mass transfer limitation is dominant was studied using diffusion models. It was observed that intraparticle diffusion mechanism is the major contributor to the resistance offered to the transport of gas molecule through polyaspartamide. The behaviour of polyaspartamide, based on the intraparticle diffusion rate parameter derived from the plots of CO_2 adsorbed versus the square root of time, signified that the adsorption mechanism involved both film and intraparticle diffusion. The intraparticle diffusion parameter (kid) obtained was dependent on temperature as well as intraparticle convection effects and ranged from 1.24×10^{-4} to 2.13×10^{-4} ms^{-1}. The Biot number (Bi) values were all greater than 10 (ranged from 17.80 – 30.74), confirming that the intraparticle diffusion was the rate-limiting step and heat transfer is more by conduction from the gas film layer than convection within the pores of polyaspartamide. Results from this study provide an important basis for future scale-up and optimisation of CO_2 capture process using polyaspartamide.

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KEYWORDS
Adsorption; CO_2 capture; diffusion mechanisms; mass transfer; Polyaspartamide

1. Introduction

Carbon capture, storage and utilisation (CCSU) is widely accepted as a promising option that aims at reducing CO_2 emissions from industrial point sources (e.g. coal-fired power plants) and it also allows for the continual use of fossil fuels (e.g. coal) for sustainable energy generation with a significant reduction of CO_2 emission. One of the technologies employed in CCSU is adsorption using CO_2-selective adsorbents. However, for adsorption of CO_2 to be economically feasible for CCSU, adsorbents with high adsorption capacities for CO_2 should be developed and the mechanism involved in the adsorption process well understood. The adsorption of

capture (Yoro, Isafiade, and Daramola 2018). Generally, it has been identified that there is a dearth of report on diffusional behaviour of adsorbents especially in gas-solid systems. The few reports available on diffusion mechanism of adsorbents dwelt majorly on liquid-solid adsorption systems with respect to the adsorption of dyes by different materials (Allen, McKay, and Khader 1989; Costa and Rodrigues 1985a, 1985b, 1985c, 1985d; Cheung, Szeto, and McKay 2007; Dotto, Buriol, and Pinto 2014; Ho and Mckay 1998b; Piccin et al. 2013). As far as could be ascertained, not much report has been published on the diffusion mechanisms involving gas-solid adsorption systems with a keen interest in polymer-based

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International Conference on Engineering for Sustainable World — IOP Publishing
Journal of Physics: Conference Series **1378** (2019) 022018 doi:10.1088/1742-6596/1378/2/022018

Synthesis of Optimal Heat Exchanger Networks with Quantified Uncertainties and Non-isothermal Mixing

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Abstract- The primary objective of this study is to develop a simultaneous approach for the synthesis of flexible heat exchanger networks (HENs) with non-isothermal mixing assumptions. The HENs synthesis procedure presented in this study took into consideration quantified uncertainties in inlet temperatures and flow rates with an unpredictable time of shift. The proposed multi-period MINLP model was used to generate a HEN with optimized heat exchanger areas and total annualized costs attributed to utility duties. A framework for generating the flexible HEN over a specified range of variations in flow rates and stream temperature was proposed in this study. The framework was based on a two-stage strategy; a HEN design stage was first performed before the testing stage where the energy-saving potential of the synthesized HEN was established. The effectiveness of the proposed approach was tested for energy minimization using a case study in literature with variation in inlet temperature and flow rate. It was observed that the inclusion of non-isothermal parameters in the non-linear model resulted in a HEN that optimally works under fluctuating conditions without losing stream temperature targets while maintaining economically-optimal energy integration.

Keywords: Energy minimization, Heat exchanger networks, MINLP models, Non-isothermal mixing

1. Introduction

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TCCS-10, 2019
Trondheim, Norway

The 10th Trondheim Conference on CO_2 Capture, Transport and Storage
17-19 June, 2019

ENERGY AND MATERIAL MINIMIZATION DURING CO_2 CAPTURE USING A COMBINED HEAT AND MASS INTEGRATION TECHNIQUE

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Abstract

Heat and mass exchange occur concurrently during CO_2 capture. Therefore, the application of a combined heat and mass exchanger network (CHAMEN) could be a very good option to reduce energy and material consumption simultaneously during CO_2 capture. In this study, a systematic technique for the synthesis of combined heat and mass exchanger networks (CHAMENs) was introduced to concurrently minimize the use of external utilities and mass separating agents (MSA) during adsorptive CO_2 capture. The method proposed in this study is based on an innovative approach that integrates a mathematical programming technique for the heat exchanger networks (HENs) synthesis and a sequentially-based composition interval technique for mass exchanger networks (MENs) synthesis with regeneration. A combined optimization approach was used to minimize the total annualized cost of the synthesized CHAMEN. An example was solved to test the efficacy of the proposed method. The cost of mass separating agents, as well as hot and cold utilities which form the total annualized costs (TAC) for the combined heat and mass exchangers, was minimized. The total annualized cost (TAC) of the synthesized CHAMEN obtained in this study (TAC=$199800/yr) showed significant improvement over the TAC reported in the literature using other synthesis techniques. Results obtained in this study confirmed that the integration of a combined heat and mass exchanger with regeneration network is an effective way to minimize heat and mass during adsorptive CO_2 capture. The combined heat and mass exchanger networks adequately satisfied the heat and mass balance of the process with a lower total annualized cost.

