Cape Peninsula University of Technology

An integrated pinch analysis framework for the development of a low carbon dioxide emissions industrial site planning which includes a fuel cell configuration

by

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DECLARATION

I, Joe Mammen John, declare that the contents of this dissertation/thesis represent my own unaided work, and that the dissertation/thesis has not previously been submitted for academic examination towards any qualification. Furthermore, it represents my own opinions and not necessarily those of the Cape Peninsula University of Technology.

Signed **Date** **08/02/2023**

ABSTRACT

The proliferation of anthropogenic greenhouse gases, of which carbon dioxide is a major constituent, has been the major driver of climate change. South Africa is one of the highest greenhouse gas emitting countries mainly caused by increased industrialisation. Industrial sites in South Africa have been clustered in industrial zones to keep toxic emissions away from residential sites. This zonal planning inadvertently created zones of high carbon dioxide concentration. The South African government has committed to sustaining the national greenhouse gas emissions at a reasonably moderate value of below the 398-440 million tonnes of CO_2 equivalent by 2030 as its contribution to lowering the global carbon dioxide emissions. To control the emissions emanating from industrial zones, industrial planners make use of an evaluation framework that accounts for the carbon footprint associated with a particular industrial zone. The existing framework focuses on greenfield sites (new planning sites), and is thus ill-adapted to brownfield sites (existing sites). This study proposes a four-stage carbon dioxide lowering framework that industrial site managers of brown-field sites could use to lower the carbon dioxide footprint of industrial sites. This work extends the current systematic framework for low carbon dioxide industrial site planning framework for a greenfield site, by proposing an alternative carbon dioxide-lowering sequential framework for a brownfield site.

The framework includes: 1. A baseline study to analyse the current carbon dioxide footprint of an industrial site. 2. A carbon capture and utilisation step to collate the carbon dioxide captured for chemical mineralisation for in-situ utilisation. The inclusion of the direct methanol fuel cell configuration is important to the site because it generates clean carbon-neutral power for the hybrid power system while utilising methanol, a carbon dioxide mineralised product. 3. The Total Sites Heat Integration technique to integrate the energy produced in the site could be integrated to reduce external utilities required. 4. The Power Pinch Analysis technique to optimise power distribution from the hybrid power system hub.

The study also proposes the option of introducing a subsidiary industry that includes carbon dioxide mineralisation plants to chemically store the captured carbon dioxide. This is because, in water-stressed South Africa, the viability of the geological storage of carbon dioxide has not been considered because of the high probability of contamination of the large water basin that is used to supplement the surface water resource. The challenge can be overcome by increasing the value of carbon dioxide emissions by creating subsidiary

industries that can utilise carbon dioxide as raw material and producing other value-added products that can be utilised within the industrial site.

This study used an illustrative example to extend the current systematic framework for low carbon dioxide industrial site planning framework used for greenfield site, by introducing an alternative four-stage carbon dioxide-lowering sequential framework for a brownfield site. it was determined that there are three possible opportunities to capture carbon dioxide from stationary. The baseline study included scoping for thermal data, which included the target temperature, supply temperature and specific heat capacity of the streams. The data scoped by the site planner also include the power required and possible power that could be generated within the site.

The study conducted a techno-economic investigation of the feasibility of including subsidiary plants producing methanol, calcium carbonate and baking soda from the carbon dioxide captured from the flue gas in the industrial site. This study included the cost of capturing carbon dioxide from selected plants within the industrial site and determined the operating and capital cost required using a bottom-up approach from mass balances. It was determined that a potential 105 ton/day of carbon dioxide could be captured from the flue gas from industries on the site. The cost of producing methanol and calcium carbonate would only be sustainable if the price of raw materials such as hydrogen and wollastonite could be brought down by producing hydrogen through solar-chemical water splitting and the wollastonite from steelmaking slag. Baking production was determined to be the most sustainable subsidiary industry in the carbon capture and utilisation framework with an annual rate of return on investment of 12%.

The Total Site Heat Integration was applied for the evaluation, generation, optimisation and usage of energy within the industrial site. it was determined that heat utility saving of 79.95% for the participating industries could be achieved for the industrial site. However, the rate of return is for the Total site Heat integration (TSHI) was a low return of 8.98%. But, since the main aim of the project is to reduce the carbon footprint and this rate of return could be improved by the carbon tax rebate incentives for the carbon dioxide reduction project

It was determined that solar and biomass energy were the two viable renewable sources of power that could be used for the illustrative example. The inclusion of a direct methanol fuel

cell configuration to the renewable energy mix was important to the site because it generated clean carbon-neutral power for the hybrid power system while utilising methanol produced by the subsidiary industry. Power Pinch Analysis was applied for the distribution of the Hybrid Power System to the existing plant, and to the new subsidiary industry. It was also determined that the renewable sources of power which incorporated the fuel cell configuration would be sufficient to provide carbon-neutral power to the industrial site. The rate of return on the investment of the hybrid power system was found to be 20.68 %. The carbon dioxide-lowering framework for existing industrial sites could provide a sustainable, impactful guide for site planners to assist the country's commitment to limit greenhouse gas emissions.

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DEDICATION

I want to dedicate this Doctoral thesis to my family, who patiently prayed and supported me during the research journey.

To my wife Manju Ansy John and son Nathan Joe John for always loving, inspiring and pushing me to improve.

To my Parents, Oommathumkattil Mammen John and Sally Elizabeth John for your love, prayers and encouragement.

PREFACE

- Chapter 1 includes a brief introduction and background to process integration. It provides the rationale and motivation for doing this project and provides information with regards to the proposed pinch analysis framework for lowering the CO_2 framework in an existing industrial site.
- Chapter 2 is a literature review relating to CO_2 reduction tools, the total site heat integration, power pinch analysis and CO_2 capture utilisation and storage.
- Chapter 3 is a materials and methods chapter which includes a systematic approach for an integrated pinch analysis framework to change a high carbon dioxide-emitting industrial site to a lower-impact carbon dioxide emissions site with the inclusion of a fuel cell configuration. A cost analysis methodology of CO_2 capture and utilisation with the inclusion of a fuel cell configuration is also presented, as are the methodology of the graphic and numerical representation of the Total Site Heat Integration (TSHI) tool set. Further, the methodology of the cost analysis of the proposed TSHI is described, together with the methodology of the numerical methods for the Power Pinch Analysis (PoPA) tools for the optimised use and distribution of renewable energy (RE) power for the Hybrid Power System (HyPS) to the existing plant, and to the new subsidiary industry. Finally, a methodology on the cost analysis of the proposed HyPS is also presented.
- Chapter 4 is a results and discussion chapter that presents the potential CO_2 lowering framework for an existing site, the cost analysis of the CO_2 capture and utilisation with the inclusion of a fuel cell configuration. These results and discussion will detail how the proposed integrated pinch analysis framework is applied to a high carbon dioxide-emitting industrial site to a lower-impact carbon dioxide emissions site with the inclusion of a fuel cell configuration. A cost analysis of the CO_2 capture and utilisation with the inclusion of a fuel cell configuration is also discussed, together with the results of the numerical representation of the TSHI toolset. A cost analysis of the proposed TSHI of the illustrative example is given. The results are presented of the numerical methods for the PoPA tools for the optimised use and distribution of RE power for the HyPS to the existing plant, and the new subsidiary industry. A cost analysis of the proposed HyPS is also presented, and the sensitivity of multi-sensitivity analysis to

determine the robustness of the TSHI system and HyPS for the framework is explained.

- Chapter 5 provides the conclusions drawn for the study, based on the proposed objectives, and includes recommendations for future studies.

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LIST OF ABBREVIATIONS

AC	-	Alternating current
AEEND	-	Available Excess Electricity for Next Day
BFW	-	Boiler Feedwater
CC	-	Composite Curves
CCS	-	Carbon Capture Storage
CCU	-	Carbon Capture and Utilisation
CCUS	-	Carbon Capture Utilisation and Storage
CEPA	-	Carbon Emission Pinch Analysis
CHP	-	Combined Heat and Power
CMH	-	Carbon Management Hierarchy
CPA	-	Carbon Pinch Analysis
CPCC	-	Continuous Power Composite Curves
CSCA	-	Carbon Storage Cascade Analysis
CW	-	Cooling Water
DC	-	Direct Current
DMFC	-	Direct Methanol Fuel Cell
FiT	-	Feed in Tarif
GCC	-	Grand Composite Curve
GHGs	-	Greenhouse Gases
HEN	-	Heat Exchanger Network
HI	-	Heat Integration
HPS	-	High Pressure Steam
HyPS	-	Hybrid Power System
IEA	-	International Energy Agency
LIES	-	Locally Integrated Energy Sector
LPS	-	Low Pressure Steam
MEA	-	Membrane electrode assemblies
MER		Maximum Energy Recovery
MHA	-	Maximum Heat Allocation
MILP	-	Mixed Integer Linear Programming
MINLP	-	Mixed Integer Non-Linear Programming
MOES	-	Minimum Outsourced Electricity Supply
MP	-	Mathematical Programming
MPS	-	Medium Pressure Steam
PA	-	Pinch Analysis
PCC	-	Power Composite Curves

PCT	-	Power Cascade Table
PEMFC	-	Proton Membrane Fuel Cell
PFSA	-	Perfluorosulfonic Acid
PI	-	Process Integration
PoCA	-	Power Cascade Analysis
PoPA	-	Power Pinch Analysis
PTA	-	Problem Table Algorithm
RE	-	Renewable Energy
SCC	-	Site Composite Curves
SCT	-	Storage Cascade Table
SDC	-	Source and Demand Curves
SGCC	-	Site Level Grand Composite Curve
SSSP	-	Site Source Sink Profiles
SUGCC	-	Site Utility Grand Composite Curves
TSHI	-	Total Site Heat Integration
TSP	-	Total Site Profiles
TSPTA	-	Total Site Problem Table Algorithm
TSST	-	Total Site Sensitivity Table
TSUD	-	Total Site Utility Distribution
UGCC	-	Utility Grand Composite Curve
VHPS	-	Very High-Pressure Steam
WtE	-	Waste to Energy

OUTPUTS FROM THIS STUDY

Publications

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CHAPTER ONE

INTRODUCTION

1.1 Background

The Glasgow Climate Pact, an agreement reached at the 2021 United Nations Climate Change Conference (COP26), declared that limiting global warming required rapid, deep and sustained reductions in global greenhouse gas emissions. This included reducing the global carbon dioxide (CO_2) emissions by 45% by 2030 relative to the 2010 level (UNFCCC, 2021). The importance of lowering the carbon dioxide footprint of a high emitting industrial site through devolution of CO_2 processes and the introduction of cleaner production has become important in the retardation of the greenhouse effect. South Africa ranks thirteenth largest carbon dioxide emitter in the world with an annual CO_2 emission of 435 $MtCO_2$ in 2020 (worldpopulationreview.com, 2023). The South African government has committed to sustaining national greenhouse gas emissions to below the 398-440 million tonnes of CO_2 equivalent by 2030 (Modise, 2021). The adverse effects of climate change due to the global increase in greenhouse gases has resulted in an increase in ocean levels, hotter summers, colder winters, and other natural disasters, as reported in the Intergovernmental Panel on Climate Change report (IPCC, 2018). Maintaining the global average temperature to under 2°C above pre-industrial levels and ensuring that the temperature increase is kept to within 1.5°C above pre-industrial levels has become essential in avoiding permanent climate change. The

The depletion of fossil fuel reserves and the impact of carbon dioxide emissions are the key reasons for finding alternative methods for a sustainable fossil fuel-free energy system (Polley et al., 1990; Rozali et al., 2018). In South Africa, industries are clustered together to form industrial areas. These industrial areas present ideal opportunities for integrating waste energy and sustainable renewable energy such as wind, solar and biomass by installing a hybrid energy central hub to meet some of the energy requirements of these industrial areas. Carbon dioxide capture from industrial emissions has also become a worldwide priority because of the adverse impact on global warming of greenhouse gases such as carbon dioxide emissions (Gibbins & Chalmers, 2008).

Pinch analysis (PA), as described by Linnhoff, (1979), was initially used for energy targeting and conservation and heat exchanger network design. John and Rabiu (2013) applied the energy targeting technique to a petroleum plant to realise a potential 34% energy saving. Pinch analysis has also seen practical applications in mass recovery (El-Halwagi & Manousiouthakis, 1990), supply chain planning (Singhvi & Shenoy, 2002), water recovery (Wang & Smith, 1994), hydrogen recovery (Alves & Towler, 2002), renewable and traditional power usage and recovery (Wan Alwi et al., 2012), and waste management (Ho et al., 2017). Singh and Leena (2019) used linear pinch analysis (LPA) to target the reduction of greenhouse gases (GHG) in the development of a sustainable municipal solid waste management system. Bandyopadhyay (2020) introduced economic pinch analysis (EPA) for an economic appraisal of project sustainability. Chin et al. (2021) applied pinch analysis to target multiple contaminant water recycling/reuse networks by assigning separate plots and analysing them sequentially to meet the sink requirements. The development of a hybrid power hub, which sources power from sustainable renewable sources in conjunction with the mainstream national power grid, has gained increased popularity in recent times. Pinch analysis, as shown by Rozali et al. (2016), has been used to integrate a hybrid power system into an existing diesel plant to effectively manage electricity demands.

Carbon capture has in recent times come to the fore as a significant route to reducing the amount of carbon and carbon dioxide emissions from coal- and petroleum-derived fuels. The global warming phenomenon has been widely attributed to the greenhouse gases and carbon dioxide proliferation from industry. It is therefore important to recapture and store, and where possible, utilise the carbon dioxide for processes that require carbon dioxide (Cuéllar-Franca & Azapagic, 2015). One of the main consumers of carbon dioxide could be the food industry.

Fuel cells, such as high temperature polymer electrolyte membrane fuel cells (PEMFC) and direct methanol fuel cells, have in recent times found favour with small office and domestic customers due to their low emission and high efficiency technology (Radenahmad et al., 2016). The heat emitted from this process could be integrated into the total site heat integration system. The captured carbon dioxide emitted from fuel cells and captured from stack gas, according to Kiatphuengporn et al. (2017), could be used to produce methanol - the fuel required to run fuel cells.

1.2 Problem statement

Carbon dioxide emissions have become an omnipotent force in the global warming phenomena that is adversely affecting climate change today (Zhou & Wang, 2016). Burning of coal causes the proliferation of carbon dioxide, making South Africa one of the main contributors of greenhouse gases globally. The current drought that is experienced in South Africa has been directly attributed to the global warming phenomenon (Amjath-Babu et al., 2016). According to Eskom (2017), 77% of South Africa's electricity demand is produced by coal with oil and gas contributing 5% of the electricity generation mix. This results in 232 TWh of electricity from coal, producing 438 million tonnes CO_2 emissions and making the country the largest emitter of CO_2 in Africa (Jain & Jain, 2017).

Electricity is a significant driver of South Africa's economic growth. The erratic supply of electricity and the high annual increase in electricity tariffs in South Africa since 2008 have had detrimental effects on the economy (Inglesi-Lotz and Ajmi, 2021). The unpredictable rolling blackouts have caused severe losses due to disrupted production, including reagent/product spoilage due to mid-process stoppages. The disruptions have also negatively affected the amount and quality of value-added products. Industries in South Africa, according to Davies and Van der Merwe (2016) use 47% of the energy produced by Eskom, making this sector the largest consumer of electricity in the country. The authors further claim that many of the industries need to utilise energy more efficiently to be sustainable, and to help mitigate the load shedding that has affected South Africa for over a decade. The locality of industries in clusters in South Africa has presented ideal opportunities for total site heat integration harvesting and energy redistribution.

Hybrid renewable energy systems, as presented by Esfahani et al. (2016), could bring a reliable alternative power source to meet the power demands of a selected site. The pinch analysis technique (Rozali et al., 2013) has previously been used to distribute the optimum power allocation of a renewable energy sources to a site. It is proposed that the pinch application could be extended to incorporating the use of fuel cells. South Africa has huge potential for capturing solar and wind energy (Pegels, 2010; Winkler, 2005), because of favourable sunlight and wind conditions that exist in the sub-Saharan region. Fluri (2009) claimed that a nominal potential 10.5GW of solar energy in the Western Cape Province in South Africa could be extracted for use. However, due to their dependency on ideal climatic conditions for solar and wind energy to produce consistent energy, it is important to set realistic targets for these intermittent power sources.

In order to mitigate the effects of carbon dioxide, Yang et al. (2008) suggests three options for the reduction of carbon dioxide:

1. Efficient energy usage;
2. Switching from fossil fuels to renewable and hydrogen fuels; and
3. Developing technologies that capture and sequestrate the carbon dioxide.

Once the carbon dioxide is captured and stored, Mohd Nawi et al. (2016) showed that pinch analysis could be used to redistribute carbon dioxide to different customers depending on its purity. It is hence important to identify industries at a site that require carbon dioxide for usage.

Fuel cells have few viable applications for domestic and industrial use. The Hydrogen South Africa (HySA) programme, supported by the Department of Science and Technology and approved by the South African Parliament, was set up to develop indigenous hydrogen and fuel cell technology (Pollet, 2013). In the current study, the use of a fuel cell configuration for supplementing hybrid power and the main grid power supply will be investigated.

Pollet et al. (2015) reported that the constant underinvestment, mismanagement and human capacity constraints faced by Eskom have severely affected its ability to provide power consistently, leading to chronic and increasingly severe load shedding. This has severely affected industrial productivity, leading to the need for industrial sites to produce their own hybrid energy to mitigate the electricity shortages. There are currently no reported energy integration initiatives taking place at industrial sites in South Africa. There have, however, been a few feasibility studies reported with regard to individual plants. For example, Pachón et al. (2018) considered the feasibility of transitioning a sugar mill into a biorefinery by including heat integration and electricity production from the discarded lignocellulose waste. In 2021, the South African government announced that industries would be permitted to produce up to 100 MW of power to avoid the consequences of load shedding and improve economic growth by raising the licence-exemption cap for embedded generation projects from 1 MW to 100 MW (Creamer, 2021).

The problem statement is as follows:

> Taking into consideration a cluster of various plants in a high CO_2 footprint industrial site, this study aims to develop a comprehensive CO_2 reduction framework by applying distribution and pinch analysis tools such as Total Site Heat Integration (TSHI) and Power Pinch Analysis (PoPA) to an existing industrial site with the inclusion of a fuel cell configuration. This study also aims to establish the robustness and sustainability of cleaner production interventions, namely a TSHI system and a hybrid power system (HyPS).

1.3 Research objectives

The main objective of this research is to advance an integrated pinch analysis framework for the development of a low carbon dioxide emissions industrial site that includes a fuel cell configuration. In support of the main objective, the following sub-objectives are identified:

1. To set up and utilise a sequential 4 step framework that will consider:
    a. A baseline study to establish the current CO_2 footprint of the industrial site;
    b. CO_2 capture, purification, ratio distribution, CO_2 chemical fixation and usage;
    c. TSHI and total site utility distribution; and
    d. The introduction of renewable sources of power and fuel cell configuration to an integrated HyPS, as well as the use of PoPA for the optimum distribution of power to the industries in the site.
2. To conduct a sensitivity analysis of the TSHI and HyPS to evaluate its robustness.
3. To conduct an economic viability study to ascertain the feasibility of a third party running the following:
    a. CO_2 capture and purification system;
    b. A single high purity CO_2 distribution hub;
    c. A subsidiary industry consisting of CO_2 mineralisation plants;
    d. A fuel cell configuration fed by methanol produced from a of CO_2 mineralisation plant;
    e. A total site heat integration system that has a centralised cooling and heating utility hub;
    f. A hybrid power system that incorporates RE power sources, the direct methanol fuel cell (DMFC) configuration and national grid electricity.

From this study, it is expected that a comprehensive CO_2 lowering framework applied to a typical industrial site can be developed in a sustainable and compressive way and that can be replicated similarly to other high-emitting industrial sites.

1.4 Scope of the research

The scope of this study includes:

1. A state-of-the-art review of the application and development of pinch analysis in relation to HyPS, TSHI and carbon capture utilisation and storage (CCUS) systems to identify the research gaps.
2. Development of a ratio distribution approach of the captured and purified CO_2 for low carbon dioxide emission industrial site planning.
3. The development of a suitable CO_2 mineralisation plant for a subsidiary industry for the use of the captured CO_2 and the production of value-added products for use within the plant and the envisaged DMFC configuration.
4. The application of existing pinch analysis techniques to maximize the usage and distribution of energy and power within the industrial site, taking into consideration the CO_2 capture and distribution units, the subsidiary industry and the fuel cell configuration. The system will include consideration of a hybrid power system, centralized steam system, cooling water header, carbon dioxide header, fuel cell configuration and power storage.
5. An economic analysis of the integrated system taking into consideration:
   a) The capital and operating costs of running the hybrid power system, considering the parking lot roof area for solar energy, and the management of a biomass system and battery storage capacity.
   b) The capital cost and operating costs of fuel cells: the methanol costs, the running and maintenance of the membrane, the cathode and the anode.
   c) Capital costs and costs of operating of the heat and power storage, lines, piping and pumps required for the utility headers.
   d) The heating and cooling requirements of the selected industries.
6. A cost analysis to approximate viability for the third party running the CCU, TSHI and HyPS system. The analysis should also include a fuel cell configuration and subsidiary industry.
7. Calculation of the rate of return on investment of the TSHI system and HyPS.
8. A sensitivity analysis on the integrated system taking into consideration:
   a) The effect of plant shutdown and erratic plant operating conditions (upsets) on the overall integrated system.
   b) The effect of the shutdowns of the solar and biomass power on the overall integrated system.

1.5 Significance of the study

This study will present a novel approach that could be used by brownfield site managers to develop and sustain a low CO_2-emitting industrial site. The study will introduce a *four-step framework* that can be used to reduce the CO_2 in an industrial site, by introducing a post CO_2 capture system to capture and purify the CO_2. The framework will also inform the industrial site of appropriate CO_2 fixing processes that could produce products that could be used within the industrial site. The framework utilises pinch analysis to optimise the heat integration as well as the use of renewable sources of power in the industrial site.

The reduction of CO_2 in a brownfield site could assist in South African government's goal of reducing the emissions below the 398-440 million tonnes of CO_2 equivalent threshold by 2030. Further, the reduction of CO_2 is essential in preventing the existential threat to humanity arising from climate change.

This study will also provide a useful insight into how to conduct a techno-economic analysis of a low CO_2-emitting industrial site. This will be done by taking into account the following factors:

1. The cost of CO_2 capture: by considering purification techniques and distribution.
2. The capital and operating cost of the selected CO_2 fixing plants.
3. The sale of the CO_2 fixed products within the brownfield site.

1.6 Delineation

The study will use a case study to illustrate how steps could be followed to achieve a lower CO_2 footprint of a brownfield site. The case study will be limited to an industrial site that includes the following industries:

1. Wastewater treatment plant
2. Paper recycling plant
3. Glass manufacturing plant
4. Industrial bakery
5. Steel processing plant.

The resources that are studied for symbiosis will be limited to:

1. Energy
2. Power
3. Carbon dioxide

The CO_2 mineralisation plants that will be considered for the study are:

1. Baking soda production plant.
2. Calcium carbonate production plant.
3. Methanol production plant.

The following assumptions were made for this work:

- The captured flue gas after purification is 90% CO_2 concentration.
- The co-generation potential will not be considered for the HyPS.
- The pressure drop will not be considered for the TSHI.
- The hot and cold utilities will be provided from a centralised utility.
- The renewable sources of energy will be assumed to be consistent average solar and biomass power for the time interval suggested for the case study.
- There is sufficient space in the site for the CCU system, the TSHI system and HyPS, including the centralised hub for the management of the capture, purification and utilisation of the CO_2.
- There should be space in the site for the management of the distribution of the hot and cold utilities for the TSHI system, power storage, inverter, rectifier and fuel cell configuration were available at the existing sites.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

Climate change has been primarily caused by the proliferation of greenhouse gases. The dire effects of global warming, as articulated by the Intergovernmental Panel on Climate Change (IPCC) report, could lead to rising ocean levels, colder winters, hotter summers, frequent droughts, and other natural disasters (IPCC, 2018). According to the report, it is imperative to keep the rise in global average temperature to under 2°C above pre-industrial levels while limiting the temperature increase to 1.5°C above pre-industrial levels to avoid irreversible calamities on the planet and its population. The concentration of carbon dioxide (CO_2) in the atmosphere reached a record high of 415 parts per million in 2019 for the first time. According to the National Oceanic and Atmospheric Administration (NOAA) Earth System Research Laboratory (2005), the world must keep CO_2 emissions below 350 ppm to avoid dangerous levels of climate change. A drastic reduction of greenhouse gases (GHG), of which anthropogenic CO_2 is a major constituent, is vital to achieving these temperature goals.

The most cost effective means of decarbonisation in an industrial site is to employ carbon capture and storage (CCS) technology to capture CO_2 from stationary CO_2-emitting sources. According to Zhang & Huisingh (2017), there are two main avenues to store captured CO_2 permanantly:

1. Geological storage and
2. CO_2 mineralisation.

Due to the thermodynamic stability of these chemically fixed CO_2 products, the carbon capture and storage by mineralisation (CCSM) technique, according to Wang & Maroto-Valer (2013), offers a non-monitoring and leakage-free CO_2 storage option. The main barrier to mass scale-up mineralisation remains the costs associated with CO_2 mineralisation. Industrial utilisation schemes, using the chemicals produced from CO_2 mineralisation, are essential in keeping the mineral storage of CO_2 more cost-effective.

2.2 Process integration

Process integration using the pinch technology, introduced by Linnhoff (1979), initially used heat recovery pinch for the optimization of thermal energy using heat exchanger networks (HENs) based on the laws of thermodynamics. The pinch point based on the context of heat recovery represents the closest approach point between hot and cold stream composite curves and is a bottleneck of practical heat energy recovery. The idea is to match existing heat sources within the plant with the appropriate heat sinks to maximize energy recovery so as to minimise the use of external utilities. There are two main methodologies (Klemeš et al., 2018) to present a pinch bottleneck:

1. A graphical representation using variants of the composite and grand composite curve; and
2. Numerical methods using variants of a problem table algorithm and heat cascades.

2.3 Total site energy integration

The term "total site", first coined by Dhole & Linnhoff (1993), refers to a centralized utility hub that services the energy requirements of the industrial site by integrating processes from different factories. The authors proposed a two-stage system using the pinch technology approach. Firstly, site-wide targets are set based on pressures levels of the process stream and secondly, designing a total site system based on the site targets. Klemeš et al. (1997) further optimized the targeting and design methodology of the streams involved in the total site integration (TSI) and gained improved energy savings.

Total sites targeting methodologies used a single ΔT_{min} for all processes in a total site study. Varbanov et al. (2012) asserted that such an assumption was too simplistic and could lead to unrealistic estimation of the overall total site heat recovery targets. The authors proposed a methodology that allows separate ΔT_{min} specifications for heat exchange between *process and process* and also *process and utilities*. The method the authors proposed, which includes the total sites profile (TSP), is concisely captured in Figure 2.1 below.

