

**A SYSTEMATIC APPROACH TO COUPLING ENERGY WITH CARBON
INTEGRATION TO REDUCE CARBON FOOTPRINT FROM INDUSTRIAL
PARKS**

A Thesis

by

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ABSTRACT

The depletion of natural resources and the increase in greenhouse gases emissions, which constitute mainly from carbon dioxide, has led many policymakers to issue policies to reduce carbon emissions and fuel consumption. However, reducing the energy consumption is constrained by meeting the increase in goods demands governed by the growth in global population. This problem can be tackled by improving process efficiencies which leads to a decrease in fuel consumption and hence the emissions. Moreover, end-of-pipe treatment approaches reduce carbon emissions by capturing carbon dioxide and store it or utilize it. While the first method is achieved via heat integration, the second method is achieved through carbon integration. In the first method, heat is exchanged between processes to minimize fuel consumption whereas the additional low grade heat is removed using cooling utilities. Moreover, carbon integration requires heat and power to capture and ship carbon dioxide from sources to sinks. This introduces a potential for synergy, where excess heat is used in the capture unit. This work explores this potential via two approaches: sequential and simultaneous. In the first approach, the energy and carbon integration are applied separately to minimize fuel consumption and carbon dioxide emissions. Afterwards, the excess waste heat is utilized to partially or fully offset the carbon integration heat and power demand, resulting in additional savings and further carbon reduction. This approach was demonstrated through a case study, where substantial savings were realized. In the second approach, the energy and the carbon problems were implemented simultaneously through an MINLP model. The same case study was used in

order to demonstrate the further benefits that can be obtained from solving the problems simultaneously.

DEDICATION

To my parents

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NOMENCLATURE

Latin Letters

A	regression parameter for steam turbine
B	regression parameter for steam turbine
b_0	regression parameter for steam turbine
b_1	regression parameter for steam turbine
b_2	regression parameter for steam turbine
b_3	regression parameter for steam turbine
$C_{b,fuel}$	Cost of boiler fuel
C_{CI}^{AEI}	Cost of carbon integration network after energy integration
C_{CI}^{BEI}	Cost of carbon integration network before energy integration
$C_{s,k}^{compressor}$	Annualized cost of compressor
C_{steam}^{LP}	Cost of Low Pressure steam
$C_{s,k}^{pipes}$	Annualized cost of pipe to transport carbon from source (s) to sink (k)
$C_{s,k}^{pump}$	Annualized cost of pump
C_{steam}^{VHP}	Cost of Very High Pressure steam
F_k	Total carbon mass balance around sink (k)
$F_{CO_2}^{BI}$	Total carbon dioxide mass flowrate from industrial city before integration
$F_{CO_2}^{Process}$	Carbon dioxide mass flowrate from processes
$F_{CO_2}^{utility}$	Carbon dioxide mass flowrate from utility system

L	intercept ratio of the Willian's line coefficient
L_s	Minimum total flow out of raw source
$m_{j,p,i}$	Mass flowrate of steam through turbine (p) in turbine level (j) to steam header (i)
m_{HRSG}	Mass flowrate of steam generated from heat recovery steam generation
$m_{i,o}$	Mass flowrate of steam (i) into energy sink (o)
$m_{inlet,hdr}$	Mass flowrate of steam into a steam header
$m_{m,i}$	Mass flowrate of steam at level (i) generated from waste heat recovery from energy source plant (m)
m_{stm}	Mass flowrate of steam generated from the boiler
$m_{outlet,hdr}$	Mass flowrate of steam at an outlet steam header
$m_{total,hdr}$	Total mass flowrate entering a steam header
m_i^{LS}	Mass flowrate of steam into header (i) through a let-down station
$m_{i,j,p}^{max}$	Maximum mass flowrate of steam through turbine (p) in turbine level (j) to header (i)
$m_{i,j,p}^{min}$	Minimum mass flowrate of steam through turbine (p) in turbine level (j) to steam header (i)
m_{LP}^{rec}	Mass flowrate of recovered low pressure steam
$n_{j,p}$	Willan's line slope for steam turbine (p) in turbine level (j)
P	Power (kW)
P_{CI}	Power demand of carbon integration

P_{export}	Power exported from utility system to the grid
P_{GT}	Power generated from gas turbine
P_{import}	Power imported from the grid to the utility system
$P_{\text{VHP} \rightarrow \text{LP}}$	Power generation from expanding VHP to LP steam (kWh)
$P_{\text{rec} \rightarrow \text{LP}}$	Power generation from expanding recovered steam to LP steam (kWh)
$P_{\text{rec} \rightarrow \text{cond}}$	Power generation from expanding recovered steam to condensate (kWh)
P_{ST}	Sum of power generated from all steam turbines in the utility system (kW)
$P_{s,k}^{\text{compressor}}$	Compressor power demand to transport carbon from source (s) to sink (k)
$P_{s,k}^{\text{pump}}$	Pump power demand to transport carbon from source (s) to sink (k)
$P_{\text{policy}}^{\text{export}}$	Maximum power allowed to be exported from the utility system to the grid
$P_{\text{policy}}^{\text{import}}$	Maximum power allowed to be imported from the grid to the utility system
Q_{BF}	Heat from fuel combustion in the steam boiler
Q_{stm}	Heat required to generate steam
R_s	Raw source plant carbon mass flowrate
$T_{s,k,t}$	Treated source mass flow from source (s) to sink (k)
U_s	Untreated source mass flow from carbon source (s)
$W_{j,p}$	Power generated by steam turbine (p) in turbine level (j)
$W_{\text{int},}$	Intercept of the Willian's line for steam turbines
$X_{j,p}$	Binary associated with steam turbine state (on/off)

$X_{s,k}$	Binary associated with flow of the combined treated and untreated carbon streams from carbon source (s) to carbon sink (k)
y_s	Mass composition of carbon source (s)
Z_k^{\min}	Carbon sink (k) minimum concentration

Greek Letters

Δh_{gen}	Enthalpy difference between boiler feed water and steam
$\Delta P_{s,k}$	Pressure difference between carbon sink (s) and carbon source (k)
$\Delta P_{s,k}^{\text{pipe}}$	Pressure drop across pipeline from carbon source (s) to carbon sink (k)
ΔT_{sat}	Saturation temperature difference between inlet and exit steam from steam turbine
θ	Carbon dioxide emissions parameter for steam at specified level
η_{Blr}	Boiler thermal efficiency
η_s	Carbon sink efficiency
$\chi_{\text{power}}^{\text{export}}$	Cost of power exported from utility system (\$/kWh)
ψ_{power}	Carbon dioxide emissions parameter for electricity

List of Abbreviations

BP	Backpressure
CC	Carbon Capture
CCUS	Carbon Capture, Utilization and Sequestration

CF	Conversion Factor
CI	Carbon Integration
CT	Condensing Turbine
E&CI	Energy and Carbon Integration
EIA	Energy International Agency
EIP	Eco-Industrial Park
EOR	Enhanced Oil Recovery
EU	European Union
GCC	Grand Composite Curves
GHG	Greenhouse Gas
HEN	Heat Exchanger Network
HP	High Pressure
HRSG	Heat Recovery Steam Generation
LP	Low Pressure
MEA	Monoethanolamine
MEN	Mass Exchange Network
MILP	Mixed-Integer Linear Programming
MINLP	Mixed-Integer Non-Linear Programming
MP	Medium Pressure
NCRT	Net Carbon Reduction Target
SCC	Site Composite Curve
SMLIP	Successive Mixed-Integer Linear Programming

SSSP	Site Sources-Sinks Profiles
THM	Turbine Hardware Model
TSA	Total Site Analysis
TSHI	Total Site Heat Integration
TSP	Total Site Profile
VHP	Very High Pressure

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1. INTRODUCTION

Threats of global warming, which are caused by greenhouse gases (GHG) emissions, have led many governments to implement regulations and sign agreements to reduce these emissions, such as the Kyoto Protocol and the European Union Climate and Energy Package. The package dictates the participating countries to reduce the GHG emissions by 20% from 1990 levels, incorporate renewable energy to supply 20% of EU energy demand, and enhance energy efficiency by 20% by 2020 [1]. Carbon dioxide emissions dominate the GHG emissions globally, thus, emissions reduction targets have focused on carbon dioxide. Many themes to reduce emissions have been proposed, including energy efficiency, renewable energy, and capturing and sequestering carbon dioxide. While energy efficiency gains can often be realized at low cost, the latter two options are relatively costly and, in the case of carbon capture, it require significant energy input [2].

The rapid expansion of industry in the last decades led to a drastic increase in energy consumption and carbon dioxide emissions. The world's energy consumption has increased by more than 40% from 1990 to 2012, from 6288 million tons of oil equivalent to 8980 million tons of oil equivalent [3]. Similarly, the global carbon dioxide production from human activities has increased by more than 60% for the same period, from 22.7 billion ton of CO₂ to 34.6 billion tons of CO₂. Consequently, the CO₂ concentration in the atmosphere has increased by more than 10% over this 22 year-period [4].

Carbon dioxide emissions are a result of fossil fuels combustion or as byproducts from processes such as the cement and ammonia industries. The Industrial and power sectors are two of the main energy consumers and CO₂ contributors. Those sectors emit about 60% of the total CO₂ emissions. Also, the manufacturing industries account for one-third of the world's energy consumption and 36% of carbon dioxide emissions [2,5]. Thus, it is important to develop methods to mitigate carbon emissions from industrial parks.

Due to significant economic benefits from process energy efficiency gains, significant research programs have been delivered over the past four decades to optimize energy management [6]. The area of energy integration has emerged to determine efficient heat and power management options for a process or an integrated site. In heat integration, heat is recovered from source streams into sink streams, while the excess heat is ejected into cooling utilities. These strategies aim to reduce energy consumption, which leads to economic savings and carbon dioxide emission reduction. The second measure to reduce the carbon footprint is capturing and sequestering or utilizing the carbon dioxide. While energy integration is a mature area, carbon capture and integration is a developing area. More recently, a comprehensive systematic approach for carbon integration in industrial parks was developed by Al-Mohannadi [7]. The approach considers a source-sink carbon allocation to achieve a specific carbon footprint cut at minimum cost.

The carbon integration approach consists of two main components: capturing carbon dioxide and transporting carbon dioxide from sources to sinks. The amine-based carbon capture processes are the current mature technology and commonly used in power plants, which unitizes post-combustion capture unit; however, this technology is energy

intensive [8]. The high energy requirements for the capture units is one of the main obstacles that prevents the wide utilization of this process. Various sources estimated that the regeneration energy demand is between 3 – 4.2 GJ/ton CO₂ for monoethanolamine (MEA) [9–12]. In addition to the heat requirements, power is required to capture, compress, pump, and ship the carbon dioxide from the carbon sources to the carbon sinks.

Many research activities have been conducted to decrease the energy requirements for regeneration. These activities include optimizing the operating conditions of the unit or synthesizing a solvent with low regeneration energy demand. For example, it was found that optimizing the operating conditions of the process decreases the energy requirements by more than 25% [10]. Also, different solvents are being tested that requires less energy such as KS-1 and AMP, which requires 3.2 GJ/ton CO₂ and 2.1 GJ/ton CO₂, respectively [9,11]. This energy is supplied to the stripper boiler in the form of low pressure (LP) steam, with a temperature less than 140°C, which was generated by combusting fossil fuel [10]. This results in an increase in the carbon dioxide emissions and a reduction in the overall efficiency of the capture unit.

As seen earlier, the research activities focused on different area separately. Another unexplored approach is merging energy and carbon integration, which will enhance the unit performance. This can be achieved by utilizing excess waste heat from the background processes into the carbon capture units. Typically, after process integration and Total Site Analysis (TSA), excess waste heat is ejected into cooling utilities. This introduces an opportunity for synergy between the processes in the industrial city and the carbon integration. The demand of the capture unit can be offset by utilizing

excess waste heat, which would improve the unit's efficiency and reduce the capture cost. This work provides a systematic approach to couple energy with carbon integration via two approaches: sequential and simultaneous. A case study for each approach is presented to demonstrate the benefits of the approaches. While energy and mass integration are mature topics, carbon capture and carbon integration is an emerging field. In the next section, a summary of energy and mass management approaches are presented.

2. LITERATURE REVIEW

In this section, a summary of the previous research activities in energy and mass management is included. The literature review covers energy and mass integration in the context of process integration (intra-plant) and Eco-Industrial Park (EIP), which is inter-plant integration.

2.1 Eco-Industrial Park

The many benefits that were realized by intra-plant integration has led many companies and researchers to investigate the possibility of expanding these tools from intra-plant to inter-plant integration [13–17]. The output of these works has led to the development of tools to assess the potential of inter-plant integration. This led to the introduction of EIP, which is based on the concept that the collective benefits of the plants working together surpasses the benefits of them working individually [18]. The goal of EIP is to bring different entities to work together to reduce raw material and energy consumption, reduce waste material disposal, and increase the value of the materials and products leaving the industrial park [18].

EIP is defined as a cluster of plants concentrated in an industrial city that are owned by different stakeholders with a common infrastructure aiming to exchange resources to enhance the overall performance of the cluster [19]. The industrial park may consist of plants from various industries such as power plant, oil refineries, pharmaceutical industry, food processing, manufacturing industries and others. Some of the successful examples of EIP are Kalondborg Park and Nanning Sugar Co., which are located in Finland and China,

respectively [19]. Similar to the methods developed for single plants, the scope of the tools that are being developed for EIP covers the following areas: energy, water, and/or materials management [20]. The following sections will elaborate on these areas.

2.2 Energy Integration

2.2.1 Site-wide Energy Integration

Although not explicitly called EIP, Total Site Analysis (TSA) is one of the earliest works on site-wide energy integration [21]. Total Site Heat Integration (TSHI) technique was first proposed in early 1990s by Dhole and Linnhoff [21], which is applied to a site containing various processes that are served by a central utility system. In their work, the Site Sources-Sinks Profiles (SSSP) was introduced, which is constructed using the Grand Composite Curves (GCCs) of single processes. The SSSP provides a graphical approach to target steam generations from source processes, steam requirements for sink processes and the co-generation potential. This will allow the user to calculate the Very High Pressure (VHP) steam load from the boiler and the co-generation potential of the utility system, which determines the fuel consumption and carbon dioxide emissions from the site [21].

In addition, the SSSP aids in determining the new energy targets to accommodate site expansion. For example, any newly added process would either import or export steam at different pressures from or to the utility system, and hence change the steam balance in the system, which might impact the co-generation potential. There is an important trade-off between VHP steam generation and co-generation potential. The VHP steam is expanded to various steam main levels through steam turbines. Thus, reducing VHP steam

generation reduces the fuel cost. However, it increases the cost of purchased power from the power plant, and vice versa. Thus, it is important to determine the optimum balance between reducing fuel consumption and importing power to minimize the total utility operating cost. Also, SSSP would provide a visual insight to identify promising options, such as changing the steam level temperature or processes operating temperature to reduce the overall cost. The case study presented by Dhole and Linnhoff [21] demonstrates the importance of this tool and how it aids in the generation of a what-if analysis.