Keywords: *Adsorption, CO_2 capture, Combined heat and mass exchanger network, Energy minimization, Mass*

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Chapter #

SYNTHESIS OF MASS EXCHANGER NETWORKS USING SEQUENTIAL TECHNIQUES

Kelvin Odafe Yoro[1], Adeniyi Isafiade[2], and Michael Olawale Daramola [3]

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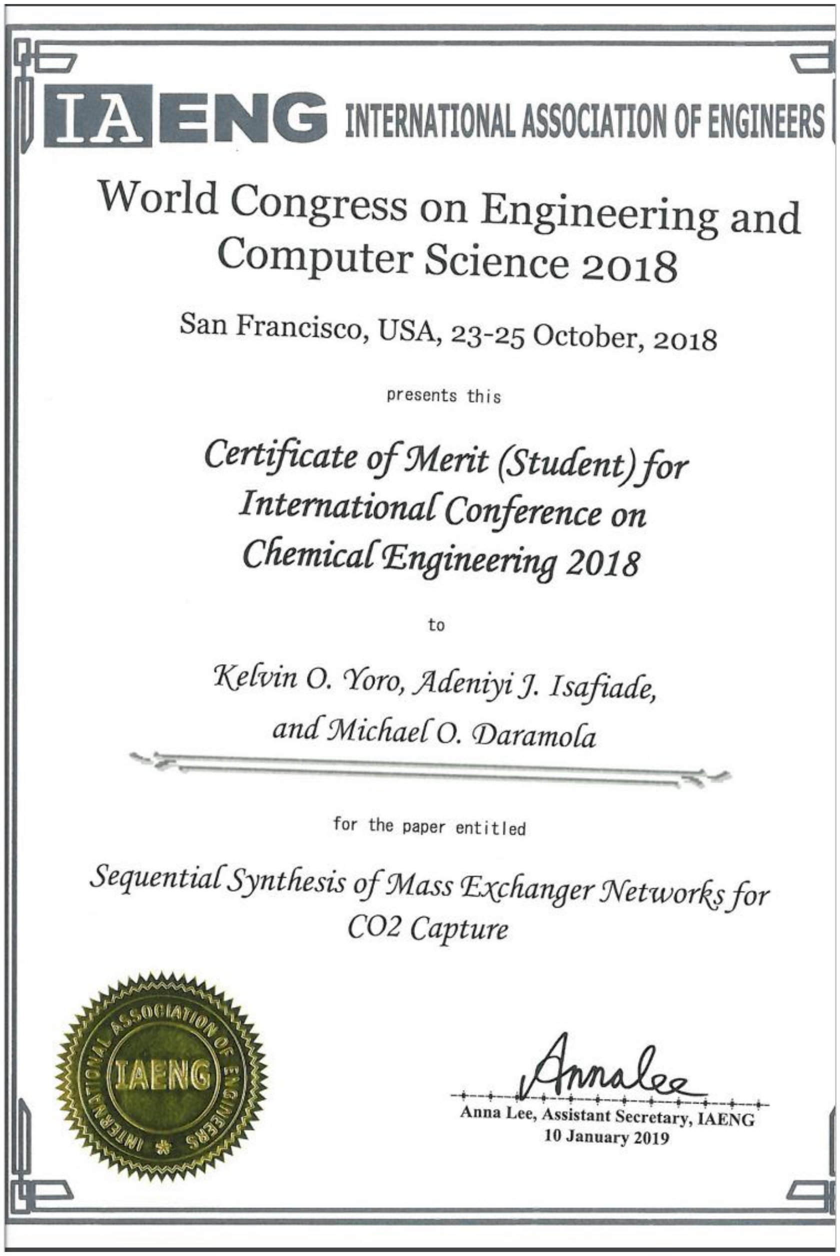
Abstract: Mass exchange units are important units in many industrial processes. Therefore, there is a need to design and operate these units in a coordinated and integrated manner. This chapter presents a systematic approach for the synthesis of mass exchanger networks involving utility and capital cost targeting. A sequential technique for targeting external mass separating agent and developing an optimal network design is discussed. The proposed technique was applied to a CO_2 adsorption process involving two mass separating agents (MSAs) that do not overlap. A thermodynamic analysis of the CO_2 adsorption process was outlined using the composition interval method. Feasible structures were formulated, and the synthesis task was expressed in a two-stage targeting procedure as an optimization task. This chapter also discussed a trade-off between the process and external MSA in the case study considered to determine the minimum amount of external MSA required for a typical CO_2 capture process. The results obtained indicated that mass integration via process synthesis is an effective strategy to