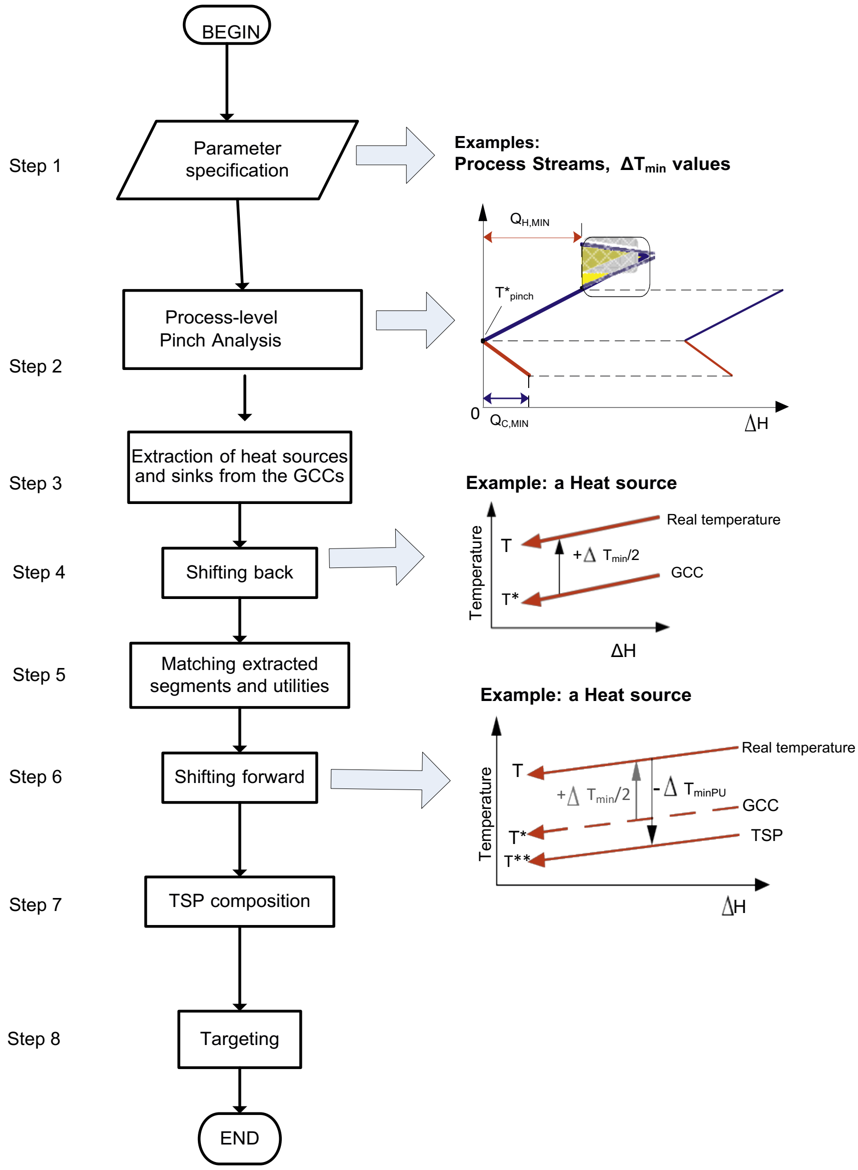

Figure 2.1: Modified total site targeting procedure, incorporating the TSP construction algorithm, adapted from Varbanov et al. (2012)

Tarighaleslami et al. (2017) further claimed that their recently developed unified total site heat integration targeting method (UTST) would calculate better TSHI targets for sites involving isothermal (e.g. steam) and non-isothermal (e.g. hot water) utilities than the method proposed by Varbanov et al. (2012). This new targeting method uses total site utility targets which are calculated by adding all the process level utility targets rather than the total site profile-based targeting method that uses heat deficits/surpluses to set total site targets. Bandyopadhyay et al., (2010) claimed that removing pockets from the grand composite curves may not be beneficial, the authors proposed a procedure where the pockets are not removed but intersecting regions of different segments is identified and eliminated because of insufficient temperature driving force for inter-process heat integration. The site level grand composite curve (SGCC) is generated using the different pseudo streams created from the shifted and modified GCC generated from eliminating intersecting portions of two GCC of different processes.

The concept of total site integration has gained traction in combined heat and power (CHP) systems, which uses heating and cooling from site sources and when necessary, utilities from the central hub. Power from various renewable energy sources such as biomass, solar cell and wind are stored at the central hub for the total site power utilisation supplementing electricity from the national grid (Perry & Bulatov, 2008).

Liew et al. (2012) advanced four new contributions (Figure 2.2) to the total site heat integration field, namely the total site problem table algorithm.

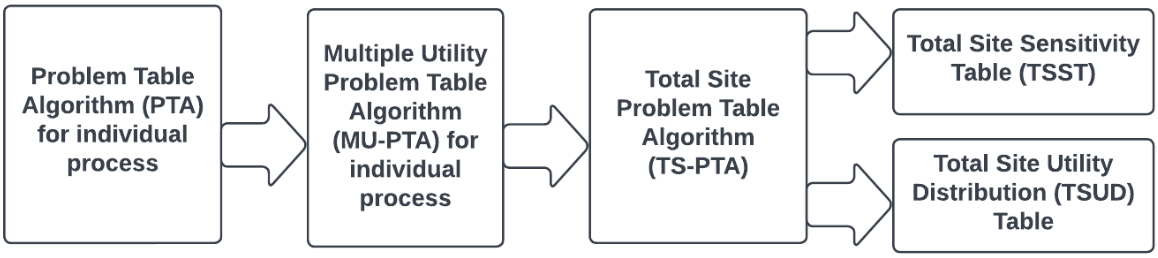

Figure 2.2: Hierarchy of total site analysis, adapted from Liew et al. (2012)

The first step, as described by Liew et al. (2012), is the multiple utility problem table algorithm (MU-PTA) that follows the principles of the PTA designed originally by Linnhoff and Flower in 1978. The procedure for dealing with above and below the pinch region is elaborated to determine the type of utilities for each temperature interval. The second step, the total site problem table algorithm (TS-PTA) is a continuation of the PTA table with a four-column methodology to balance heating and cooling deficits of the TS. The third tool, the total site utility distribution (TSUD) table is constructed using heat sources and sinks from each site, with arrows indicating possible utility exchanges between sites. Finally, the total sites sensitivity table (TSST) is used for analysing the effects of plant operating variations such as shutdowns on the total site.

The effects of pressure drop in pinch technology have gained importance because of the distances that cold and hot streams travel. Neglecting pressure drop, as elucidated by Polley et al. (1990), can lead to some very expensive mistakes, making the project unviable. The authors suggested in their paper that incorporating the pressure drop factor for each individual stream to the area-energy graph could indicate the cost benefit of pump placement or replacement with regards to the capital cost. Chew et al. (2015) expanded the effect of pressure drop on total site heat integration by including the pressure drop factor during the Maximum Energy Recovery (MER) targeting stage of the graphical pinch-based TSHI methodology. They claimed that by including the pressure drop factor in the TSHI, a better estimation of the MER targets could be achieved. The mathematical programming-based methodologies, whilst providing adequate MER targeting buffers due to pressure drop, fail to give sufficient design insights for TSHI projects. The methodology that incorporates the pressure drop can be summarised as shown in the algorithm in Figure 2.3 below.

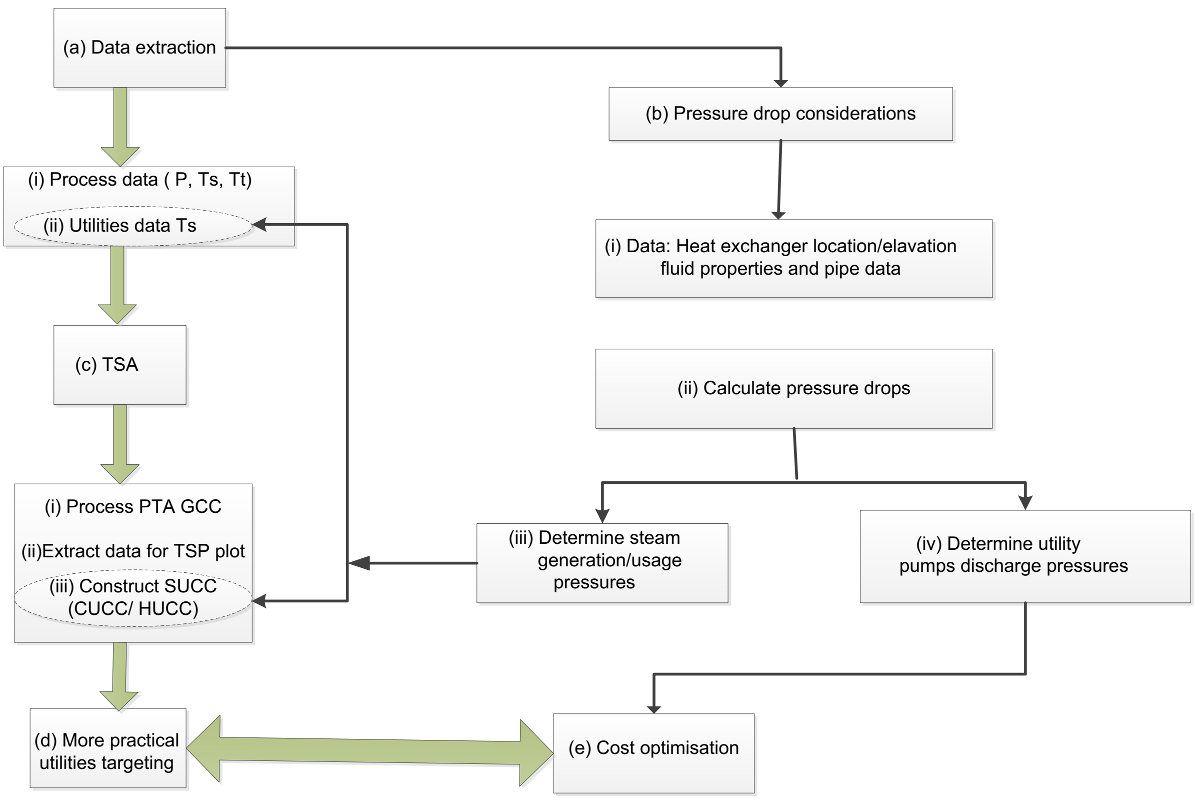

Figure 2.3: Algorithm to consider pressure drops in TSHI, adapted from Chew et al. (2015)

Jamaluddin et al. (2019) extended TSHI to a trigeneration system by introducing a new method, trigeneration system cascade analysis (TriGenSCA), to estimate the optimum size of utilities for generating power, heating and cooling by a trigeneration power plant. Varbanov et al. (2017) explored the integration of wastewater with the aim of reducing the fresh water usage in a total site scenario by introducing the total site centralised water integration (TS-CWI) tool. Fan et al. (2021) extended pinch analysis to a circular economy in a total site context by integrating solid waste, water and energy to achieve symbiosis by implementing a total ecosite integration (TESI) design. The integration of waste hydrogen of differing concentrations using pinch analysis for a total site using principles of circular economy, as described by Gai et al. (2021), turns waste hydrogen into valuable products.

2.4 Power pinch analysis

Electricity is one of the most important resources needed for industries to operate successfully. In South Africa, as recently as 2015, intermittent and erratic electric power supply disrupted industrial production and development, thus eroding investor confidence. Due to the advances of renewable energy (RE) sources such as solar and wind (Wan Alwi et al., 2012), it has become more attractive to create a central hub that incorporates renewable, sustainable and the national grid electricity sources for an industrial site. This central hub which incorporates renewable energy sources along with reliable national power sources is referred to as a hybrid power generation system (HyPS) (Zhou et al., 2009). Power pinch analysis (PoPA) can be applied to this HyPS to establish the minimum outsourced electricity targets from the national grid. RE power sources may be intermittent due to the nature of the energy source (Wan Alwi et al., 2012). This implies that solar power sources will be dependent on the quality and availability of sunshine, while wind power sources will be dependent on the speed and quality of the prevailing winds. It is therefore necessary to supplement a sustainable RE source with a more reliable national grid electricity source.

PoPA, using the new power cascade analysis (PoCA) and storage cascade table (SCT) numerical tools, was introduced by Rozali et al. (2013). These tools can be used to determine:

1. The minimum (target for) outsourced electricity supply (MOES);
2. The excess electricity for storage during start-up and normal operations;
3. The transferrable power;
4. The maximum storage capacity;
5. The outsourced electricity needed at each time interval; and
6. The time interval where the maximum power demand occurs.

Furthermore, Rozali et al. (2013) studied various scenarios to find the optimal size of generators of RE in an HPS using PoPA in order to find the lowest payback period. Esfahani et al. (2015) further introduced extended power pinch analysis (EPoPA) as an extension to the existing PoPA by storing wasted electricity that cannot be stored in the existing batteries. In this approach, the energy is stored in the form of hydrogen and released back as electricity. EPoPA was used to design renewable energy systems incorporating both battery and hydrogen storage (RES-BH). Rozali et al. (2014) expanded PoPA to allocate the optimum power allocation of the renewable energy sources to the site. They also applied PoPA to integrate a HyPS into an existing diesel plant to effectively manage electricity demand (Rozali et al., 2016).

The approach of integrating heat and carbon dioxide from an industrial park, as shown by Hassiba et al. (2017), uses the surplus energy to power the carbon dioxide compression and capture process. The proposed method has 3 steps:

1. Energy integration throughout the industrial park;
2. Carbon dioxide integration throughout the industrial park;
3. Utilising excess energy from Step 1 to improve carbon dioxide integration.

Wienchol et al. (2020) described a waste incineration plant at the Twence waste incineration plant in the Netherlands that was used for the production of electricity and thermal energy whilst capturing CO_2. The CO_2 was captured by scrubbing the flue gas with sodium carbonate to produce a sodium bicarbonate slurry that can be transported to CO_2 end-users.

2.5 CO_2 emission reduction analysis through capture, distribution and storage

CO_2 emission reduction techniques through process integration, capture, and storage are discussed in the subsections below.

2.5.1 CO_2 emission Pinch Analysis tools

Process integration methodologies, to exploit the waste and excess resources by integrating them for use by other industries within an industrial park, could play an important part in reducing the carbon footprint of a site. Tan and Foo (2007) introduced a procedure for low CO_2 energy planning by applying a pinch analysis (PA) graphical procedure that considered expected energy usage (range of zero CO_2, low CO_2 to high CO_2 emission energy sources) and the CO_2 emissions limit. Foo et al. (2008) dealt with the constraints of this PA graphical procedure by extending it to the tabular algebraic targeting approach of the cascade analysis technique. Atkins et al. (2009) introduced the concept of carbon emissions pinch analysis (CEPA) to study the effects of the renewable energy target on the various electricity generation sources and emissions levels. Their study showed that a possible 90% renewable energy target could be achieved by 2025.

In the holistic waste to resource planning of an industrial park with a low carbon footprint, Munir et al. (2012) designed a minimum carbon use network for carbon planning by identifying sources and sinks for possible matches and determining the minimum CO_2 targets using source and demand curves (SDC). This study was extended by Manan et al. (2014) by introducing a generic carbon cascade analysis technique (GCCA) as an algebraic alternative to the graphical SDC to determine the minimum CO_2 targets. Both of these targeting methodologies work in conjunction with the carbon management hierarchy (CMH) to determine the holistic CO_2 emissions management of the site. The CO_2 total site problem table algorithm (CTS-PTA), introduced by Muster-Slawitsch et al. (2011), used the concept of the achievement of a green brewery by optimizing unit operation and using PA to integrate all the energy sinks with the energy sources, and the integration of renewable sources within the production site. It did so in order to reduce CO_2 caused by the use of fossil fuel sources. The importance of considering exergy when integrating renewable energy sources such as solar energy was also highlighted. The authors claimed to have the potential of saving 5,000 t/y of fossil CO_2. Meylan et al. (2015) proposed numerous utilisation pathways for CO_2 usage in an industrial ecology setup. However, due to the difficulty in estimating the purity of CO_2 from various emitting sources, the capture of CO_2 from biological processes (such as fermentation) was considered as usage feedstock because of its relatively low cost and high purity of CO_2.

Patricio et al. (2017) developed a top-down matrix-based approach that matched CO_2 sources of different qualities to CO_2 receiving processes. This matrix-based approach considered the minimum acceptable levels of CO_2 purity, the required CO_2 flowrate and CO_2 receiving process conditions. Marchi et al. (2018) exploited greenhouse horticulture installations to offset emissions from energy intensive industries by using the captured CO_2 emissions without purification. Sanghuang et al. (2019) extended the methodology for the development of the total site CO_2 integration (TSCI) by considering different CO_2 purity ranges for the distribution of a variety of carbon sinks and storages for the enhancement of sustainable, systematic planning and management of CO_2 emission to improve the air quality of an industrial site.

Industrial symbiosis is a strategy for eco-industrial parks to reduce their carbon footprint by the exchange of energy and resources. Zhao et al. (2020) proposed an industrial symbiosis system which would operate under financial and economic constraints and include upstream manufacturers, a downstream manufacturer, the government, and a bank. Lopez et al. (2021) developed a modified CEPA approach to determine the minimum renewable energy target for countries with an electricity trading agreement with the aim of combining electricity sources and demands and reducing the increase of new renewable energy generation.

2.5.2 Carbon capture and utilisation

The ever expectant need of emerging economies such as China and India for rapid economic growth has caused a proliferation of carbon dioxide due to the use of carbon-based fuels for energy production (Perry & Bulatov, 2008). The authors proposed a mix of renewable, biomass and fossil fuels to meet the heating and electricity needs of small scale industrial and social environments (such as hospitals and schools) to cut down CO_2 emissions. Another option for reducing CO_2 in the atmosphere is to capture and store it. Page et al. (2009) proposed that an emission/energy penalty could be used as an added incentive to CO_2 capture and storage. A case study conducted in New Zealand showed an energy penalty of 43.5% and 48% for 100% capture of liquefied CO_2, and of CO_2 compressed to 11 MPa respectively. Harkin et al. (2010) used pinch analysis and heat integration to decrease the overall carbon fuel usage for a CCS plant and therefore reduce the amount of carbon dioxide emissions. A combined pinch analysis and linear programming methodology was used to determine targets for the energy penalty of the existing power plants.

There are three viable broad conceptual methods of capturing carbon dioxide. These methods are post-combustion capture systems (Thiruvenkatachari et al., 2009), pre-combustion capture systems (Bolland & Mathieu, 1998), and oxy-fuel capture systems (Damen et al., 2006). The post-combustion capture system functions by capturing of carbon dioxide in the flue gas after carbon-based fuel combustion. The absorption process is used for the extraction of low concentrations of carbon dioxide in the flue gas and depends on the purity of the carbon dioxide needed. The pre-combustion capture system involves reforming carbon-based fuels by using oxygen and steam. A mixture of carbon dioxide and hydrogen are the main components formed from the reformatting reaction. The carbon dioxide and hydrogen are separated by adsorption or by membrane technology and the

hydrogen can then be combusted with air. Biomass fuel is the most important beneficiary of this conceptual method of separating carbon dioxide from the fuel to create a carbonless fuel. The last conceptual method is the oxy-fuel system. The main aim of oxy-fuel capture systems is to purify the air to increase the concentration of oxygen and hence have a higher purity of carbon dioxide - more than 80% v/v in the flue gas (Pires et al., 2011).
South Africa uses coal as a primary fuel in the production of electricity (Beidari et al., 2017), making it one of the largest contributors of CO_2 per capita in the world. Arndt et al. (2016) claimed that the decarbonisation of South African economy would have to be anchored by a combination of carbon tax implementation and cross-border acquisition of electricity from regional countries without drastically impacting economic growth in South Africa. In 2018, South Africa introduced the Carbon Tax Bill (RSA, 2018) to encourage industries to reduce GHG emissions. Van Heerden et al. (2016) claimed that these carbon taxes, if usage behaviour was not modified, would make industrial products uncompetitive to similar imported products and drive inflation. It would therefore be important for the South African government to take an incentive-based approach as a start to get industries compliant-ready by using tax rebates for reduction of GHG. The reduction of mainstream electricity usage for the energy needs in an industrial site would be vital in the creation of a low carbon dioxide industrial site.

The concept of carbon capture and utilisation (CCU), as explained by Zimmermann and Kant (2017), is an umbrella of technologies that capture CO_2. Utilisation describes a range of technologies that consume CO_2 chemically to provide products that are either economically or environmentally beneficial or both. The sequestration of CO_2 for permanent storage in building materials, products, landfills or in the ocean can be used as an alternative to geological storage. The life cycle environmental impact, as explained by Cuéllar-Franca and Azapagic (2015), using stable CCU is essential in reducing the global warming potential.

Adding value to waste products/by-products can be accomplished through industrial symbiosis (IS) by reusing them in a network of industrial operations (Frosch and Gallopoulos, 1989). The use of IS prioritises the conversion of waste to resource by improving the environmental and economic benefits of otherwise discarded effluents. Lee Chan et al. (2020) developed network models where CO_2 process is allocated between existing ammonia plants and methanol plants, including numerous models restricting the CO_2 between the source and sinks. One of the challenges of capturing CO_2 emissions from various stationary sources is the varied concentration of the CO_2 that is captured. Hasan et al. (2015) presented a multi-scaled framework that should be considered when designing a CO_2 capture, utilisation, and sequestration/storage (CCUS) supply chain network with the aim of reducing the cost. The framework used the following CO_2 reduction routes:

1. Selection of advanced CO_2 capture processes by using innovative materials;
2. Simultaneous selection of materials and process optimisation;
3. Selecting CO_2 capture options for various emission sources; and
4. Optimisation of the supply chain networks.

In South Africa, the carbon dioxide emissions from the stationary sources amount to 20.66 million tons/y of CO_2 that could be captured, stored and reused in various industries (Palmer, 2018). In 2018/2019, Eskom, South Africa's monopoly power producer, started using diesel to supplement their current lack of sufficient electricity generation. It was estimated that Eskom used up to 7.1 million litres of diesel during the 2019 period to mitigate the energy crisis faced in South Africa (Isaacs, 2019). This contributed a significant 19 million kg of CO_2 emissions to the atmosphere.

2.5.2.1 Post-combustion carbon dioxide capture

The process flow diagram for the adsorption process considers particulate, sulphur removal and sorbent regeneration. The SO_x are removed using SO_X polishers to remove undesirable and toxic compounds before they are sent to the adsorber and desorption vessel for CO_2 extraction, dewatering, and finally to the storage vessel via the compression block. The lean sorbent is then mixed with the fresh sorbent to maintain adsorption capacity. According to Mukherjee et al. (2019), adsorption is one of the most promising and cost-effective post-combustion CO_2 separation systems because of its lower energy cost requirements for sorbent regeneration, lower maintenance requirements, reduced waste generation, faster reaction and better sorption stability. A typical flow sheet diagram showing the post-combustion process adsorbent CO_2 capture process that uses solid sorbents in a regenerative system to separate CO_2 from flue gas is shown in Figure 2.4:

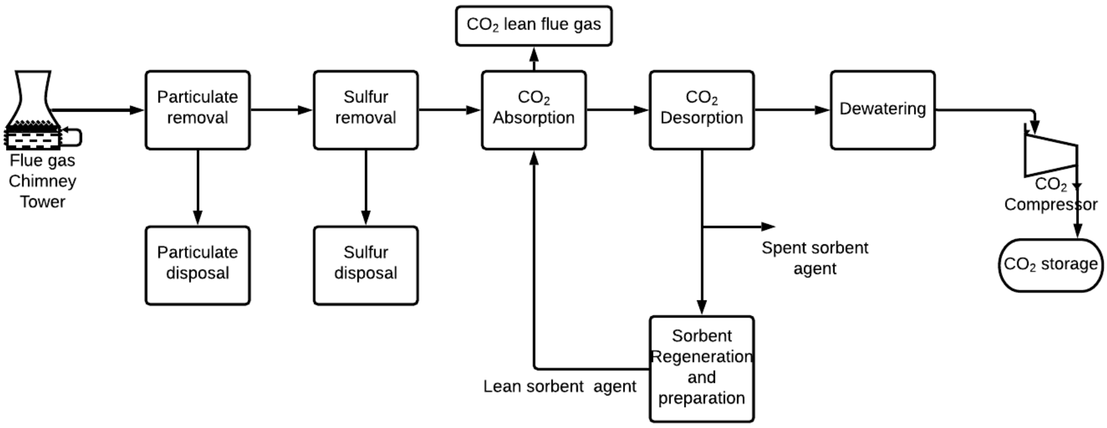

Figure 2.4: Post-combustion process adsorbent CO_2 capture process using solid sorbents in a regenerative system to separate CO_2 from flue gas

There are numerous ways to reduce the CO_2 impact in an industrial park. These include:

1. Improving the energy efficiency of a site through intensification of plant operation and energy integration to reduce utility usage;
2. Selecting carbon-neutral energy and power sources as a replacement for fossil-based fuel;
3. Capturing of CO_2 from stationary sources within the site for reuse and storage;
4. Converting the CO_2 into other useful products; and
5. Sequestration of uncaptured CO_2 from non-stationary sources by adding an artificial photosynthesis system to a site.

The capture of CO_2 using a low-temperature purification technology, as proposed by De Guido and Pellegrini (2019), could be used as a low energy CO_2 capture for flue gas of different concentrations. Four main CO_2 capture techniques can be applied to capture CO_2 from the fuel combustion:

1. Pre-combustion, which involves the CO_2 removal from the fuel source before combustion. Usman et al. (2018) reported a 90% efficiency of CO_2 gas absorption.
2. Oxy-fuel combustion, which utilises high purity oxygen (O_2) instead of air for its combustion, resulting in the capturing of a high concentration of CO_2. Wu et al. (2018) reported cost-effective O_2 separation processes from air to enable cost-efficient CO_2 capture.
3. Chemical looping combustion, which involves the introduction of a solid oxygen carrier for indirect combustion and where the fuel is combusted in an environment deprived of direct contact with air (Mantripragada & Rubina, 2013).

4. Post-combustion, which involves the removal of CO_2 directly from flue gas. This methodology is more widely used during retrofit, as elucidated in a review paper by Mukherjee et al. (2019), because it does not modify the existing process dynamics and equipment.

According to Rubin et al. (2015), several factors influence the cost estimation of post-combustion separation technique. These include:

- The space within the industrial plant to accommodate the post-combustion capture primary and auxiliary equipment;
- The age of the existing plant, which influences the type and size of the CO_2 capture equipment.
- The concentration of secondary species, i.e. nitrogen oxide (NO_x), sulphur oxide (SO_x), water and dust particulates which influences the addition of flue gas cleaning equipment such as desulphurisation units, electrostatic precipitators, membranes, etc.

Post-combustion separation techniques can be categorized into five technologies, as shown in Table 2.1. The techniques for post-combustion have inherent advantages and disadvantages which inevitably makes the selection of a uniform solution difficult. The cost estimates of these techniques are significantly dependent on 2 main aspects, namely contaminants of the flue gas and the quality of the CO_2 required.

Table 2.1: Summary of post-combustion techniques

Post-combustion technique	Advantages	Disadvantages	Estimated CO_2 capture cost ($/t CO_2)
Absorption	• High CO_2 yield >90% (Dubois and Thomas, 2018). • Extensively researched, technology easily available (Laribi et al., 2019).	• High power and heat requirements (Laribi et al., 2019). • Cost of sorbent regeneration (Laribi et al., 2019). • Progressive corrosion of equipment (Dubois and Thomas, 2018).	(~$31-$43)

Micro-algal bio-fixation	• It can produce valuable microalgae oil (Packer, 2009)(Packer, 2009).	• Scale-up for large industrial use is difficult (Wiesberg et al., 2017). • Very expensive (Singh et al., 2019).	(~$136-$155)
Membrane	• High CO_2 yield >90% (Wang et al., 2017).	• Relatively expensive to run the technology (Xu et al., 2019). • It requires a large membrane area (Bounaceur et al., 2006).	(~$25-$48)
Cryogenic	• Requires no solvent or pressure drop (Mat & Lipscomb, 2019).	• Long start-up time (Song et al., 2019; Bounaceur et al., 2006) • Progressive deterioration of CO_2 capture (Mat & Lipscomb, 2019).	~$53
Adsorption	• High CO_2 yield >90% (Zhao et al., 2019). • The durability of sorbents (Plaza et al., 2010).	• High energy demand (Zhao et al., 2019) • Expensive to run (Dhoke et al., 2019). • Adsorption affected by the concentration of NO_x and SO_x (Plaza et al., 2010).	(~$44-$51)

2.5.2.2 Geological storage of carbon dioxide

Saran et al. (2017) stated that the viability of CO_2 storage systems has different longevity, porosity and cost implications. In South Africa, underground storage is currently being researched by the newly established public-private research collaboration, the South African Centre for Carbon Capture and Storage (SACCCS), where projects are still ongoing (Beck, 2014). The policy for geological storage in South Africa has yet to be published.