On the downside, Dhole and Linnhoff used the exergy model to estimate the co-generation potential, which was proved to be inaccurate. In order to overcome this inaccuracy, Raissi [22] has proposed an alternative way to approximate the co-generation potential. The new method calculates the co-generation via Temperature-Enthalpy (T-H) Shaftwork model and is based on the observation that for a specified input pressure, the available heat in the outlet steam is almost constant at different outlet pressures. The coefficient of the correlation that relates heat load of the steam and saturation temperatures is defined as the Conversion Factor (CF). The CF is obtained from the operation data of specific turbines [22]. Klemes et al. [23] extended the previous works by introducing the Total Site Profile (TSP), the Site Composite Curve (SCC) and the Site Utility GCC (SUGCC). The TSP and SSSP are similar, while the SCC gives unique insight to the problem. The Total Site Pinch, VHP steam supply, heat recovery, and co-generation potential can be targeted and determined from the aforementioned graphical techniques.

While TSHI used to assess sites served by central utility system, other methods have been developed to reduce energy consumption across different processes that has

independent utility systems. Linke and Stijeopvic [24] presented a mathematical programming approach to determine the maximum waste heat recovery and optimum waste for an industrial city with decentralized utility systems. Later on, they published a similar work that accounts for co-generation [25].

2.2.2 Utility System

As shown in the previous section, the utility system plays an important role in energy integration and TSA. In addition to providing steam and power to the processes, the utility system acts as a link between the processes in the site. Thus, it is important to predict the behavior of the utility systems and estimate the fuel required to meet the site requirements. The utility system is complex and contains many nonlinear relationships. The complexity of the system arises from the interdependency of the steam turbine power output, size of the steam turbine, mass flowrate via the turbine, and the turbine efficiency. Therefore, a robust model is needed to predict the utility system output. This led to the development of many models to address this complexity and the non-linearity and to explore the co-generation potential and the change in steam and power demand. Mavromatis and Kokossis [26,27] developed a Turbine Hardware Model (THM), which estimates the power generation by steam turbines in utility site. The developed model predicts the turbine efficiency based on its load, unlike the T-H model, which assumes constant efficiency [22,26]. The THM model was used to develop and optimize networks of steam turbines [27].

However, the THM model focused on steam turbines and did not explore other power and steam generation options, such as gas turbines and Heat Recovery Steam

Generation (HRSG). Varbanov et al. [28] incorporated these elements and improved the steam and gas turbines models, to construct an overall model for utility systems and account for co-generation [28]. The developed method was a Successive Mixed-Integer Linear Programming (SMILP) model. The successive technique was used to overcome the non-linearity in the problem, which is caused by the non-linear relationship between steam flowrate and the efficiency of steam turbine. As the efficiency of turbine changes, the enthalpy of the exhaust steam changes, and consequently the temperature of the steam changes. In addition to the previous work, a top level analysis of site utility systems was developed by Varbanov et al. [29] to provide a strategy for steam saving and alternative route to decrease fuel cost [29].

2.2.3 Single Process Energy Integration

The development of site-wide energy integration is attributed to the success of intra-plant heat integration. The methods and techniques of intra-plant heat integration was developed over 20 years, to overcome the hike in energy prices that occurred in the early 1970s, which increased the operating cost of the plants. The goal of these research activities was to design an optimal heat exchanger network (HEN) [30–39]. Such networks would feature a maximum energy recycle at minimum cost. The main costs associated with designing HENs are the utility cost and capital cost. Various methods have been developed to achieve the aforementioned targets based on three concepts: heuristics, mathematical program and graphical solutions [6].

The first step of setting an optimum network is determining the energy target. This is defined as the maximum energy can be recovered from energy sources to energy sinks

constrained by thermodynamic limitations for a given minimum approach temperature. One of the methods to find the target is Table Interval method introduced by Linhoff and Flower [40], which is a mathematical programming model. Table Interval method is a systematic approach to identify the maximum energy recovery, minimum utility requirements, and aid in designing an optimal network. This is achieved by partitioning the problem into temperature intervals and ensuring that each interval is in energy balance. The solution of the problem does not guarantee an optimal solution; however, it provides a good estimate for a near-optimum network, as the network is usually dominated by energy costs.

Whilst mathematical programming has many advantages, it also has some drawbacks. One of the methodology's weaknesses is that it lacks the ability to give an insight about the problem. On the other hand, pinch based methodology and graphical techniques give a thermodynamic and visual insight about the problem. Similar to the TI method, Linnhoff and Hindmarsh [35] used the pinch concept to analyze the system. It was observed from the graphs that the system is divided into two regions. The point that divides the system into two region is called the pinch point and the regions are above and below the pinch. The significance of the pinch point is that it dictates the type of the utility that can be used, as hot utility can be used only above the pinch, while cold utility can be used only below the pinch [35]. This insight can help in reducing the computational time for complex designs.

2.3 Mass Integration

2.3.1 Mass Integration

Similar to energy integration, methods have been developed for mass integration. The aim of mass integration is to reduce the consumption of fresh resources, minimize waste discharge and maximize profit [41]. Many techniques have been developed to target minimum fresh materials and maximum recycle. Analogous to energy composite curves and Table Interval problem, mathematical and graphical approaches, were developed for direct recycling by El-Halwagib [42,43]. Also, comparable to designing heat exchanger network approach, the pinch point plays an important role in mass integration. When designing the direct recycling, the fresh material is used only for sinks below the pinch and no mass transfer across the pinch. Earlier, Mass Exchange Networks (MEN) method was introduced to systematically synthesis a cost-effective mass exchange network. In MEN, external mass-separating agents are used to reduce contamination in source streams to meet sinks requirements. The proposed approach is applicable for single and multiple contaminants [44]. In addition to intra-plant integration, Inter-plants integration was introduced [45,46]. An example of mass integration is water integration, which received the attention of many researchers. Many graphical and mathematical approaches were developed to target and design water networks for process integration and EIP [19,45,47–49]. Similarly, the work was extended to include the recycling of other materials such as carbon dioxide, in the context of process integration or EIP [7,50–54]. The next section provides an overview of the previous efforts to reduce carbon dioxide emissions through mass integration.

2.3.2 Carbon Integration

2.3.2.1 Carbon Sequestration and Utilization

In addition to heat integration, Carbon Capture, Utilization, and Sequestration (CCUS) and Carbon Integration (CI) are other ways to reduce carbon emissions into the atmosphere [7,55]. While Energy integration reduces the emissions by minimizing the source emissions, CCUS and CI reduce carbon emissions into atmosphere by recycling carbon dioxide as feedstock or store it in geological formation. Carbon dioxide can be used as a feedstock for various products such as methanol, ethanol and carbonates [50,56]. Furthermore, carbon dioxide can be captured and either be sequestered in geological formation or recycled for Enhanced Oil Recovery (EOR) [51–53].

Few methods have been proposed for carbon storage and fixation. For example, Tan and Foo have presented a pinch analysis approach to minimize the zero-emission energy sources while meeting the regional regulations and energy demand [57]. The same problem was later solved using Linear-Programming formulation [58]. For sink and source allocation, Middleton and Bielicki have proposed a MILP formulation to capture and store carbon dioxide. The formulation considers various sources of carbon dioxide and various sinks locations. The carbon dioxide sinks considered in this problem were oil reservoirs. The objective of the formulation was to design a network to allocate the carbon dioxide from the emission sources to the reservoirs to achieve a specified carbon footprint reduction, while minimizing the cost [54]. However, the formulation does not account for the carbon footprint associated with capturing and compressing carbon dioxide to be suitable for storage. Moreover, the paper considers only storing the carbon dioxide and

does not consider utilizing it to produce value-added products. Furthermore, the model lacks the ability to predict energy and power demand for different end-users pressure requirements. Additionally, the calculations are based on the assumption that all sinks have similar composition requirements.

2.3.2.2 Carbon Integration

In order to overcome the earlier issues, a systematic approach to allocate carbon dioxide to appropriate sinks is needed. Al-Mohannadi [7] introduced CI, which is a systematic approach to reduce carbon footprint. The objective function of the proposed MINLP formulation is to achieve a specific carbon footprint cut at minimum cost. The result of this formulation is a carbon network allocating sources emissions to various carbon sinks. The sinks can either be for storage or chemical transformation for CO₂. The paper considers the capital and operating cost for the treatment unit, compression and pumping unit, if needed, and the pipelines capital investment. The approach also accounts for the emissions associated with energy demand for treating and compressing the carbon dioxide [7]. The results obtained from the case study shows that the treatment cost is the dominant cost in the carbon network. Thus, to reduce the overall cost of the network, the treatment unit should be optimized. The treatment unit is needed to capture carbon dioxide from the diluted exhaust stream. The following section discusses different approaches to capture carbon dioxide.

2.3.2.3 Carbon Capture

In addition to heat integration, another approach was developed to reduce carbon emissions into the atmosphere. While the earlier techniques reduce emissions from the

source, carbon capture deal with end-of-pipe treatment. Typically, the carbon dioxide stream emitted into the atmosphere consists of carbon dioxide, in addition to many other components. The carbon molar composition of the exhaust stream may vary from 3% from gas turbines up to 44% in the steel industry [59]. Thus, different processes were proposed to purify the carbon stream. These processes take the composition of the stream into consideration. These processes are: post-combustion, oxy-fuel and pre-combustion.

As the power plants are one of main emitter of carbon dioxide, many studies have been conducted to optimize the carbon capture from their flue gases. Post-combustion is one of the main candidates for capture technology. The technology contains many separation technologies. However, the amine-based absorption treatment technology is currently the promising technology for the power generation sector. In this process, the flue gas is passed through an absorber, where the gas comes in contact with an amine-based solvent (lean solvent). The outlet of the column's top is the clean gas, while the other stream is the rich solvent, which contains carbon dioxide. The rich solvent is routed to a stripper, where the solvent is regenerated and a high concentrated carbon dioxide stream leaves at the column [8]. The disadvantage of this process is the high energy demand for the stripper reboiler to regenerate the solvent. Many research activities is being conducted to minimize the reboiler duty by optimizing the process or introducing a more efficient amine solution [9,10].

The second process is utilizing oxy-fuel. The low carbon concentration in the exhaust stream is due to combusting fuel in air. Therefore, in addition to carbon dioxide, the flue gas contains substantial amount of nitrogen, which may constitute more than 75%

of the stream on molar basis. Hence, combusting fuel with pure oxygen produces a carbon dioxide enriched flue gas. This approach makes it easier to separate carbon dioxide from the other components for further treatment or storage. However, due to fossil fuel combustion with oxygen, instead of air, new equipment might be required. For example, a new gas turbine that can withstand oxygen combustion might be needed, which requires large capital expenditure. In addition, an Air Separation Unit (ASU) is required to separate oxygen from air, which requires additional capital and operating cost [60].

The third approach is pre-combustion. In this method the fuel is converted into syngas, which is composed of carbon monoxide and hydrogen, where hydrogen is used as fuel. On the other hand, the carbon monoxide is further reacted in a gas-shift reactor with steam to obtain additional hydrogen as fuel and carbon dioxide as byproduct. The carbon dioxide is then separated from the product stream while the hydrogen is used as a fuel. On the downside, pre-combustion capture requires installation of additional equipment and energy input to produce syngas. In power plants, this reduces the plant's efficiency and increases their capital cost. Currently, there is no power plant utilizes this technology [61].

Although there are various capturing techniques that are available and strong candidates, the post combustion amine-based technology is selected for this work. This technology was selected as it is considered the mature technology with highest potential [2,62]. However, the capture unit operating cost, in addition to the compression units operating cost, constitute a large portion of the carbon network overall cost. This is due to the regeneration energy in the separation unit and power required for compressors. The objective of this work is to develop an approach to reduce the fuel combustion in the utility

system boiler that is used to generate the required steam and power requirements for the separation and compression units. The next section elaborates on the focus, objective, and boundaries of this work.

3. SCOPE AND OBJECTIVE

This section provides an overall summary about the focus of this work and the assumptions that were made. The focus of this work is to investigate the potential synergy between waste heat and carbon integration, in addition to linking the heat and power requirements of carbon integration to the utility system and power plant. This synergy can be used to design a carbon network to allocate carbon sources to carbon sinks at minimum cost, to achieve an overall carbon reduction. The recovered waste heat from energy sources is used to offset the demand of energy sinks. This measure reduces the steam generation from the boiler and, consequently, decreases fuel combustion and carbon emissions. Also, the work will explore the potential of utilizing the excess waste heat in the carbon capture units to improve the unit's efficiency.

The work considers linking a developed utility system with a developed carbon integration model. The developed technique is achieved without compromising the operability or the design of the existing processes. The processes in the studied park is assumed to be fully integrated and receive its energy demand from the common utility system, whereas the surplus heat from the processes is recovered and exported to the utility system or ejected into cooling utilities. The carbon dioxide emissions considered in this work are the ones that are resulted from materials processing, byproducts, and/or combusting fuels.

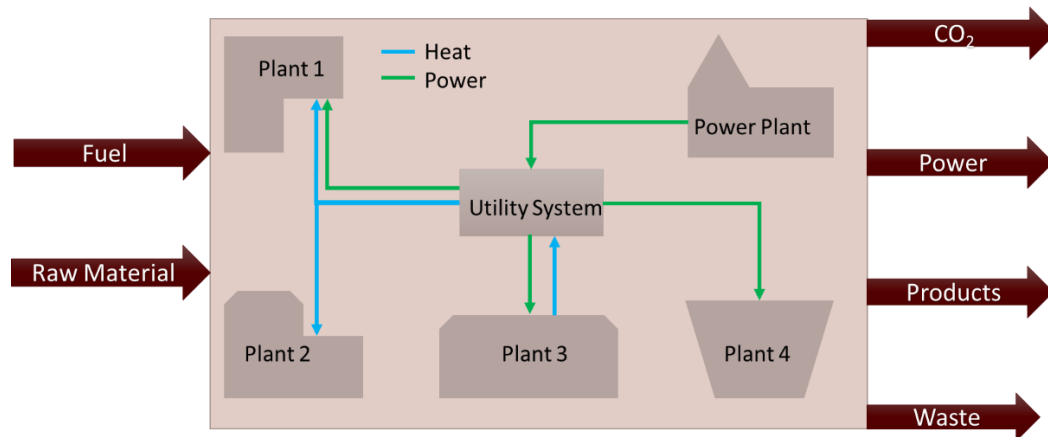


Figure 1: Industrial park schematic

The developed methods in this work are applicable for an industrial park served by a common utility system, similar to the one shown in Figure 1. The work considers the addition of carbon dioxide sinks. The heat and power demand for the processes are supplied from the utility system, which are generated from combusting fossil fuel. The utility system may import or export electricity to the grid to offset any deficit or surplus electricity. The utility system considered in this work is similar to the one shown in Figure 2. The presented approach aims to retrofit an existing design by alternating flow via different turbine paths, increase or decrease steam generation from boiler, and export or import power if necessary, without installing new equipment. Typically, the steam loads for various steam levels are known, based on the processes in the industrial park. However, due to the capture unit, the total amount of steam will change depending on the capture target. Therefore, the total amount of steam is unknown, as it highly depends on the carbon reduction target.