Appendix B- Laurels/Awards from this PhD research



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Kelvin O. Yoro, Adeniyi J. Isafiade, and Michael O. Daramola

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Title: Modelling and experimental investigation of effects of moisture and operating parameters during the adsorption of CO_2 onto polyaspartamide

Author: Kelvin O. Yoro, Mutiu K. Amosa, Patrick T. Sekoai et al

Publication: International Journal of Coal Science & Technology

Publisher: Springer Nature

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Title: Diffusion mechanism and effect of mass transfer limitation during the adsorption of CO2 by polyaspartamide in a packed-bed unit

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Appendix E- GAMS Files

The GAMS codes

```
*$Title Simultaneous Optimization for HEN Synthesis (CHAPTER 6)

$Ontext

This model synthesizes a flexible non-isothermal heat exchanger network with
minimized Total Annualized Cost (TAC) which satisfies heating and cooling
requirements. The superstructure consists of two stages with eight possible
exchangers.

Written by Kelvin Yoro, University of the Witwatersrand, Johannesburg. 2019

$Offtext

Scalar

    nhut number of hot utilities /1/

    ncut number of cold utilities /1/

 Sets

 i hot streams /1*4/

  j cold streams /1*5/

 k temperature locations  nok + 1 /1*7/

     data  data /tin,tout,h,f,cost/

 hut(i)          hot utilities

 hps(i)          hot process streams

 cps(j)          cold process streams

 cut(j)          cold utilities

 st(k)           stages
```

```
first(k)          first temperature location
last(k)           last temperature location
hx_st(k)          heat recovery stages
hut_st(k)         hot utility stages
cut_st(k)         cold utility stages
fhps(k)           first temperature location of hps(i)
fcps(k)           first temperature location of cps(j)
first_tlhot(K)    intervals where hps(i) exist
last_tlhot(K)     last temperature location of hps(i)
first_tlcold(K)   intervals where cps(j) exist
last_tlcold(K)    last temperature location of cps(j);
st(k)             = yes$(ord(k) < card(k))  ;
first(k)          = yes$(ord(k) eq 1)       ;
last(k)           = yes$(ord(k) eq card(k))  ;
hut(i)            = yes$(ord(i) <=nhut);
cut(j)            = yes$(ord(j) > 1+ncut);
hps(i)            = yes$(ord(i) >nhut);
cps(j)            = yes$(ord(j) <=1+ncut);
hut_st(k)         = yes$(ord(k)=1);
cut_st(k)         = yes$(ord(k)=card(k)-1);
hx_st(k)          = yes$(ord(k)>1 and ord(k)<=card(k)-2);
fhps(k)           = yes$(ord(k)=2);
fcps(k)           = yes$(ord(k)=card(k)-1);
```

```
 first_tlhot(k)    = yes$(ord(k)>=2 and ord(k) <card(k));
 last_tlhot(k)     = yes$(ord(k)=card(k));
 first_tlcold(k)   = yes$(ord(k)<=card(k)-2);
 last_tlcold(k)    = yes$(ord(k)=1);
$ONTEXT
TABLE HOTS(I,DATA) Hot streams data
         TIN     TOUT    H       F       COST
1         180     90     0.5     100       60
2         160     100    0.5     140      50
3         160     50     0.5     80       20
4         140     40     0.5     400      0
5         170     170    0.5     0        0      ;
TABLE COLDS(J,DATA) Cold streams data
         TIN  TOUT    H     F     COST
1         100  160  0.5     100    0
2         70   140  0.5     60     0
3         80   120  0.5     250    5
4         90   130  0.5     200    5
5         20    80  0.5     0     6      ;
$OFFTEXT
```

```
*$ONTEXT
TABLE HOTS(I, DATA) Hot streams data
        TIN     TOUT    H       F       COST
1       200     250     0.2     0.00    115.2
2       106     60      0.2     205.0   0.0
3       160     40      0.2     198.8   0.0
4       162     60      0.2     136.4   0.0;
TABLE COLDS(J, DATA) Cold streams data
        TIN     TOUT    H       F       COST
1       72      165     0.2     210.3   0
2       62      110     0.2     141.0   0
3       220     170     0.2     175.4   0
4       250     190     0.2     318.7   0
5       0       10      0.2     0.0     1.3;
*$OFFTEXT
PARAMETER
*Capital cost parameters
AF      Annualisation factor
CF      Investment cost
AC      Area cost
AE      Area cost index
gamma(i,j)
EMAT    Exchanger minimum approach temperature;
```

```
AF= 0.2;    CF=8333.3;     AC = 641.7;       AE = 1;
gamma(i,j) =max(0,colds(j,'tin') - hots(i,'tin'), colds(j,'tin') - hots(i,'tout'),
                colds(j,'tout') - hots(i,'tin'), colds(j,'tout') - hots(i,'tout')) ;
*Flags
Parameter
AREX(i,j,k)
a_hps(i,k)        intervals in which hps(i) are present
a_cps(j,k)        intervals in which cps(i) are present
a_hut(i,k)        intervals in which hot utilities are present
a_cut(j,k)        intervals in whc cold utilities are present
match(i,j,k)        define possible macthes between streams i and j in interval k
temp_in_hot(i,k)
temp_in_cold(j,k);
*Initialise flags
a_hps(i,k)$(hps(i) and first_tlhot(k))= 1;
a_cps(j,k)$(cps(j) and first_tlcold(k))= 1;
a_hut(i,k)= 0;
a_cut(j,k)= 0;
match(i,j,k)=0;
temp_in_hot(i,k)=0;
temp_in_cold(j,k)=0;
*Assign flag values
a_hut(i,k)$(hut(i) and hut_st(k))=1;
```