Geological storage of CO_2 is usually chosen from the following storage options: oil and gas reservoirs, deep saline aquifers, deep seated coal beds (enhanced coal-bed methane recovery), caverns and mines (Lokhorst & Wildenborg, 2005). In selecting a geological site, Raza et al. (2016) stated that key parameters required for a suitable storage site selection include:

1. Storage capacity, which is the total volume in the geological medium that could be utilised to store captured CO_2. The evaluation of the medium considers the storage capacity of the geological formation excluding the formation water during and after the production stage.
2. Injectivity, which refers to the ease with which fluids can flow through stratigraphic intervals.
3. Trapping mechanisms, as a result of CO_2 injections to confine CO_2 in a geological medium. The efficiency of the trapping mechanism, however, depends mainly on reservoir characteristics, e.g. stratigraphic trapping and solubility trapping.
4. Containments of a storage site, which are important to prevent CO_2 leakage. The containments depend mainly on the nature of caprocks and the fracture surrounding the proposed CO_2 reservoir. The most vital aspects of containment are seal capacity, and the geometry and integrity of the seals.
5. Cost: the main costs are associated with site preparation, and transportation, operation and maintenance costs.

Impediments to the geological storage of CO_2 are the environmental lobby groups that oppose geological drilling for CO_2 storage without assurances of its long-term environmental impact. As a water-stressed country, South Africa has turned to underground aquifers to source portable water to curb the effects of the ubiquitous threat of droughts that have affected South African society, industry, and farmlands. Geological storage of CO_2 are vigorously opposed by the environmental lobby groups due to the threat of water contamination on these portable sources of water. Given these circumstances, CO_2 fixation as an alternative storage option can be explored, provided the cost efficiency is sustained.

2.5.2.3 Chemical fixation of carbon dioxide

Chemical fixation of carbon dioxide into valuable products such as carbonates and methanol has gained favour because of the recovery of some costs accrued from carbon capture. Teir et al. (2016) investigated the possibility of producing calcium carbonate, ($CaCO_3$) from wollastonite and captured CO_2. It was proposed that the precipitated $CaCO_3$ would then be reused in the pulp and paper process in three different applications. One of the major advantages of $CaCO_3$ is that it is inert and very stable and can therefore be used in a variety of applications where fillers are required such as the pharmaceutical industry, building industry, paper industry and glass industry. The practicality of the production of

$CaCO_3$ is dependent on the reduction in the cost of both the raw materials as well as the energy costs. The appeal of methanol production from flue gas is that methanol has ten times the energy density of hydrogen and sixteen times the energy density of lithium-ion batteries (Ovidiu, 2014). Bellotti et al. (2017) illustrated the feasibility of methanol (CH_3OH) production from captured CO_2 and hydrogen (H_2) produced from pressurised water electrolysis. The production of sodium bicarbonate ($NaHCO_3$) from flue gas, as described by Bonaventura et al. (2017), offers a better economic output than the other two CO_2 chemical fixation options. Direct methanol fuel cells (DMFCs) have also been considered because they are safer, simpler to operate and more cost-effective than other fuel cell configurations (Sgroi et al., 2016).

2.5.2.4 Industrial symbiosis in relation to CO_2 distribution and usage

Industrial symbiosis is a strategy for eco-industrial parks to reduce their carbon footprint by the exchange of energy and resources (Marchi et al., 2018). It exploits greenhouse horticultural installations to offset emissions from energy-intensive industries by using the captured CO_2 emissions without purification. Meylan et al. (2015) proposed numerous utilisation pathways for CO_2 usage in an industrial ecological setup. However, due to the difficulty in estimating the purity of CO_2 from the various emitting sources, the capture of CO_2 from biological processes such as fermentation was considered as usage feedstock because of the relatively low cost of capturing high purity CO_2. Patricio et al. (2017) developed a top-down matrix-based approach that matches CO_2 sources of different qualities to CO_2 receiving processes. The matrix considers the minimum acceptable levels of CO_2 purity, the required CO_2 flowrate and CO_2 receiving process conditions.

In South Africa, the Department of Economic Development and Tourism of the Western Cape Government has developed a project that encourages companies from different industrial sectors to recover and reprocess excess resources (Western Cape Government, 2014). No record could be found of any ongoing symbiosis project currently active in South Africa. This could possibly be because of a lack a framework to guide these industrial sectors on how to systematically utilise pathways for potential exchange of resources, by-products and wastes.

2.6 Fuel cell

One of the compelling reasons for incorporating fuel cells in a renewable energy mix is to introduce an independent source of high density portable energy to a small office environment to maintain a sustainable energy supply. Sharaf and Orhan (2014) noted that fuel cells provide an efficient, clean and flexible chemical to electrical energy source that is compatible with a renewable energy source mix. Furthermore, fuel cells are very quiet operators and therefore very useful for the office environment. Because of the modular design of fuel cells, they can be designed for any confined spaces and hence are an attractive option to add to the TSHI study.

There are two viable fuel cell types that can be considered, the direct methanol fuel cell (DMFC) and the high temperature polymer electrolyte membrane fuel cell which is also known as a proton exchange membrane fuel cell (PEMFC) (Larminie & Dicks, 2003). The DMFC described by Aricò et al. (2001) is ideal because it works at low and intermediate temperatures whilst producing continuous power at high efficiency with extremely limited emissions to the atmosphere. Methanol is the source of energy for fuelling the DMFC. Kamarudin et al. (2009) argued that whilst it is really easy to refuel when depleted, the DFMC does have a few disadvantages. These include:

1. Methanol crossover: This happens when methanol molecules diffuse through the membrane in the fuel cell and are directly oxidized on the cathode. This reaction reduces the current output production and in time, fuel utilisation in the fuel cell.
2. Durability and stability: the longevity of the DMFC is diminished due to methanol poisoning of the membrane electrode assemblies (MEA). The MEA is the most important component of a fuel cell, necessary for the electrochemical reaction needed to separate electrons.
3. Heat and water management: the electro-chemical reaction that takes place in the DMFC produces heat. This heat increases the rate of reaction, but also increases methanol poisoning of the MEA. The reaction also produces water which could lead to water flooding.
4. Cost and commercialization: the price of fuel cells is exorbitant because of the use of precious group metals such as platinum as catalysts.

The difficulty of hydrogen storage for conventional fuel cells such as alkaline electrolyte fuel cells and polymer electrolyte membrane as opposed to the simplicity of use of DMFC, according to Larminie and Dicks (2003), is the main determining factor that would persuade a designer to choose the DMFC. The DMFC can provide exceptional alternatives to lithium-ion batteries.

The overall reaction in the DMFC is represented by Equation 2.1:

$$CH_3OH + 1\frac{1}{2}O_2 \rightarrow 2H_2O + CO_2 \qquad \text{Eq 2.1}$$

The production of carbon dioxide, as explained by Larminie and Dicks (2003), is an inevitable occurrence that has prevented extensive applications. However, this carbon dioxide, that is produced at the anode, can be captured and sold as a high-quality product.

To reduce methanol crossover, multilayer membranes made up of an inner layer consisting of SiO_2 mixed with poly(sulphone) (APSu) packed in between two outer layers made of sulphonate poly(sulphone) (SPSu) can be used (Branco et al., 2016). The authors attribute this to the tortuosity of the multilayer membrane that prevents the permeability of the methanol molecule, which is better than other commonly used membranes. The durability and effectiveness of these membranes are particularly attractive for DMFCs that use methanol.

It is important to note that the DMFC has a few drawbacks. These include the cost of the fuel cell, methanol crossover, and water flooding. Lo Vecchio et al. (2019) forward the option of platinum group metal-free cathodic electrocatalysts which demonstrated high power density whilst counteracting the effects of methanol crossover. The other major drawback of the DMFC, as elucidated by Gong et al. (2018), is the poisoning of the platinum anode by carbon monoxide. This phenomenon can be mitigated by alloying it with transitional metals such as Cu, Ni, Sn, Ru, Rh, Pd, Os, Ir, etc., to increase the stability of the anode surface, improving activity and longevity of the DMFC.

PEMFC was first used by NASA as an early application for in-space travel with short term usage (up to 500 hours) and low temperatures applications (Larminie & Dicks, 2003). This technology however, had limited use due to its low durability. In recent times, PEMFC as described by Li et al., (2003), has adopted the use of perfluorosulfonic acid (PFSA) polymer membranes which can operate at higher temperatures. With the use of a PFSA membrane (such as Nafion) a lifespan of over 60 000 hours for this fuel cell was achieved. There are three major issues that exist with this high temperature PEMFC:

1. Water management issues: At high temperatures the issue of two-phase water states, namely water and steam, have to be managed.

2. Carbon monoxide poisoning: At low temperatures, carbon monoxide poisoning takes place, although this is less pronounced at higher temperatures. This requires purer hydrogen for more efficient voltage output.
3. Hydrogen storage and usage issues: The difficulty of storing hydrogen is well known. The safety aspect of using hydrogen also cannot be understated. In recent times, complex hydrates such as sodium aluminium hydrate ($NaAlH_4$) has been used for the storage of hydrogen. An excessive amount of heat is however required to then extract the hydrogen.

The impurities of air such as CO_2, NO_2 and SO_2 produced at the cathode of the PEMFC causes both reversible and irreversible damage to the platinum catalyst supported by carbon. Prithi et al. (2017) synthesized unsupported mesoporous platinum by the hard template method. This improved the SO_2 tolerance at the cathode side of the PMFC and enabled the ability of the mesoporous platinum to recover quickly to its original state.To date, fuel cells have found limited use as a low carbon solution in industrial sites. Milewski and Lewandowski (2012) showed how the molten carbonate fuel cell (MCFC) could reduce CO_2 emissions from a coal-fired power plant by capturing CO_2 from flue gas. Wee (2011) stated that MCFC could be used as the concentrator for CO_2 from a high temperature flue gas mixture in a gas turbine in an MCFC/GT hybrid energy system. The use of DMFC as an option for a hybrid system for an industrial system has not fully been explored. It has shown potential applications for portable devices, the automobile industry, and stationary power plants because of the ease of handling of the liquid fuel (Xia et al., 2019). It is therefore an attractive option to include in an industrial symbiosis project. DMFCs have been considered because they are safer, simpler to operate and more cost-effective than other fuel cell configurations (Sgroi et al. 2016).

2.7 Low carbon emission planning

Munir et al. (2012) proposed a new technique for achieving holistic minimum carbon targets. The technique follows four steps as follows:

1. Planning the carbon dioxide demand;
2. Maximising carbon exchange by using modified sources and demand curves;
3. Managing the "carbon management hierarchy" (Figure 2.5) showing the order of priority of how carbon is managed methodically to achieve holistic minimum carbon targets;
4. Formation of the minimum carbon utilisation network using a network allocation

diagram.

The authors claimed a reduction of 95% of carbon dioxide using the holistic approach as shown in Figure 2.5.

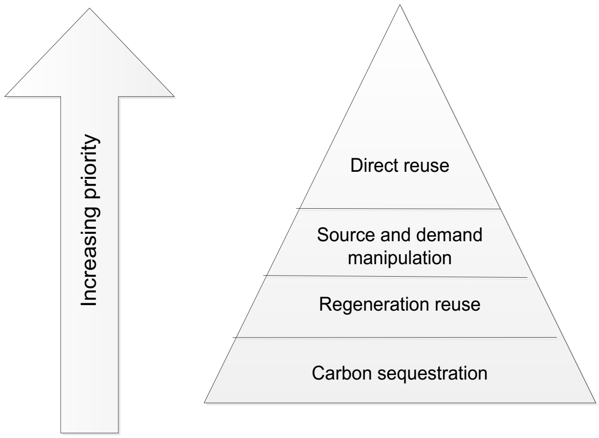

Figure 2.5 The carbon management hierarchy (CMH), adapted from Munir et al. (2012)

The framework for low carbon dioxide impact planning for new industries in a vacant site (Aziz et al., 2017) proposes four stages that the site planner should follow.

1. Stage 1 requires the site planners to acquire resource information that includes, power consumption, heating and cooling consumption and CO_2 emissions. This is essential to ensure the industries are placed correctly to ensure optimum symbiosis takes place.
2. Stage 2 utilises total site heat integration analysis to create a centralized system that will provide the optimum amount of heating and cooling utilities for the industries.
3. Stage 3 uses power pinch analysis to create a centralized hybrid power system to provide the optimum amount of renewable energy as a power source to the industries in the site.
4. Stage 4 captures and exchange of CO_2 of various concentrations to industrial CO_2 sinks using the principles of carbon dioxide emission pinch analysis.

2.8 Research gap

There has been little guidance in the state-of-the-art literature searched that industrial site managers can use to lower the CO_2 footprint of an existing industrial site through a systemic framework that holistically includes CO_2 capture from stationary industrial sources, industrial symbiosis, RE power sources and fuel cell configuration. This study is an extension of the work done by Aziz et al. (2017) that provided a framework for industrial site planners to lower the CO_2 footprint for a new industrial site using a suite of pinch analysis tools.

This study proposes a new framework that industrial site managers or third-party companies could use to reduce the CO_2 footprint for an existing industrial site. This study proposes a four-step sequential approach that introduces appropriate post-combustion CO_2 capture, purification and permanent storage using CO_2 fixing plants, including a fuel cell configuration. The study will also utilise a case study in an industrial site situated in the Western Cape, South Africa, to illustrate the applicability of the proposed four-step sequential approach.

This study investigates the economic sustainability of a multipronged CO_2 utilisation approach that includes a fuel cell configuration. The case study illustrates the creation of a subsidiary industry producing value-added products from captured CO_2 for consumption within the industrial site. In the main, the literature presented proposes a CO_2 pinch method that utilises CO_2 of varying qualities for existing plants in the industrial site. A uniform high quality captured CO_2 feedstock (>90%) will be distributed to proposed CO_2 fixing plants. The distribution of CO_2 to the CO_2 fixing plants will be conducted through a ratio distribution approach. This will be determined by the most profitable process and the demand for the products from these CO_2 fixing plants. This work uses a case study to investigate the economic feasibility of building new CO_2 fixation plants for usage distribution within an industrial site with a fuel cell configuration to reduce its CO_2 impact.

The CO_2 footprint is further reduced by using total site heat integration pinch analysis techniques to reduce the external utility requirement by maximising heat recovery from processes within the site, including the new subsidiary CO_2 fixation plants. The use of a HyPS that incorporates mainstream electricity, renewable sources of electricity and the fuel cell configuration is then used to supply the electricity requirements of the industrial site, which includes the carbon capture system and the subsidiary CO_2 fixation plants.

After an extensive review of literature, a comprehensive economic analysis of CO_2 reducing tools to determine the economic impact of the CO_2 reducing framework could not be found. A multi-sensitivity analysis to determine the robustness of CO_2 lowering tools could also not be found. This study will conduct an economic evaluation of the CO_2 reducing tools and perform a multiple sensitivity analysis in order to propose a more comprehensive model to determine the impact of the CO_2 reducing framework.

CHAPTER THREE

METHODOLOGY

3.1 Introduction

This chapter will detail the research approach used to lower the carbon dioxide footprint of an existing industrial site. The chapter will detail:

1. A systematic approach for an integrated pinch analysis framework to change a high carbon dioxide-emitting industrial site to a lower impact carbon dioxide emission site with the inclusion of a fuel cell configuration.
2. A cost analysis methodology of CO_2 capture and utilisation with the inclusion of a fuel cell configuration.
3. A methodology for the numerical representation of the TSHI tool set.
4. A methodology of the cost analysis of the proposed TSHI.
5. A methodology of the numerical methods for the PoPA tools for the optimised use and distribution of RE power for the HyPS to the existing plant and the new subsidiary industry.
6. And finally, a methodology for the cost analysis of the proposed HyPS.

The study will also determine the sensitivity and cost analysis of the TSHI system and the HyPS, as shown in the research approach in Figure 3.1.

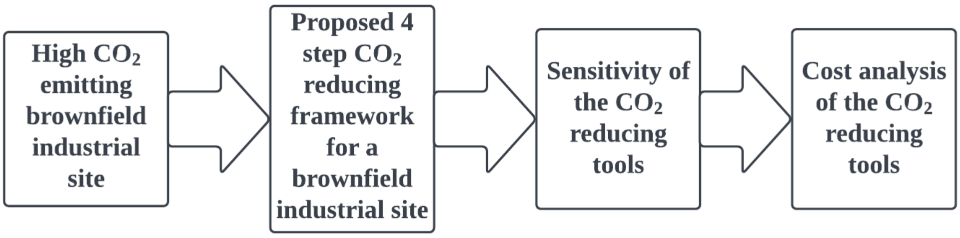

Figure 3.1: Overview of the research approach

3.2 Framework to lower the carbon dioxide footprint of an existing industrial site

Process integration plays a critical role in industrial site planning by taking into account the topology of the site by placing plants near to each other based on the 'best fit' material and energy integration between plants - determined by economic and environmental benefits (Ch'ng et al., 2021). The best location of the centralised heating, power and resource hubs can also be determined to optimise the distances between these hubs and the industries. Industrial sites have been established to cluster industries zonally. These sites have emerged spontaneously in the identified zones over a long period, without centralized planning to direct undesirable emissions away from the residential and farming sectors of a region. However, this clustering of industries has created a concentrated area of high CO_2 emissions that adversely contribute to the regional carbon footprint. The framework that is presented in this study takes into account the fact that there are established production facilities in industrial site that are running their operations independently of each other.

The proposed framework to lower the CO_2 footprint of an existing site can be identified by two essential processes, namely the removal of CO_2 emissions of the site, and cleaner production methodologies through process integration, intensification and use of RE sources of power.

Figure 3.2 proposes a framework that site managers can systematically follow. The framework assumes that the site has vacant space to install the following:

1. The CO_2 emissions capture and purification system;
2. The CO_2 storage and distribution hub;
3. The subsidiary industry consisting of CO_2 fixing plants;
4. The TSHI system;
5. The centralized utility hub producing, storing and distributing the requisite hot and cold utilities to the site
6. The HyPS that includes the biomass power production unit and the solar PV units; and
7. The centralized power storage hub that includes battery storage, invertor, rectifier and the fuel cell configuration.

The framework proposes three tools that should be applied sequentially in the site:

Tool 1: Target reduction of CO_2 by capturing it from stationary sources by post-combustion in the selected industrial site using a ratio-based approach to distribute the captured CO_2 to the subsidiary industry. A cost analysis of the CCU approach will be presented.

Tool 2: Target total site heat recovery for selected plants that include the subsidiary industry with TSHI pinch analysis method. The numerical method will be used to scope the utility saving as well as the distribution of utilities to the industries in the brownfield site.

Tool 3: Target a hybrid power system with PoPA for the industrial site, including the subsidiary industry. In this study, the numerical pinch approach is used to ensure that optimum distribution and storage of the RE power source.

Framework to Lower CO_2 Footprint of an existing industrial site

Step 1

Baseline study

- Identify the correct mix of industries in the industrial site for Low CO_2 footprint study.
- Request energy and power usage from the invited industries.
- Identify space in the industrial site for the centralized steam generation.
- Identify space in the industrial site for the Centralised CO_2 hub for the purification, storage and distribution of CO_2.
- Identify space for the suitable CO_2 fixing plants for the subsidiary industry.
- Identify the energy and power usage from the subsidiary industry.
- Identify the appropriate Fuel cell configuration for Low CO_2 footprint study.
- Identify the appropriate RE mix for the Hybrid power system.
- Identify space in the industrial site for the Centralised Hybrid power distribution hub that incorporates the fuel cell configuration.

Step 2

Tool 1: Target of reduction of CO_2 by Capturing of CO_2 from stationary sources in the selected industrial site using a ***ratio based approach***

- Data extraction of the potential CO_2 sources from flue gas.
- Identify the appropriate post-combustion CO_2 capture and purification method.
- Identify the potential mix of CO_2 fixing chemical plants for the subsidiary industry.
- Identify the correct ratio for the CO_2 distribution to CO_2 fixing chemical plants based on product. demand by existing industries in the industrial site and envisaged Fuel cell configuration.
- Conduct a cost analysis to determine impact of the CCU system.

Step 3

Tool 2: Target of total site heat recovery including the subsidiary industry with ***TSHI***

- Data extraction of Energy sources and demands from industries from the industrial site including the subsidiary industry.
- Generate the PTA for all the plants in the study to get the individual minimum heating and cooling requirements.
- Generate MU-PTA to obtain targets for heat sources and sinks for the TSHI.
- Generate TS-PTA to determine the external Energy utility requirement for the industrial site.
- Generate TSUD to determine the possible distribution of heat from heat sources and utilities to the heat sink.
- Perform a sensitivity analysis to determine the amount of external energy utility requirement due to individual chemical plant shutdowns.
- Perform a cost analysis the TSHI system with the use of TSP to calculate the HE area.

Step 4

Tool 3: Target for hybrid power system with ***PoPA*** for the industrial site including the subsidiary industry.

- Analyse the potential RE that could be harvested from the industrial site as well as integrating the fuel cell configuration.
- Data extraction of power sources and demands from industries from the industrial site including the subsidiary industry.
- Generate PCT to target the amount of electricity that could be stored for transfer to the next day operation.
- Generate SCT, taking into account battery discharge, AC to DC conversion and DC-AC conversion.
- Evaluate addition external power requirement for the industrial site.
- Perform a sensitivity analysis to determine the amount of external power requirement due to individual RE source shutdowns.
- Perform a cost analysis the HyPS with the use of FiT to calculate the potential loss due to the RE power shutdown.

Figure 3.2 Framework to lower CO_2 in an existing industrial site that includes a fuel cell configuration

In order to conceptualize the low carbon dioxide footprint framework, the case study of a typical mix of industries in an industrial site will be used as the baseline study.

3.2.1 Baseline study

The baseline study for the lowering of the CO_2 footprint of a brown field site would have to consider industries that have accepted the call to participate in the project. The industrial site planner for the CO_2 reduction project for the brownfield site would then request emissions data from selected industries that have the potential for post-combustion CO_2 capture. The site planner then determines the correct mix of CO_2 fixing industries that would produce value-added products that could be used in the site. The site planner would then request heat and power data from the existing industries in the site as well as extrapolate the heat and power data from the envisaged subsidiary industry. The thermal data is then used to target total site heat recovery with TSHI. The site planner would then determine the renewable resources available in the site, e.g., solar PV power potential, amount of biomass and possibly wind power potential. This data could then be used to target the HyPS using PoPA. The site planner would then find potential space within the site for the centralised utility and power distribution hub. The baseline study in this work will consider typical industrial mix in an industrial site in the Western Cape, South Africa.

3.2.2 Procedures to establish a low CO_2 footprint for the industrial site

To reduce the CO_2 footprint of the industrial site, it is proposed that a framework be introduced to guide industrial role players on systematic CO_2 reduction tools that should be followed to achieve sustainable low CO_2 footprint in an industrial site. Figure 3.3 illustrates a summary of the sequential procedures for the CO_2 footprint reduction through CCU from stationary sources, cleaner production, i.e., TSHI for the reduction of external utilities, and the introduction of renewable power sources in conjunction with the DMFC for the proposed HyPS.

After the identification of the potential plants in the industrial site for the study, the next step is to request flue gas emissions data as well as the energy and power usage from the invited plants to establish the baseline data for which all the calculations are based. This scoping of the existing baseline data establishes the possible CO_2 mineralisation processes that would be beneficial to the site. The appropriate RE power mix of the site is identified based on the availability of the RE source/s and its/their impact on the activity of the site. The site manager would also identify, during the baseline study the space available within the site to house all the envisioned storage, the potential subsidiary industries and the HyPS.

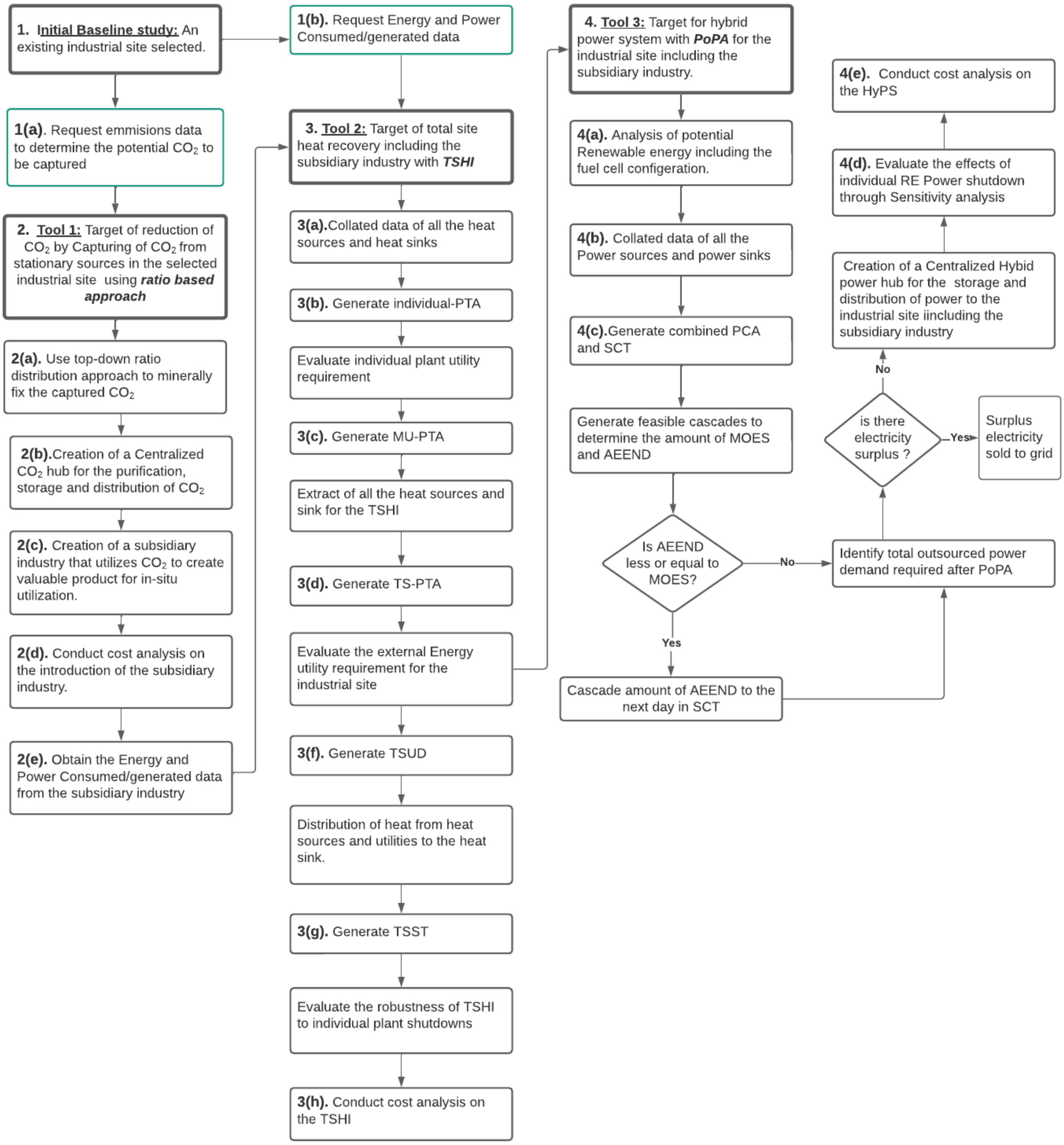

Figure 3.3: Procedure of sequential routes to CO_2 reduction of an existing industrial site

3.3 Carbon dioxide capture and utilisation mechanism

The most essential aspect in the devolution of CO_2 from a site is the permanent stable storage of the captured gas. The distribution of the single high concentration of gas to chemical fixing industries using Equation 3.1 is the most effective way of introducing industrial symbiosis in the site.

$$m_{CO_2} R_T = m_{CO_2} R_1 + m_{CO_2} R_2 + m_{CO_2} R_3 + m_{CO_2} R_i + \cdots \qquad \text{Eq 3.1}$$

where

m_{CO_2} is the amount of CO_2 captured per day (tons/d);

$R_T = 1$, and R_i is the fractional ratio for distribution to a CO_2 mineralisation plant, i.e., for this work, the methanol production plant, the baking soda production plant and the calcium carbonate plant.