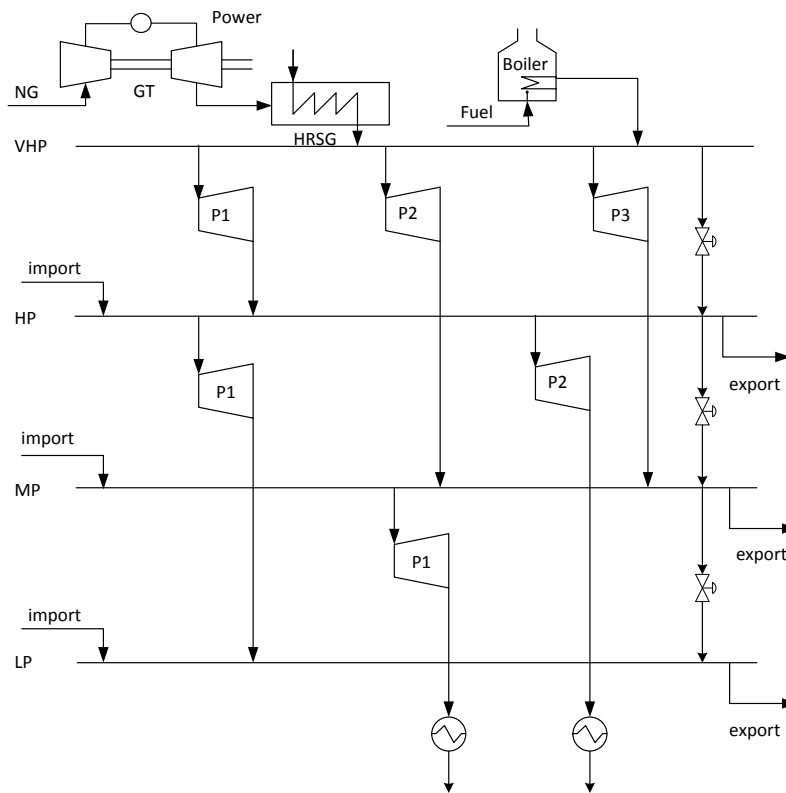


Figure 2: Utility system schematic

The proposed methods tackle this issue by determining the useful excess heat and linking the treatment unit with the utility system. An overview of the approaches that are used in this work is presented in the next section. The approaches used are sequential and simultaneous.

4. OVERALL APPROACH

This section outlines the overall approaches to reduce carbon emissions and fuel consumption in an industrial city. The approaches employ energy and carbon integration (E&CI) to achieve the aforementioned goal. In previous works, the carbon footprint emitted into atmosphere is reduced by two measures: reducing carbon emissions resulted from fossil fuel combustion, and end-of-pipe treatment for carbon dioxide. The fossil fuel consumption is reduced via heat integration, while part of the remaining emissions are captured and either stored or utilized as a raw feedstock into another carbon sink. The objective of this work is to couple E&CI. This section presents the developed approaches to achieve the aforementioned objective.

4.1 Data Acquisition

The first step in the approach is data acquisition. Similar to the work proposed by Al-Mohannadi [7], the following data are needed:

- 1- Industrial park data acquisition
- 2- Identification of carbon sinks
- 3- Carbon treatment and transmission data acquisition

In addition to the data collected in previous steps the following data are needed:

- 4- Heat sources and Steam System Composite (SSC).
- 5- Utility system and power plant data.

Heat source processes data are collected to construct the GCCs, which is used to construct TSP and finally SSC. In addition, the temperature and the duty of each stream

that is cooled using cooling utilities is required. This data is used to determine the available waste heat to be recovered. The SSC allows the user to determine the steam demand, co-generation potential and available waste heat.

The utility system information is needed to predict fuel requirements and carbon emissions from the site. The following data is needed:

- Boiler capacity and technical data
- Gas turbine capacity, exhaust flow rate, temperature and efficiency data
- Heat Recovery Steam Generation (HRSG) type
- Fuel type and cost
- Limits of importing and exporting electricity from utility system
- Steam turbines capacity, type, and performance data
- Steam turbines network design
- Steam mains pressure and temperatures

4.2 Energy and Carbon Integration

As mentioned earlier, this work proposes two approaches: sequential and simultaneous. The following subsections discuss how to apply them and points out the differences between them.

4.2.1 Energy and Carbon Integration: Sequential

In the sequential approach, the problem is solved step-by-step to combine energy and carbon integration. In addition to the data acquisition shown in the previous section, carbon integration is performed as described by Al-Mohannadi [7], then an additional step is added to combine energy and carbon integration. In section 5, these steps are explained

more in-depth. The energy problem is solved using TSA, while the carbon allocation problem is solved using carbon integration. Afterwards, the excess waste heat from the background processes, which was calculated from TSA, is used to offset the carbon integration demand.

4.2.2 Energy and Carbon Integration: Simultaneous

This approach is similar to previous one in terms of the data collection. However, the optimal design is based on a mathematical model. In this approach, MINLP model is used to find the optimal carbon network. The proposed model solves the energy and carbon allocation problem simultaneously. Section 6 presents the problem statement and formulation for this approach.

5. ENERGY AND CARBON INTEGRATION: SEQUENTIAL APPROACH

5.1 Introduction

This section elaborates on the approach used for coupling energy and carbon integration, as shown in section 4.2.1. The proposed approach solves the energy and carbon problems separately. The excess waste heat, which is identified from TSA, and steam and power requirements for carbon integration are calculated. The excess waste heat found from the first TSA is used to partially or fully offset the energy requirements for carbon integration. Moreover, the utility system is used to calculate the steam cost, and the emissions parameters associated with steam and power generation. The next section explains in detail the approach used.

5.2 Approach

In this section, a step-wise approach is proposed. The approach aims to minimize carbon emissions by reducing fuel consumption and end-of-pipe treatment. The fuel requirements can be minimized via heat integration, which targeted using TSA. This also identifies the waste heat ejected into cooling utilities. Then, the end-of-pipe treatment is achieved via carbon integration. Afterwards, further carbon and cost reduction can be realized from merging the energy and carbon integration via the utility system. Finally, the actual carbon reduction and the cost of the carbon network can be calculated by crediting the cost and the carbon dioxide resulted from energy consumption to the network. This problem is solve sequentially, which is consisted of three steps:

- 1- Energy integration and management

- 2- Carbon integration
- 3- Explore potential synergy, savings and additional carbon reduction

Step 1: Energy integration and management

The first measure in reducing carbon emissions is achieved by reducing fuel consumption through waste heat recovery. The TSP is constructed from combining the grand composite curves of various processes in the industrial park. From TSP, the industrial park fuel requirements, VHP steam load, co-generation potential, carbon dioxide emissions and heat recycle potential can be targeted. Also, this analysis aids in constructing SSC, which helps in identifying the quantity and quality of the waste heat that is ejected into cooling utilities. Figure 3 shows a sketch for a SSC.

Afterwards, the utility system is modelled and optimized to accommodate for the imported steam from energy source processes. The imported steam is routed via different paths to maximize power generation, while meeting the energy sinks demand, as shown in Figure 4. The figure shows the optional paths for importing HP steam. The red lines shows the steam flow for maximum power paths, while the blue line shows the co-generation option. Importing steam from energy sources reduces the steam generated from the boiler and HRSG. However, reducing steam generation from the firing machines might reduce the co-generation potential. Thus, a utility system model is used to optimize the steam generation and flow through the steam turbine network. The importance of this step is to determine the following:

- 1- Fuel cost
- 2- Carbon dioxide emissions from the utility system

- 3- Power import or export to the grid
- 4- VHP steam generation from the boiler
- 5- Steam flowrates through different turbines

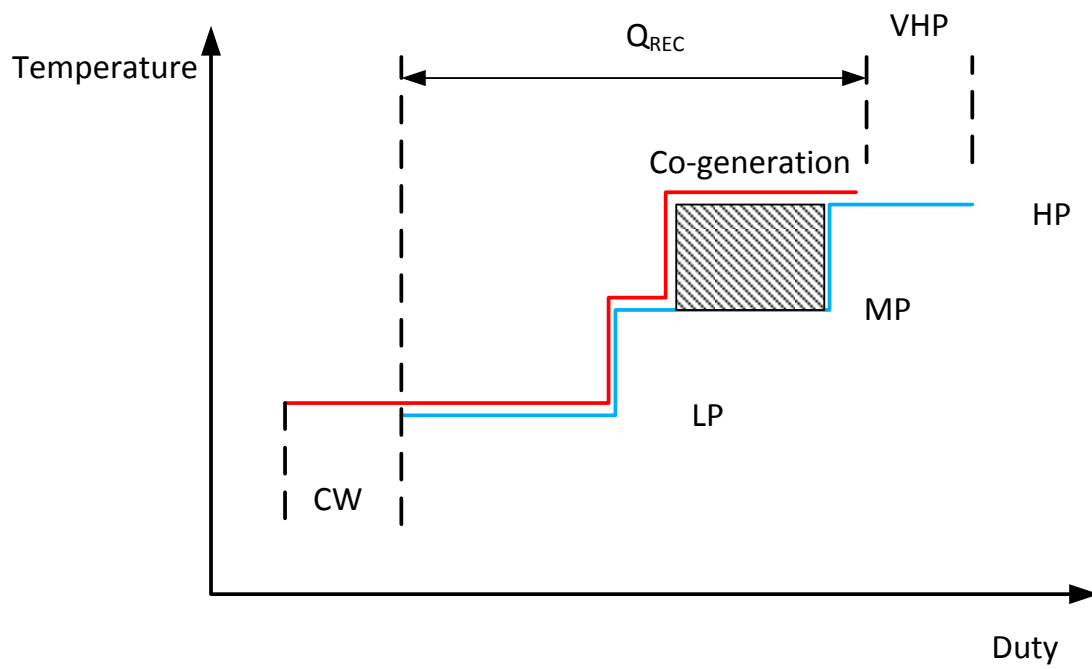


Figure 3: Steam system composite

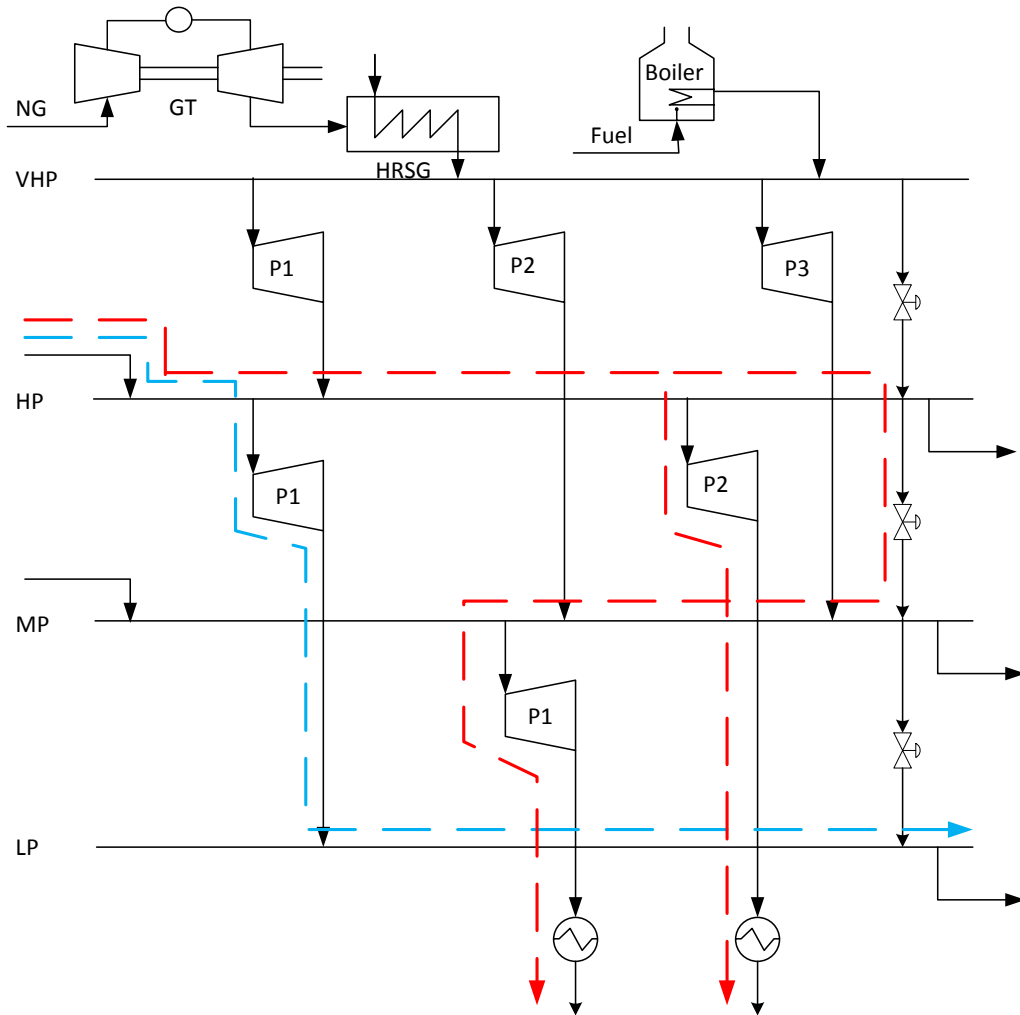


Figure 4: Utility system optional paths

Step 2: Carbon integration

The first step in carbon integration is to estimate the cost and the emissions parameters for various steam levels. This step is an important step, as it allows the user to accurately estimate the cost of the network. The utility model shown in section 6.3 was used for these estimation. While calculating the cost and carbon dioxide emissions for

VHP steam is a straight forward problem, it is not the case for other steam levels. The complexity of the problem arises from the co-generation. In the first case, fuel is combusted to generate VHP steam exclusively, thus, the cost of fuel and the resulted emissions from fuel combustions can be credited directly to the VHP steam. However, due to the co-generation, the fuel costs and the carbon dioxide emissions should be credited adequately to steam and the power generated from expanding VHP to the given steam level. This will aid in estimating the actual change in cost and carbon emissions caused by changing in heat and power demand. Accounting for these parameters adequately aids in accurately estimating the monetary and emission saving when waste heat is recovered in the form of steam at different levels.

As mentioned above, the calculations for VHP steam cost and associated carbon dioxide emissions were simply calculated based on the cost of the fuel to generate one ton of steam. Also, the emissions associated with VHP steam was equal to carbon emissions from fuel combusted to generate one ton of VHP steam. These values were computed based on the following equations:

$$\theta_{CO_2}^{VHP} = \frac{\Delta h_{gen}}{\eta_{Blr}} * \psi_{b,fuel} \quad (1)$$

$$C_{steam}^{VHP} = \frac{\Delta h_{gen}}{\eta_{Blr}} * C_{b,fuel} \quad (2)$$

where $\theta_{CO_2}^{VHP}$ is the carbon dioxide emissions parameter (ton CO₂/ton VHP steam), Δh_{gen} is the enthalpy difference to generate one ton of VHP steam from boiler feed water (GJ/ton VHP steam), η_{Blr} is the boiler efficiency, and $\psi_{b,fuel}$ is the carbon dioxide emissions per

unit of energy for the boiler (ton CO₂/ GJ). Also, C_{steam}^{VHP} is the VHP steam cost and $C_{b,fuel}$ is the fuel cost.