a_cut(j,k)$(cut(j) and cut_st(k))=1;

match(i,j,k)$(st(k) and ((a_hps(i,k) and a_cps(j,k)$(hps(i) and cps(j))) or (a_cut(j,k)$((hps(i) and cut(j)))) or (a_hut(i,k)$((hut(i) and cps(j))))))=1;

temp_in_hot(i,k)$hps(i)=fhps(k);

temp_in_cold(j,k)$cps(j)= fcps(k);

Display hut, hps, cps, cut, k, st, first, last, hut_st, cut_st, hx_st, fhps,

fcps, first_tlhot, last_tlhot, first_tlcold, last_tlcold, a_hps, a_cps,

a_hut, a_cut, match,temp_in_hot, temp_in_cold ;

VARIABLES

dtin(i,j,k) approach between i and j in period p at location k

dtout(i,j,k);

Binary Variables

y(i,j,k);

Positive Variables

th(i,k)   temperature of hot stream i as it enters stage k

tc(j,k)   temperature of cold stream j as it leaves stage k

q(i,j,k)   energy exchanged between i and j in stage k

thot(i,j,k)

tcold(i,j,k)

FLHOT(I,J,K)

FLCOLD(I,J,K)

AX(i,j,k)   ;

Equations

THOT_IN(I,K) ASIGNMENT OF HOT PROCESS STREAM INLET TEMPERATURES

TCOLD_IN(J,K) ASIGNMENT OF COLD PROCESS STREAM INLET TEMPERATURES

TOTAL_HEAT_HOT(I)   TOTAL HEAT BALANCE OF HOT PROCESS STREAM HPS(I)

TOTAL_HEAT_COLD(J) TOTAL HEAT BALANCE OF COLD PROCESS STREAM CPS(I)

STAGE_HEAT_HOT(I,K)   STAGE HEAT BALANCE OF HOT PROCESS STREAM HPS(I)

STAGE_HEAT_COLD(J,K)   STAGE HEAT BALANCE OF COLD PROCESS STREAM CPS(I)

FLOWHOT(I,K)

FLOWCOLD(J,K)

EXUNITH(i,j,k)

EXUNITC(i,j,k)

MONOT_HOT(I,K) MONOTONICITY ON TEMPERATURES - CONSTRAINT

MONOT_COLD(J,K) MONOTONICITY ON TEMPERATURES - CONSTRAINT

MONOT_HOTSUB(I,J,K)

MONOT_COLDSUB(I,J,K)

LOG_Q_HPS_CPS(I,J,K) LOGICAL CONSTRAINT ON HEAT EXCHANGED BETWEEN HPS(I) AND CPS(J)

LOG_Q_HPS_CUT(I,J,K) LOGICAL CONSTRAINT ON HEAT EXCHANGED BETWEEN HPS(I) AND CUT(J)

LOG_Q_HUT_CPS(I,J,K) LOGICAL CONSTRAINT ON HEAT EXCHANGED BETWEEN HUT(I) AND CPS(J)

LOG_DT_HPS_CPS_HS(I,J,K) LOGICAL CONSTRAINT ON HOT SIDE TMEPERATURE DIFFERENCE BETWEEN HPS(I) AND CPS(J)