This study will consider the cost of capturing CO_2 from selected industries with chimney stacks that emit flue gas containing a significant concentration of CO_2 that could be captured for reuse within the industrial site as a resource. The approach taken will consider the chemical fixing processes relevant to the industries for reuse within the industrial site to create a subsidiary industry that is run by a third party for a sustainable low CO_2-emitting industrial park. The product from this CO_2 chemical fixing process will then be sold to the industries in the industrial park.

This study aims to conduct a techno-economic analysis of CO_2 capture, distribution and usage system from selected plants in an industrial site with the aim of evaluating the economic sustainability of the CCU system. To achieve this aim, the following objectives will be considered:

1. Proposal of a framework to be used to lower the CO_2 footprint through CO_2 capture, distribution and utilisation within an industrial site;
2. Determination of the appropriate chemical fixing plants, appropriate for the industrial mix of the industrial park;
3. Conduct a cost analysis of all the processes in the CCU system which includes:
   a. The cost of Carbon dioxide Capture (CC),
   b. The cost of producing and selling of valuable CO_2 fixing products, and
   c. The running of the fuel cell system.

This cost analysis must be conducted to establish the sustainability of the mix of these subsidiary CO_2 chemical fixing industries in the CCU system for the third party.

The summary of the strategy used in this study to reduce CO_2 in an industrial site using the chemical fixation option is illustrated in Figure 3.4. The strategy considers a four-step methodology to determine the most suitable chemical fixing processes whilst determining the cost implications for this approach to lower the CO_2 footprint in an industrial site.

1.	**Select the most cost-effective post-combustion system commercially available.** this includes a. Selecting a long lifespan CCS system. b. Ensuring there should be enough space for the retrofit of the CCS system. c. Selecting the correct suite of impurity cleansing solvents and filters to achieve the recommended CO_2 purity (CO_2 treatment). and d. Selecting the most cost effective transport and storage system of the captured CO_2.

↓

2.	**Determine the cost of the carbon capture.** this includes a. The cost of power. b. The labour and maintenance cost. c. The operating cost. and d. Selecting the most cost effective transport and storage system of the captured CO_2

↓

3.	**Determine the optimal CO_2 chemical fixing plants that would be suitable for the industrial site.** the products produced by these CO_2 fixing plants will be a. Used within the site as a reagent for existing industries. b. Sold as value added products outside the site . c. Used as alternative energy sources to sustain the CCUS system.

↓

4.	**Determine the cost analysis (T.C) of the industries and systems associated with running the subsidiary industry.** this includes a. Initial Capital (annualised). (C.C) b. The required energy and power costs. (C.E) c. The operating labour cost. (C.L) e. The cost of raw materials. (C.R)and f. The market value of the CO_2 fixed product. (C.P) $T.C=C.P-(C.C+ C.E+C.L+C.R)$ (Eq.3.2)

Figure 3.4: Step-by-step methodology proposed for the creation of a low CO_2-emitting industrial site

The approach of this research is to evaluate the economic feasibility of industrial subsidiaries which can utilise CO_2 via chemical fixation of CO_2 and the cost of post-combustion capture (Rubin et al., 2015). Bottom-up mass balance analysis is conducted by using a ratio distribution approach to distribute the CO_2 captured to the three subsidiary industries (see Table 4.4 from case study). The calculation that is typically used to estimate the cost of post-combustion carbon capture is shown in Equation 3.3.

$$C_{cc} = C_E + C_A + C_M + C_L \qquad \text{(Eq. 3.3)}$$

where

C_{CC} is the annual total cost of CO_2 capture ($/y),

C_E is the cost of operating electricity cost ($/y),

C_M is the maintenance cost($/y),

C_L is the annual operating labour costs($/y) and

C_A is the annualized capital cost over the projected life of the post-combustion capture system.

To evaluate the sustainability of this CCU system, the rate of return on investment is calculated as a percentage of the average annual net profit over the annualised fixed capital investment (Turton et al., 2018).

3.3.1 Carbon dioxide capture method

For an existing plant, the most effective method of capturing the stationary CO_2 is the post-combustion CO_2 capture method because it can be retrofitted in the existing flue gas stack chimneys without affecting the routine operations of the plant. The post-combustion CO_2 capture method that should be chosen for the site is determined by:

1. The cost of the post-combustion CO_2 capture system;
2. The size of the post-combustion CO_2 capture system;
3. The availability of post-combustion CO_2 capture system in the region.

The most commercial and technologically mature post-combustion CO_2 removal route, according to Cormos and Cormos (2017), is based on gas-liquid absorption using various basic solvents such as alkanol amines like methyl-di-ethanol-amine (MDEA). The CO_2 capture is done in an absorption–desorption cycle using the following reversible reaction, (Equation 3.4).

$$MDEA + CO_2 + H_2O \rightarrow MDEAH^+ + HCO_3^- \qquad \text{Eq 3.4}$$

The solvent, saturated with CO_2 as a result of the absorption process, is then thermally regenerated. The main problem associated with this thermal regeneration process is the high heat duty (~ 3 MJ/kg CO_2) required for solvent regeneration. Glier and Rubin (2013) performed a comparison between the liquid absorption and solid adsorption option and ascertained that solid sorbents are potentially a viable alternative to liquid sorbents because of the lower heat requirement for sorbent regeneration. The study used the following parameters to ascertain the comparison:

1. CO_2 capacity;
2. Operating adsorption and desorption temperature window;
4. Regeneration ability;
5. Rate of the sorbent replacement.

3.3.2 Identification of the CO_2 mineralisation processes for the selected site

The identification of the CO_2 mineralisation processes for the site is dependent on the possible uses of the CO_2 mineralised products within the site. For this study, the suite of plants in the site as well as the proposed fuel cell configuration informed the suitable CO_2 fixing plants for the subsidiary industry.

The proposed framework, as seen in Figure 3.5, shows the framework that sequences the process of evaluating the CO_2 footprint in an industrial park by proposing the post-combustion method. CO_2 is captured, distributed and utilised by determining the appropriate CO_2 fixing plants for the industrial site. The suite of subsidiary industries could change depending on the composition of industries in the brownfield.

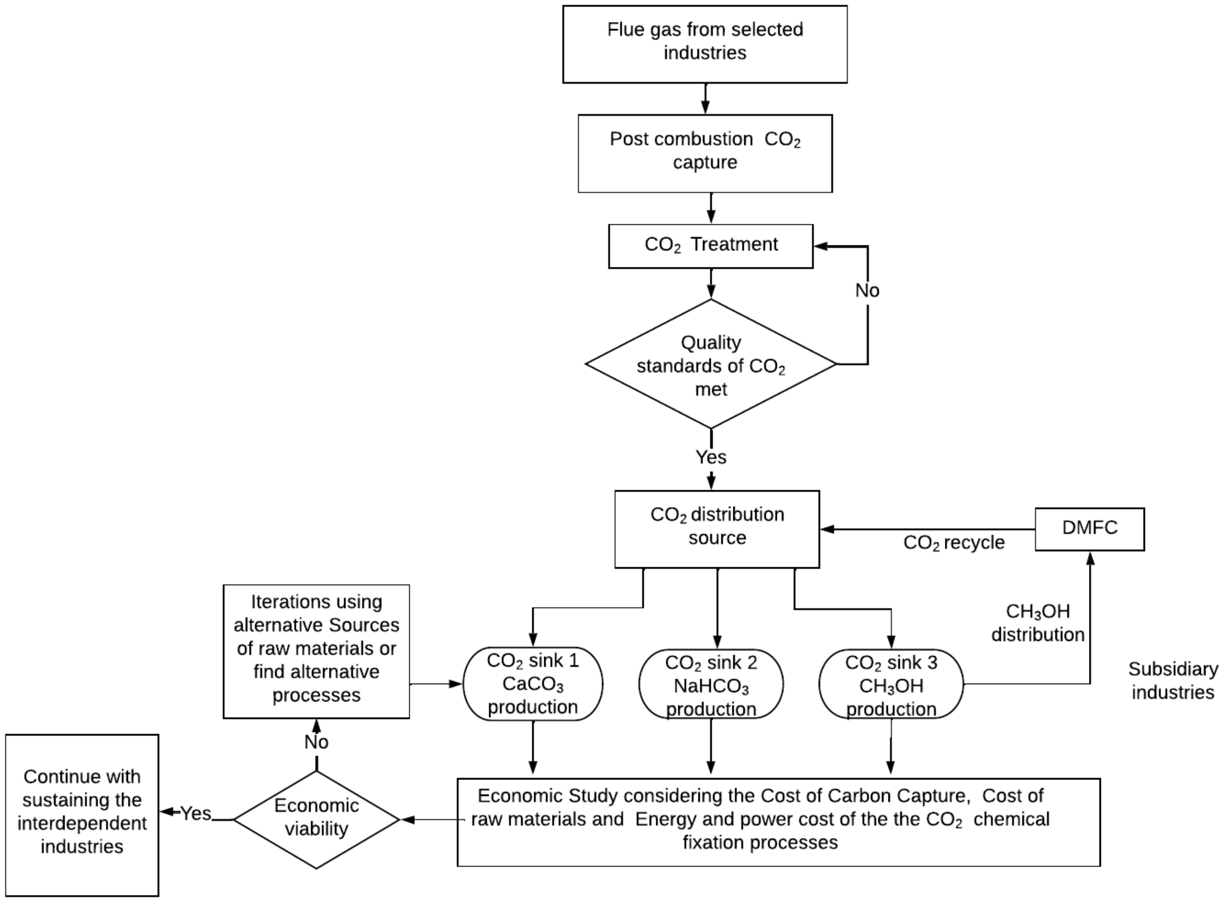

Figure 3.5. Framework for the capture, distribution, and usage of CO_2 from flue gases

The illustrative example in Figure 3.5 shows the CO_2 from the flue gas of three selected plants' gas stacks from an industrial site post-combustion capture and utilisation, and usage of technology. Flue gas undergoes a purification process through various scrubbing and filtration techniques to remove impurities to achieve the recommended CO_2 purity. If the quality standards of the CO_2 are not met, the gas is then recycled through the CO_2 purification process again. In this study the prescribed purity recommended is 90% CO_2.

The utilisation of the captured CO_2 into resources to be reused within the industrial site has not been explored fully as a means of reducing the CO_2 footprint of an industrial site. In this study, CO_2 from the flue gas of the stack chimneys of a steel processing plant, waste paper processing plant and a glassmaking plant, as shown in Figure 3.5, is captured and scrubbed to become a CO_2 resource for CO_2 fixing plants producing $CaCO_3$, $NaHCO_3$, and CH_3OH. It is envisaged that baking soda could be sold to a bakery and could also be used as a reagent in the purification of CO_2 in the CCS system. The $CaCO_3$ could be sold to the paper and glassmaking industry and the methanol could be used to feed the DMFC, which will provide an independent mobile source of high-density energy to the site. The possible CO_2 utilisation technology is considered on the basis of profit, reuse viability, and market demand. The CO_2 sinks consider subsidiary industries that consume CO_2 as their feedstock and include the baking soda plant, the calcium carbonate plant and the methanol plant. The site will also utilise a fuel cell configuration to add an independent power source for all the office space of the considered plants.

3.3.3 The fuel cell inclusion

The inclusion of a fuel cell to the site is dependent on the source of fuel available. In this study, one of the products of the CO_2 mineralisation processes is methanol. The inclusion of the fuel cell would then play a twofold role. It would be used as utilisation tool and for power generation as part of the HyPS. The factors that would be considered when choosing the fuel cell configuration are the cost of the fuel cells, the ease of use and the stack size.

The addition of the DMFC will utilise the methanol produced by the subsidiary industry. The size of the DMFC is directly linked to the daily production of methanol from the methanol production plant. The fuel cell configuration used in this study is a two-molar utilisation DMFC. It is assumed that the fuel cell configuration runs at a 90% efficiency level. The following factors also need to be taken into consideration when determining the size of the DMFC:

1. The size of the fuel cell is determined by taking into account the energy density of methanol, which is 6.1 kWh/kg (Scott & Xing, 2012).
2. A typical 200W stack of DMFC that occupies approximately $1m^2$ (Sgroi et al., 2016) is used to estimate the size of the fuel cell configuration. The size of the DMFC configuration is estimated by using Equation 3.5:

$$A_{FC} = A_{FC} = \frac{A_{ref}}{P_{ref}} \times P_{potential}$$

3.3.4 Economic analysis of the carbon dioxide capture and utilisation

The capital cost of all the CO_2 fixing industries was determined by using CAPCOST software. This software package uses the Lang factor method to estimate preliminary capital cost by applying the *Chemical Engineering* Plant Cost Index (CEPCI) for the 2019 time period. The Lang factor is derived from historical cost data from similar processes developed by Hans Lang in 1948 to estimate capital cost of chemical plants based on the cost of the major equipment from preliminary process flow diagrams. The Lang factor method for capital cost estimation takes into consideration the cost of the equipment, installation, land use, pipes, compression, pumps, and instrumentation, labour, insurance and taxes, as seen in some of the typical percentages of fixed-capital investment values for direct and indirect cost segments for multipurpose plants in Table 3.1. The initial capital cost calculated is divided over a payback period of 10 years. The operating labour cost, according to Peters et al. (2003), can be divided into highly skilled and low skilled employees needed to operate the plant optimally. It is estimated that the operating labour cost amounts to about 10 - 20% of the total product cost. For this study, the ratio used to estimate the cost of operating labour is 10%, as seen in Equation 3.2 within Figure 3.4.

Table 3.1: Typical percentages of fixed-capital investment values for direct and indirect cost segments for multipurpose plants (Peters et al. 2003)

Component	Range of FCI, %
Direct costs	
Purchased equipment	15-40
Purchased equipment installation	6-14
Instrumentation and controls (installed)	2-12
Piping (installed)	4-17
Electrical systems (installed)	2-10
Building (including services)	2-18
Yard improvements	2-5
Services facilities (installed)	8-30
Land	1-2
Indirect costs	
Engineering and supervision	4-20
Construction expenses	4-17
Legal expenses	1-3
Contractors' fee	2-6
Contingencies	5-15

3.4 Total Site Heat Integration

The term "total site" that was first coined by Dhole and Linnhoff (1993) refers to centralized utility hub services by integrating processes from different factories. The following steps are used to perform TSHI analysis:

3.4.1 Data extraction for Total Sites

The data required for the total site heat integration are extracted from process flowsheets to extract the cold stream and hot streams of the process from selected industries in the industrial site (see Klemes et al., 1997). The data from the cold stream and hot streams from the CO_2 fixing plants are collated and included for the total site heat integration. The data from the existing plant, the envisaged CO_2 fixing plant, the CO_2 capture system and fuel cell configuration that can be extracted are:

1. The target and supply temperatures of the streams;
2. The heat capacity of the steams;
3. The power requirements; and
4. The CO_2 sources and demands for the site.

3.4.2 Total site problem table algorithm

The total site problem table algorithm (TS-PTA), developed by Liew et al. (2012), is a numerical tool that compliments the visual insights provided by the graphical TSHI method. It represents the numerical version of the site composite curve (SCC), which is a part of the graphical TSHI analysis.

The following steps summarise the procedure by Liew et al. (2012).

1. Net heat sinks, which are heat sinks above the pinch region and net heat sources, which are heat sources below the pinch region, are identified for the utility region.
2. The net heating requirement for each utility level is calculated by subtracting the net heat source from the net heat sink.
3. The net heating requirements are cascaded from top to bottom for the utility region.
4. The highest negative value from the last cascade is used to start the new cascade by altering it to a positive value.
5. The PTA involving multiple utilities is performed by cascading from top to bottom for the utility region's net heat requirement for above the total site pinch region, and cascading the net heat requirement from the coldest utility to the pinch region. A negative cold utility value is included when a positive value occurs in a cascade with a utility region.

3.4.3 Total site utility distribution

The total site utility distribution (TSUD) is constructed by listing the heat sources and heat sinks of each plant according to utility levels, which includes the external utility requirements. The arrows are used, as shown in the example below in Table 3.2, to designate possible utility exchanges from heat sources/external utilities to heat sinks within the site.

Table 3.2. Total site utility distribution (TSUD) table adapted from Liew et al. (2012)

Utility	Heat Source (kW)			Heat Sink (kW)		
	Plant A	Plant B	Site Utility	Plant A	Plant B	Site Utility
HPS			7,000	6,000	1,000	
MPS		2,165				
LPS		9,963	4,372	16,500		
CW	4,000	3,302				7,302

3.4.4 Total site sensitivity analysis

The total site sensitivity analysis (TSST) is constructed to analyse the effects of plant shutdown of participating industries. The sensitivity of the TSHI is calculated by determining the variation of individual plant shutdown from normal operation. The variation is determined by subtracting the utility requirement from individual plant shutdown from the utility requirements during normal operations.

3.4.5 Economic analysis of the total site heat integration system

The cost estimate of the TSHI will utilise the total site profiles to evaluate the heat recovery potential between processes with the industrial site of the TSHI system. The assumptions made for the economic analysis is that the system is running at 90% efficiency. The total annualised cost considers that the initial capital cost calculated is divided over a payback period of 10 years. The operating labour cost, according to Peters et al. (2003), can be divided into highly skilled and low skilled employees to optimally operate the plant. It is estimated that the operating labour cost amounts to about 10- 20% of the total product cost. For this study, the ratio used to estimate the cost of operating labour was assumed to be 10% of the annualised capital cost. The estimated capital cost of the TSHI was calculated on the basis of the estimated costs of the waste heat boiler and water chiller. The typical cost factors as shown in Table 3.2 were used to estimated total cost of the TSHI network. The annual operating labour cost and fixed operation and maintenance cost are estimated as 10% of the annualised capital cost.

Table 3.3: Cost factors (Smith, 2005)

Item (installed)	cost multipliers
Waste heat boiler	
Water chiller	
Site preparation for the central utility hub	0.1
Equipment erection	0.4
Headers and pumping	0.7
Instrumentation & controls	0.2
Electrical connections	0.1

The annual utility operating cost of a network considering multiple utility types (Reza et al. (2004) is given by Equation 3.6:

$$C_U = H_Y(C_H Q_{Hmin} + C_C Q_{Cmin}) \quad \text{(Eq.3.6)}$$

where,

Q_{Hmin}	is the minimum hot utility target
Q_{Cumin}	is the minimum cold utility target
C_H	is the unit cost of hot utility
C_C	is the unit cost of the cold utility
H_Y	represents the hours of operation of network per year

The price of utilities varies immensely in different countries depending on the market fluctuations and to a huge extent the country's own available natural resource. Ulrich and Vasudevan (2006) proposed a two-factor utility price equation (Equation 3.7):

$$C_{S,u} = a(CEPCI) + b(C_{S,f}) \quad \text{(Eq.3.7)}$$

where,

$C_{S,u}$ is the price of the utility

a and b are utility cost coefficients (Ulrich & Vasudevan (2006)) ,

$C_{S,f}$ is the price of fuel in $/GJ

CEPCI is the inflation parameter for projects

Using the calculated price of the utilities, the cost of utilities required for the TSHI system can be established. The calculated price of the utilities is also used to calculate the cost of potential utility saving from TSHI.

The total annual cost estimate is calculated by using the capital cost of the waste heat boiler and water chiller. The annual operating labour cost and the annual fixed operation and maintenance cost are estimated as 10% of the annualised capital cost. The total cost analysis of the process is conducted by subtracting the annualised capital cost, annual operating labour cost, the amount of the utility required by the TSHI; and annual fixed operation and maintenance cost from the monetary saving from the amount of utility avoided in the TSHI system. A positive value in the cost column denotes the monetary saving from the amount of utility avoided from the TSHI, while a negative value in the cash column denotes the cost of running the plant, as well as the annualised capital cost.

3.5 Power integration for hybrid power systems (HyPS)

The targeting for the HyPS is done using power pinch analysis (PoPA) to plan for the optimisation and distribution of the renewable sources and the power generated from the fuel cell configuration. The HyPS should be able to provide electricity to the existing industries in the site, the post-combustion of CO_2 capture and storage and distribution system, the power needs of the envisaged subsidiary industry and the power needs of the TSHI system. Rozali et al. (2013a) introduced the power cascade analysis (PoCA) and the storage cascade table (SCT) to complement the graphical PoPA methods (Wan Alwi et al., 2012). After acquiring all the power sources and power demands at each time interval, this data is used to determine:

1. The minimum outsourced electricity supply (MOES); and
2. The available excess electricity for the next day (AEEND), the amount power that should be transferred from HyPS to demands, and the maximum battery required for sustaining the HyPS.

For this study, numerical tools (instead of the graphical tools) were used to allocate power accurately and to determine targets for each time interval. They were also used to determine the sensitivity of the HyPS when a RE power source shuts down for intended or unintended reasons. The disturbance due to power generation fluctuation was not factored in the sensitivity analysis. Figure 3.3 shows the sequential procedures that site managers of high carbon footprint sites can use to lower their site carbon footprint using the tools as mentioned above. The procedure of each of the tools in the framework will not change depending on any other brownfield. However, following need to be considered:

1. The suite of industries in the site determines the CO_2 fixed products for the site. The study recommends having a DMFC as a part of the HyPS (methanol production will be part of the subsidiary industry).
2. The procedures for the TSHI and PoPA will not essentially change. The results will entirely depend on the internal resources within the site.
3. The cost of the CO_2 lowering tools will be affected depending on the internal resources available within the site.

3.5.1 Data extraction

The power demands and sources (Table 3.4 and Table 3.5 respectively) for the selected site are considered at this point in the framework. The sources that will be considered are:

1. The power demand of the existing industries,
2. The power demands of the CCUS and distribution system and
3. The CO_2 fixing plants of the newly envisaged subsidiary industry.

The power sources will consider the potential renewable sources of power according to:

1. The renewable power resources available in the site,
2. The DMFC configuration considering the amount of methanol produced and
3. The outsourced main grid power source.

3.5.2 Power cascade table

The power cascade table (PCT) is used to determine the amount of power that can be transferred or introduced to the national electricity grid. The sequential steps, as described by Rozali et al. (2013a), can summarised by using Table 3.4 and Table 3.5 to explain the process in constructing the PCT.

Table 3.4: Example of power sources in an industrial site

Power sources		Time, h		Time interval, h	Power generated, MW	Electricity generation, MWh
AC	DC	From	To			
Biomass		06:00	18:00	13	2	24
	Fuel cell	00:00	23:59	24	0.183	4.383
	Solar	08:00	17:00	9	1.785	16.065

Table 3.5: Example of power demands in an industrial site

Power demands	Time, h		Time interval, h	Power consumed, MW	Electricity consumption, MWh
AC DC	From	To			
Industrial bakery	00:00	23:59	24	0.049	1.181
Steel processing	00:00	23:59	24	0.563	13.5
Wastewater treatment	00:00	23:59	24	0.033	0.792
Glassmaking industry	00:00	23:59	24	0.379	9.096
Paper recycling industry	00:00	23:59	24	0.096	2.304
Calcium carbonate production plant	00:00	23:59	24	0.090	2.170
Methanol industry	00:00	23:59	24	0.023	0.552
Baking soda production plant	00:00	23:59	24	0.198	4.752
CO_2 capture system	00:00	23:59	24	0.045	1.080

There are two main steps in the construction of the PCT:

Step 1 entails locating the net electricity excess and deficits within the time intervals. After the time intervals for the PCT are determined, the power sources and power demands are arranged per time interval, and the power rating for each time interval is calculated by adding all the sources to get the total power source per time interval and adding all the demands to get the total power demands for each time interval. The net electricity surplus or deficit is obtained by subtracting the total electricity demand from the total electricity source for each time interval, as shown in Equation 3.8. The net positive electricity value indicates that that there is electricity excess while net negative electricity value indicates electricity deficit.

$$n\mathrm{EE}_{\mathrm{su/df}} = \sum \mathrm{EE}_{\mathrm{S}} - \sum \mathrm{EE}_{\mathrm{D}} \qquad \text{Eq. 3.8}$$

where

$nEE_{su/df}$ is the net electricity surplus/deficit

EE_S is the net electricity sources, and

EE_D is the net electricity demand

Step 2 entails establishing the surplus electricity for storage and verifying the possible electricity requirement from the outsourced main grid power source. This is conducted by adding the excess electricity and deficit electricity from the initial to the last time interval. The unfeasible electricity cascade is conducted by cascading net electricity from the top time interval downwards, including the negative electricity flow values. The feasible electricity cascade is conducted by cascading the absolute value of the most negative electricity flow quantity from the top time interval downwards to obtain the MOES and AEEND. The excess electricity can either be stored or sold to the national electricity supplier. The deficit electricity requirements can be supplemented by the electricity provided from the national electricity supplier.

3.5.3 Storage cascade table

In order to establish the SCT, the MOES and AEEND from the PCT are used. The purpose of the SCT is to ascertain:

- The amount of electricity that can be transferred by each electricity producing source. This is done taking the lower of the values between the sum of electrical sources and the sum of electrical demands.
- The electricity required from the national electricity supplier at each time interval, the possible electricity that could be sent for storage, and the maximum storage capacity.

A net electricity excess indicates the amount of electricity that can be stored for a given time interval, while a net electricity deficit shows the electricity required from the national electricity supplier.

3.5.4 Sensitivity analysis

The sensitivity of the HyPS system to individual RE power shutdown could significantly affect the stability of the HyPS system. The sensitivity analysis approach that this study takes is to look at the effect of the individual plant shutdown and determine how it influences the electricity supply and demands of the HyPS. Rozali et al. (2016b) use the feed-in tariffs

(FiTs) to determine the cost implication of the individual RE power source shutdown. The on-grid problem table is then constructed to ascertain the impact of the individual plant shutdown. This information is then used in the HyPS sensitivity table to determine the cost implication based on the FiTs of the individual RE power sources as well as the penalty rates. This is done by subtracting the impact of the individual RE power sources from the normal operation.

3.5.5 Economic analysis of hybrid power system

For the purposes of the cost estimate calculation for the HyPS, the study considered the solar PV and the biomass power generating systems. The cost analysis of the fuel cell is included in the discussion to show how the viability of the fuel cell configuration can be sustained from the income generated from both the biomass and solar PV power generation for the HyPS. For this study, it was assumed that the biomass material would be provided by the landfill site as a way of mitigating the amount of material filling the landfill. The study also assumed free rental roof space for the PV solar power system. The HyPS cost estimation methodology is as follows:

1. After the area of the parking lot in the industries where the solar panels would be installed has been determined, the first step would be to determine the number of solar panels required for the installation. The cost of the panels and installation usually come as a package from a solar PV company (Solar Advice (PTY) LTD, 2021). The average size of the panels in the South African context is approximated to occupy 8m^2/kW using Equation 3.9 (Howell, 2021):

$$N_P = \frac{A_I}{A_P} \qquad \text{(Eq.3.9)}$$

where

N_P Number of panels that can be installed in the installation area

A_I Size of the installation area, (m^2), and

A_P Size occupied by 1 kWp of solar panels, (m^2)

2. The cost of the inverter (Live Stainable, 2021a) is determined using Equation 3.10b and battery storage (Live Stainable, 2021b) using Equation 3.10a required for the solar PV system. The inverter was slightly oversized to cater for the fuel cell configuration. This was done using the latest prices available in South Africa at the time.

$$TC_B = N_B \times C_B \quad \text{(Eq.3.10a)}$$

$$TC_I = N_I \times C_I \quad \text{(Eq.3.10b)}$$

where

TC_B	Total cost of required Battery
N_B	The number of 17,75 kW battery units ((Live sustainable, 2021b))
C_B	Cost of individual battery
TC_I	Total cost of the invertor units
N_I	The number of 100kW invertor units (Live sustainable, 2021a))
C_I	Cost of the invertor unit

3. The estimated maintenance fee for the solar PV system, as shown in Tidball et al. (2020), is calculated as MW per annum. It is estimated that the maintenance cost is $11,680/MW/y, as shown in Table 3.6.