On the other hand, the cost of the various steam levels and their associated carbon emission parameters were calculated based on the power generation potential from expanding the steam from VHP to the specified pressure. The profit generated from the power generation and the cost of the steam should equal to the cost of the VHP. Moreover, the carbon dioxide associated with generating power and steam at various level, should equal the carbon emissions associated with generating VHP.

This complexity is solved by knowing the cost and the carbon dioxide emission associated with power generation. The cost and emissions parameters of the electricity were chosen as they can be easily obtained from power plants. In this approach, we are interested in the LP steam parameters, as LP steam is used in the amine-based capture unit. The following equations were used to compute the parameters:

$$\theta_{CO_2}^{LP} = \theta_{CO_2}^{VHP} - \psi_{power} * P_{VHP \rightarrow LP} \quad (3)$$

$$C_{steam}^{LP} = C_{steam}^{VHP} - \chi_{power}^{export} * P_{VHP \rightarrow LP} \quad (4)$$

where $\theta_{CO_2}^{LP}$ is the carbon dioxide emissions parameter (ton CO₂/ton LP steam), ψ_{power} is the carbon dioxide emissions per unit of energy (ton CO₂/kWh), $P_{VHP \rightarrow LP}$ is the power generated from expanding one ton of VHP to LP steam (kWh/ton steam). Also, C_{steam}^{LP} is LP steam cost (\$/ton LP steam), and χ_{power}^{export} is the cost of power that utility system export to the grid (\$/kWh). The ψ_{power} is obtained from a local power plant, as the power plant

has a fixed emissions power. It is noteworthy that these steps can be applied to any steam level.

Afterwards, carbon integration technique is applied to further reduce carbon footprint. While the first step is to minimize emissions by minimizing fuel consumption, this step minimize emissions by end-of-pipe treatment. The result of carbon integration is an optimal carbon network, allocating carbon sources to carbon sinks, while meeting the specified carbon cut. Moreover, the results obtained from carbon integration show the steam and power required to achieve the network. These results aid in calculating the cost and carbon dioxide associated with steam and power consumption.

Step 3: Explore potential synergy, savings and additional carbon reduction

In this step, the waste heat transferred into the cooling utility is identified and the potential of steam generation is explored. Figure 5 shows the potential synergy by exporting the waste heat to treatment unit, instead of cooling utilities.

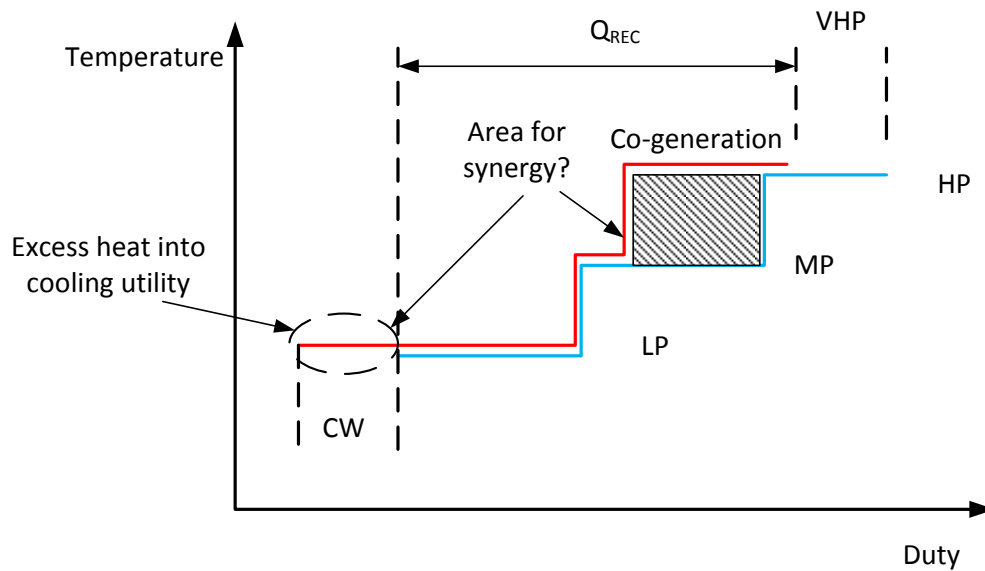


Figure 5: Steam system composites and areas for synergy

The excess waste heat is routed via different paths, as mentioned earlier and shown in Figure 4. The first step is maximize the co-generation flow through co-generation paths, afterwards, the steam is routed through condensing turbines to maximize power output. It is important to route the steams via the most efficient paths to maximize the power output from the system.

Afterwards, the potential savings and additional carbon reduction from utilizing waste heat is calculated. The first step is to determine the steam and power consumption of the network. If the steam requirements for CI is higher than the available waste heat, then all excess heat is used to offset the reboiler duty, while expanded via the most efficient path. Otherwise, the remaining steam is routed to the condensing turbine to offset the power demand. Thus, the value of steam and power saved are credited back to the CI

network cost, and the associated carbon emissions are credited back to the net carbon reduction, as shown in the following equation:

$$C_{CI}^{AEI} = C_{CI}^{BEI} - (m_{LP}^{rec} * C_{steam}^{LP}) - (P_{rec \rightarrow LP} + P_{rec \rightarrow cond}) * \chi_{power}^{export} \quad (5)$$

$$NCRT^{AEI} = NCRT - (m_{LP}^{rec} * \theta_{CO_2}^{LP}) - (P_{rec \rightarrow LP} * \psi_{power}) \quad (6)$$

where C_{CI}^{AEI} is the carbon network cost after energy integration, m_{LP}^{rec} is the mass flowrate of LP steam that was offset by recovered waste heat, $P_{rec \rightarrow LP}$ and $P_{rec \rightarrow cond}$ are the power generation-by expanding the recovered steam to LP steam and condensing main. $NCRT^{AEI}$ is the new net carbon reduction target.

5.3 Case Study

This section provides an illustrative example demonstrates the abovementioned steps to couple energy and carbon integration. Also, it shows the benefits realized from utilizing excess waste heat to offset the carbon integration energy demand. In this example, an industrial city containing the following plants is being studied: Methanol plant, refinery, fertilizer complex, power plant and a utility system. The methanol plant is planning to expand its production by adding a new process using renewable energy, based on the information provided by Van-Dal and Boullaou [63] and Olah et al [64]. The data of the plants that are used in this study are based on the data from Hasan et al [59], Gharaie et al [65], EIA [66], Canadian Natural Resources [67,68], and simulation results.

Table 1 and 2 shows the cost of fuel and electricity, and the steam levels pressures for the utility system. These data were used to cost the steam at different levels. Moreover Table 3 and 4 shows the steam demand and the available waste heat from different plants in the industrial park.

Table 1: Fuel and electricity prices

Utility	Unit	Price (\$/unit)
Fuel	MMBtu	3.9
Electricity (export)	MWh	50
Electricity (import)	MWh	51

Table 2: Steam levels

Steam level	Pressure (bara)
VHP	90
HP	48
MP	16
LP	2.7
Condensate	0.1

Table 3: Steam and power requirements

Process	Steam level	Steam flow (t/h)	Power demand (kW)
Methanol	HP	15.3	23975
	LP	5.6	
Refinery	MP	7.9	18000
Ammonia	MP	60.6	46200
	LP	54.6	
Urea	MP	33	0
	LP	16.5	

Table 4: Waste heat recovery steam generation

Process	Steam level	Steam generation (t/h)
Methanol	MP	86.1
Ammonia	HP	240

The utility system, shown in Figure 6, is licensed to export 10 MW of electricity to the grid, while importing 30 MW. Table 3 and 4 shows the steam requirement for each process and potential waste heat recovery from each process after performing process

integration for the individual plants. It can be seen from Table 3 that the total power and steam requirements for the industrial city is 88.175 MW, 15.3 t/h HP steam, 101.5 t/h MP steam, and 83.9 t/h LP steam, while the recovered waste heat is 240 t/h and 86.t/h of HP and MP steam, respectively.

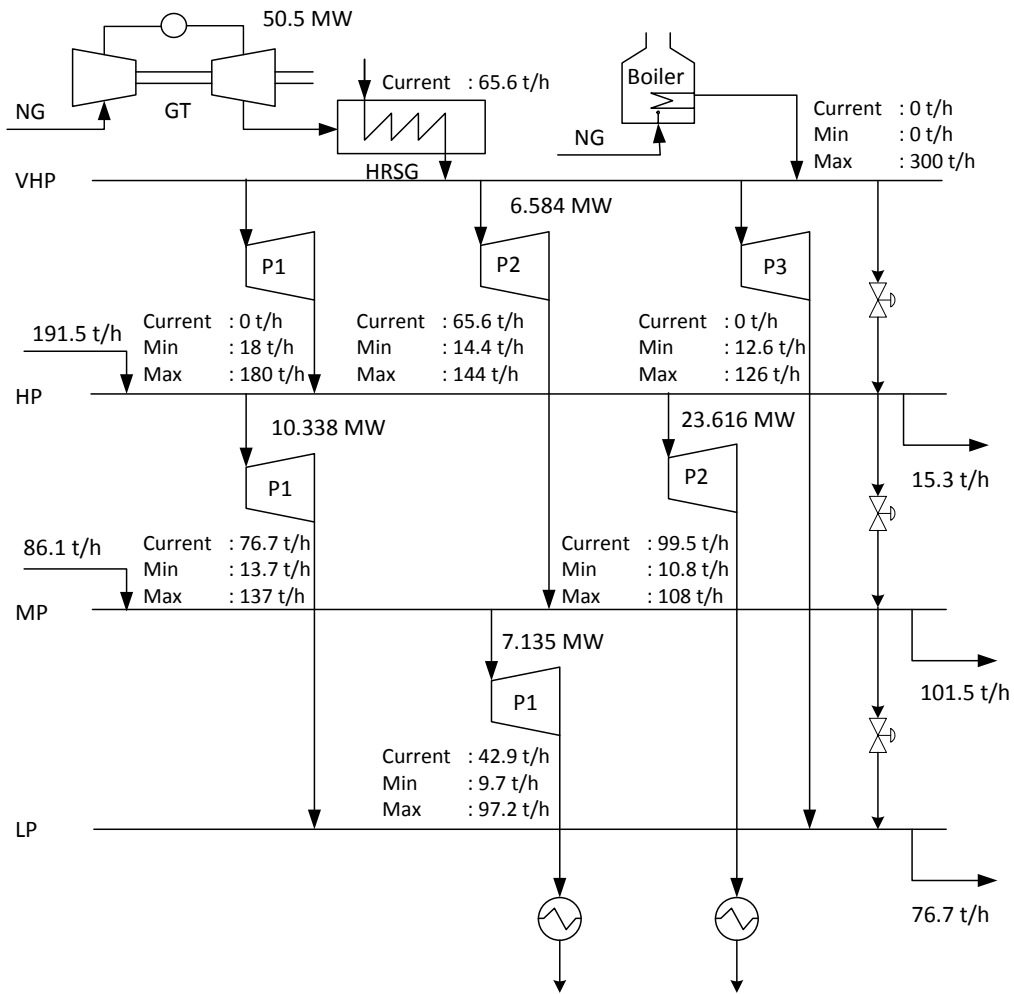


Figure 6: Utility system configuration and steam flow

The figure above displays the utility system configuration and the steam flowrate after TSA. The utility system in this example consists of: A gas turbine, a HRSG, a boiler, and 6 steam turbines, 2 of which are condensing turbines. The figure shows the minimum and maximum flowrate per steam turbine. If a turbine has steam flow lower than the minimum flow, then the turbine is turned off and the steam is routed via another path. The gas turbine technical data are shown in Table 5. These data are similar to the one published by Siemens for SGT-800 model. The total power output from the utility system is 98.175 MW, from which 10 MW is being exported to the grid.

Table 5: Gas turbine technical data

Data	Value
Fuel	Natural gas
Electrical efficiency	38.3%
Power generation	50.50 MW _e
Exhaust gas flow	132.8 kg/s
Exhaust temperature	553° C

It can be observed that only 191.5 t/h out of 240 t/h of HP steam is imported from the ammonia process. The remaining steam was not utilized as the processes' steam demand was offset by current flow from HRSG, and the utility system exported the maximum allowable power into the grid.

The second step is to apply carbon integration. The carbon integration approach that is used in this paper follows the approach published by Al-Mohannadi [7]. The cost parameters to evaluate the cost of the network can be found in the appendix. Moreover, the carbon sources data for the site can be found in the following tables.

Table 6: Industrial city carbon sources plants data

Plant	Capacity	Emitted CO ₂ , MTPD
Methanol	1400 MTPD Methanol	175
Refinery	100,000 bbl/d	710
Fertilizer Complex	900 MTPD Ammonia 1020 MTPD Urea	1450
Power Plant	1 GW	10764
Utility System	72 t/h VHP steam 98.2 MW	624
Total Emission		13723

Table 7: Carbon source stream data

Source stream	Composition		Estimated $C_{s,t}^T$ USD/tCO ₂	CO ₂ Capacity (MTPD)
	wt %	mol %		
Methanol – off gases	18%	4%	48.6	32
Methanol – topping column	55%	34%	14.3	143
Refinery – local furnaces	11%	7%	30.3	710
Ammonia – CO ₂ amine unit	100%	100%	0	1450
Power Plant (gas turbine)	7%	3%	41.4	10764
Utility system	14%	9%	26.5	624

Table 6 shows the carbon dioxide flowrate from each plant and the plant production capacity. The total emissions from the industrial park is 13723 MTPD. In addition, Table 7 shows the data of each source stream. The plant may have one or more source streams. For example, methanol plant contains two carbon source streams, each with different flowrate and composition. It is recommended to account for each stream separately, as it gives an extra degree of freedom. The treatment cost accounts only for the capital cost of the treatment unit.

The purpose of carbon integration is to allocate the carbon sources to the sinks. Table 8 shows the available and potential sinks, their costs, capacity and efficiency. The

sink type, composition, pressure and sink efficiency are the same as the ones published by Al-Mohannadi [7]. However, the sink costs were decreased to accommodate for current prices. The sinks consists of biological transformation, chemical treatment, and sequestration. The biological transformation sinks are algae and greenhouses, which consumes part of the carbon dioxide via photosynthesis. While the algae was assumed to be cost neutral, the greenhouse sink generates revenue, \$5 per metric ton of carbon dioxide. The chemical fixation for carbon dioxide is taking place in the solar methanol synthesis process and urea processes, which are purchasing carbon dioxide at \$19 and \$18 per metric ton, respectively. The third type of sinks is the sequestration, while EOR generates profit, additional cost is required to store carbon dioxide in geological formation.