LOG_DT_HPS_CPS_CS(I,J,K) LOGICAL CONSTRAINT ON COLD SIDE TMEPERATURE DIFFERENCE BETWEEN HPS(I) AND CPS(J)

LOG_DT_HPS_CUT_HS(I,J,K) LOGICAL CONSTRAINT ON HOT SIDE TMEPERATURE DIFFERENCE BETWEEN HPS(I) AND CUT(J)

LOG_DT_HPS_CUT_CS(I,J,K) LOGICAL CONSTRAINT ON COLD SIDE TMEPERATURE DIFFERENCE BETWEEN HPS(I) AND CUT(J)

LOG_DT_HUT_CPS_HS(I,J,K) LOGICAL CONSTRAINT ON HOT SIDE TMEPERATURE DIFFERENCE BETWEEN HUT(I) AND CPS(J)

LOG_DT_HUT_CPS_CS(I,J,K) LOGICAL CONSTRAINT ON COLD SIDE TMEPERATURE DIFFERENCE BETWEEN HUT(I) AND CPS(J)

AX1(i,J,k)

OBJECTIVE FUNCTION;

```
*Model equations

*=====================================================================================

*assignment of stream inlet temperatures

thot_in(i,k)$(hps(i) and temp_in_hot(i,k))..

  th(i,k) =e= hots(i,'tin');

tcold_in(j,k)$(cps(j) and temp_in_cold(j,k))..

  tc(j,k) =e= colds(j,'tin');

*=====================================================================================

*stream overall enthalpy balance

TOTAL_HEAT_HOT(I)$(HPS(I))..  HOTS(I,'F')*(HOTS(I,'TIN')-HOTS(I,'TOUT')) =E=

                         SUM((J,K)$(Arex(i,j,k)), Q(I,J,K));

TOTAL_HEAT_COLD(J)$(CPS(J)).. COLDS(J,'F')*(COLDS(J,'TOUT')-COLDS(J,'TIN')) =E=

                         SUM((I,K)$(Arex(i,j,k)), Q(I,J,K));

*=====================================================================================

*stream stage heat exchange
```

STAGE_HEAT_HOT(I,K)$(HPS(I) AND SUM(J,MATCH(I,J,K)))..

HOTS(I,'F')(TH(I,K)-TH(I,K+1)) =E= SUM(J$MATCH(I,J,K), Q(I,J,K));*

STAGE_HEAT_COLD(J,K)$(CPS(J) AND SUM(I,MATCH(I,J,K)))..

COLDS(J,'F')(TC(J,K)-TC(J,K+1)) =E= SUM(I$MATCH(I,J,K), Q(I,J,K));*

FLOWHOT(I,K)$(HPS(I) AND SUM(J,MATCH(I,J,K)))..

HOTS(I,'F')=E=SUM(J$MATCH(I,J,K), FLHOT(I,J,K));

FLOWCOLD(J,K)$(CPS(J) AND SUM(I,MATCH(I,J,K)))..

COLDS(J,'F') =E= SUM(I$MATCH(I,J,K), FLCOLD(I,J,K));

EXUNITH(i,j,k)$(HPS(I) AND MATCH(I,J,K))..

FLHOT(I,J,K)(TH(I,K)-THOT(I,J,K))=E=Q(I,J,K);*

EXUNITC(i,j,k)$(CPS(J) AND MATCH(I,J,K))..

FLCOLD(I,J,K)(TCOLD(I,J,K)-TC(J,K+1))=E=Q(I,J,K);*

*==

*Logic equations

*monotocity of temperature

MONOT_HOT(I,K)$(HPS(I) AND ST(k) AND A_HPS(I,K)).. TH(I,K) =G= TH(I,K+1);

MONOT_COLD(J,K)$(CPS(J) AND ST(k) AND A_CPS(J,K)).. TC(J,K) =G= TC(J,K+1);

MONOT_HOTSUB(I,J,K)$(HPS(I) AND ST(k) AND A_HPS(I,K)).. TH(I,K) =G= THOT(I,J,K);

MONOT_COLDSUB(I,J,K)$(CPS(J) AND ST(k) AND A_CPS(J,K)).. TCOLD(I,J,K) =G= TC(J,K+1);

LOG_Q_HPS_CPS(I,J,K)$(HPS(I) AND CPS(J) AND MATCH(I,J,K))..