Table 3.6: Estimated fixed operation and maintenance cost ($/MW/y) obtained and adapted from Tidball et al. (2020)

Renewable energy power source	Estimated fixed operation and maintenance cost ($/MW/y)
Solar PV	11,680
Wind (onshore)	30,300
Wind (offshore)	89,480
Biomass	64,450

4. The cost of the biomass power plant takes into account the most cost effective biomass power system (Indiamart, 2021). The cost of the site preparation, installation and electrical connections are taken into account by using cost multipliers introduced by Smith (2005). These cost multipliers were presented as estimated typical factors in proportion to the equipment cost depending on the dominant phase being processed i.e., the fluid processing or solid processing taking place in the equipment.
5. The estimated maintenance fee of the biomass power plant, as shown in Tidball et al. (2020), is calculated in MW per annum. It is estimated as $64,450/MW/y (see Table 3.2). This amount is more than 5 times the maintenance amount required for the PV solar power plant.
6. The initial capital cost calculated is divided over a payback period of 10 years as explained previously. For this study, this ratio will be used to estimate the cost of operating labour at 10%.

The total cost analysis of the process was conducted by subtracting the capital cost, fixed operation and maintenance cost, and the cost of operating labour requirements for the plant from the market value of the product. A positive value in the cost column as shown in Table 3.7 denotes the amount of cash returning to the investment from the sale of RE power to the site based on renewable energy feed in tariffs (FiT), and a negative value in the cash column denotes the cost of running the plant, as well as the annualised capital cost.

Table 3.7: Summary of cost estimates of the HyPS

RE power source	Solar PV source	Biomass source	General HPS
Annualised Capital cost ($/y)	-149583	-162000	
Fixed operation and maintenance cost ($/y)	-196350	-289170	
Invertor for HPS ($/y)			-52093
Battery for HPS ($/y)			-599919
Operating labour cost ($/y)	-34593.30	-45117	-65201
Selling price of power produced using feed in tariffs ($/Y)	1318568	674739	
Total cost analysis (annualised) ($/y)		**478990**	

CHAPTER FOUR

RESULTS AND DISCUSSION

Extracts from this chapter were published as:

John, J.M., Wan Alwi, S.R. & Omoregbe, D.I. 2020. Techno-economic analysis of carbon dioxide capture and utilisation analysis for an industrial site with fuel cell integration. *Journal of Cleaner Production*: 124920.

and

John, J.M., Wan Alwi, S.R., Liew, P.Y., Omoregbe, D.I., Narsingh, U., 2022. A comprehensive carbon dioxide reduction framework for industrial site using pinch analysis tools with a fuel cell configuration. *Journal of Cleaner Production*: 132497. https://doi.org/10.1016/J.JCLEPRO.2022.132497

4.1 Introduction

The results of this work demonstrate the efficacy of a proposed framework that could be used to comprehensively lower the CO_2 footprint of an existing industrial site. The study utilised an illustrative example of a typical industrial site. This framework was used in the case study of a high CO_2 footprint site. The existing industries in this high CO_2 footprint site were assumed to work independently of each other with no symbiosis between them.

Using the procedure of sequential routes to CO_2 reduction of an existing industrial site as shown in Figure 3.3 with regard to the illustrative case study, this chapter demonstrates the implementation of the methodology applied.

These results and discussion detail:

1. How the integrated pinch analysis framework was employed to change a high carbon dioxide emitting industrial site to a lower impact carbon dioxide emissions site with the inclusion of a fuel cell configuration by using an illustrative example.
2. The cost analysis of the CO_2 capture and utilisation with the inclusion of a fuel cell configuration.
3. The results of the numerical representation of the TSHI toolset.
4. The cost analysis of the proposed TSHI of the illustrative example.
5. The results of the numerical methods for the PoPA tools for the optimised use and distribution of RE power for the HyPS to the existing plants, and the new subsidiary industry.
6. The cost analysis of the proposed HyPS.
7. The use of a multi-sensitivity analysis to determine the robustness of the TSHI system and HyPS for the framework.

4.2 Baseline study: the illustrative example

The illustrative case study as shown in Figure 4.1 used in this work considered a typical mix of industries that occupy a site. The industries historically have functioned without any form of symbiosis. The clustering of these industries created a zone of high CO_2 emissions that would benefit from the proposed four step CO_2 reducing framework. The following industries were selected to represent a sample of industries that would typically occupy a site such as in the Sacks Circle Industria, Western Cape, South Africa (City of Cape Town, 2017) as seen in Figure 4.1. The industries selected are:

1. A glassmaking plant
2. A paper recycling plant
3. A steel processing plant
4. An industrial bakery
5. A wastewater treatment plant and
6. A Landfill site for domestic garden waste.

Figure 4.1 shows the scenario of the creation of a subsidiary industry that utilises the captured CO_2 emissions. The subsidiary industries were chosen based on the most beneficial CO_2 mineralised products for the site. In this study three products were identified as potential valuable CO_2 mineralised products for the site.

1. Methanol, which could be used for the DMFC configuration.
2. Baking soda, which could be used in the industrial bakery and
3. Calcium carbonate for the paper recycling plant and the glassmaking plant.

The data that could be requested from the existing plants (1(a) and 1(b)., Figure 3.3), as well as the required data from the envisaged subsidiary industries the site is shown in Table 4.1. The data extracted for this illustrative example includes thermal data, which includes the target temperature, supply temperature and specific heat capacity of the streams. The data would also include the power required and power generated by the site. Finally, the data would include the CO_2 generated from the selected industries in the site and supplied to the subsidiary CO_2 fixing industries.

The example also shows through the arrow distribution as shown in Figure 4.1, the possible TSHI with the supply of various level hot and cold utilities for the further development of a low CO_2 footprint framework, a hybrid power system which uses solar PV power, and power from biomass resources from the landfill site for domestic garden waste as the power sources as well as the introduction of a battery storage system. The electricity provided by the hybrid power system as well as the fuel cell configuration can be directly delivered to the consumer or sent to the battery storage system when the electricity demand of the supplied industries has been met. The sale of excess electricity generated back to the grid in South Africa is currently not available (Electricity regulatory act, 2006) and must, therefore, be utilised fully within the site. The outsourced main electricity grid will be included in the hybrid power system to ensure that the industrial site has sufficient and consistent power for the existing industries as well as the envisaged subsidiary industry.

The post-combustion capture system is the preferred CO_2 capture method because it lends itself to retrofitting. The CO_2 that is captured and purified from the flue gas is then converted to more valuable products for on-site utilisation. The subsidiary industries created from the waste to product system would be baking soda, calcium carbonate, and methanol production, as noted above. The focus of this work is to perform an early evaluation of the feasibility of creating these CO_2 fixing processes that includes the DMFC. For the purpose of early decision making on the viability of the subsidiary industry, the reagent and product amounts are calculated from the material balances from the primary CO_2 fixing reaction(s). The amounts calculated from these material balances will be used to select the appropriate size of the major equipment for the subsidiary plants.

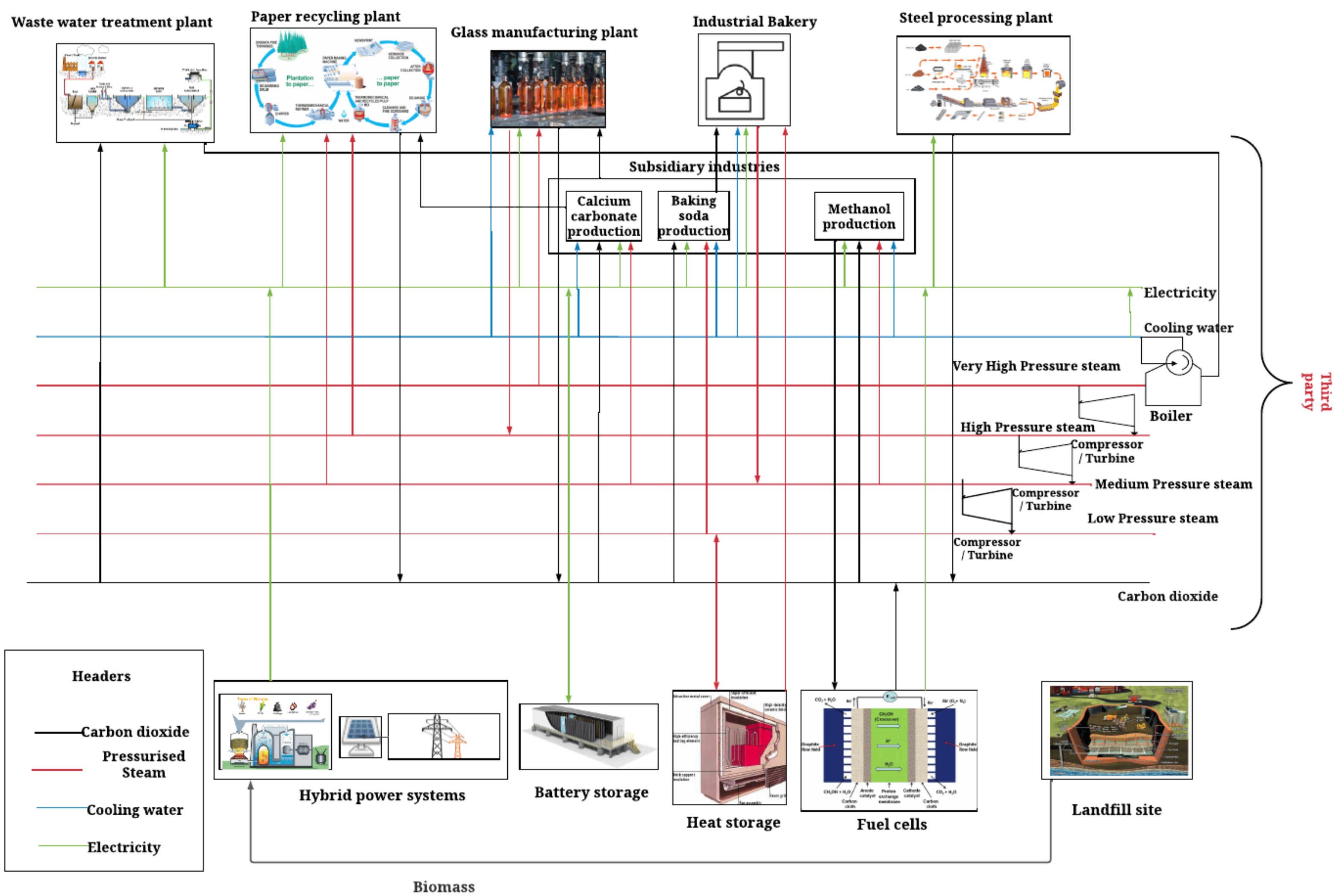

Figure 4.1: Illustration of the conceptual design of the integrated CCUS, TSHI and HyPS system with a fuel cell configuration for the site

Table 4.1: Data extraction table for the integrated CCUS, TSHI and HyPS system with a fuel cell configuration for the site

Industries	**Thermal data**					**Power (MWh)**		**CO_2 source and demands data**		
								CO_2 flow rate	**CO_2 purity. generated**	**CO_2 purity required**
Existing industries	Streams	Type	Ts(°C)	Tt(°C)	CP(MW/°C)	Generated(+)	Needed(−)	(kg/hr)	(%)	(%)
Industrial bakery	1	cold	28	40	2.8		1.18	Not considered		
	2	cold	40	230	2.8					
	3	hot	230	90	3.3					
	4	hot	90	20	3.6					
Wastewater treatment	1	hot	35	25	4.184		0.79	Not considered		
Glassmaking industry	1	cold	25	400	0.84		9.1	1455.21	35.5	
	2	cold	400	1100	1.124					
	3	hot	1100	600	1.214					
	4	hot	600	300	1.124					
	5	hot	300	20	0.95					
Paper recycling plant	1	cold	20	35	1.79		2.3	1659.09	24.2	
	2	cold	35	60	3.74					
	3	cold	60	120	3.8					
	4	cold	120	175	3.8					
	5	hot	175	80	2.64					
	6	hot	80	25	1.47					
Steel processing	Not considered						13.5	18364.04	22.8	

Subsidiary industries										
Calcium carbonate production	1	cold	20	80	0.0224		2.17	1148.65		100
	2	cold	80	150	0.0406					
	3	cold	150	375	0.0074					
	4	hot	375	20	0.0263					
Baking soda production	1	cold	60	175	0.078		4.76	2297.3		100
	2	hot	175	60	0.021					
	3	hot	190	60	0.037					
	4	hot	60	20	0.078					
Methanol production	1	cold	41	46	0.078		0.55	1148.65		100
	2	cold	46	52	0.078					
	3	cold	52	62	0.223					
Fuel cell	Not applicable					4.38				
Carbon capture system	Not applicable						1.08			

4.3 Carbon dioxide capture and utilisation mechanism

The abatement of CO_2 of the site in this study takes place through the placement of post-combustion CO_2 capture placed on the chimney stacks to collect flue gas from the following selected facilities: the steel processing plant, the paper recycling plant and the glassmaking plant as shown in Figure 4.2. The captured high-quality CO_2 are used by the CO_2 fixing plants of the subsidiary industry to produce $CaCO_3$, $NaHCO_3$, and CH_3OH for use within the site. The methanol produced in the site will be used the direct methanol fuel cell (DMFC).

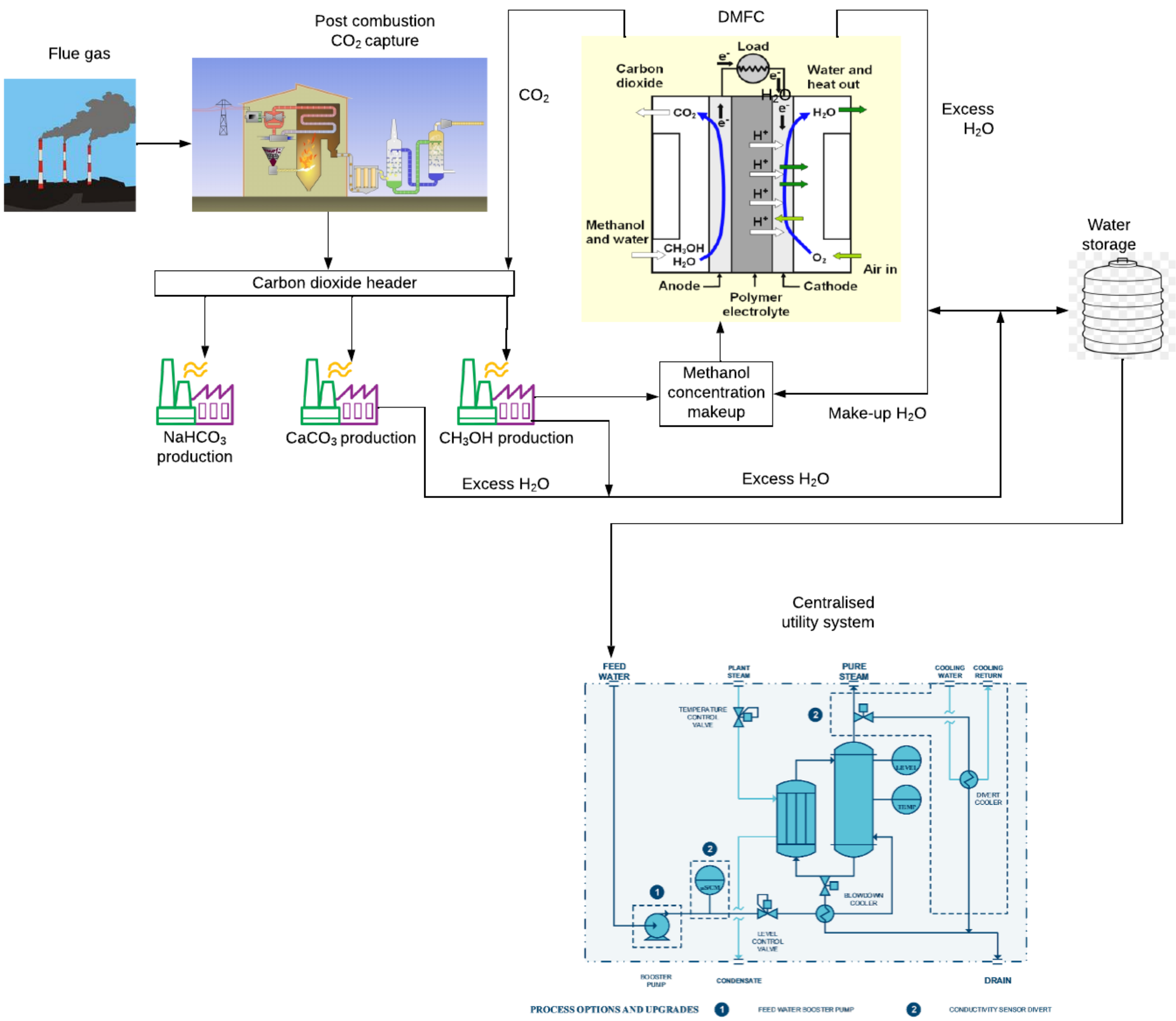

Figure 4.2: Illustration showing CO_2 capture, distribution, and usage

The excess water produced from the reactions, as shown in Equations 4.4 and Equation 4.7, as well as the excess water from the DMFC reaction as shown in Equation 4.1, will be sent to storage where it is envisaged that it will be utilised as a reserve for the water requirement of the centralised utility. The pure CO_2 produced by the DMFC is recycled for use for the subsidiary industry. The next section considers the sustainability of the CCU system, taking into account the post-combustion CO_2 capture system, the CO_2 fixing plants, and the fuel cell configuration.

4.3.1 Carbon dioxide capture method

Table 4.2 shows the flue gas compositions for the three plants in the case study. The estimated energy requirements for the post-combustion CO_2 capture based on the flue gas flow rate and composition are 0.44 MWh for the steel plant, 0.25 MWh for the waste paper processing facility and 0.39 MWh for the glassmaking industry as shown in Tables 4.6 to 4.8. These values are the basis of the calculations of the cost estimates that are shown in Table 4.3.

Table 4.2 Composition values of flue gas of industries

Steel industry		Waste paper industry		Glassmaking industry	
Components	% Composition	Components	% Composition	Components	% Composition
H_2	3.6	H_2	24.1	Cl comp	0.9
CO	22.1	CO	30	CO	4.9
CO_2	22.8	CO_2	24.2	CO_2	35.5
N_2	48.3	N_2	0.2	NO_2	7.2
H_2O	3.2	H_2O	15.9	NO_x	12.9
		HC's	5.6	O_2	5.4
				SO_2	31.6
				F comp	0.14
				Dust	1.44

Using Equation 3.3, Table 4.3 shows that the case study uses a plant lifetime of 10 years for the post-combustion CO_2 system. The purity of CO_2 required for the CO_2 fixing process is recommended to the prescribed CO_2 purity of 90% (John et al., 2020). The capital cost was estimated based on the flue gas flow rate of the three plants and the Chemical Engineering Plant Cost Index (CEPCI) of the 2019 time period. The operating and maintenance cost, as well as operating labour cost, were estimated as 10% of the annualized capital cost (Finkenrath, 2011). From the calculation, it was also found that the average cost of CO_2 capture was 57 $/t as shown in Appendix 2 .

Table 4.3: Summary cost estimates for post-combustion capture

Flue gas sources	Glassmaking industry	Waste paper processing	Steel processing
Cost of electricity ($/y)	546,624	350,400	616,704
Annualised Capital cost ($/y)	204,750	131,250	231,000
Maintenance cost ($/y)	20,475	13,125	23,100
Operating labour cost ($/y)	20,475	13,125	23,100
CO_2 flow rate (t/y)	13,838	9,010	15,681
Total CO_2 capture cost ($/y)	792,324	507,900	896,214

4.3.2 Identification of the CO_2 mineralisation processes for the selected site

A ratio distribution system of the purified CO_2 was conducted taking into consideration the reagent requirements for the industries in the site, i.e., calcium carbonate for the papermaking and glassmaking industry, baking soda for the industrial bakery, methanol for the DMFC configuration, and the economic viability of the CCUS system.

The distribution of the CO_2 using a selling price of 57 $/t from the post-combustion capture process shown in Table 4.4 was the basis for the calculations for this study using Equation 3.1. This ratio of CO_2 distribution (2(a), Figure 3.3) was chosen because the baking soda process as reported by Harrabin (2017) is a more profitable chemical fixing process than the other CO_2 fixing processes, as shown in Table 4.4.

Table 4.4: Distribution of CO_2 to chemical fixing plants

Flue gas sources	Methanol plant	Baking soda plant	Calcium carbonate plant
The ratio of CO_2 distribution	1	2	1
Total CO_2 distribution (t/d)	26.39	52.78	26.39
Cost per day of CO_2 ($)	1,502	2,786	1,502
Cost per annum ($)	548,075	1,016,770	548,075

By purifying the CO_2 from all the flue gas sources to >90% CO_2 purity, the distribution (2(b)., Figure 3.3) to the subsidiary plants becomes uncomplicated. The distributed CO_2 was then used bottom-up to calculate the stoichiometric mass for the other reagents and products based on the chemical reactions as shown in the subsections below. The power and requirements were extrapolated from similar plants as shown in the sections below, considering the proportional sizing requirements of the proposed carbon sink plants. The size of the CO_2 mineralisation plants was solely based on the amount of captured CO_2 per day as well as the proposed CO_2 ratio distribution as shown in Table 4.4. In this study, it was assumed that the plant would operate 365 days a year between 8:00 and 17:00 daily. The maintenance of the plant would be done after hours to sustain the operating days per annum.

4.3.3 The fuel cell inclusion

The fuel cell configuration chosen for this study was the DMFC (see Sgroi et al., 2016) because of its ease of use and low-temperature start-up requirements. A 2 Molar solution of CH_3OH was prepared for the direct feeding of the fuel cells. The cost of production of CO_2 was also included to mitigate the high cost of the DMFC and methanol. The reaction in Equation 4.1 was the main reaction taking place in the fuel cell:

$$CH_3OH + H_2O \rightarrow CO_2 + H_2O \quad \text{Eq. 4.1}$$

Using a 2 Molar solution of CH_3OH, the annualised total cost analysis was calculated by applying Equation 4.2 considering a fuel cell life of 15 years. The area of the fuel cell was inferred from the volume of CH_3OH fed to the DMFC per day. The projected power produced per day, as shown in Table 4.5, would be around 4.4 MW/d that would be sold to the industrial site at the recommended FiT rate for renewable power of \$ 0.16 per kWh as shown in Table 4.25.

$$T.C_{FC} = C_E + C_{CO_2} - C_{CH_3OH} - C_{A_{Fc}} \quad \text{Eq. 4.2}$$

where

$T.C_{FC}$	is the is the annual total cost of CO_2 capture (\$/y)
C_E	is the selling price of electricity cost (\$/y)
C_{CO_2}	is the selling price of CO_2 (\$/y)
C_{CH_3OH}	is the cost of methanol (\$/y)
$C_{A_{Fc}}$	is the annualized capital cost over the projected life of the fuel cell configuration (\$/y)

Table 4.5: The costing that considers the size and power output for DMFC

DMFC	Values	Cost (\$)
CH_3OH (t/d)	17,27	-6,053
Area of the DMFC(m^2)	2.44	-78,110,256
CO_2 contribution(t/d)	23.74	-1,351
The power produced (MW/d)	4.39	+16,906
Total cost analysis(annualized) (\$/y)		-**753,013**

4.3.4 Economic analysis of the carbon dioxide capture and utilisation

The subsidiary industries considered for this case study (2(c)., Figure 3.3) are presented in the section below. The CO_2 fixing plants presented include the baking soda production, methanol production, the calcium carbonate production plants and the DMFC. The total cost analysis of the process was conducted by subtracting the capital cost, cost of raw materials, cost of operating labour, and the energy and power requirements for the plant from the market value of the product. A positive value in the cost column denotes the amount of cash returning to the investment from the sale of products while a negative value in the cash column denotes the cost of running the plant, as well as the annualised capital cost (2(d)., Figure 3.3).

4.3.4.1 Baking soda production

The chemical fixing industries including the fuel cell configuration are considered to be part of the subsidiary industries. Equation 4.3 shows the primary reaction that was considered for the baking soda manufacture process considered for the site. The power and energy requirements (2(e)., Figure 3.3) shown in Table 4.6 were interpolated from data of a similar baking soda production plant (see Bonaventura et al., 2017). Baking soda provided the best chemical CO_2 fixation option with a potential rate of return of investment of 12%. This is important to establish the sustainability of the whole CCU system. The baking soda sold to the bakery could also be used for cleaning the working surfaces, floors, baking equipment and utensils. It can also be argued that using baking soda produced within the site for internal use also reduces the carbon footprint within the site over and above the purpose of the product because an external source is avoided, thus avoiding the carbon footprint attributed to transport.

$$NaCl + NH_3 + H_2O + CO_2 \rightarrow NaHCO_3 + NH_4Cl \qquad \text{Eq. 4.3}$$

Table 4.6: Costing that includes materials, energy, and power for a baking soda production plant

Baking soda reagents, products, energy and power	Flowrate (t/d)	Energy demand MW/d	Cost per day ($/d)	Cost ($/ton of CO_2)	Annualized cost ($/y)
NaCl	70.2		-4,212	80	-1,537,380
NH_3	20.4		-8,160	155	-2,978,400
H_2O	21.6		-216	4	-78,840
CO_2	52.8		-2,786	53	-1,016,995
$NaHCO_3$	90.7		+25,402	481	+9,271,584
Energy requirement		3.939	-433	8	-158,155
Power requirement		6.045	-950	18	-347,079
Capital cost					-548,000
Operating Labour cost					-625,871
Total cost analysis ($)					**1,980,969**

The major cost factor for baking soda production, as illustrated in Figure 4.3, is the acquisition of ammonia (NH_3) which accounts for 41% of the total annual cost. The total cost, in spite of the high cost of NH_3 acquisition, realises a profit margin of around $ 2M.

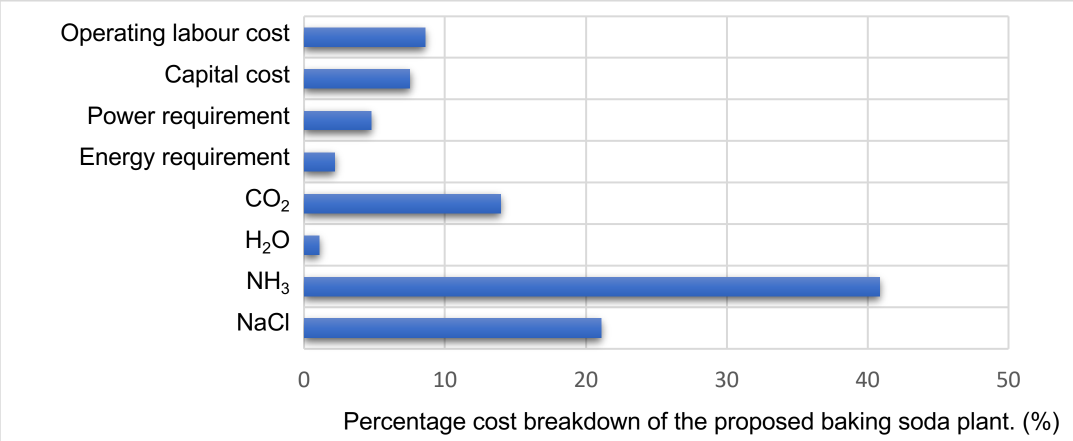

Figure 4.3: Cost breakdown of the baking soda production process

4.3.4.2 Methanol production

Methanol production from flue gas was considered as an attractive option for this study because it could directly be fed to the fuel cell for the generation of electricity for usage within the industrial site. The biggest cost component in the production of methanol is the price of hydrogen (H_2). Abdelaziz et al. (2017) introduced a novel process technology to convert CO_2 from flue gas into methanol. The authors claim that a profit of 56.55 M$/y could be achieved from the study. However, the reason for such a decidedly positive outcome is that the cost of H_2 was negated completely because the study utilised H_2 produced from the chlor-alkali industry existing in the industrial park. In the current study, the market value of the H_2 was used for the calculation of the total cost analysis for the production of CH_3OH. As seen in Table 4.7, it has a detrimental impact on the sustainability of the methanol production industry. Equation 4.4 is the primary reaction used to account for the production of methanol. The energy and power calculations for the methanol processing plant were interpolated from data collected from a similar plant (see Kumabe et al., 2008). In this study, as noted above, it was assumed that the plant would operate 365 days a year between 8:00 and 17:00 daily. The maintenance of the plant would be done after hours to sustain the operating days per annum.