Table 8: Carbon sinks

Sinks	CO ₂ composition, wt%	Flow CO ₂ , MTPD	P, KPa	Sink cost (USD/ton)	η_k
Algae	6%	500	101	0	0.42
Greenhouses	94%	1030	101	-5	0.5
Saline Storage	94%	8317	15198	8.6	0
Methanol	99.9%	1710	8080	-19	0.098
Urea	99.9%	1126	14140	-18	0.39
EOR	94%	1500	15198	-25	0

Moreover, Tables 9 to 11 provide additional data necessary for carbon integration. Table 9 shows the specific power requirement for compressors to compress one kilogram of carbon dioxide from source pressure to sink pressure. Table 10 shows the pressure drop

parameter for the flow between the specific source and sink. Moreover, Table 11 shows the distances between the plants.

Table 9: Compressor specific power (kWh /kg CO₂)

Source/Sink	Algae	Greenhouse	Storage	Methanol	Urea	EOE
Methanol (1)	0.0111	0.0559	0.1424	0.1424	0.1424	0.1424
Methanol (2)	0.0107	0.0558	0.1424	0.1424	0.1424	0.1424
Refinery	0.0126	0.0572	0.1424	0.1424	0.1424	0.1424
Ammonia	0.0091	0.0554	0.1424	0.1424	0.1424	0.1424
Power Plant	0.0135	0.0575	0.1424	0.1424	0.1424	0.1424

Table 10: Pressure drop parameter (kPa)

Source/Sink	Algae	Greenhouse	Storage	Methanol	Urea	EOE
Methanol (1)	71.1	846.9	64.3	8.2	65.6	65.6
Methanol (2)	67.9	843.6	61.0	8.2	62.3	62.6
Refinery	83.0	888.2	88.9	88.9	21.6	26.9
Ammonia	56.4	832.1	49.5	49.5	50.8	51.1
Power Plant	90.8	896.1	96.7	96.7	29.8	16.7

Table 11: Distances between carbon sources and sinks (km)

Source/Sink	Algae	Greenhouse	Storage	Methanol	Urea	EOE
Methanol (off gases)	2.17	25.83	1.96	0.25	2	2
Methanol (topping column)	2.07	25.73	1.86	0.25	1.9	1.91
Refinery	2.53	27.09	2.71	2.71	0.66	0.82
Ammonia	1.72	25.38	1.51	1.51	1.55	1.56
Power Plant	2.77	27.33	2.95	2.95	0.91	0.51
Utility system	2.97	27.66	3.25	3.25	1.1	0.8

Compressors and pumps are used to meet the sinks pressure demands and overcome pressure drop in the pipes. The compressors are used to compress the fluid up

to 7.38 MPa, then a pump is used to raise the pressure of the fluid to a higher level[7]. The total annualized costs of the compressors and the pumps are divided into operating cost and annualized capital cost. The dominant operating cost for compressors and pumps are the power cost. Also, the capital cost of the compressor is estimated based on the equipment duty. The costs parameters can be found in the appendix.

In this example, the cost of generating VHP steam was calculated to be 14.55 \$/ton, based on fuel cost of 3.9 \$/MMBtu. Also, the power is purchased at 0.051 \$/kWh. Moreover, the cost of LP steam was estimated to be 5.95 \$/ton. Besides the utility cost, carbon dioxide is emitted while generating the required utility. The carbon dioxide penalty for generating steam from using natural gas as fuel was calculated to be 0.22 t CO₂/t VHP steam and 0.12 tCO₂/t LP steam. The calculation for these values can be found in the appendix. Moreover, the electricity penalty was assumed to be 0.55 kg CO₂/kWh for the same fuel type, according to EIA [66]. Similarly, the calculations for these values can be found in the appendix.

Carbon integration method that was proposed by Al-Mohanndi[7] was implemented for different carbon footprint reduction. The total annualized cost (TAC) of the different networks were calculated. Figure 7 shows the TAC of the various CI networks. Also, it can be observed from the figure that with proper CI, an annual profit of \$ 8.7 million can be realized, while reducing the carbon footprint by 1425 MTPD (approximately 10% of the industrial city emissions). In addition, 2250 MTPD (16%) carbon reduction can be achieved with no additional cost. However, the cost increases drastically for larger cuts.

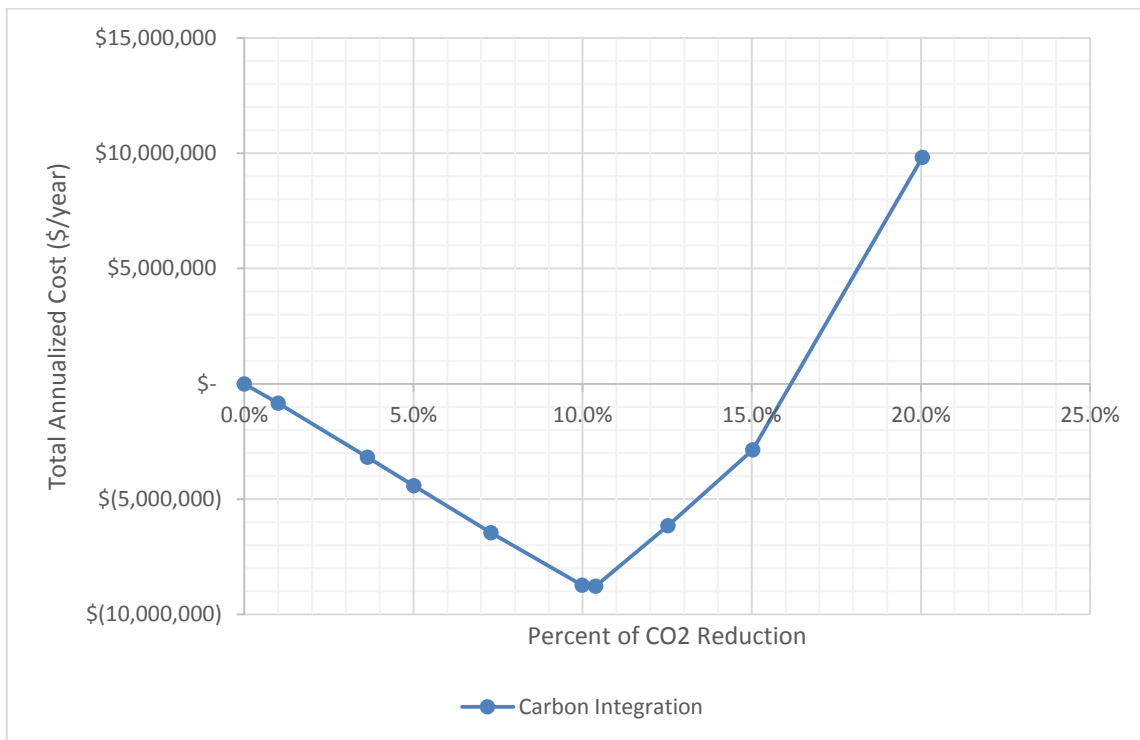


Figure 7: Total annualized cost of carbon integration

The TAC of the network was broken down into operating cost and annualized capital cost. The operating cost consisted of steam and power costs, as they are the dominant costs in carbon integration. The power and steam demand for the carbon integration networks are plotted in Figure 8 and 9, respectively. The graphs give an insight on the development of power and energy demand over a range of different carbon reduction cuts.

It can be observed from the figures below that steam and power demands increases with increasing carbon reduction. The power demand increases steadily with carbon reduction until approximately 10% carbon reduction is achieved, beyond that the power

demand increases rapidly. This is due to the fact that up to 10% carbon reduction, power was only used to compress and pump the carbon dioxide, and no treatment was required. This is evident by the steam demand. The reason behind these results is that ammonia plant emits pure carbon dioxide at ambient conditions, which is allocated to the EOR sink. Whilst no steam is needed to treat the stream, power was required to compress and pump the carbon dioxide. After exhausting the ammonia source, a lower quality source was allocated to another sink, which required treatment.

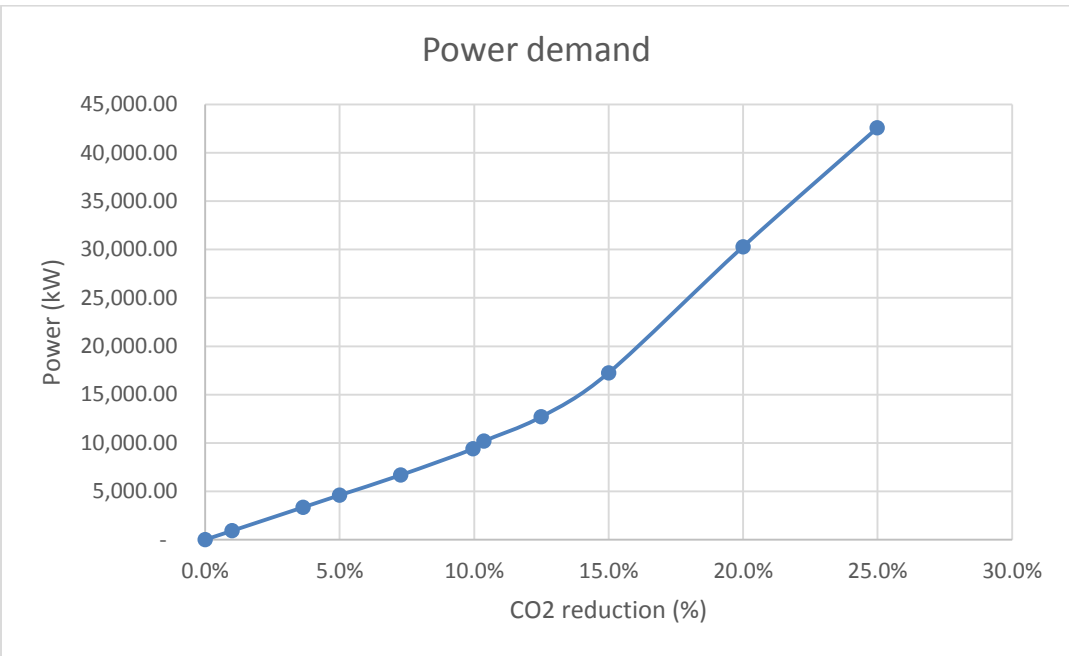


Figure 8: Power demand for carbon integration

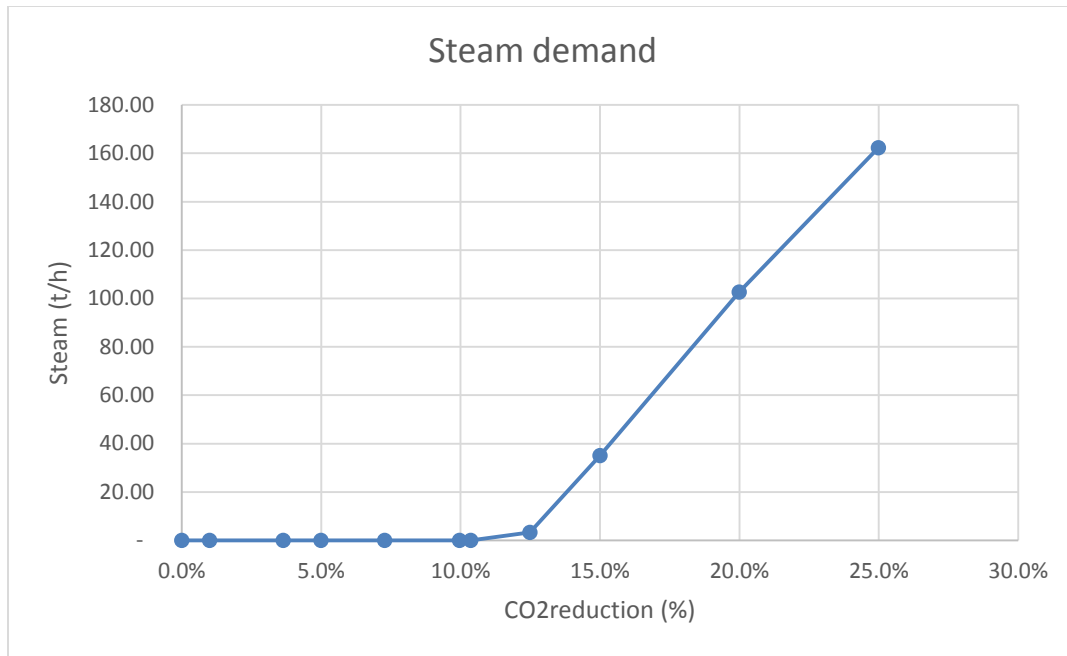


Figure 9: Steam demand for carbon integration

As stated earlier, the economic and emissions penalties reduce the carbon integration efficiency. Hence, utilizing waste heat to generate electricity and LP steam eliminates the emissions caused by the fuel combusting and the cost for purchasing fuel and power.

Looking at the utility system results obtained earlier, only 191.5 t/h of HP steam was utilized out of 240 t/h, after optimizing the utility system. Thus, there is an opportunity to utilize the excess waste heat to reduce the steam demand from the boiler and/or importing power from the power station to meet the network demand. The excess waste heat can be expanded via various paths for co-generation or power generation. In this example, the recovered HP steam can be expanded via three paths, one for co-generation and two for power generation. For co-generation, the steam is routed through HP-P1

turbine to be exported as LP steam to the treatment unit. For the power generation option, there are two paths: through HP-P2 turbine or via let-down station then MP-P1. Table 12 summarizes the different paths. The capacity limit is determined by the current flow of steam and the maximum allowable flow in the turbine. Also, while the steam turbine efficiency vary with the current flow of steam, the specific power output is a good estimate for small variation and as initial calculations.

Table 12: Steam path power output

Path	Path type	Capacity limit (t/h)	Specific power output (kJ/kg)
Path 1	co-generation	60.3	485
Path 2	Power generation	8.5	823
Path 3	Power generation	54.3	598

As the steam is the main cost in treatment unit, the co-generation path was preferred over the maximum power generation path. After the steam demand is satisfied for the carbon network, the surplus steam is expanded to the condensing main to maximize power generation. The cost of the steam and power that was offset by waste heat, and its associated carbon dioxide are credited back to the cost of carbon integration network.

For example, looking back at the carbon network for 15% carbon reduction, the network required 35.1 t/h of LP steam and 17.252 MW of electricity. Thus, out of the 48.5 t/h HP steam, 35.1 t/h was expanded to LP steam and the remaining was used to generate power. The steam took the following paths: 35.1 t/h via Path 1, 8.5 t/h via Path 2, and the balance via Path 3. The power generation from the three paths amounted for 7.4 MW. Thus, the savings from steam and power reductions are 1.8 million and 3.3 million dollars

per year, respectively. Also, the emissions were reduced by 105.3 and 97.7 MTPD by partially offsetting the fuel combustion in the utility system and power plant. Therefore, the overall savings for the improved network is 5.1 million dollars per year and 203 MTPD of carbon dioxide. This step was repeated for all the cuts.