Q(I,J,K) =L= MIN(HOTS(I,'F')(HOTS(I,'TIN')-HOTS(I,'TOUT')),COLDS(J,'F')*(COLDS(J,'TOUT')-COLDS(J,'TIN')))*Y(I,J,K);*

LOG_Q_HPS_CUT(I,J,K)$(HPS(I) AND CUT(J) AND MATCH(I,J,K))..

```
Q(I,J,K) =L= HOTS(I,'F')*(HOTS(I,'TIN')-HOTS(I,'TOUT'))*Y(I,J,K);

LOG_Q_HUT_CPS(I,J,K)$(HUT(I) AND CPS(J) AND MATCH(I,J,K))..

Q(I,J,K) =L= COLDS(J,'F')*(COLDS(J,'TOUT')-COLDS(J,'TIN'))*Y(I,J,K);

LOG_DT_HPS_CPS_HS(I,J,K)$(HPS(I) AND CPS(J) AND MATCH(I,J,K))..DTIN(I,J,K) =L=
TH(I,K) - TCOLD(I,J,K) + GAMMA(I,J)*(1-Y(I,J,K));

LOG_DT_HPS_CPS_CS(I,J,K)$(HPS(I) AND CPS(J) AND MATCH(I,J,K))..DTOUT(I,J,K)
=L= THOT(I,J,K) - TC(J,K+1) + GAMMA(I,J)*(1-Y(I,J,K));


LOG_DT_HPS_CUT_HS(I,J,K)$(HPS(I) AND CUT(J) AND
MATCH(I,J,K))..DTIN(I,J,K)$(HPS(I) AND CUT(J) AND MATCH(I,J,K)) =L= (TH(I,K) -
COLDS(J,'TOUT')) + GAMMA(I,J)*(1-Y(I,J,K));

LOG_DT_HPS_CUT_CS(I,J,K)$(HPS(I) AND CUT(J) AND
MATCH(I,J,K))..DTOUT(I,J,K)$(HPS(I) AND CUT(J) AND MATCH(I,J,K)) =L= (THOT(I,J,K)
- COLDS(J,'TIN')) + GAMMA(I,J)*(1-Y(I,J,K));

LOG_DT_HUT_CPS_HS(I,J,K)$(HUT(I) AND CPS(J) AND MATCH(I,J,K))..DTIN(I,J,K
)$(HUT(I) AND CPS(J) AND MATCH(I,J,K)) =L= (HOTS(I,'TIN') - TCOLD(I,J,K)) +
GAMMA(I,J)*(1-Y(I,J,K));

LOG_DT_HUT_CPS_CS(I,J,K)$(HUT(I) AND CPS(J) AND
MATCH(I,J,K))..DTOUT(I,J,K)$(HUT(I) AND CPS(J) AND MATCH(I,J,K))
=L=(HOTS(I,'TOUT') - TC(J,K+1)) + GAMMA(I,J)*(1-Y(I,J,K));

*=============================================================
============================================================
============================================================
========================

AX1(i,J,k)$(AREX(i,j,k))..

AX(i,J,k)=e= (Q(i,J,k)*(1/HOTS(i,'H')+1/COLDS(J,'H'))/

(((1e-6)**3+((DTIN(I,J,K)*DTOUT(I,J,K))**0.5)+(1/3*(DTIN(I,J,K)+

DTOUT(I,J,K))*0.5))+1E-6)+1E-6);
```

```
*=============================================================
====================================================
*OBJECTIVE
OBJECTIVE..DUMMY=E= AF*((CF*(SUM((I,J,K),Y(I,J,K))))+
*       (SUM((I,J,p,k)$(AREX(i,j,p,k)),(AX(i,J,k))))
        (AC*((SUM((I,J,k),(AX(i,J,k)))))))
        +((1/3)*SUM((I,J,K),COLDS(J,'COST')*Q(I,J,K)))
        +((1/3)*SUM((I,J,K),HOTS(I,'COST')*Q(I,J,K))) ;
*+SUM((P),(DOP(P)/NOP)* SUM((I,J,K)$(HPS(I,p) AND CUT(J,p) AND
MATCH(I,J,p,K)),COLDS(J,p,'COST')*Q(I,J,p,K)))
*       +SUM((P),(DOP(P)/NOP)*SUM((I,J,K)$(HUT(I,p) AND CPS(J,p) AND
MATCH(I,J,p,K)),HOTS(I,p,'COST')*Q(I,J,p,K)))
*AF*((CF*(SUM((JH,JC,I)$(INTERVAL(I)),NHC(JH,JC,I))))+
*AC*SUM((JH,JC,I)$(INTERVAL(I)),(Q(JH,JC,I)*(1/HOTS(JH,'H')+1/COLDS(JC,'H'))/
*((((1e-6)**3+(ATHC(JH,JC,I)*ATHC(JH,JC,I+1))*((ATHC(JH,JC,I)
*+ATHC(JH,JC,I+1))*0.5))**0.3333)+1E-6)+1E-6)**AE))
*=============================================================
======================================================
MODEL TEST /ALL/;
*$ONTEXT
*Initialisation for exchanger approach temperatures between HPS(I) AND CPS(J)
EMAT=2;
DTIN.L(I,J,K)$(HPS(I) AND CPS(J) AND MATCH(I,J,K))=HOTS(I,'TIN')-COLDS(J,'TIN') ;
DTOUT.L(I,J,K)$(HPS(I) AND CPS(J) AND MATCH(I,J,K))=HOTS(I,'TIN')-COLDS(J,'TIN');
DTIN.LO(I,J,K)$(HPS(I) AND CPS(J) AND MATCH(I,J,K))=EMAT;
```

```
DTOUT.LO(I,J,K)$(HPS(I) AND CPS(J) AND MATCH(I,J,K))=EMAT;
DTIN.UP(I,J,K)$(HPS(I) AND CPS(J) AND MATCH(I,J,K))=600;
DTOUT.UP(I,J,K)$(HPS(I) AND CPS(J) AND MATCH(I,J,K))=600;
*Initialisation for exchanger approach temperatures between HPS(I) AND CUT(J)
DTIN.L(I,J,K)$(HPS(I) AND CUT(J) AND MATCH(I,J,K))=HOTS(I,'TIN')-COLDS(J,'TIN');