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad \text{Eq. 4.4}$$

Table 4.7: Costing that includes materials, energy, and power for a methanol production plant

Methanol reagents, products, energy and power	Flowrate (t/d)	Energy demand MWh/d	Cost per day ($/d)	Cost ($/ton of CO_2)	Annualized cost ($/y)
H_2	3.6		-5,398	205	-1,970,270
CO_2	26.39		-1,502	57	-548,230
CH_3OH	17.271		6,045	229	+2,206,535
Energy requirement		3.09	-484	18	-176,624
Power requirement		0.567	-62	2	-22,776
Capital cost					-1,048,000
Operating Labour cost					-338,361
Total cost analysis ($)					**-1,897,727**

The total cost analysis is detrimentally affected by the cost of H_2, as shown in Figure 4.4. The breakdown reveals that H_2 dominates the cost breakdown by 48% of the total annual costs required. It would be prudent to investigate methods that could drive the cost of H_2 down. Driving down the hydrogen cost is key to sustaining the CH_3OH production.

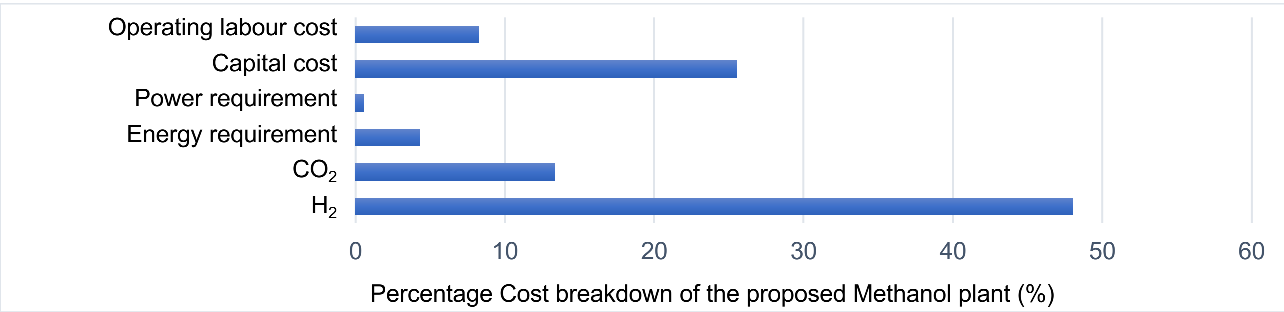

Figure 4.4: Cost breakdown of the methanol production process

4.3.4.3 Calcium carbonate production

The $CaCO_3$ production was chosen as another option for chemical CO_2 fixation because it would be used as a raw material in the paper processing and glassmaking plants within the industrial site. The three major reactions that are essential in the production of $CaCO_3$ are shown in Equations 4.5 to 4.7. The Wollastonite ($CaSiO_3$) as proposed by Svensson et al. (2018) was reacted in the presence of CO_2 in aqueous conditions to calcite and amorphous silicon oxide. The interpolation of the energy and power requirements (2(e), Figure 3.3) for the $CaCO_3$ plant was conducted using data from a similar plant (see Teir et al.,(2016).

$$CaSiO_3 + 2HCl \rightarrow CaCl_2 + SiO_2 + NH_4Cl \quad \text{Eq. 4.5}$$

$$CaCl_2 + 2Mg(OH)Cl \rightarrow Ca(OH)_2 + MgCl \quad \text{Eq. 4.6}$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \quad \text{Eq. 4.7}$$

The cost of the $CaSiO_3$, as shown in Table 4.8, is essential for this process. It could be supplemented from the slag by-product of the steel manufacturing process. In this study, the market value of $CaSiO_3$ was used for the primary process and this cost had a detrimental impact on total cost analysis. The $CaCO_3$ has a few applications that could be used in the total site apart from supplying it to the paper recycling and glassmaking industry. Carlos and Rozada (2017) patented a process that utilises $CaCO_3$ in conjunction with calcium oxide as a sorbent in the treatment of flue gas. The patented process uses heat exchanges from high-temperature flue gas to reduce the cost of post-combustion CO_2 capture.

Table 4.8: Costing that includes materials, energy, and power for a calcium carbonate production plant

Calcium carbonate reagents. products, energy and power	Flowrate (t/d)	Energy demand MWh/d	Cost per day ($/d)	Cost ($/ton of CO_2)	Annualized cost ($/y)
$CaSiO_3$	69.6		-6,957	264	-2,539,305
HCl	43.8		-3,941	149	-1,438,283
Mg(OH)Cl	92.1		-921	35	-336,165
CO_2	26.4		-1,502	57	-548,230
$CaCO_3$	66.6		11,995	454	+4,378,339
Energy requirement		4.17	-655	25	-238,966
Power requirement		3.63	-399	15	-145,745
Capital cost					-796,000
Operating labour cost					-661,202
Total cost analysis ($)					**-2,325,556**

The cost breakdown for the $CaCO_3$ production, as shown in Figure 4.5, reveals that 38% of the total cost accrues from the cost of acquiring the $CaSiO_3$. This process can be made viable by acquiring $CaSiO_3$ for a rate that could make the production of $CaCO_3$ profitable. If the wollastonite could be acquired for free from the site, the potential profit from the site would be around $1.5M. For this study, the assumption was made that the wollastonite would be bought at market value.

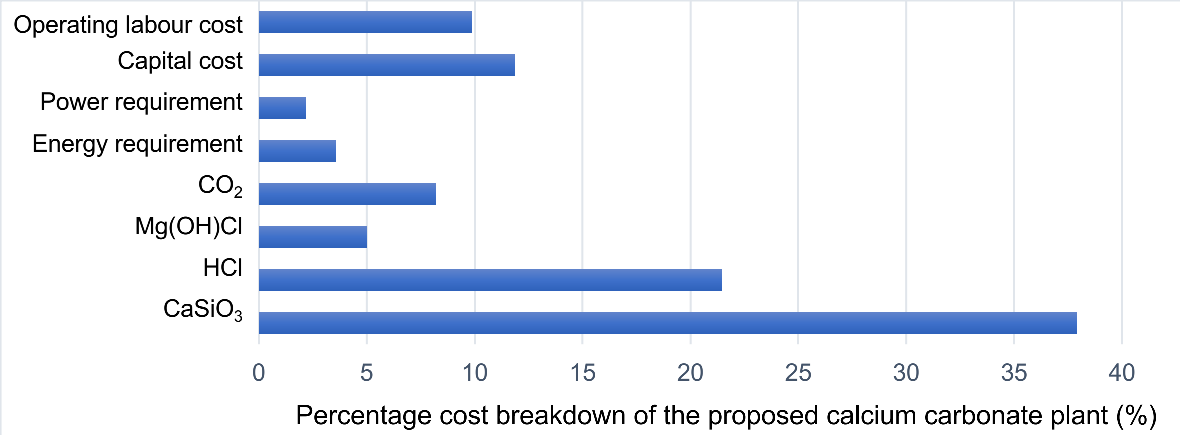

Figure 4.5: **Cost breakdown of the calcium carbonate production process**

4.3.5 Total annual cost analysis

To evaluate the sustainability of the whole system, a total annual cost analysis revealed that an overall loss of $2.75M was obtained from the summation of the annual cost of all the CCU processes. The only profitable CO_2 fixing process in the current configuration of the CCU system, as shown in the total cost analysis summary in Table 4.9, was the baking soda production process. The cost of the DMFC could be better sustained if the cost of obtaining methanol from the subsidiary industry could be lowered.

Table 4.9: Summary of the total cost analysis

	Baking soda production plant	Methanol production plant	Calcium carbonate production plant	Running of the DMFC
Total cost analysis ($/y)	1,980,969	-1,897,727	-2,325,556	-753,013

4.4 Total site heat integration

The TSHI is a suite of pinch technology tools used for the evaluation, generation, optimisation and usage of energy within a total site scenario. This study used the established numerical methodology as articulated by Liew et al. (2012) to perform the TSHI. There are four basic analysis tools that the TSHI employed:

1. Individual problem table algorithm
2. Multiple problem table algorithm (PTA)
3. Total site problem table algorithm, and
4. Total site utility distribution table

4.4.1 Individual problem table algorithm (PTA)

The first step was to determine the QH_{min}, the $QC_{min,}$ and the pinch temperature of each of the individual industries on the site as well as the envisaged CO_2 fixing plants (3(a)., Figure 3.3) by constructing the individual PTA. The single utility PTA tables (3(b), Figure 3.3) are considered for the site which housed an industrial bakery, paper recycling plant, glassmaking industry, methanol production plant, calcium carbonate production plant, and the baking soda production plant. Table 4.10 shows the thermal data, which includes the minimum heating and cooling requirements derived from the individual PTA (Tables 1A to 1F- Appendix 1). The steel industry was not considered for the TSHI because the plant manager requested exclusion from the TSHI project. The individual PTA was required to construct the multiple utility problem table algorithm (MU-PTA) which was used to target for heat sources and sinks.

Table 4.10: Heating and cooling requirements of the individual plants of the CO_2 reduction study

Thermal data	Industrial bakery	Paper recycling plant	Glassmaking industry	Methanol production plant	Calcium production plant	Baking soda production
Minimum temperature difference ΔT_{min} (°C)	10	10	20	5	10	10
Shifted pinch temperatures (°C)	225	25	1090	43.5	370	65
Hot utility requirement (MW)	28	233.05	22.48	3.09	0.074	2.325
Cold utility requirement (MW)	173.6	14.7	126.13	0	3.539	3,7

4.4.2 Multiple Utility Problem Table Algorithm

The MU-PTA (3(c), Figure 3.3) for each plant participating in the TSHI is constructed to obtain targets for multiple utility levels as heat sources and sinks for the TSHI (Tables 1G - 1L, Appendix 1) following the procedural methodology shown in Liew et al. (2012). The illustrative example used the utility temperature levels in Table 4.11 for the TSHI. As explained earlier, the MU-PTA is an algebraic representation of the GCC that uses utility temperature boundaries to differentiate the amounts of heat sources and sinks by utility type. The multiple utility cascades would have to be performed based on the pinch regions, i.e., above and below the pinch region. Above the pinch, the heat is cascaded starting from the temperature point towards the pinch temperature. When there is a negative value during the cascading between temperature intervals, an external utility is added to that point (column 8 of the MU-PTA Tables 1G - 1L, Appendix 1). The multiple utilities below the pinch are cascaded from the bottom to the pinch temperature. When there is a positive value during the cascading between temperature intervals, the cascading must be zeroed to generate utilities (column 8 of the MU-PTA Tables 1G - 1L, columns 7 and 8, Appendix 1). The amount of utilities generated was determined by summing the amounts of excess heat per utility interval (above the utility temperature to the next utility level) to obtain the total amount of the utility per utility interval, as summarised in Table 4.12.

Table 4.11: Proposed site utility data

Utility	Temperature (°C)
Very high-pressure steam (VHPS)	500
High pressure steam (HPS)	240
Medium pressure steam (MPS)	198
Low pressure steam (LPS)	150
Hot water (HW)	50
Cold water (CW)	20
Chilled water (ChW)	10

Table 4.12: Summary of results from multiple utility heat cascade table

Utility	Utility Temp (^oC)	Heat source (MW)						Heat sinks (MW)					
		Bakery	Paper making	Glass making	Methanol	Calcium Carbonate	Baking soda	Bakery	Paper making	Glass making	Methanol	Calcium carbonate	Baking soda
VHPS	500			45								0.074	
HPS	240			39.58		2.835		28					
MPS	198	13.5		4.62		0.7938			38				0.645
LPS	150	24		5.28		0.1562			96.45		4.93		1.7
CW	20	118.1	7.35	26.9			3.31						
ChW	10	18	7.35	4.75		0.263	0.39						

4.4.3 Total site problem table algorithm

The total site problem table algorithm (TS-PTA) (3(d)., Figure 3.3) was applied to establish the utilities exchanged between processes within the total sites. It is an algebraic representation of the graphical site composite curve. The utilities generated below the pinch region were added to determine the total heat sources. Above the pinch region, the utilities used by the industries in the TSHI study were added together to determine the total heat sink. The heat requirement was acquired by subtracting the heat sink from the heat source. As shown in column 5 of Table 4.13, the positive value, as seen in Column 5, is heat surpluses, and the negative values represent the heat deficits. The initial heat cascade represented by Column 6 of Table 4.13. was found by starting at zero and cascading by adding the heating requirements acquired in Column 5 from top to bottom. The most negative value was used to determine the external heating utility requirement by making it positive, as seen in column 7 of Table 4.13 by cascading its heating values and getting an external heating requirement of 34.03 MW and cooling requirement of 186.41MW (of which there were 155.66 MW of cooling water utility and 30.75 MW chilled water).

Table 4.13: Total site problem table algorithm

1	2	3	4	5	6	7	8	9
Utility	Utility temp (^{O}C)	Net heat source (MW)	Net heat sink (MW)	Net heat requirement (MW)	Initial heat cascade	Final single heat cascade	Multiple utility heat cascade	External Utility requirement (MW)
					0	34.034	44.926	
VHPS	500	45	0.074	44.926				0
					44.926	78.96	14.415	
HPS	240	42.415	28	14.415				0
					59.341	93.375	0	
MPS	198	18.9138	38.645	-19.7312				0
					39.6098	73.6438	0	
LPS	150	29.4362	103.08	-73.6438				34.034
					-34.034	0 (Pinch)	0	
CW	20	155.66		155.66				-155.66
					121.626	155.66	0	
ChW	10	30.753		30.753				-30.753
					152.379	186.413	0	

4.4.4 Total site utility distribution

The distribution of utilities in a total site scenario can be a complicated task depending on the distances between processes and the sensitive nature of the streams to cross-contamination. The TSUD tool (3(f), Figure 3.3) developed by Liew et al. (2012) provides a visual representation, as shown in Table 4.14, of how heat sources and utilities can be distributed to heat sinks. The arrows show the proposed distribution to the same or lower utility levels. The plant manager could then use this tool to determine the best distribution option for processes on the site.

4.4.5 Total site sensitivity analysis

The most important feature of the TSHI was to ensure the system's robustness with regard to plant shutdowns and to ensure the utility cushions the utility loss due to individual plant shutdowns. Plant shutdowns could be due to predictable reasons such as planned maintenance or unpredictable reasons such as unit operation failures and accidents. According to Liew et al. (2012), the consequence of the sensitivity study using the total site sensitivity table (TSST) would be to provide insights to the TSHI designer on planning for the maximum heating and cooling utility requirements for individual shutdowns (3(g), Figure 3.3). The excess heating and cooling duties could be sold to interested parties or stored in heat storage, as shown in the conceptual diagram in Figure 4.1. Table 4.15 shows the impact of the individual plant shutdowns by discounting the impact of the individual plant heat sinks and heat source data. For example, if the bakery shuts down, the heat requirements of 28 MW of HPS, cooling requirement of 118 MW of cooling water and 18 MW of chilled water, as well as the heating source of 13.5 MW of MPS and 24 MW of LPS, would be removed from the TSUD. Its variance from normal operations is explored in column 3 in Table 4.15. it is recommended that maximum external utilities required is always available as shown in Table 4.15.

Table 4.14: Total site utility distribution (TSUD) table.

Utility	Utility Temp (°C)	Heat source (MW)							Heat sinks (MW)						
		Bakery	Paper making	Glass making	Methanol	Calcium carbonate	Baking soda	Site utility	Bakery	Paper making	Glass making	Methanol	Calcium carbonate	Baking soda	Site utility
VHPS	500			45									0.074		
HPS	240			39.58		2.835			28						
MPS	198	13.5		4.62		0.7938				38				0.645	
LPS	150	24		5.28		0.1562		34.034		96.45		4.93		1.7	
CW	20	118.1	7.35	26.9			3.31								155.66
ChW	10	18	7.35	4.75		0.263	0.39								30.753

Table 4.15: Total site sensitivity table (TSST)

Utility	Total Site external utility requirement, MW												
	Normal operation	Bakery plant shutdown	Variance from normal operation	Paper recycling plant shutdown	Variance from normal operation	Glassmaking plant shutdown	Variance from normal operation	Methanol production plant shutdown	Variance from normal operation	Calcium carbonate production Plant shutdown	Variance from normal operation	Baking soda production plant shutdown	Variance from normal operation
VHPS	0	0	0	0	0	45	-45	0	0	-0.074	0.074		0
HPS	0	-28	28	0	0	39.58	-39.58	0	0	2.835	-2.835		0
MPS	0	13.5	-13.5	-38	38	4.62	-4.62	0	0	0.7938	-0.7938	-0.645	0.645
LPS	34.034	24	10.034	-96.45	130.484	5.28	28.754	-4.93	38.964	0.1562	33.8778	-1.7	35.734
	Pinch												
CW	155.66	118.1	37.56	7.35	148.31	26.9	128.76	0	155.66	0	155.66	3.31	152.35
ChW	30.753	18	12.753	7.35	23.403	4.75	26.003	0	30.753	0.263	30.49	0.39	30.363

4.4.6 Economic analysis of the total site heat integration system

The estimated capital cost of the TSHI (3(h)., Figure 3.3) was calculated based on the estimated cost of the waste heat boiler (Madeinchina.com, 2022a), the water chiller (Madeinchina.com, 2022b) and the utility headers. The typical cost factors (Smith, 2005) were used to estimate total cost of the TSHI network, as shown in Table 4.16. It was found that the total estimated capital cost would be $ 1,650,000. The steam at different pressure levels would be supplied to the various industries as shown in the TSUD table (see Table 4.14).

Table 4.16: Estimated capital cost based on delivered equipment costs (Smith, 2005)

Item (installed)	cost multipliers	Estimated capital cost
Waste heat boiler		440,000
Water chiller		220,000
Site preparation for the central utility hub	0.1	66,000
Equipment erection	0.4	264,000
Headers and pumping	0.7	462,000
Instrumentation & controls	0.2	132,000
Electrical connections	0.1	66,000
Total		1,650,000

This study utilised the proposed two-factor utility cost Equation 3.9 to calculate the estimated cost of utilities at different temperature and pressure levels. Table 4.17 and Table 4.18 shows a summary of the estimated annual cost of required utility for the TSHI and the potential cost saving from the heat integration of the TSHI network. It was found that $1,252,605 of utilities were required to meet the energy requirements of the TSHI network. It was also found that a potential cost saving of $1,483,194 could be realised due to the HI from the TSHI.

Table 4.17: Estimated cost of required utility for the TSHI

Utility	CEPCI	$C_{S,u}$	a	b	$C_{S,f}$ ($/Gj)	A_S ($/Y)
Chilled water	607.5	74.92	0.12	0.03	2	479,062
Cooling water	607.5	29.62	0.05	0.03	1	479,581
LPS	607.5	0.630	0.001	0.0037	3	293,963
					Total utility cost ($/y)	1,252,605

The utility avoidance cost savings, calculated and summarised in Table 4.18, determined if the TSHI could be economically viable. This cost-saving considered the maximum potential saving from heat integration.

Table 4.18: Estimated potential utility cost saving from the TSHI

Utility	CEPCI	$C_{S,u}$	a	b	$C_{S,f}$ ($/Gj)	A_S ($/Y)
LPS	607.5	0.717	0.0012	0.00368	3	632,414
MPS	607.5	1.371	0.00223	0.00389	4.5	268,644
HPS	607.5	0.952	0.00149	0.00417	11	290,885
VHPS	607.5	1.0094	0.00157	0.00426	13	291,251
				Total saving ($/y)		**1,483,194**

The estimated total annual cost analysis was calculated considering that the initial capital cost was divided over a payback period of 10 years. The annual operating labour cost and fixed operation and maintenance cost was estimated at 10% of the annualised capital cost. The total cost analysis of the process was found to have an annual loss of $1,749,411 (see Table 4.19).

Table 4.19: Summary of cost estimate of TSHI

TSHI	Cost ($/Y)
Annualised capital cost ($/y)	-1,650,000
Operating labour cost ($/y)	-165,000
Amount of the utility required for TSHI	-1,252,605
Fixed operation and maintenance cost ($/y)	-165,000
Amount of saving from the utility saving from TSHI	1,483,194
Total cost analysis (annualised) ($/y)	**-1749411**

The rate of return for the project was 8.98 %. This is low, but the main purpose of the study was to lower the CO_2 footprint of the industrial plant. The TSHI played an important role in lowering the amount of utilities required in the industrial site. It is estimated that hot utilities saving, valued at $1,483,194, could be obtained from the TSHI network. One of the main contributors to the escalated loss was the cost multipliers added to the original cost of the total sites heat exchanger network. If the multipliers were reduced, the effect on the total cost analysis would be significant. The carbon tax incentives and international sponsorship for CO_2 reducing projects could also be used to alleviate the economic impact of the TSHI on the suite of CO_2 reduction projects in the industrial site.

4.5 Power integration for hybrid power systems

The introduction of renewable sources for power generation is one of the most consequential ways to reduce the carbon footprint from outside sources. PoPA is an ideal tool that can be utilised for the power allocation of HyPS comprising renewable energy sources. The numerical tools by Rozali et al. (2013a) were used to determine the minimum target for outsourced electricity, the maximum power storage required for the HyPS, and the system's sensitivity to shut down during operations (Rozali et al., 2016b).

4.5.1 Data extraction

The first step in developing a HyPS is to evaluate the possible power sources apart from the outsourced mainstream electricity supply. Table 4.20 summarises the possible RE sources of power and the proposed DMFC that could be sourced to provide the electricity needs for the selected plants in the industrial site (4(a), Figure 3.3). The amount of solar power obtained was determined using the parking area of the selected plants in the industrial area. It was determined that the available area from (Table 4.27) for the placement of the solar panels was 14,280 m^2. The amount of electricity that could be generated by evaluating the placing of solar panels on parking lot rooftops in the identified parking areas of the selected industries is shown in Table 4.27. As a result, it was determined that the possible electricity generated per day as calculated from Equation 4.9 (Rozali et al., 2017), would 16.065 MWh, by assuming maximum solar production during the selected time period of the day. The industrial site also has a landfill area that collects garden waste comprising mainly felled trees and excess branches from garden service vendors from the surrounding residential and company premises. The biomass plant was presumed to operate optimally between 06:00 and 18:00, generating 24MWh of possible electricity per day (as calculated from Equation 4.8). The fuel cell configuration was expected to deliver 4.383 MWh of electricity supply per day, operating 24 h.

$$\mathrm{EE_{su/df}} = \sum P_R \times t_i \qquad \text{Eq. 4.8}$$

where

$\mathrm{EE_{su/df}}$ is the net electricity surplus/ deficit

$\mathrm{P_r}$ is the power rating

$\mathrm{t_i}$ is the time interval

Table 4.20: Power sources for the case study

Power sources		Time, h		Time interval, h	Power generated, MW	Electricity generation, MWh
AC	DC	From	To			
Biomass		06:00	18:00	13	2	24
	Fuel cell	00:00	23:59	24	0.183	4.383
	Solar	08:00	17:00	9	1.785	16.065

The electricity demands for the envisaged TSHI system considered the consumption for the existing plants, i.e., the industrial bakery, steel processing plant, wastewater treatment plant, glassmaking plant and paper recycling plant. The power demands also considered the chemical fixing plants, namely the calcium carbonate, methanol, and baking soda production plants. The post-combustion CO_2 capture system also considered the power demands because of the high-power consumption requirements for capturing and purifying the CO_2. Table 4.21 summarises all the electricity requirements for the proposed low CO_2 footprint industrial site. In this study it was assumed that there would be a constant consumption of electricity during the plant's operation. This study considered the power losses due to conversion from direct current (DC) to alternating current (AC) using a rectifier, as calculated using Equation 4.9 and power losses (due to conversion from AC to DC with the use of a rectifier as in Equation 4.10).

$$\mathrm{EE_{AC}} \underset{\mathrm{convert}}{\Longrightarrow} \mathrm{EE_{DC}} = \mathrm{E_{AC}(surplus)} \times \eta_{\mathrm{R}} \qquad \text{Eq. 4.9}$$

where

$EE_{AC} \underset{convert}{\Longrightarrow} EE_{DC}$ is the amount of converted AC electricity to DC electricity (kWh),

$E_{AC}(surplus)$ is the AC electricity surplus (kWh) and

η_R is the rectifier efficiency

$$\mathrm{EE_{DC}} \underset{\mathrm{convert}}{\Longrightarrow} \mathrm{EE_{AC}} = \mathrm{E_{DC}(surplus)} \times \eta_{\mathrm{I}} \qquad \text{Eq. 4.10}$$

where

$EE_{DC} \underset{convert}{\Longrightarrow} EE_{AC}$ is the amount of converted DC electricity to AC electricity (kWh),

$E_{DC}(surplus)$is the DC electricity surplus (kWh) and

η_I is the invertor efficiency

Table 4.21: Power demands for the case study

Power demands	Time, h		Time interval, h	Power consumed, MW	Electricity consumption, MWh
AC DC	From	To			
Industrial Bakery	00:00	23:59	24	0.049	1.181
Steel processing	00:00	23:59	24	0.563	13.5
Waste water treatment	00:00	23:59	24	0.033	0.792
Glassmaking industry	00:00	23:59	24	0.379	9.096
Paper recycling industry	00:00	23:59	24	0.096	2.304
Calcium carbonate production plant	00:00	23:59	24	0.090	2.170
Methanol industry	00:00	23:59	24	0.023	0.552
Baking soda production plant	00:00	23:59	24	0.198	4.752
CO_2 capture system	00:00	23:59	24	0.045	1.080

The power sources and demands data (4(b), Figure 3.3) for the illustrative study, as shown in Table 4.22, considers the power losses due to the conversion arranged on an hourly basis, showing the possible power sources and sinks within the industrial site. The power generation changes based on the availability of resources, e.g., it is assumed that Electricity generated from Solar PV takes place between 08:00 and 17:00. It is assumed that all the industrial sinks require AC to meet their electricity requirements. Therefore, the total power sinks and power sources at each hourly interval are calculated as shown in the last two columns in Table 4.22. These total power sinks and power sources at each hourly interval are shown in the Power Cascade Table (PCT), Table 4.23.