Figure 10 shows the cost and emissions reductions, when excess waste heat from the background processes is integrated with carbon integration. Also, it can be seen from Figure 10 that the data from merging energy and carbon integration are shifted down and to the right. It is shifted down as the TAC was reduced and to the right as carbon dioxide emitted to achieve the network was also reduced. Moreover, it can be seen that incorporating waste heat reduced the annual costs for some networks by almost 5 million USD and increased the emissions reduction by more than 200 MTPD, which is equivalent to an additional 1.5% reduction. These substantial savings and increasing the CI efficiency show the importance of understanding the background processes and incorporating waste heat, when considering carbon integration.

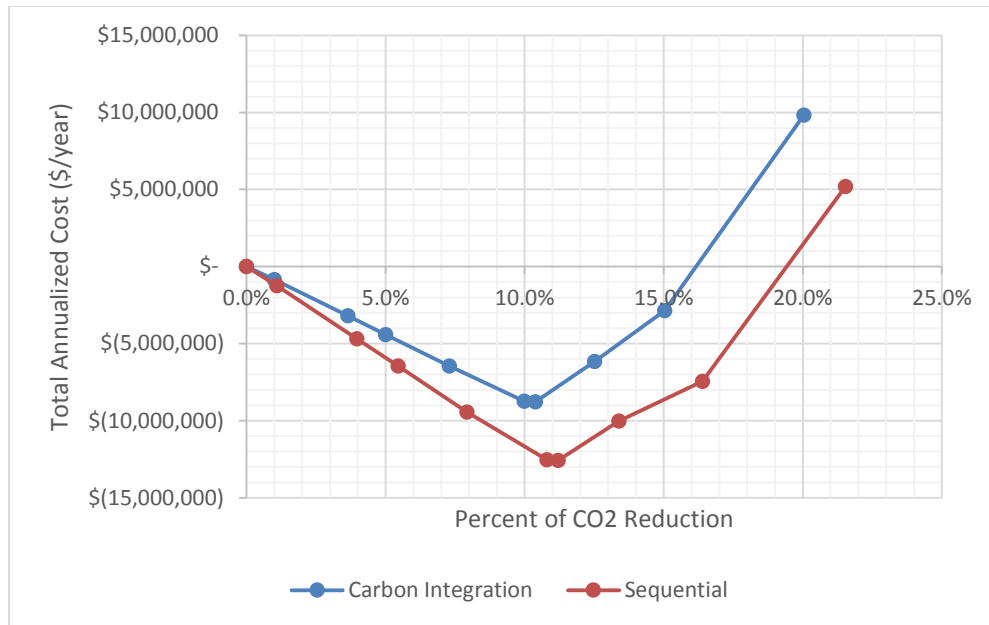


Figure 10: Carbon and energy integration

5.4 Conclusion

Exploiting the synergy between energy and carbon integration is an important activity. This activity can be achieved through sequential approach. The steps are: performing TSA and optimizing utility system, applying carbon integration technique, and finally utilizing excess waste heat to partially or fully meet the carbon network demand. The recovered waste heat is mainly used to meet the capture unit energy demand. The additional steam generated from waste heat is then expanded through condensing turbines to maximize power generation. While expanding the steam, the most efficient path is selected. As it was demonstrated in the case study, utilizing excess waste heat has a positive impact on the carbon integration network and overall economics. It can be seen

from the case study that almost 5 million dollars can be saved annually and the carbon reduction was increased by %1.5 for carbon cuts larger than 15%.

6. ENERGY AND CARBON INTEGRATION: SIMULTANEOUS APPROACH

6.1 Introduction

The previous section demonstrated the significance of using excess waste heat from background processes to partially or fully meet the carbon integration demand. However, this approach was performed sequentially by retaining the carbon network configuration, which constrains the problem and limit the search for other optimal solutions. This raises the following question: does implementing carbon and energy integration simultaneously provide cheaper and more efficient networks? Thus, a systematic optimization-based approach to link energy and carbon integration simultaneously is needed to investigate and determine the optimum network.

6.2 Problem Statement

The formal problem statement for this problem is presented as the following:

Given:

- Industrial city with a number of plants
- Spatial representation of the industrial city
- Structure and technical data of the utility system
- Power requirement of the industrial city
- The maximum allowable power to export/import for the utility system from/to the grid
- Number of energy sources and sinks in industrial city
- Energy demand of each plant (steam level and duty) – energy sink

- Waste heat available from each plant (temperature and duty) – energy source
- Number of CO₂ sources and sinks in industrial city
- CO₂ sinks temperature, pressure and composition requirements and capacity
- CO₂ sources temperature, pressure, composition and flow:
- Treatment unit type

Determine:

- The minimum fuel requirement to meet the energy and power demand of the city.
- The cost of minimum fuel and power to meet the city demand.
- The minimum amount of fuel required to meet the carbon integration network demand
- The amount of carbon dioxide flow between sources and sinks
- The carbon dioxide source-sink mapping that achieve the carbon footprint reduction at minimum cost

In the simultaneous approach, all the tasks are solved instantaneously. The following sets are defined:

$S \{ s | s = 1,2,3, \dots, N_{sources} | S \text{ is a set of carbon sources} \}$

$K \{ k | k = 1,2,3, \dots, N_{sinks} | K \text{ is a set of carbon sinks} \}$

$T \{ t | t = 1,2,3, \dots, T_{max} | T \text{ is a set of carbon treatment technology} \}$

$M \{ m | m = 1,2,3, \dots, N_{energy sources} | M \text{ is a set of energy sources} \}$

$O \{ o | o = 1,2,3, \dots, N_{energy sinks} | O \text{ is a set of energy sinks} \}$

$I \{ i | i = 1,2,3, \dots, N_{steam levels} | I \text{ is a set of steam levels} \}$

$J \{ j | j = 1, 2, 3, \dots, N_{\text{turbine levels}} \mid J \text{ is a set of turbine levels} \}$

$P \{ p | p = 1, 2, 3, \dots, N_{\text{turbines}} \mid P \text{ is a set of steam turbine} \}$

$L \{ l | l = 1, 2, 3, \dots, N_{\text{paths}} \mid L \text{ is a set of steam paths} \}$

6.3 Problem Formulation

The utility system model used in this work is similar to the work presented by Varbanov et al. [28], which is a Successive Mixed Integer Linear Programming (SMLIP). The model accounts for different type of firing machines: gas turbines, boilers, and heat recovery steam generation system. Also, the gas turbine exhaust can be integrated with a HRSG unit to generate VHP steam. The main consumers of fuel in the utility system is the boiler and gas turbine. The boiler energy balance is found in Equation 7:

$$Q_{BF} = \frac{1}{\eta_{Blr}} * m_{stm} * \Delta h_{gen} \quad (7)$$

$$\eta_{Blr} = \frac{Q_{stm}}{Q_{BF}} \quad (8)$$

where Q_{BF} is the heat from fuel combustion in the boiler needed to generate steam, η_{Blr} is the boiler thermal efficiency, m_{stm} is the boiler current steam load, and Δh_{gen} is the heat required to generate one unit of steam. The mathematical definition of the boiler efficiency is presented in Equation (8), where Q_{stm} is the energy needed to generate steam. The model used in this work assumes constant boiler efficiency.

Simple mass and energy balances are carried around the steam headers. The steam balance are modelled as follow:

$$\Sigma_{inlets} m_{inlet,hdr} - m_{total,hdr} = 0 \quad (9)$$

$$\Sigma_{inlets} m_{outlet,hdr} - m_{total,hdr} = 0 \quad (10)$$

where $m_{inlet,hdr}$ is the mass flowrate of the steam into a steam header. The inlet streams are from the following sources: HRSG, boiler, steam turbine, let-down station or heat recovered from an energy source plant:

$$m_{inlet,hdr,i} = \sum_{m \in M} m_{m,i} + \sum_{j \in J} \sum_{p \in P} m_{j,p,i} + m_i^{LS} \quad \forall m \in M, j \in J, p \in P \quad (11)$$

$$m_{stm} = \sum_{p \in P} m_{j,p,i} - m_{HRSG} \quad \forall p \in P, \text{ For } j = 1 \quad (12)$$

$$m_{stm} \geq 0 \quad (13)$$

$$m_{j,p,i} \geq 0 \quad \forall j \in J, p \in P, i \in I \quad (14)$$

$$m_i^{LS} \geq 0 \quad \forall i \in I \quad (15)$$

where $m_{m,i}$ is the waste heat recovered from an energy source process m at steam level i , $m_{j,p,i}$ is the mass flowrate of steam through turbine p in turbine level j to steam header i , m_i^{LS} is the steam mass flowrate into header i through a let-down station, and m_{HRSG} is the steam mass flowrate from the HRSG. Equation (13) - (15) are the non-negativity constraints.

Also, $m_{outlet,hdr}$ is the steam mass flowrate at the header outlet. The outlet steam can be expanded via steam turbine, let-down stations, or supplied to an energy sink process:

$$m_{outlet,hdr,i} = \sum_{p \in P} \sum_{i \in I} m_{j,p,i} + \sum_{o \in O} m_{i,o} + \sum_{t \in T} \sum_{s \in S} m_{t,s,i} + m_{i+1}^{LS} \quad \forall p \in P, i \in I, o \in O, t \in T, s \in S \quad (16)$$

where $m_{i,o}$ is the steam demand of steam level i to energy sink o , and $m_{t,s,i}$ is the energy demand of treatment unit t in carbon source s .

While the mass balance equation is linear, the energy balance is bi-linear, where $h_{inlet,hdr}$ is the specific enthalpy of steam entering the steam header and h_{hdr} is the specific average enthalpy of the steam header:

$$\Sigma_{inlets} m_{inlet,hdr} * h_{inlet,hdr} - m_{total,hdr} * h_{hdr} = 0 \quad (17)$$

The steam turbine efficiency depends heavily on three parameters: steam turbine size, pressure drop across the turbine, and the current load. Willan's line was used to capture these aspects and determine the steam turbine power output. The steam turbine model is shown below:

$$W_{j,p} = n_{j,p} * m_{i,j,p}, -W_{int,j,p} \quad (18)$$

$$X_{j,p} * m_{i,j,p}^{min} \leq m_{i,j,p} \leq X_{j,p} * m_{i,j,p}^{max} \quad (19)$$

where $W_{j,p}$ is the power generated by steam turbine p in turbine level j , $n_{j,p}$ is the slope for Willan's line for steam turbine p in turbine level j , and $W_{int,j,p}$ is the intercept of the Willan's line for the steam turbine. $X_{j,p}$ is a binary (1,0) associated with steam turbine. The value of the binary is 1 if the flow in the turbine is within the lower and upper limit, otherwise it is zero. Also, $m_{i,j,p}^{min}$ and $m_{i,j,p}^{max}$ are the minimum and maximum allowable steam mass flowrate in the specific steam turbine.

Generally, the intercept of the Willan's line can be calculated according to Equation (20) and (21):

$$W_{int,} = \frac{L}{B} * (\Delta h_{is} * m_{max} - A) \quad (20)$$

$$n = \frac{L+1}{B} * (\Delta h_{is} - \frac{A}{m_{max}}) \quad (21)$$

where L is the steam turbine intercept ratio, Δh_{is} is the isentropic enthalpy change across the steam turbine, and A and B are regression parameters in the steam turbine model. The regression parameters are calculated using Equation 22 and 23, respectively:

$$A = b_0 + b_1 * \Delta T_{sat} \quad (22)$$

$$B = b_2 + b_3 * \Delta T_{sat} \quad (23)$$

where b_0, b_1, b_2, b_3 are regression parameters and can be found in the literature. The parameters are also included in Appendix I. The parameter differs depending on the size and the type of the steam turbine, whether it is backpressure or condensing turbine.

As shown earlier, power is generated in the utility system is through either steam or gas turbines. The deficit power is imported from a local power plant, while the surplus power is exported to the grid:

$$P_{ST} = \sum_{j,p} W_{j,p} \quad \forall j \in J, p \in P \quad (24)$$

$$P_{industrial\ park} = P_{ST} + \sum_{GT} P_{GT} + P_{import} - P_{export} \quad (25)$$

$$P_{industrial\ park} = \sum_{process} P_{process} \quad (26)$$

where P_{ST} is the power generated from steam turbines, P_{GT} is the power generated from gas turbines, P_{import} and P_{export} are the power imported and exported to the grid, respectively. $P_{process}$ is the power demand from existing processes.

The maximum power imported or exported into the grid depends on the utility system, industrial city and power plant capacity and are modelled as following:

$$0 \leq P_{import} \leq P_{policy}^{import} \quad (27)$$

$$0 \leq P_{export} \leq P_{policy}^{export} \quad (28)$$

where P_{policy}^{import} and P_{policy}^{export} are the maximum power can be imported or exported to the grid set by the user, respectively.

The emissions from the industrial city is then calculated:

$$F_{CO_2}^{BI} = \sum_{processes} F_{CO_2}^{Process} + F_{CO_2}^{utility} + F_{CO_2}^{Power} \quad (29)$$

where $F_{CO_2}^{BI}$ is the total carbon dioxide flowrate from industrial city before carbon integration, $F_{CO_2}^{Process}$ is the carbon dioxide flowrate from the processes in industrial city, including the power plant emissions to meet the initial power plant capacity, $F_{CO_2}^{utility}$ is the carbon dioxide flowrate from the utility system, and $F_{CO_2}^{power}$ is the additional carbon dioxide flowrate from the power plant due to importing power from or exporting power to utility system. This term can be negative, which means that the power plant production is decreased, as the utility system is exporting power to the grid.

$$F_{CO_2}^{utility} = Q_{BF} * \psi_{b,fuel} + Q_{GT} * \psi_{GT,fuel} \quad (30)$$

$$F_{CO_2}^{Power} = (P_{import} - P_{export}) * \psi_{power} \quad (31)$$

where $\psi_{b,fuel}$ and $\psi_{GT,fuel}$ are the carbon dioxide emissions per unit of energy for the boiler and gas turbine, respectively, and ψ_{power} is the carbon dioxide mass emission per unit of power.

The carbon integration problem is formulated similar to the work that was published and explained in Al-Mohannadi[7]:

$$L_s \leq R_s \leq M_s ; \quad \forall s \in S \quad (32)$$

$$R_s = \sum_{k \in K} \sum_{t \in T} \epsilon_t T_{s,k,t} + \sum_{k \in K} U_{s,k} ; \quad \forall s \in S \quad (33)$$

$$R_s y_s = \sum_{k \in K} \sum_{t \in T} \epsilon_t T_{s,k,t} y_{s,t} + \sum_{k \in K} U_{s,k} y_s^u ; \quad \forall s \in S \quad (34)$$

$$F_k = \sum_{s \in S} \sum_{t \in T} T_{s,k,t} + \sum_{s \in S} U_{s,k}; \quad \forall k \in K \quad (35)$$

$$F_k Z_k^{min} \leq \sum_{s \in S} \sum_{t \in T} T_{s,k,t} y_{s,t} + \sum_{s \in S} U_{s,k} y_s^u; \quad \forall k \in K \quad (36)$$

$$y_s^u = y_s; \quad \forall s \in S \quad (37)$$

$$L_{s,k} X_{s,k} \leq T_{s,k,t} + U_{s,k} \leq M_{s,k} X_{s,k}; \quad \forall s \in S, k \in K, t \in T \quad (38)$$

$$T_{s,k,t} \geq 0; \quad \forall s \in S, k \in K, t \in T \quad (39)$$

$$U_{s,k} \geq 0; \quad \forall s \in S, k \in K \quad (40)$$

$$y_{s,k,t} \geq 0; \quad \forall s \in S, k \in K \quad (41)$$

$$y_{s,k} \geq 0; \quad \forall s \in S, k \in K \quad (42)$$

The following modification are introduced to the published model to incorporate the utilization of excess surplus heat and the utility system. Firstly, the following parameters and costs were excluded:

- 1- The emitted carbon dioxide from the treatment unit energy use parameter
- 2- Carbon footprint from power consumption parameter.
- 3- Operating cost for compressor and pump
- 4- Operating cost for treatment unit.