DTOUT.L(I,J,K)$(HPS(I) AND CUT(J) AND MATCH(I,J,K))=HOTS(I,'TIN')-COLDS(J,'TIN');
DTIN.LO(I,J,K)$(HPS(I) AND CUT(J) AND MATCH(I,J,K))=EMAT;
DTOUT.LO(I,J,K)$(HPS(I) AND CUT(J) AND MATCH(I,J,K))=EMAT;
DTIN.UP(I,J,K)$(HPS(I) AND CUT(J) AND MATCH(I,J,K))=600;
DTOUT.UP(I,J,K)$(HPS(I) AND CUT(J) AND MATCH(I,J,K))=600;
*Initialisation for exchanger approach temperatures between HUT(I) AND CPS(J)
DTIN.L(I,J,K)$(HUT(I) AND CPS(J) AND MATCH(I,J,K))=HOTS(I,'TIN')-COLDS(J,'TIN');
DTOUT.L(I,J,K)$(HUT(I) AND CPS(J) AND MATCH(I,J,K))=HOTS(I,'TIN')-COLDS(J,'TIN');
DTIN.LO(I,J,K)$(HUT(I) AND CPS(J) AND MATCH(I,J,K))=EMAT;
DTOUT.LO(I,J,K)$(HUT(I) AND CPS(J) AND MATCH(I,J,K))=EMAT;
DTIN.UP(I,J,K)$(HUT(I) AND CPS(J) AND MATCH(I,J,K))=600;
DTOUT.UP(I,J,K)$(HUT(I) AND CPS(J) AND MATCH(I,J,K))=600;
*$OFFTEXT
FLHOT.L(I,J,K)=0;
FLHOT.LO(I,J,K)=0;
FLHOT.UP(I,J,K)= hots(i,'f');
FLCOLD.L(I,J,K)=0;
FLCOLD.LO(I,J,K)=0;
```

```
FLCOLD.UP(I,J,K)=colds(j,'f');

thot.L(i,j,k)=HOTS(I,'TIN');

thot.LO(i,j,k)=HOTS(I,'TOUT');

thot.UP(i,j,k)=HOTS(I,'TIN');

tcold.L(i,j,k)=COLDS(J,'TIN');

tcold.LO(i,j,k)=COLDS(J,'TIN');

tcold.UP(i,j,k)=COLDS(J,'TOUT');

*Initialisations for Q(I,J,K) between HPS(I) and CPS(J)

Q.L(I,J,K)$(HPS(I) AND CPS(J) AND MATCH(I,J,K))=MIN(HOTS(I,'F')*(HOTS(I,'TIN')-
HOTS(I,'TOUT')),COLDS(J,'F')*(COLDS(J,'TOUT')-COLDS(J,'TIN')));

Q.L(I,J,K)$(HPS(I) AND CUT(J) AND MATCH(I,J,K)) = HOTS(I,'F')*(HOTS(I,'TIN')-
HOTS(I,'TOUT'));

Q.L(I,J,K)$(HUT(I) AND CPS(J) AND MATCH(I,J,K))= COLDS(J,'F')*(COLDS(J,'TOUT')-
COLDS(J,'TIN'));

Q.UP(I,J,K)$(HPS(I) AND CPS(J) AND MATCH(I,J,K))=MIN(HOTS(I,'F')*(HOTS(I,'TIN')-
HOTS(I,'TOUT')),COLDS(J,'F')*(COLDS(J,'TOUT')-COLDS(J,'TIN')));

*Q.UP(I,J,P,K)$(HPS(I,P) AND CUT(J,P) AND MATCH(I,J,P,K)) = 100000;

*Q.UP(I,J,P,K)$(HUT(I,P) AND CPS(J,P) AND MATCH(I,J,P,K))= 100000;

Q.UP(I,J,K)$(HPS(I) AND CUT(J) AND MATCH(I,J,K)) = HOTS(I,'F')*(HOTS(I,'TIN')-
HOTS(I,'TOUT'));

Q.UP(I,J,K)$(HUT(I) AND CPS(J) AND MATCH(I,J,K))= COLDS(J,'F')*(COLDS(J,'TOUT')-
COLDS(J,'TIN'));

*$offtext

*Intialisations and bounds for intermediate temperatures

*$ONTEXT

TH.L(I,K)$(first(k))=HOTS(I,'TIN');
```

```
TC.L(J,K)$(last(k))=COLDS(J,'TIN');

TH.LO(I,K)$(last(k))=HOTS(I,'TOUT');

TH.UP(I,K)$(first(k))=HOTS(I,'TIN');

TC.LO(J,K)$(last(k))=COLDS(J,'TIN');

TC.UP(J,K)=COLDS(J,'TOUT');

*$OFFTEXT

test.optfile=0;

OPTION LIMROW =10;

OPTION DOMLIM =1000 ;

SOLVE TEST USING MINLP MINIMIZING DUMMY;

*$ONTEXT

SCALAR

HEAT_EXCHANGED

HOT_UTILITIES

COLD_UTILITIES

AOCCOST

AREA

Total;

HEAT_EXCHANGED= SUM((I,J,K)$(HPS(I) AND CPS(J)), Q.L(I,J,K));

HOT_UTILITIES = SUM((I,J,K)$(HUT(I) AND CPS(J)), Q.L(I,J,K));

COLD_UTILITIES = SUM((I,J,K)$(HPS(I) AND CUT(J)), Q.L(I,J,K));

AOCCOST=SUM((i,J,k),Q.L(i,J,k)*HOTS(I,'COST'))+

SUM((I,J,K),Q.L(I,J,K)*COLDS(J,'COST'));
```

```
AREA=SUM((I,J,K),(AX.L(I,J,K)));
*AREA=SUM((I,J,K),((Q.l(i,J,k)*(1/HOTS(i,'H')+1/COLDS(J,'H'))/
*(((1e-6)**3+((2/3)*(DT.l(I,J,K)*DT.l(I,J,K+1))**0.5)+(1/3*(DT.l(I,J,K)+
*DT.l(I,J,K+1))*0.5))+1E-6)+1E-6)));
*Total = AOCCOST+AREA;
DISPLAY "MATCHES:"
DISPLAY Y.L;
DISPLAY "TOTAL HEAT EXCHANGED:"
DISPLAY HEAT_EXCHANGED ;
DISPLAY "TOTAL HOT UTILITY CONSUMPTION:"
DISPLAY HOT_UTILITIES;
DISPLAY "TOTAL HOT UTILITY CONSUMPTION:"
DISPLAY COLD_UTILITIES;
DISPLAY "Annual operating cost:"
DISPLAY AOCCOST;
*DISPLAY "AREA"
*DISPLAY AREA;
*DISPLAY "Total"
*DISPLAY Total;
*$OFFTEXT
```