Table 4.22: Power sources and demands data for Illustrative study

Time (hr)		Site Power sources (MWh)					Site Power Demands (MWh)									Total power (MWh)	
From	To	Solar (DC)	Conversion to AC	Biomass	Fuel cell (DC)	Conversion to (AC)	Waste water	Glassmaking	Industrial bakery	Paper recycling	Steel processing	Carbon capture	Methanol	$CaCO_3$	Baking soda	∑ power source	∑ power demands
0	1				0.183	0.1735	0.033	0.379	0.0492	0.096	0.5625	0.045	0.023	0.09	0.198	0.1735	1.5665
1	2				0.183	0.1735	0.033	0.379	0.0492	0.096	0.5625	0.045	0.023	0.09	0.198	0.1735	1.5665
2	3				0.183	0.1735	0.033	0.379	0.0492	0.096	0.5625	0.045	0.023	0.09	0.198	0.1735	1.5665
3	4				0.183	0.1735	0.033	0.379	0.0492	0.096	0.5625	0.045	0.023	0.09	0.198	0.1735	1.5665
4	5				0.183	0.1735	0.033	0.379	0.0492	0.096	0.5625	0.045	0.023	0.09	0.198	01735	1.5665
5	6				0.183	0.1735	0.033	0.379	0.0492	0.096	0.5625	0.045	0.023	0.09	0.198	2.1735	1.5665
6	7			2	0.183	0.1735	0.033	0.379	0.0492	0.096	0.5625	0.045	0.023	0.09	0.198	2.1735	1.5665
7	8			2	0.183	0.1735	0.033	0.379	0.0492	0.096	0.5625	0.045	0.023	0.09	0.198	2.1735	1.5665
8	9	1.785	1.696	2	0.183	0.1735	0.033	0.379	0.0492	0.096	0.5625	0.045	0.023	0.09	0.198	3.8692	1.5665
9	10	1.785	1.696	2	0.183	0.1735	0.033	0.379	0.0492	0.096	0.5625	0.045	0.023	0.09	0.198	3.8692	1.5665
10	11	1.785	1.696	2	0.183	0.1735	0.033	0.379	0.0492	0.096	0.5625	0.045	0.023	0.09	0.198	3.8692	1.5665
11	12	1.785	1.696	2	0.183	0.1735	0.033	0.379	0.0492	0.096	0.5625	0.045	0.023	0.09	0.198	3.8692	1.5665
12	13	1.785	1.696	2	0.183	0.1735	0.033	0.379	0.0492	0.096	0.5625	0.045	0.023	0.09	0.198	3.8692	1.5665
13	14	1.785	1.696	2	0.183	0.1735	0.033	0.379	0.0492	0.096	0.5625	0.045	0.023	0.09	0.198	3.8692	1.5665
14	15	1.785	1.696	2	0.183	0.1735	0.033	0.379	0.0492	0.096	0.5625	0.045	0.023	0.09	0.198	3.8692	1.5665
15	16	1.785	1.696	2	0.183	0.1735	0.033	0.379	0.0492	0.096	0.5625	0.045	0.023	0.09	0.198	3.8692	1.5665
16	17	1.785	1.696	2	0.183	0.1735	0.033	0.379	0.0492	0.096	0.5625	0.045	0.023	0.09	0.198	3.8692	1.5665
17	18			2	0.183	0.1735	0.033	0.379	0.0492	0.096	0.5625	0.045	0.023	0.09	0.198	2.1735	1.5665
18	19				0.183	0.1735	0.033	0.379	0.0492	0.096	0.5625	0.045	0.023	0.09	0.198	0.1735	1.5665
19	20				0.183	0.1735	0.033	0.379	0.0492	0.096	0.5625	0.045	0.023	0.09	0.198	0.1735	1.5665
20	21				0.183	0.1735	0.033	0.379	0.0492	0.096	0.5625	0.045	0.023	0.09	0.198	0.1735	1.5665
21	22				0.183	0.1735	0.033	0.379	0.0492	0.096	0.5625	0.045	0.023	0.09	0.198	0.1735	1.5665
22	23				0.183	0.1735	0.033	0.379	0.0492	0.096	0.5625	0.045	0.023	0.09	0.198	0.1735	1.5665
23	24				0.183	0.1735	0.033	0.379	0.0492	0.096	0.5625	0.045	0.023	0.09	0.198	0.1735	1.5665

4.5.2 Power cascade table

The PCT, a tool in the PoPA, as described by Rozali et al. (2013a), is a method to target the amount of electricity stored for transfer to the next day's operation. The amount of electricity sources and demands for each hourly interval is calculated in Columns 3 and 4 of Table 4.23 using Equation 4.11.

$$\mathrm{EE}_{\mathrm{su/df}} = \sum P_R \times t_i \qquad \text{Eq. 4.11}$$

where

$\mathrm{EE}_{\mathrm{su/df}}$ is the net electricity surplus/ deficit

$\mathrm{P_S}$ is the power rating

$\mathrm{t_i}$ is the time interval

The net electricity surplus and deficit are seen in Column 8 of Table 4.23 and determined using Equation 4.12. The positive net electricity value represents the stored electricity sources, and the negative net electricity value represents the sinks. Electricity is supplied from external sources to meet the deficit.

$$\mathrm{nEE}_{\mathrm{su/df}} = \sum \mathrm{EE_S} - \sum \mathrm{EE_D} \qquad \text{Eq. 4.12}$$

where

$\mathrm{nEE}_{\mathrm{su/df}}$ is the net electricity surplus/deficit

$\mathrm{EE_S}$ is the net electricity sources

$\mathrm{EE_D}$ is the net electricity demands

The unfeasible electricity cascade from Column 9 of Table 4.23 shows negative electricity flows due to the net electricity being cascaded down. The feasible electricity cascade from Column 10 of Table 4.23 takes the largest negative value (-6.965MW), making it positive and cascading it cumulatively across the surplus and deficit (as seen in Column 8). The minimum amount during start-up is 6.965 MW of outsourced electricity, which would be required to ensure stability to the HyPS. This means that a net avoidance of 6,834 ton CO_2 per annum during HyPS normal operation could be achieved using the estimated 0.53kg CO_2/kWh of electricity production from coal (Hawkes, 2014).

Table 4.23: Power Cascade Table

							8	9	10
							Start-up and Operation		
1	2	3	4	5	6	7	PCT		
Time	Time interval h	∑ power source (MW)	∑ power demand (MW)	∑ Electricity source (MWh)	∑ Electricity demand (MWh)	Amount of electricity transfer, MWh	Net Electricity surplus/deficit, MWh	Unfeasible electricity cascade, MWh	Feasible electricity cascade, MWh
0								0	6.965
	1	0.1735	1.5665	0.1735	1.5665	0.1735	-1.393		
1								-1.393	5.572
	1	0.1735	1.5665	0.1735	1.5665	0.1735	-1.393		
2								-2.786	4.179
	1	0.1735	1.5665	0.1735	1.5665	0.1735	-1.393		
3								-4.179	2.786
	1	0.1735	1.5665	0.1735	1.5665	0.1735	-1.393		
4								-5.572	1.393
	1	0.1735	1.5665	0.1735	1.5665	0.1735	-1.393		
5								-6.965	0
	1	2.1735	1.5665	2.1735	1.5665	2.1735	0.607		
6								-6.358	0.607
	1	2.1735	1.5665	2.1735	1.5665	2.1735	0.607		
7								-5.751	1.214
	1	2.1735	1.5665	2.1735	1.5665	2.1735	0.607		
8								-5.144	1.821
	1	3.8692	1.5665	3.8692	1.5665	3.8692	2.303		
9								-2.841	4.124
	1	3.8692	1.5665	3.8692	1.5665	3.8692	2.303		
10								-0.539	6.426
	1	3.8692	1.5665	3.8692	1.5665	3.8692	2.303		
11								1.764	8.729
	1	3.8692	1.5665	3.8692	1.5665	3.8692	2.303		
12								4.067	11.032
	1	3.8692	1.5665	3.8692	1.5665	3.8692	2.303		
13								6.370	13.335
	1	3.8692	1.5665	3.8692	1.5665	3.8692	2.303		
14								8.672	15.637
	1	3.8692	1.5665	3.8692	1.5665	3.8692	2.303		
15								10.975	17.940
	1	3.8692	1.5665	3.8692	1.5665	3.8692	2.303		
16								13.278	20.243
	1	3.8692	1.5665	3.8692	1.5665	3.8692	2.303		
17								13.885	22.546
	1	2.1735	1.5665	2.1735	1.5665	2.1735	0.607		
18								14.492	23.153
	1	0.1735	1.5665	0.1735	1.5665	0.1735	-1.393		
19								13.099	21.758
	1	0.1735	1.5665	0.1735	1.5665	0.1735	-1.393		
20								11.706	20.367
	1	0.1735	1.5665	0.1735	1.5665	0.1735	-1.393		
21								10.313	18.974
	1	0.1735	1.5665	0.1735	1.5665	0.1735	-1.393		
22								8.920	17.581
	1	0.1735	1.5665	0.1735	1.5665	0.1735	-1.393		
23								7.527	16.187
	1	0.1735	1.5665	0.1735	1.5665	0.1735	-1.393		
24								6.134	14.795

4.5.3 Storage cascade table

The sustainability of a HyPS to ensure that there is sufficient reliable power to the industrial site is fundamental for the decarbonisation of the site. The storage cascade table (SCT) (4(c)., Figure 3.3) was used to gauge the maximum power storage capacity for a battery configuration to ensure that the excess power produced per hourly interval would be stored and the battery storage could provide for the power deficit per hourly interval. The SCT as shown in Table 4.24, was used to find the maximum power storage of 20.20 MW after considering 5% rectifier and inverter losses, and a battery charge and discharge loss of 10%, as well as the self-discharge rate losses of 0.004%/h while storing as DC power, as explained in Rozali et al. (2013b). Considering all these losses, it was also determined that the AEEND was 8.55 MW, that was cascaded to the next day operation. Therefore, it was established that the HyPS requires only RE sources of power to supply electricity to the industrial during normal operation apart from the 6.965 MW of outsourced electricity required during start-up.

Table 4.24: Storage cascade table

Time (hr) From	Time (hr) To	Total power (MWh) ∑ power source	Total power (MWh) ∑ power demands	Electricity surplus/ deficit (MWh)	Converted surplus MWh AC-DC (MWh)	Discharge for AC deficit MWh	Battery capacity AC-DC (MWh)	Outsourced electricity (MWh)	Battery capacity AC-DC (MWh)
	AEEND								8.55
0	1	0.1735	1.5665	-1.3930		-1.47		1.47	6.92
1	2	0.1735	1.5665	-1.3930		-1.47		1.47	5.29
2	3	0.1735	1.5665	-1.3930		-1.47		1.47	3.66
3	4	0.1735	1.5665	-1.3930		-1.47		1.47	2.03
4	5	0.1735	1.5665	-1.3930		-1.47		1.47	0.40
5	6	2.1735	1.5665	0.6070	0.58		0.52		0.92
6	7	2.1735	1.5665	0.6070	0.58		1.04		1.44
7	8	2.1735	1.5665	0.6070	0.58		1.56		1.96
8	9	3.8692	1.5665	2.3027	2.19		3.53		3.93
9	10	3.8692	1.5665	2.3027	2.19		5.49		5.90
10	11	3.8692	1.5665	2.3027	2.19		7.46		7.87
11	12	3.8692	1.5665	2.3027	2.19		9.43		9.84
12	13	3.8692	1.5665	2.3027	2.19		11.40		11.80
13	14	3.8692	1.5665	2.3027	2.19		13.37		13.77
14	15	3.8692	1.5665	2.3027	2.19		15.34		15.74
15	16	3.8692	1.5665	2.3027	2.19		17.31		17.71
16	17	3.8692	1.5665	2.3027	2.19		19.28		19.68
17	18	2.1735	1.5665	0.6070	0.58		19.80		20.20
18	19	0.1735	1.5665	-1.3930		-1.47	18.17		18.57
19	20	0.1735	1.5665	-1.3930		-1.47	16.54		16.94
20	21	0.1735	1.5665	-1.3930		-1.47	14.91		15.31
21	22	0.1735	1.5665	-1.3930		-1.47	13.28		13.68
22	23	0.1735	1.5665	-1.3930		-1.47	11.65		12.05
23	24	0.1735	1.5665	-1.3930		-1.47	10.02		10.42
				Total surplus =	22.00	AEEND =	8.55	7.33	

Storage capacity limit

4.5.4 Sensitivity analysis

The sensitivity of the HyPS (4(d), Figure 3.3) to resource shutdown is an important consideration for the site manager to plan for how much extra electricity would be required to fulfil the electricity deficits due to individual renewable energy shutdowns. Rozali et al. (2016b) approached the sensitivity of a HyPS by looking at the system's profitability by considering the feed-in tariff (FiT) as shown in Table 4.25 related to the RE resource. The sensitivity table shown in Table 4.25 shows the potential losses based on FiT penalty rates (Table 4.25) to the HyPS when the solar PV power source or the biomass power source fails. The FiT of renewable sources, as ratified by the DEA (2021), shows the tariff discrepancy between solar PV power source and the biomass power source as almost fourfold. From the sensitivity table (Table 4.26) it can be seen that a loss of $1,461 per day is experienced if the biomass fails and a loss of $1,327 per day is experienced if the solar PV fails on FiT penalty rates.

Table 4.25: Feed-in tariff rates of renewable sources (DEA, 2021)

Technology	Tariff (South African Rand/kWh)	Tariff (US dollar/kWh)	FIT penalty (US dollar/kWh)
Landfill gas power plant	0.9	0.06	0.0060
Small hydro power plant (less than 10MW)	0.94	0.063	0.0063
Wind power plant	1.25	0.083	0.0083
Concentrating solar power (CSP) with storage	2.1	0.140	0.0140
Concentrating solar power (CSP) without storage	3.14	0.209	0.0209
Biomass solid	1.18	0.079	0.0079
Biogas	0.95	0.063	0.0063
Photovoltaic systems (large ground or roof mounted)	3.94	0.263	0.0263
Concentrating solar power (CSP) Central tower with storage capacity of 6 hours	2.31	0.154	0.0154

Table 4.26: Sensitivity analysis of hybrid power systems using feed-in tariff

1. Operation	2. RE electricity MW/d		3. FIT paid USD			4. Deviation MW/d		5. Penalty, USD			6. Outsourced electricity	7. Electricity cost,	8. Total profit/Loss,
	Biomass	Solar	Biomass	Solar	Total	Biomass	Solar	Biomass	Solar	Total	MW/d	USD/d	USD/d
Normal	5.46	17.08	429.90	4492.80	4922.70	-	-	-	-	-	16.72	1425.90	3496.80
Biomass system fails	0	2.73	0	716.70	716.70	5.190	13.503	40.80	354.70	395.60	20.90	1782.30	-1461.30
Solar system fails	6.67	0	524.90	0	524.90	0	16.229	0	426.30	426,30	16.72	1425.90	-1327.30

4.5.5 Economic analysis of hybrid power system

The economic analysis of the HyPS (4(e), Figure 3.3) considers the solar PV system and the biomass power generation system.

4.5.5.1 Solar PV system cost estimates

The roof area of the parking space of the industries in the industrial site was considered for the installation of the solar PV panels as shown in Table 4.27. In this study, monocrystalline solar panels were considered as the preferred PV sources because of their higher efficiency (Hidayanti, 2020) and longevity (Sadek, 2016). Using the manufactures' solar PV panel size of four panels occupying 8 m^2/kW, it was determined that the number of panels needed for the proposed amount of power required would 7140. An installation fee of $76 per panel was considered (Solar Advice (PTY) LTD, 2021). It would cost $1,495,830 for the total installed panels required as seen in Table 4.27.

Table 4.27: Cost of monocrystalline solar panels for the industrial site (Solar Advice (PTY) LTD, 2021)

	Industry	Total covered parking area (m^2)	Power generated (kW)	Number of Panels	Cost of solar panel ($)	Cost per Installation($)
1	Industrial bakery	1,300	162.5	650	86,775	49,400
2	Wastewater treatment industry	280	35	140	18,690	10,640
3	Glassmaking industry	3,800	475	1,900	253,650	144,400
4	Paper recycling industry	2,700	337.5	1,350	180,225	102,600
5	Steel processing plant	5,900	737.5	2,950	393,825	224,200
6	Calcium carbonate production plant	100	12.5	50	6,675	3,800
7	Methanol industry	100	12.5	50	6,675	3,800
8	Baking soda production plant	100	12.5	50	6,675	3,800
Total		14,280	1,785	7,140	**953,190**	**542,640**
					Total installed solar panel cost	**1,495,830**

It was further determined that 21 invertor units of 100 kW (Live Stainable, 2021b) would be required for the study. This would cost approximately $ 520,934, as shown in Table 4.28. It was determined that the maximum storage capacity required for the HyPS stored would be 20.20 MW. The number of battery units with a 17.75 KW capacity (Live Stainable, 2021a) required for the power storage of the HPS would be 1,138 units. The capital cost of the battery storage required is $ 5,999,194 as shown in Table 4.29. The total capital cost of the

PV solar system that includes the installed PV cells, the invertor and battery storage system is $8,015,959 (Table 4.30). Although the maintenance of running a PV solar plant is low compared to other renewable sources of energy, the cost of maintenance for the PV system was estimated to be $20,850 (Table 4.31).

Table 4.28: Cost of invertor system for the industrial site (Live Stainable, 2021b)

Item	Cost ($)
Cost of100KW inverter($)	24,806
Cost of the required invertors for the system (20 units)	**520,934**

Table 4.29: Cost of battery storage system required for AEEND for the industrial site (Live Stainable, 2021a)

Item	Units(kW)	Cost($)
Maximum storage	20,200	
Battery unit	17.75	5,272
Number of units	1,138	**5,999,194**

Table 4.30: Summary of capital costs for the solar PV system including storage

items		Cost($)
Capital cost of the solar panels required		953,190
installation		542,640
Cost of required invertors		520,934
Cost of required batteries		5,999,194
	Total cost	**8,015,959**

Table 4.31: Summary of maintenance costs for the solar PV system (Tidball et al., 2020)

Solar PV: Operation& maintenance cost ($/MW/y)	Cost ($/y)
Fixed operation and maintenance fee ($/MW/y)	11,680
1,785 MW solar photovoltaic plant	20,849

4.5.5.2 Biomass gasifier power unit

For this study, three units of 1 MW biomass gasifier power plants were considered due to the efficiency of the biomass plant. Dividing the biomass plants into three modules prevents complete plant shutdowns when conducting maintenance. The three modules could also be advantageous if the biomass material becomes a limiting factor – in this case either 1 or 2 of the units could be used instead of all three biomass gasifier power units. The cost multipliers uses the typical factors for capital cost as explained by Smith (2005) to estimate the capital cost for the biomass plant, as shown in Table 4.32. The maintenance cost of the biomass plant (Table 4.33) could be conducted in three or two phases because the three 1 MW biomass plants could run concurrently. The reason for selecting three 1 MW biomass plants was to cater for the efficiency losses and to ensure that a steady reliable 2 MW of power source was available for the site.

Table 4.32: Capital cost of biomass power plant for the industrial site (Indiamart, 2021)

Item	Cost Multipliers	Cost($/y)
Capital cost ($) of a 1 MW biomass plant		400,000
3 x 1 MW biomass power plant	1	1,200,000
Site preparation	0.1	120,000
Installation ($)	0.15	180,000
Electrical connections	0.1	120,000
Total ($)		**1,620,000**

Table 4.33: Summary of maintenance costs for the biomass power system (Tidball et al., 2020)

Biomass: operation & maintenance cost ($/MW/y)	Cost($/y)
Fixed operation and maintenance fee ($/MW/y)	65,450
3 x1 MW biomass plant ($)	**196,350**

The HyPS would estimate the selling price of the solar and biomass produced power at the approved FiTs (see Table 4.25). It was found that the HyPS would be economically viable, with a potential annual profit of $476,990. The negative values in Table 4.34 are due to the annual capital and operational cost required to run the HyPS. The positive values of $1,318,568 and $674,739 is the maximum expected annual cash flow from the project. The rate of return for the project was 20.68%, making it highly desirable for the site to include a HyPS as a crucial tool to lower the CO_2 footprint. This profit realised from the RE power sources assists in reducing the cost of the fuel cell configuration (that was calculated to be $753,013) - giving a potential total annual cost reduction of 63%.

Table 4.33: Summary of cost estimates of the HyPS

RE- power source	Solar PV source	Biomass source	General HPS
Annualised capital cost ($/y)	149,583	162,000	
Fixed operation and maintenance cost ($/y)	196,350	289,170	
Invertor for HyPS ($/y)			52,093
Battery for HyPS ($/y)			599,919
Operating labour cost ($/y)	34,593	45,117	65,201
Selling price of power produced using FiTs ($/y)	1,318,568	674,739	
Total cost analysis (annualised) ($/y)			**478,990**

4.6 Summary of results

The decarbonisation of an industrial site through a multiple approach is essential in sustaining the reduction of anthropogenic carbon dioxide emissions of a brownfield. In this work, a four-step sequential framework is proposed (as summarised in Figure 4.6) that would lead to a low carbon footprint site. The framework as presented, started with the application of post-combustion CO_2 capture and purification to above 90% concentration. The next step was the selection of suitable subsidiary CO_2 fixing industries that would directly use reagents within the industrial site. The CO_2 footprint of the site was further reduced with the implementation of pinch analysis tools for heat integration and to optimise the distribution of renewable sources of power for a HyPS. The TSHI for the project revealed a 79.95% of hot utility usage reduction.

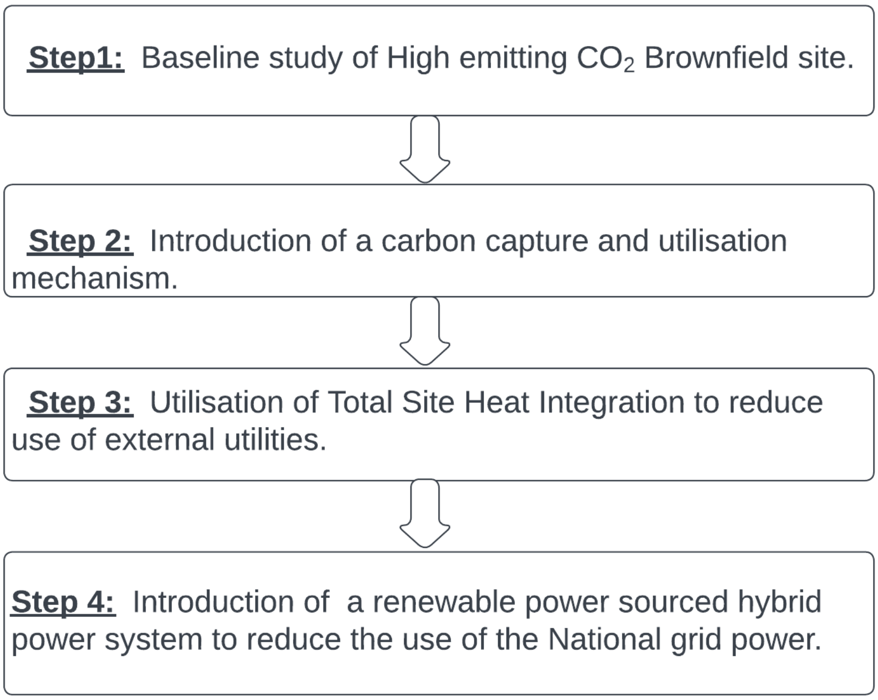

Figure 4.6: Summary of four stage CO_2 reducing framework

It was found from the analyses in Tables 4.4 to 4.6, that only the baking soda production would have the ability to sustain a profit of around $ 2M per annum. To sustain the cost of CH_3OH production, the cost of H_2 could be brought down through electrolysis of water using solar energy. To sustain the cost of the $CaCO_3$ production, it would necessitate a cheaper alternative wollastonite source from the steel making process slag at the site. The lowering of the cost of production of CH_3OH would substantially add impetus in maintaining the fuel cell overall cost. It was established that when considering the overall system, the market value of baking soda would be able to buffer the losses incurred by the current CCU system. It was established that the total water produced from the CCU system was 48.5 t/d, which could be supplied to the waste boiler and the solar electrolysis process for the production of hydrogen.

The techno-economic analysis conducted on the CCU system, which included a DMFC configuration, could be considered as a more viable alternative to the geological CO_2 storage option because the current geological storage landscape in South Africa has yet to be practically explored. The cost of capturing, transporting and maintaining the storage site with no payback stimulus makes it an expensive CO_2 reduction option. It is therefore significant that a viable localised option such as the industrial symbiosis for the use of CO_2

fixed products within a site was explored. An annual CO_2 abatement of 38,000 t/y could potentially be achieved from this CCU system, which is comparable to similar studies. Chemical fixation of CO_2 can become more sustainable if the industries within a site are encouraged to buy the products at above market value. The above the market value can be justified by the reduction of the carbon footprint of the in-situ produced products due to the CO_2 fixing of flue gas produced in the site and the removal of transportation costs associated with bringing products sourced from outside the site. The recent carbon tax implemented in South Africa to encourage the lowering of GHG will also improve the viability of CO_2 fixation processes to establish a low CO_2-emitting industrial site.

Although the rate of return for the TSHI was 8.98%, the main aim of the project is to reduce the carbon footprint and this rate of return could be improved by the carbon tax incentives for the CO_2 reduction project. The study also showed that RE sources of power and the additional DMFC power supply would be sufficient to provide a sustainable power source for the industrial site. The amount of CO_2 avoided from the addition of the HyPS would be 6,834 ton/y. The rate of return for the project would be 20.68%, making it highly desirable for the site to include a HyPS as a crucial tool to lower the CO_2 footprint.

CHAPTER FIVE

CONCLUSIONS

The sustained decarbonisation of industrial sites is essential in assisting the South African government in meeting its commitment to reduce emissions to below 440 million tonnes of CO_2 equivalent by 2030. The decarbonisation of an industrial site requires a multiple-pronged approach in sustaining the reduction of anthropogenic carbon dioxide emissions. In pursuing this aim, this study had the following objectives:

1. Propose a CO_2 reducing framework that would sequentially reduce the CO_2 footprint in a site.
2. Propose chemical storage of CO_2 by creating a subsidiary industry that supplies value added products for use within the site as an alternative to geological storage.
3. Conduct a sensitivity analysis of the TSHI and HyPS to evaluate its robustness.
4. Conduct an economic viability study of the subsidiary industry, TSHI and the HyPS.

This study presented a four-stage sequential framework (using different CO_2 lowering sequences) for a brownfield site. This study is an extension of the work of Aziz et al. (2017) that presented a framework for a greenfield site. This framework, which includes a fuel cell configuration, has not been done before. The sequence started with a baseline study of a high CO_2 emissions site to identify the possible CO_2 reducing avenues, including CO_2 capture and chemical storage, TSHI and the introduction of a HyPS using renewable sources of power. The baseline study (the first stage) considered possible constraints such as embedded spatial locations between plants as well as available space within the site to locate the centralised utility as well as hybrid power systems. The second stage of the framework was the removal of CO_2 from stationary sources of CO_2 emissions. This included post-combustion CO_2 capture and the inclusion of CO_2 fixing plants as an alternative to geological storage. The third stage of the framework was the introduction of a TSHI to optimise the external use of utilities in the site. The last stage of the framework was the introduction of renewable sources of power to the site by utilising PoPA to determine the minimum outsourced electricity required for the site. At this stage, the correct mix of renewable sources of power was also determined by considering resource availability in the site.

The study proposed the creation of a subsidiary industry (CO_2 sinks) to produce value-added products from captured CO_2 that have been purified for consumption within the industrial site. The study employed a ratio-based approach for the distribution of high purity CO_2 to selected CO_2-fixing plants based on the utilisation needs of the existing plants. In this study, it was determined that there were three possible CO_2 fixing plants: baking soda, methanol, and calcium carbonate production that could produce value-added product for in-situ utilisation. The methanol would be used on site by the proposed addition of the DMFC that would be used in the electricity mix of the HyPS. It must be noted that introducing this subsidiary industry for mineral storage of CO_2 also reduced the carbon footprint within the site, despite the possibility of CO_2 re-release to the site because the external source was avoided, i.e. the carbon footprint attributed to transport.

This work also used a multi-sensitivity analysis to determine the robustness of the TSHI system and HyPS for the framework. The work studied the effects of individual plant shutdown on the TSHI by examining the differences in utility sources and demands from that of the normal TSHI operation. This sensitivity exercise aimed to give a better insight into the required waste heat boiler for the site. It was determined that a maximum of 45 MW of VHPS is required should one of the plants fail. A sensitivity analysis of the HyPS was conducted to examine the effect of individual renewable power shutdown from the normal HyPS. In order to do this, this work studied the sensitivity of the HyPS by examining the system's profitability by considering the FiTs. It was found that a loss of $1,461 per day would occur if the biomass failed and a loss of $1,327 per day if the solar PV failed.