Secondly, these excluded terms were replaced by equations to link the carbon integration model and utility systems model. The emitted carbon dioxide from the treatment unit due to energy use is accounted for in Equation (16). While, carbon footprint due power consumption is accounted for by:

$$P_{CI} = \sum_{t \in T} \sum_{s \in S} P_{t,s} + \sum_{s \in S} \sum_{k \in K} (P_{s,k}^{compressor} + P_{s,k}^{pump}) \quad (43)$$

$$\forall s \in S, k \in K, t \in T$$

where P_{CI} is the power demand for the carbon integration network, $P_{t,s}$ is the power demand for treatment technology t , in source plant s , and $P_{s,k}^{compressor}$ and $P_{s,k}^{pump}$ are the power demand for compressor and pump to transport carbon dioxide from source plant s to sink plant k , to meet the sink pressure requirements and overcome pressure drop in the pipes.

The industrial park power demand after carbon integration is modelled by modifying Equation (26)

$$P_{industrial\ park} = \Sigma_{process} P_{process} + P_{CI} \quad (44)$$

The dominant operating cost in the carbon capture is the power and energy costs. These costs are calculated based on the fuel consumption in the utility system to generate steam and power, and from purchasing electricity from the power station:

$$C_{fuel} = Q_{BF} * \chi_{b,fuel} + Q_{GT} * \chi_{GT,fuel} \quad (45)$$

$$C_{power} = P_{import} * \chi_{power}^{import} - P_{export} * \chi_{power}^{export} \quad (46)$$

where C_{fuel} is the total cost of fuel, and $\chi_{b,fuel}$ and $\chi_{GT,fuel}$ is the fuel cost per unit of energy for boiler and gas turbine, respectively. C_{power} is the total cost of power from power plant, and χ_{power}^{import} and χ_{power}^{export} are the cost of purchased and sold power, respectively.

The energy and carbon integration network needs to meet the net carbon reduction target (NCRT) for the industrial city:

$$Net\ reduction \geq NCRT$$

The *NCRT* is specified by the user, while the net reduction is defined as the difference between carbon emissions before and after energy and carbon integration (E&CI):

$$Net\ reduction = F^{BI} - F^{AI} \quad (47)$$

$$F^{AI} = F_{CO_2}^{Processes} + F_{CO_2}^{utility} + F_{CO_2}^{Power} - \sum F_k^{CO_2} (1 - \eta_k) \quad (48)$$

where F^{BI} is the total footprint of the industrial city before coupling energy and carbon integration, F^{AI} is the total carbon footprint after coupling energy and carbon integration, $F_{CO_2}^{Processes}$ is the carbon dioxide flow from the carbon sources in industrial city except utility system, $F_k^{CO_2}$ is the carbon dioxide flow into the sink and η_k is the sink efficiency.

The objective function of this problem is to minimize the cost of the network, subject to meeting the NCRT:

$$Min \sum_{s \in S} \sum_{k \in K} (C_{s,k}^{treatment} + C_k^{sink} + C_{s,k}^{transportation}) + C_{fuel} + C_{power} \quad (49)$$

$$C_{s,k}^{treatment} = T_s^{CO_2} * C_{s,t}^T \quad \forall s \in S, k \in K, t \in T \quad (50)$$

$$C_k^{sink} = \sum_{k \in K} F_k^{CO_2} * CR_k^{sink} \quad \forall k \in K \quad (51)$$

$$C_{s,k}^{transportation} = C_{s,k}^{pipes} + C_{s,k}^{compressor} + C_{s,k}^{pump} \quad \forall s \in S, k \in K \quad (52)$$

where $C_{s,k}^{treatment}$ is the annualized capital cost for the treatment unit, $T_s^{CO_2}$ is the treated flow from source s , $C_{s,t}^T$ is the treatment cost parameter, C_k^{sink} is the cost to process carbon dioxide in the sink, $C_{s,k}^{transportation}$ is the annualized capital cost to ship carbon dioxide from the source s to the sink k . C_k^{sink} is calculated by multiplying the carbon dioxide flow to the sink, $F_k^{CO_2}$, by the processing cost parameter, CR_k^{sink} . The transportation cost is the

sum of the annualized cost of pipes, $C_{s,k}^{pipes}$, compressors, $C_{s,k}^{compressor}$, and pumps, $C_{s,k}^{pump}$, in each connection between the sources to the sinks.

6.4 Case Study

This section provides an illustrative example on how to apply the proposed model. The example illustrated in section 3 is revisited to demonstrate the results of the simultaneous approach. Then, the results of the three cases: carbon integration, sequential and simultaneous approaches are compared.

In this work, the utility system and steam turbines networks are shown in Figure 6, which is the same system that was used in the first case study. Table 13 shows the steam turbine type, minimum allowable flow, maximum allowable flow, and inlet and outlet pressures. The turbine type, whether backpressure (BP) or condensing turbine (CT), plays an important role in determining the turbine efficiency. If the steam flow in the turbine is below the minimum flow, then the steam turbine is turned off and the current flow is set to zero.

Table 13: Steam turbines technical data

Steam turbine	Type	Minimum flow (t/h)	Maximum flow (t/h)	Inlet pressure (bar)	Outlet pressure (bar)
VHP-P1	BP	18	180	90	48
VHP-P2	BP	14.4	144	90	16
VHP-P3	BP	12.6	126	90	2.7
HP-P1	BP	13.7	137	48	2.7
HP-P2	CT	10.8	108	48	0.1
MP-P1	CT	9.7	97.2	16	0.1

As mentioned earlier, the treatment technology used in this study is MEA amine-based absorption technology. The treatment cost is divided into capital cost and operating cost. The annualized capital cost is based on the models that published by Hasan et al.[59]. In his work, the cost accounts for treating carbon dioxide stream and compress it to 150 bar. The model was linearized and modified to account only for the treatment unit. The operating cost is calculated by accounting for power and fuel costs. The demand calculated based on the equation proposed by Chapel et al[9]:

$$P_{s,k}^{treatment} = \left(0.4 + \frac{16.4}{\%CO_2}\right) * \left(\frac{te}{d}\right) \quad (53)$$

where $\frac{te}{d}$ is the flow rate of carbon dioxide per day. As for steam demand, Chapel et al.[9] and Abu-Zahra et al.[10] estimated the energy demand of the treatment unit between 3 – 4.2 GJ/t. A value of 3.1 GJ/t was used in this work, which is equivalent to 1.4 tLP/tCO₂.

The compressor duty was calculated by estimating the specific power, which is defined as the amount of power needed to compressor one ton of the given flow from source pressure to sink pressure and accounting for the pressure drop in the pipelines. The data used for this case study is demonstrated in Table 9, and the power demand is calculated as follow:

$$P_{s,k}^{comp} = \frac{SP * F_{s,k} * 1000}{24} \quad (54)$$

Similarly, the pump power is calculated using the following equation:

$$P_{s,k}^{pump} = \frac{1000 * 10}{24 * 36} * \left(F_{s,k} * \frac{\Delta P_{s,k} + \Delta P_{s,k}^{pipe} - 7.38 * 10^6 Pa}{\rho * \eta} \right) \quad (55)$$

where $\Delta P_{s,k}$ is the pressure difference between the sink and source pressure, $\Delta P_{s,k}^{pipe}$ is the pressure drop through the pipe, ρ is the density of the fluid and η is the pump efficiency, which is assumed to be 70%. The pressure drop across the pipe is estimated using pressure drop parameter.

6.5 Optimal Design

The Mixed Integer Non-Linear Program (MINLP) formulation presented earlier has been solved using “What’s Best 9.0” Lindo Global solver for MS-Excel 2013 via a desktop with Intel Core i7 8-processor, 8 GB RAM and 64-bit operating system.

The problem was solved for different carbon cuts, ranging from 5% up to 15%, with an interval of 2.5%. Also, the problem was solved for a 20% cut. The change of carbon network configuration and the cost of the various networks over different cuts were observed and plotted. It can be seen from the Figure 11 that substantial benefit was realized by utilizing waste heat. Moreover, additional benefit was gained by solving the energy and carbon problem simultaneously.

Furthermore, it can be seen from Figure 11 that the optimum network for the simultaneous case occurred at 11.4% cut, with an annual cost of - 13 million USD, i.e. profit. Also, it was observed that more than 20% reduction in the carbon footprint could occur at no additional cost. Similar results were obtained for the sequential method, with 19% carbon footprint reduction with no additional cost. On the other hand, performing carbon integration without including the excess waste heat resulted in an optimum network at 10.5% capture with an annual cost of -8.8 million USD, while only 17% carbon reduction can occur at no additional cost.

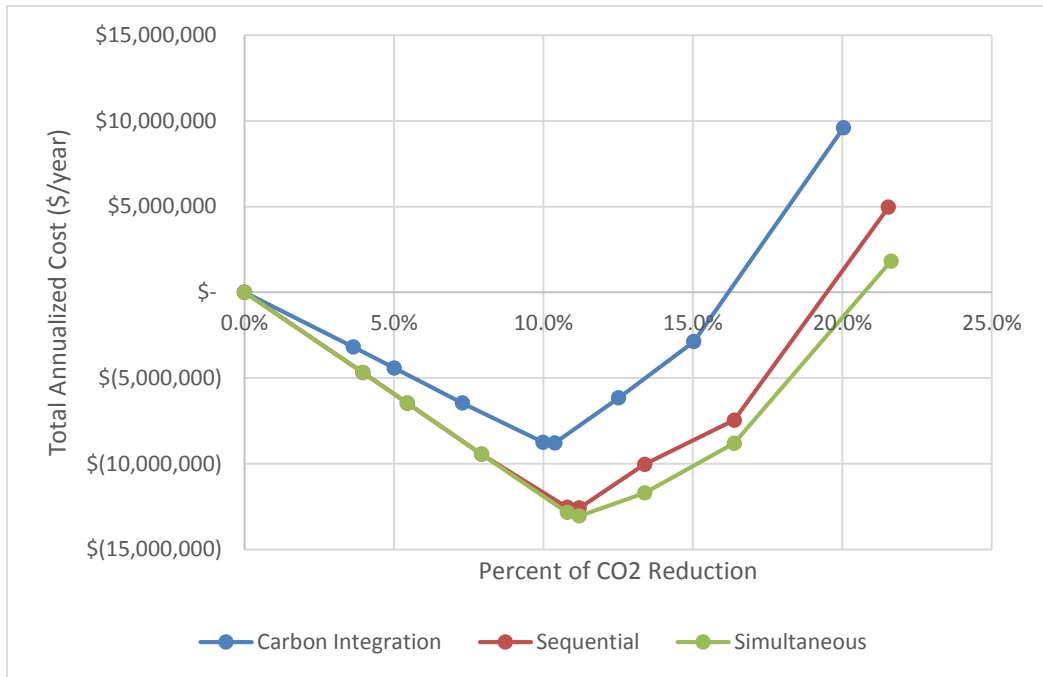


Figure 11: Carbon reduction cost

Although it is obvious that utilizing excess waste heat would reduce the overall cost of the networks, the cost reduction may vary between the different approaches. It can be seen from the figure above, up to 11% cut, the sequential and simultaneous approaches yield the same results. However, the values deviate afterwards, favoring the simultaneous approach. To understand the deviation between the sequential and simultaneous approach, an insight look at the different optimal networks is needed. Figures 12-19 show the optimal carbon integration networks for both approaches, and the consumption percentage from each source and the usage percentage of each sink at different carbon footprint cut, while Table 14 summarizes the economics of each network. The carbon reduction cuts used in this section are the same as the one selected for the first case study.

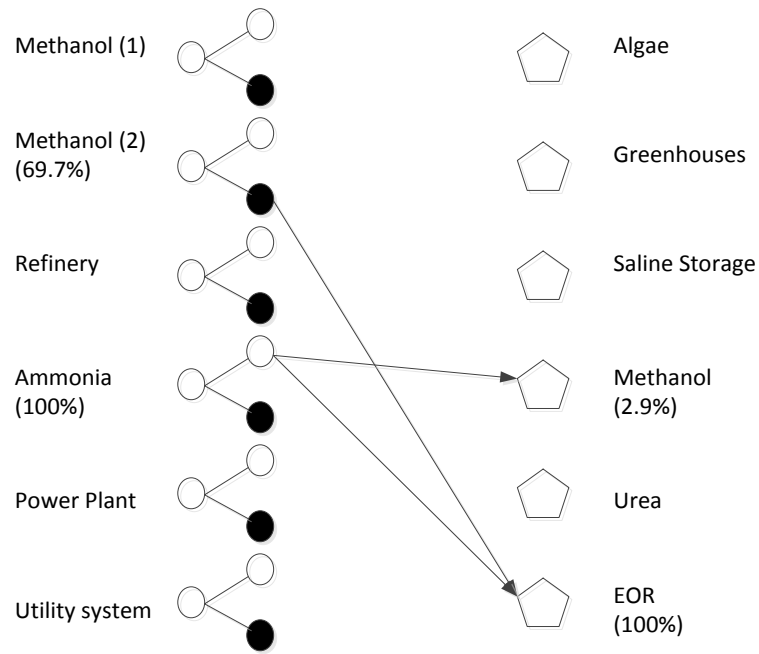


Figure 12: 11.2% carbon footprint reduction network after E&CI (Simultaneous)