GAMS PROGRAM FOR CO_2 TRANSPORT (Chapter 7)

```
$Title  A Transportation of captured CO2.

$Ontext

This problem investigates the least cost of transporting captured CO2 from the power
plant to storage sites.

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$Offtext

 Sets

     i   power-plant   / grootveli /

     j   storage-sites   / freestate, easterncape, northerncape, kwazulunatal / ;

 Parameters

     a(i)  capacity of plant(MW) i in cases

       /    grootvlei     1180/

     b(j)  distance (km) of plant to storage sites j in cases

       /    free-state      610

            northern-cape 1076

            eastern-cape  1135

            kwazulu-natal  467        / ;

 Table d(i,j)  distance in kilometers

                   free-state   northern-cape   eastern-cape  kwazulu-natal

    mpumalanga        610          1076          1135           467

    orange-basin     45               75            96           402

    karoo-basin       570          480           780             35
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;

  Scalar f  freight in dollars per case per kilometres/90/ ;

  Parameter

c(i,j)  transport cost in thousands of dollars per case ;

           c(i,j) = f * d(i,j) / 1000 ;

  Variables

      x(i,j)  shipment quantities in cases

      z       total transportation costs in thousands of dollars ;

  Positive Variable x ;

  Equations

      cost        define objective function

      cost ..        z  =e=  sum((i,j), c(i,j)*x(i,j)) ;

  Model transport /all/ ;

  Solve transport using lp minimizing z ;

  Display x.l, x.m ;
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