A techno-economic analysis of the carbon capture utilisation system was conducted using a case study approach. The systems considered in this analysis were the post-combustion CO_2 capture system, all the CO_2 fixing plants and the fuel cell configuration. It was found that the only profitable CO_2 fixing system was the baking soda production facility. In order to make the other CO_2 fixing plants more attractive, it is recommended getting alternate sources of reagents, such as using solar energy for the hydrolysis process to acquire cheaper H_2 for the methanol production process, and substituting the wollastonite with the steel making process slag for the calcium carbonate production process. This study also conducted an estimate cost analysis of the TSHI system by considering the present capital cost of the waste heat boiler and the water chiller. It was determined that the ROI for the TSHI system would 8.98%. This is low, but the benefit has to be seen through the lens of lowering the CO_2 footprint of the brownfield site. The study also conducted an estimate cost analysis of the HyPS used in the proposed case study based on the FiTs that are used in South Africa. It was found HyPS was economically viable, with a potential annual profit of $476,990.

As noted above, the sustained decarbonisation of an industrial site is essential in assisting the South African government in meeting its commitment of reducing emissions to below 440 million tonnes of CO_2 equivalent by 2030.The reduction of CO_2 in an existing industrial site is important in the establishment a low carbon impact industrial park. This study employed a solvent-based post-combustion absorption system to capture CO_2 after considering the various post-combustion options available. The study employed a ratio-based approach for the distribution of high purity CO_2 to selected CO_2 fixing plants, based on the utilisation needs of the existing plant. The study also showed that RE sources of power and an additional DMFC power supply would be sufficient to provide a sustainable power source for the industrial site. The amount of CO_2 avoided through the addition of the HyPS would be 6 834 ton/y. The rate of return for the project would 20.68%, making it highly desirable for the site to include a HyPS as a crucial tool in lowering the CO_2 footprint.

This framework could be used to assist high CO_2-emitting industrial zones to attain deep and sustainable reductions in global CO_2 emissions as per the COP26 Glasgow Climate Pact. This work presents a viable framework that would result in lowering the CO_2 footprint of a brownfield site in four sequential steps. However, the cost of holistic decarbonisation of an industrial site is impeded by the cost of the CO_2 lowering systems. Recent incentives by the European Union for decarbonisation projects could also assist in improving the viability of the proposed project.

The following recommendations for further studies are proposed:

- A deeper cost analysis needs to be conducted to establish the impact of alternative sources of raw materials. The inclusion of the DMFC has to be evaluated further to consider the efficiency of the fuel cell and its impact on the sensitivity of the hybrid power system. It is recommended that the overall market value of baking soda be considered, taking into account the demand for baking soda and the carbon footprint in the production of baking soda, methanol, and $CaCO_3$ production.
- Future work could give emphasis to the inclusion of the co-generation potential for the HyPS. The method should also consider the effects of pressure drop on the TSHI. In addition, future work should consider the fluctuation of renewable power due to seasonal changes and resource availability.

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Appendixes

Appendix 1:

Supplementary Tables: Single Utility Cascade Tables and Multiple Utility Heat Cascades Problem Table Analysis

Table 1A: Single utility cascade table for Bakery Plant

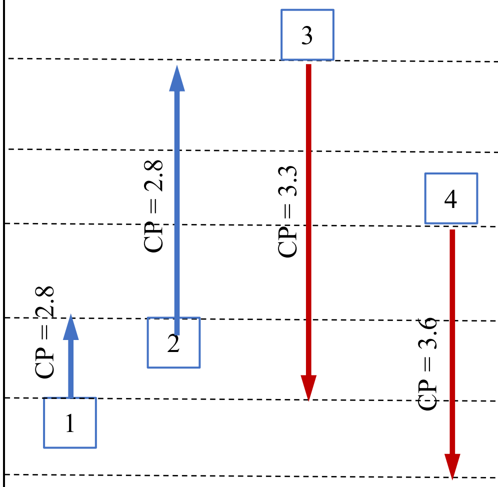
Interval Temp (^{O}C)	Stream population CP units = $MW/^{O}C$	ΔT interval (^{O}C)	$\sum CP_H - \sum CP_C$ ($MW/^{O}C$)	$\Delta H_{interval}$ (MW)	initial Cascade (MW)	Single Utility Cascade (MW)
235					0	28
		10	-2.8	-28		
225					-28	0
		140	0.5	70		
85					42	70
		40	0.8	32		
45					74	102
		13	0.8	10.4		
32					84.4	112.4
		17	3.6	61.2		
15					145.6	173.6

Table 1B: Single utility cascade table for Paper recycling Plant

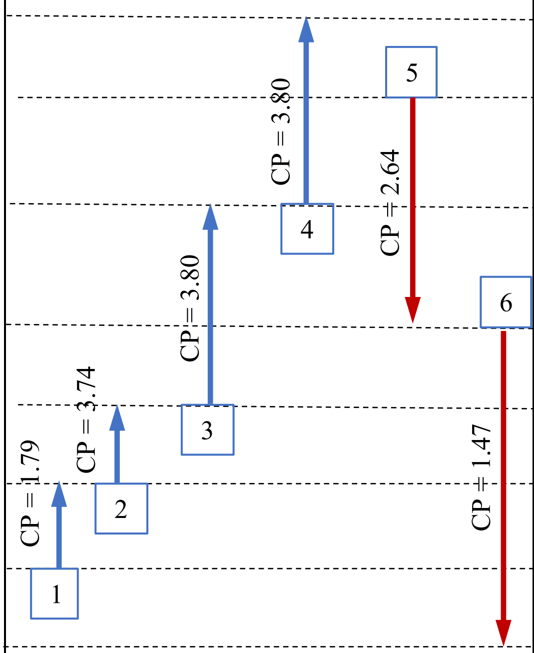
Interval Temp (^{o}C)	Stream population CP units = $MW/^{o}C$	ΔT interval (^{o}C)	$\sum CP_H - \sum CP_C$ ($MW/^{o}C$)	$\Delta H_{interval}$ (MW)	initial Cascade (MW)	Single Utility Cascade (MW)
180					0	233.05
		10	-3.8	-38.0		
170					-38	195.05
		45	-1.16	-52.2		
125					-90.2	142.85
		50	-1.16	-58.0		
75					-148.2	84.85
		10	-2.33	-23.3		
65					-171.5	61.55
		25	-2.27	-56.75		
40					-228.25	4.8
		15	-0.32	-4.8		
25					-233.05	0
		10	1.47	14.7		
15					-218.5	14.7

Table 1C: Single utility cascade table for Glassmaking Plant

Interval Temp (°C)	Stream population CP units = MW/°C	ΔT interval (°C)	∑CP$_H$-∑CP$_C$ (MW/°C)	ΔH $_{interval}$ (MW)	initial Cascade (MW)	Single Utility Cascade (MW)
1110					0	22.48
		20	-1.124	22.48		
1090					-22.48	0
		500	0.09	45		
590					22.52	45
		180	0	0		
410					22.52	45
		120	0.284	34.08		
290					56.6	79.08
		255	0.11	28,05		
35					84.65	107.13
		20	0,95	19		
15					103.65	126.13

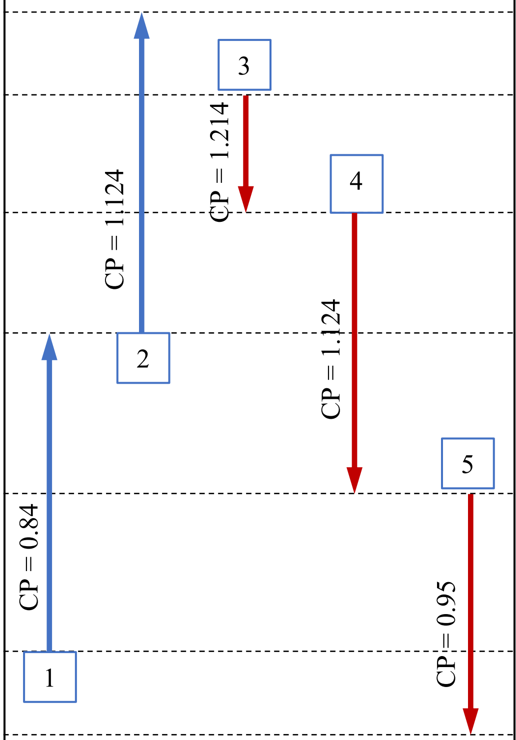


Table 1D: Single utility cascade table for Methanol production Plant

Interval Temp (°C)	Stream population CP units = MW/°C	ΔT interval (°C)	∑CP$_H$-∑CP$_C$ (MW/°C)	ΔH $_{interval}$ (MW)	initial Cascade (MW)	Single Utility Cascade (MW)
64.5					0	3.09
		10	-0.223	-2.23		
54.5					-2.23	0.86
		6	-0.078	-0.47		
48.5					-2.7	0.39
		5	-0.078	-0.39		
43.5					-3.09	0

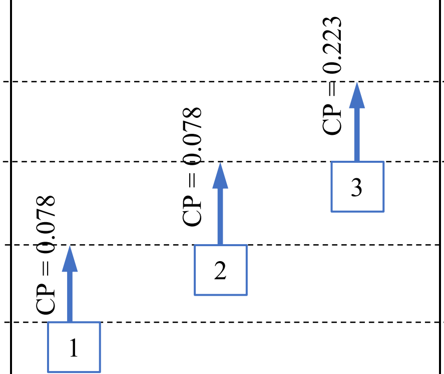
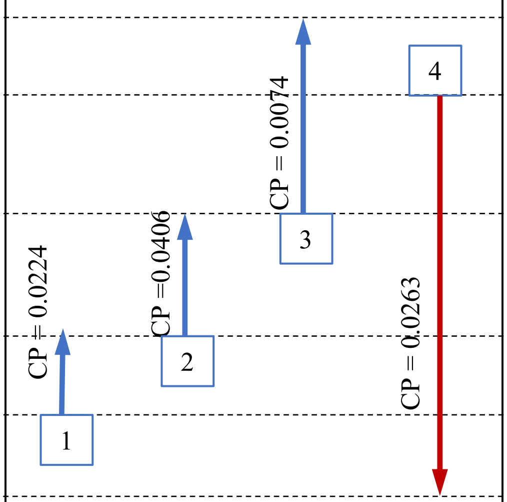
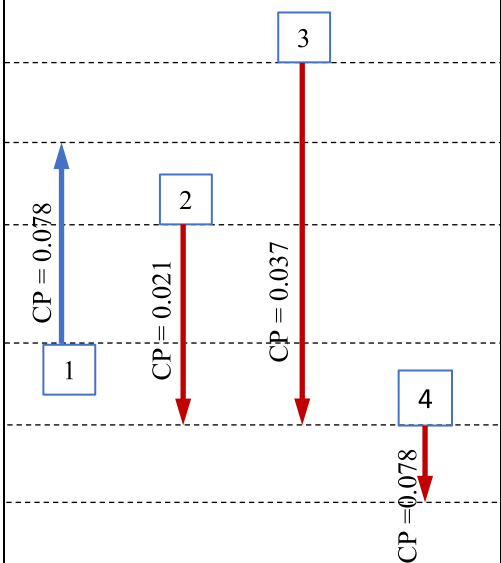


Table 1E: Single utility cascade table for Calcium Carbonate production Plant



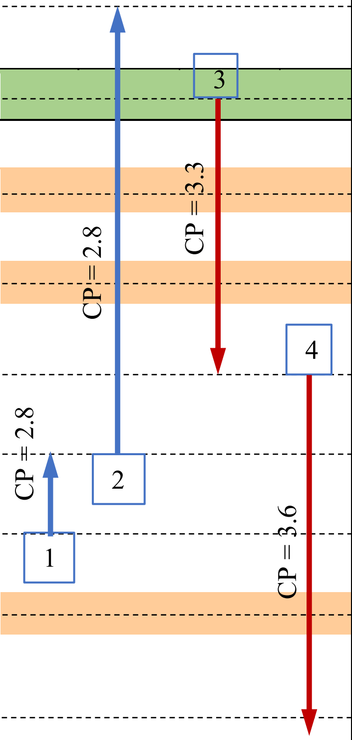
Interval Temp (°C)	Stream population CP units = MW/°C	ΔT interval (°C)	∑CP$_H$- ∑CP$_C$ (MW/°C)	ΔH interval (MW)	initial Cascade (MW)	Single Utility Cascade (MW)
380					0	0.074
		10	-0.0074	-0.074		
370					-0.074	0
		215	0.0189	4.0635	3.9895	4.064
155						
		70	-0.0146	-1.022	2.9675	3.042
85						
		60	0.0039	0.234		
25					3.2015	3.276
		10	0.0263	0.263		
15					3.4645	3.539

Table 1F: Single utility cascade table for baking soda production Plant



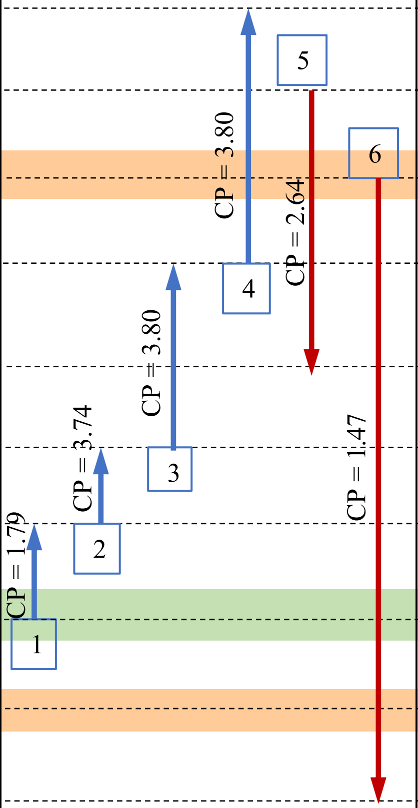
Interval Temp (°C)	Stream population CP units = MW/°C	ΔT interval (°C)	∑CP$_H$- ∑CP$_C$ (MW/°C)	ΔH interval (MW)	initial Cascade (MW)	Single Utility Cascade (MW)
185					0	2.325
		5	0.037	0.185		
180					-0.074	2.51
		10	-0.041	-0.41		
170					3.990	2.1
		105	-0.02	-2.1		
65					2.968	0
		10	0.058	0.58		
55					3.202	0.58
		40	0.078	3.12		
15					3.465	3.7

Table 1G: PTA with multiple utility heat cascades for Bakery Plant



Interval Temp (^{o}C)	Stream population CP units = $MW/^{o}C$	ΔT interval (^{o}C)	$\sum CP_{H}$- $\sum CP_{C}$ ($MW/^{o}C$)	ΔH interval (MW)	Multiple Utility Cascade (MW)	Utility consumed/ generated	Heat sink/ sources
240					0		HPS 28
		5	0	0			
235					0		
		10	-2.8	-28		28	
225					0		Pinch
		27	0.5	13.5		-13.5	
198					0		MPS 13.5
		48	0.5	24		-24	
150					0		LPS 24
		65	0.5	32.5		-118.1	
85					85,6		
		40	0.8	32			
45					53,6		
		13	0.8	10.4			
32					43,2		
		12	3.6	43.2			
20					0		CW 118,1
		5	3.6	18		-18	
15					0		
		5	0	0			
10							ChW 18

Table 1H: PTA with multiple utility heat cascades for paper making Plant



Interval Temp (°C)	Stream population CP units = MW/°C	ΔT interval (°C)	∑CPH-∑CPC. (MW/°C)	ΔH interval (MW)	Multiple Utility Cascade (MW)	Utility consumed / generated	Heat sink/ sources
198							MPS 38
		18	0				
180					0		
		10	-3.8	-38.0		38	
170					0		
		20	-1.16	23.2			
150					23,2		LPS 96.45
		25	-1.16	23.2			
125					46,4		
						11.6	
		50	-1.16	-58.0	0		
75						23.3	
		10	-2.33	-23.3	0		
65						56.75	
		25	-2.27	-56.75	0		
40						4.8	
		15	-0.32	-4.8			
25						0	Pinch
		5	1.47	7.35		-7.35	
20							CW 7.35
		5	1.47	7.35			
15						-7.35	
		5	0	0			
10							ChW 7.35

Table 1I: PTA with multiple utility heat cascades for Glassmaking Plant

Interval Temp (°C)	Stream population CP units = MW/°C	ΔT interval (°C)	∑CP$_H$-∑CP$_C$ (MW/°C)	ΔH interval (MW)	Multiple Utility Cascade (MW)	Utility consumed / generated	Heat sink/ sources
1110					0	-22.48	
		20	-1.124	22.48			
1090	3 (CP = 1.214)						Pinch
		500	0.09	45	0	-45	
590	4 (CP = 1.124)						45
		90	0	0			
500							VHPS 45
						-39.58	
		90	0	0			
410	2				39,58		
		120	0.284	34.08			
290	5 (CP = 0.95)				5,5		
		50	0.11	5.5			
240					0		HPS 39.58
		42	0.11	4.62		-4.62	
198					0		MPS 4.62
		48	0.11	5.28			
150					0		LPS 5.28
		115	0.11	12.65		-26.9	
35	1 (CP = 0.84)				14,25		
		15	0.95	14.25			
20					0		CW 26.9
		5	0.95	4.75			
15						-4.75	
		5	0	0			
10					0		ChW 4.75
;							

Table 1J: PTA with multiple utility heat cascades for Methanol manufacturing Plant

Interval Temp (^oC)	Stream population CP units = MW/^oC	ΔT interval (^oC)	$\sum CP_H - \sum CP_C$ (MW/^oC)	ΔH interval (MW)	Multiple Utility Cascade (MW)	Utility consumed / generated	Heat sink/ sources
150							LPS 4.93
		85.5	0	0	0		
64.5	3: CP =0.223					2.23	
		10	-0.223	-2.23	0		
54.5	2: CP =0.078					0.47	
		6	-0.078	-0.47	0		
48.5	1: CP = 0.078					0.39	
		5	-0.078	-0.39	0		
43.5							Pinch
		23.5	0	0			
20							CW 0

Table 2K: PTA with multiple utility heat cascades for Calcium Carbonate manufacturing Plant

Interval Temp (^oC)	Stream population CP units = MW/^oC	ΔT interval (^oC)	$\sum CP_H - \sum CP_C$ (MW/^oC)	ΔH interval (MW)	Multiple Utility Cascade (MW)	Utility consumed / generated	Heat sink/ sources
500							VHPS 0.074
		120	0	0			
380						0.074	
		10	-0.0074	-0.074	0		
370	4: CP = 0.0263						Pinch
		150	0.0189	2.835		-2.835	
240							HPS 2.835
		42	0.0189	0.7938		-0.7938	
198							MPS 0.7938
						-0.1562	
		43	0.0189	0.8127			
155	3: CP = 0.0074				-0.6565		
		5	-0.0146	-0.073			
150					-0.5835		LPS 0.1562
						0	
		65	-0.0146	-0.949			
85	2: CP =0.0406				0.3655		
		60	0.0039	0.234			
25	1: CP = 0.0224				0.1315		
		5	0.0263	0.1315			
20							CW 0
		10	0.0263	0.263		-0.263	
15					0		
		5	0	0			
10							ChW 0.263

Table 1L: : PTA with multiple utility heat cascades for Baking Soda manufacturing Plant

Interval Temp (^{O}C)	Stream population CP units = $MW/^{O}C$	ΔT interval (^{O}C)	$\sum CP_{H}$- $\sum CP_{C.}$ ($MW/^{O}C$)	ΔH interval (MW)	Multiple Utility Cascade (MW)	Utility consumed / generated	Heat sink/ sources
198							MPS 0.645
			0				
185	3						
		5	0.037	0.185			
180						0.225	
	2	10	-0.041	-0.41	0		
170							
		20	-0.02	-0.4	0	0.4	
150	CP = 0.078; CP = 0.021; CP = 0.037						LPS 1.7
		85	-0.02	-1.7		1.7	
65	1						Pinch
		10	0.058	0.58		-3.31	
55	4				2.73		
		35	0.078	2.73			
20	CP =0.078						CW 3.31
		5	0.078	0.39		-0.39	
15					0		
		5	0	0			
10							ChW 0.39

Appendix 2:

Table 2: Calculations for the average cost of CO_2 capture

Composition of flue gas of industries in the industrial site

$$C_{CC} = C_E + C_A + C_M + C_L$$

Steel industry

						525	$/kw							
					Carbon capture									
Componen	% Comp	Power (MW	Plant capac	Power(MW	PC (h/y)	c.A($/y)	c. P ($/Kwh	CoE ($/y	c.O M($/y)	c.L($/y)	F_{CO2} (kg/h)	F_{CO2} (t/y)	**CC.C ($/y)**	**CC.C ($/t)**
		13,5	8100	0,44	8760	231000	0,16	616704	23100	25410	1790,1	15681,28	896214	57,15185
H_2	3,6	13500	70956	ton/y										
CO	22,1		69204000	kg/y										
CO_2	22,8													
N_2	48,3													
O_2	0													
H_20	3,2													
HC's	0													

Paper industry

						525	$/kw							
Componen	% Comp	Power (MW	Plant capac	Power(MW	PC (h/y)	c.A($/y)	c. P ($/Kwh	CoE ($/y	c.O M($/y)	c.L($/y)	F_{CO2} (kg/h)	F_{CO2} (t/y)	**CC.C ($/y)**	**CC.C ($/t)**
		2,3	4250	0,25	8760	131250	0,16	350400	13125	13125	1028,5	9009,66	507900	56,37283
H_2	24,1													
CO	30													
CO_2	24,2													
N_2	0,2													
O_2	0													
H_20	15,9													
HC's	5,6													

Glass industry

						525	$/kw							
Componen	% Comp	Power (MW	Plant capac	Power(MW	PC (h/y)	c.A($/y)	c. P ($/Kwh	CoE ($/y	c.O M($/y)	c.L($/y)	F_{CO2} (kg/h)	F_{CO2} (t/y)	**CC.C ($/y)**	**CC.C ($/t)**
		2,3	4450	0,39	8760	204750	0,16	546624	20475	20475	1579,75	13838,61	792324	57,25459
Cl comp	0,9													
CO	4,9													
CO_2	35,5													
NO_2	7,2													
NO_x	12,9									Avg CC.C ($/t)		56,92642		2196438
O_2	5,4													
SO_2	31,6									Total F_{CO2} (t/y)		38529,55	38529,55	
F comp	0,14												105,5604	
Dust	1,44													

Appendix 3:

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Techno-economic analysis of carbon dioxide capture and utilisation analysis for an industrial site with fuel cell integration

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ABSTRACT

The emergence of global warming phenomena that has adversely affected the world today has been largely attributed to the proliferation of greenhouse gases, with Carbon dioxide, as its main constituent. The challenge to reduce the Carbon dioxide footprint can be overcome by increasing the value of Carbon dioxide emissions by creating subsidiary industries that can utilize Carbon dioxide as its raw materials and producing other added-value products that can be utilised within the industrial site. The study proposes a framework that sequences the process of evaluating the CO_2 footprint and proposing CO_2 reduction measures to decrease the CO_2 footprint of an existing industrial site. The framework considers an economic sustainability of a multipronged CO_2 utilisation approach that includes a fuel cell configuration. Fuel cell is an efficient electrical energy generation technology that can also supplement the electrical needs of a site. The objective of this study is to conduct a techno-economic investigation of the feasibility of including subsidiary plants producing methanol, Calcium carbonate and baking soda from the carbon dioxide captured from the flue gas in the industrial site. This paper investigated the cost of capturing carbon dioxide from selected plants within the industrial site and determined the operating and capital cost required using a bottom-up approach from mass balances. The energy and power cost were interpolated from data obtained from similar waste to resources plants. From the methanol produced, it was determined that a maximum potential of 4.4 MWh per day of electricity can be produced from a Direct Methanol Fuel cell, configuration. It was determined that the cost of producing methanol and calcium carbonate would only be sustainable if the price of raw materials such as hydrogen and wollastonite could be brought down by producing hydrogen through solar-chemical water splitting and the wollastonite from steelmaking slag. The baking production was determined as the most sustainable subsidiary industry in the carbon capture and utilisation, CCU framework with an annual rate of return on investment of 12%. The sustainability of the Carbon capture and utilisation system proposed depends on the reduction of certain raw material costs and the carbon tax alleviation funds. The findings could serve as a guide for future industrial site planning when inviting CO_2 fixing plants to join in the subsidiary industry.

1. Introduction

The dire effects of global warming as articulated by the Intergovernmental Panel on Climate Change (IPCC) 2018 report could lead to rising ocean levels, colder winters, hotter summers, frequent droughts, and other natural disasters (IPCC, 2018). According to the report, it is imperative to keep the rise in global average temperature to under 2 °C above pre-industrial levels and while limiting the temperature increase to 1.5 °C above pre-industrial levels to avoid irreversible calamities on the planet and its population. The concentration of Carbon dioxide (CO_2) in the atmosphere hit a record high of 415 parts per million in 2019 for the first time. According to the National Oceanic and Atmospheric Administration (NOAA) Earth System Research Laboratory (2005), the world must keep CO_2 emissions below 350 ppm to avoid dangerous levels of climate change. A drastic reduction of greenhouse gases (GHG) of which anthropogenic CO_2 is a major

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A comprehensive carbon dioxide reduction framework for industrial site using pinch analysis tools with a fuel cell configuration

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ABSTRACT

Removing anthropogenic carbon dioxide emissions from existing industrial sites is essential to slow down climate change. A multipronged approach is required to reduce the carbon dioxide footprint of an existing industrial site by including carbon dioxide capture and utilisation, industrial symbiosis, heat integration and the introduction of renewable power sources. This work extends the current systematic framework for low carbon dioxide industrial site planning by proposing an alternative carbon dioxide lowering sequential framework for existing high carbon dioxide footprint industrial sites. The sequential framework will set out a four-step process using a suite of optimisation tools to guide industrial site managers to lower the carbon dioxide footprint of an existing industrial site that also features a fuel cell configuration. The framework includes a baseline study to analyse the current carbon dioxide footprint of the industrial site. The study then proposes a carbon capture and utilisation step to collate the carbon dioxide captured for chemical mineralisation for in-situ utilisation. The inclusion of the Direct Methanol Fuel Cell configuration is important to the site because it generates clean carbon-neutral power to the hybrid power system while utilising methanol, a carbon dioxide mineralised product. The following steps involve using Pinch Analysis tools to optimise the energy usage and renewable power usage within the industrial site. The energy produced at the site would be integrated to reduce external utilities required by using the Total Sites Heat Integration technique. The Power Pinch Analysis technique optimises power distribution from the hybrid power system hub. The illustrative case study is a typical industrial site in the Western Cape province in South Africa. It was determined that a potential 105 ton/day of carbon dioxide could be captured from the flue gas from industries on the site. The overall heat utility saving of 79.95% of the hot utility requirements for the participating industries in the site. It was also determined that the renewable sources of power which incorporated the fuel cell configuration would be sufficient to provide carbon-neutral power to the industrial site. The rate of return on the investment of the hybrid power system is found to be 20.68%. The carbon dioxide lowering framework for existing industrial sites could provide a sustainable, impactful guide for site planners to assist the country's commitment to limit greenhouse gas emissions.

1. Introduction

The Glasgow Climate Pact, an agreement reached at the 2021 United Nations Climate Change Conference (COP26), declared that limiting global warming required rapid, deep and sustained reductions in global greenhouse gas emissions. This includes reducing the global carbon dioxide emissions by 45 per cent by 2030 relative to the 2010 level (UNFCCC, 2021). The importance of lowering the carbon dioxide (CO_2) footprint of a high emitting industrial site through devolution of CO_2 processes and the introduction of cleaner production has become consequential in the retardation of the effect of greenhouse effect. The South African government has committed to sustaining the national greenhouse gas emissions below the 398–440 million tonnes of CO_2 equivalent by 2030 (Modise, 2021). The adverse effects of climate change due to the global increase of greenhouse gases have started to

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