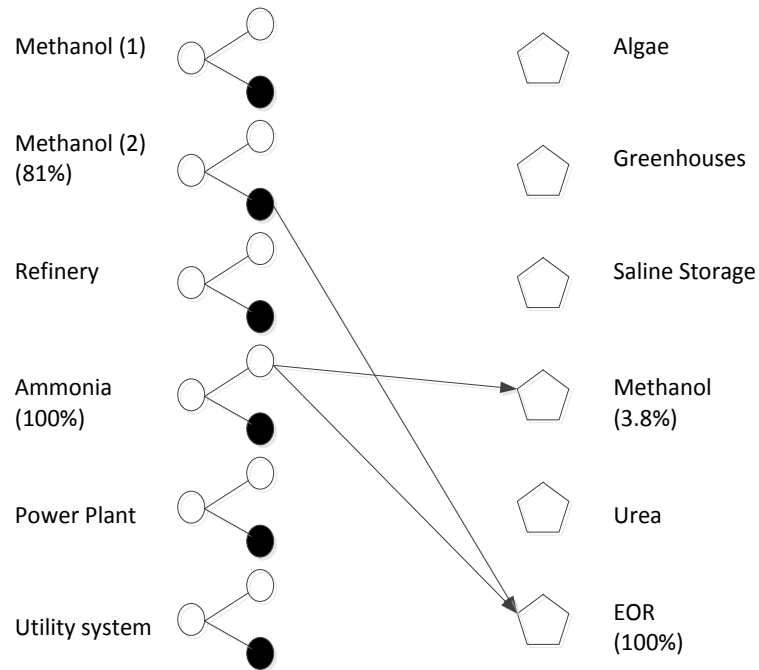


Figure 13: 11.2% carbon footprint reduction network after E&CI (Sequential)

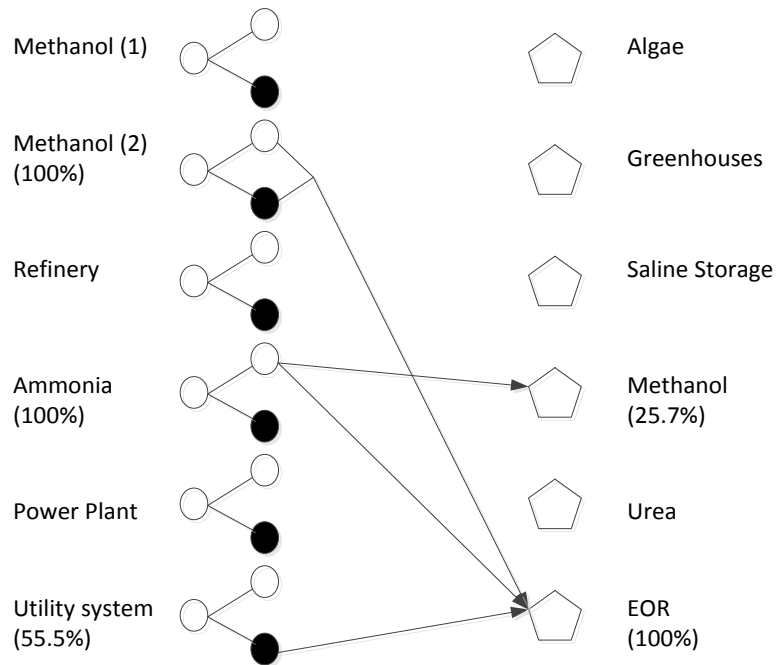


Figure 14: 13.4% carbon footprint reduction network after E&CI (Simultaneous)

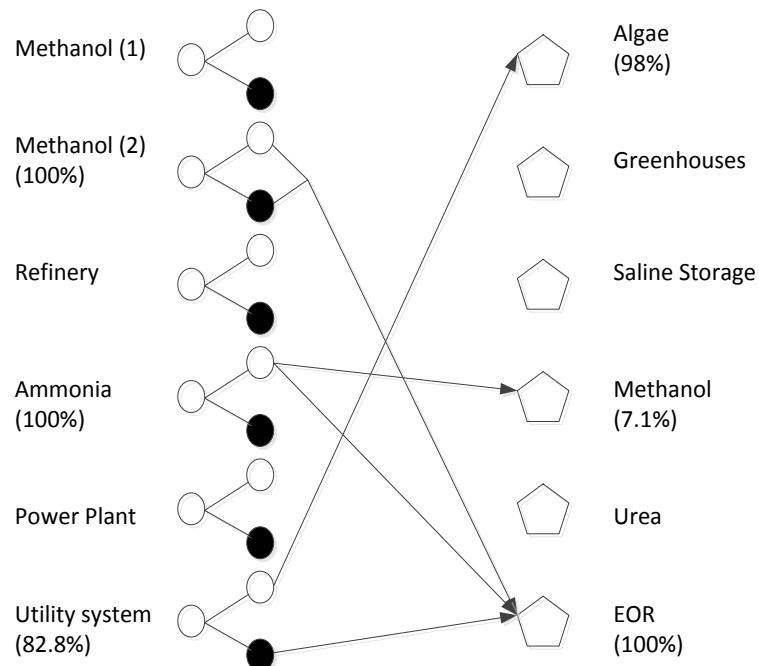


Figure 15: 13.4% carbon footprint reduction network after E&CI (Sequential)

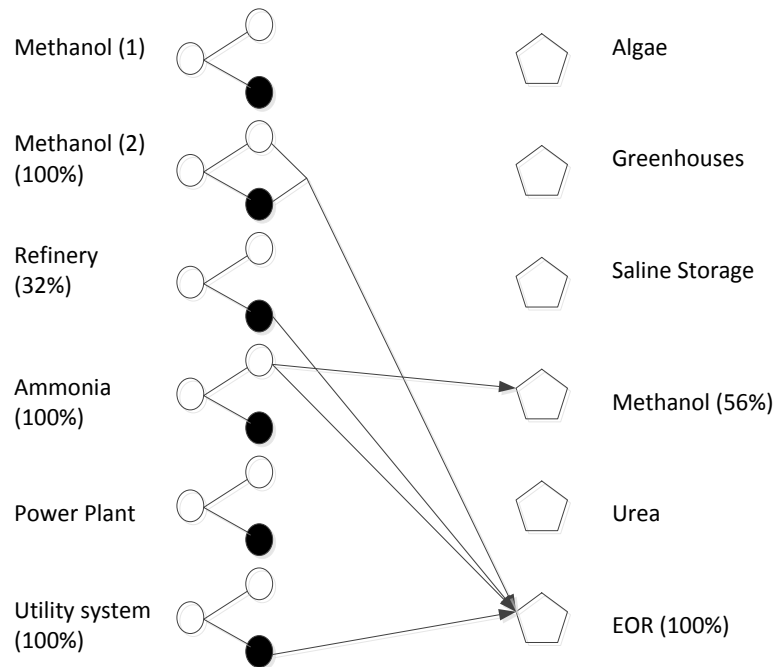


Figure 16: 16.4% carbon footprint reduction network after E&CI (Simultaneous)

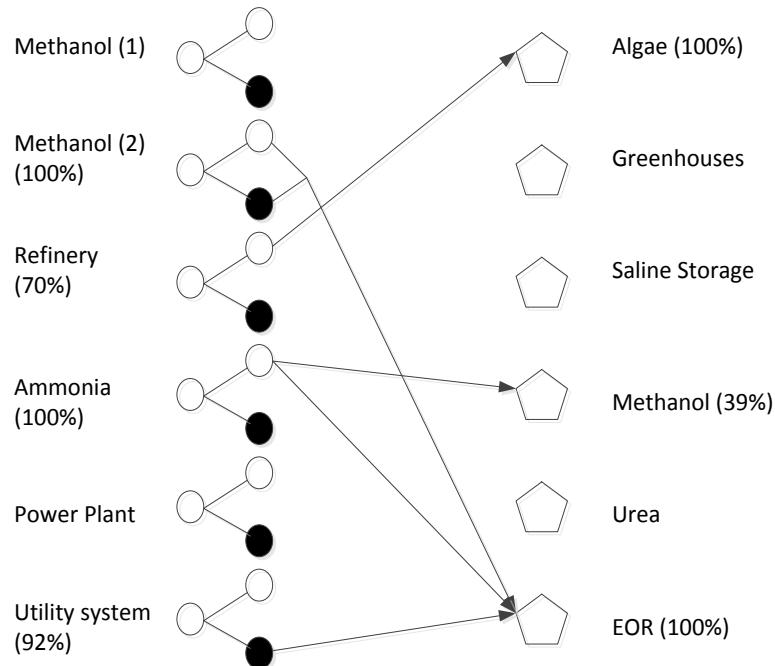


Figure 17: 16.4% carbon footprint reduction network after E&CI (Sequential)

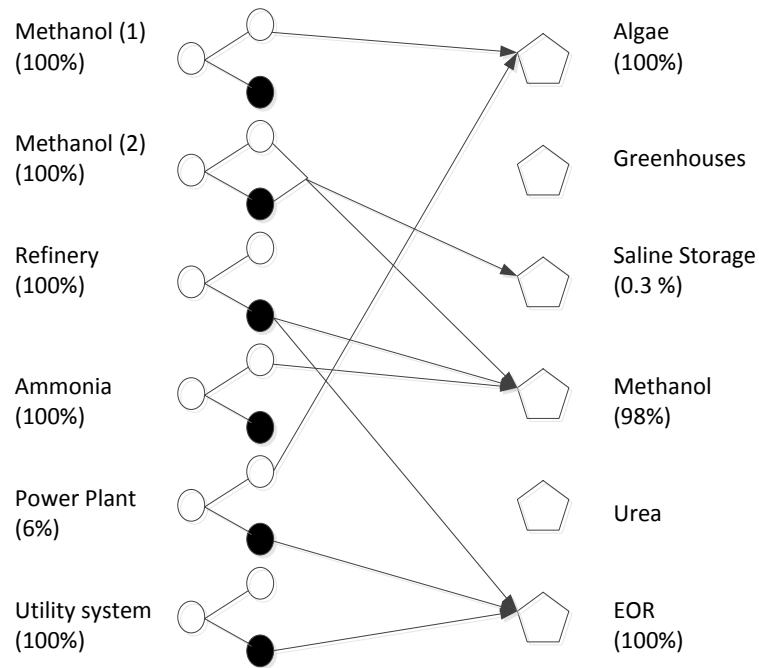


Figure 18: 21.5% carbon footprint reduction network after E&CI (Simultaneous)

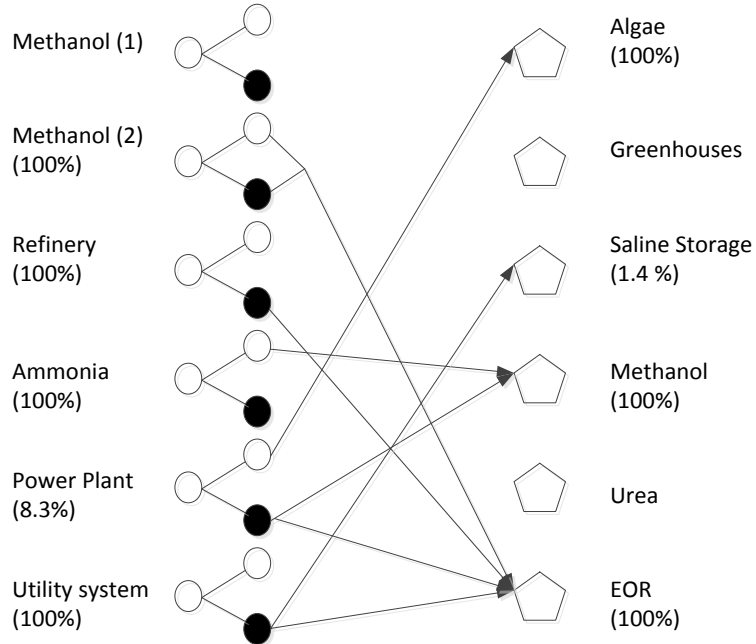


Figure 19: 21.5% carbon footprint reduction network after E&CI (Sequential)

Table 14: Potential cost (savings)

Carbon reduction (%)	Sequential (million \$/year)	Simultaneous (million \$/year)
11.2	-12.5	-13.0
13.4	-10.0	-11.7
16.4	-7.5	-8.8
21.5	5.2	1.8

The carbon reduction values were selected based on carbon integration. Then, the sequential approach was implemented to calculate the further savings and carbon reductions. Afterwards, the new reduction values were used to find an optimal network based on the simultaneous approach. The values selected for carbon integration were: optimum network (most profitable network), 12.5%, 15% and 20%. These values were enhanced to 11.2%, 13.4%, 16.4% and 21.5%, respectively, utilizing the sequential approach.

Figure 12 and 13 shows the carbon network configuration for 11.2% carbon footprint reduction for sequential and simultaneous energy and carbon integration. Comparing the figures, it can be seen that EOR was the preferred sink (100% used), followed by methanol in both cases. This is due to the high profitability of the EOR sink compared to the other ones. The second preferred sink was methanol, as it has the second highest income, and lower sink efficiency value. In addition, the selected sources were ammonia then methanol. These sources were favored as they have the highest carbon dioxide concentration at 100% and 55%, respectively.

Furthermore, the deviation that occurs at 13.4% and 16.4% can be explained from Figure 14-17. From the sequential approach, it was observed that carbon dioxide was allocated to EOR and algae then the remaining was allocated to methanol. Even though methanol forms a source of revenue, the algae sink was favored. This is due to the methanol sink pressure and purity demand. The methanol sink requires the stream to be at 8080 kPa and a purity of 94%, on the other hand, the algae sink has less stringent requirement at 101 kPa and a composition of 6%. Thus, the cost of capturing, compressing, and transporting the carbon dioxide to the methanol sink surpasses the revenue obtained from the methanol sink. This resulted in allocating the source into sink that has low pressure and composition requirements, regardless of its profitability.

On the other hand, the simultaneous approach opted to select methanol sink in the 13.4% and 16.4% cut. While in the first approach the fuel cost and the emissions caused by combusting fossil fuel that are offset by utilizing waste heat are credited it back to the network, in the simultaneous approach, the information of the excess heat was provided to the model while solving for the optimum network. Hence, the carbon dioxide was allocated to the methanol sink, which generated profit. This is due to the fact that the model maximized the usage of excess waste heat and the network was constructed at no additional cost.

From Figures 11, additional deviation occurs with 21.5% cut. This is due to the carbon dioxide concentration from the source and the source selection. It is noteworthy that in the sequential method, the emissions caused by power and steam generation are calculated as a penalty toward the total carbon capture. However, in the simultaneous

approach, the emissions increase due to power and steam generation for the networks is incorporated in the utility system and power plant sources. This difference causes the aforementioned sources' sizes to change in the simultaneous approach. Therefore, the flowrate from utility system source to the sinks in Figure 18 and 19 are not the same, even though in both cases the sources are fully consumed.

It is important to account for the change in carbon source flowrate. Each source has a different composition, and thus, different treatment costs. The composition of the treated stream affect the power demand, and hence affect the emissions resulting from treating the specific stream. In this example, the utility system's flue gas had a higher carbon concentration compared to the power plant one. Therefore, the network always preferred capturing the utility system flue gas over the power plant.

Moreover, the costs of capturing one metric ton of carbon dioxide over different cuts were plotted. Figure 20 shows the development of the specific cost reduction for carbon dioxide per metric tons. It can be seen that the industrial city may cut its emissions up to 10% at a cost of -17.5 USD/metric tCO₂, using the carbon integration technique. This cost is reduced to -23.5 USD/metric tCO₂ and up to 11.2% when excess waste heat was utilized. Also, breakeven point (i.e. specific cost is zero), occurs at 16%, 19.8%, and 20.9% for CI, sequential E&CI, and simultaneous E&CI, respectively.

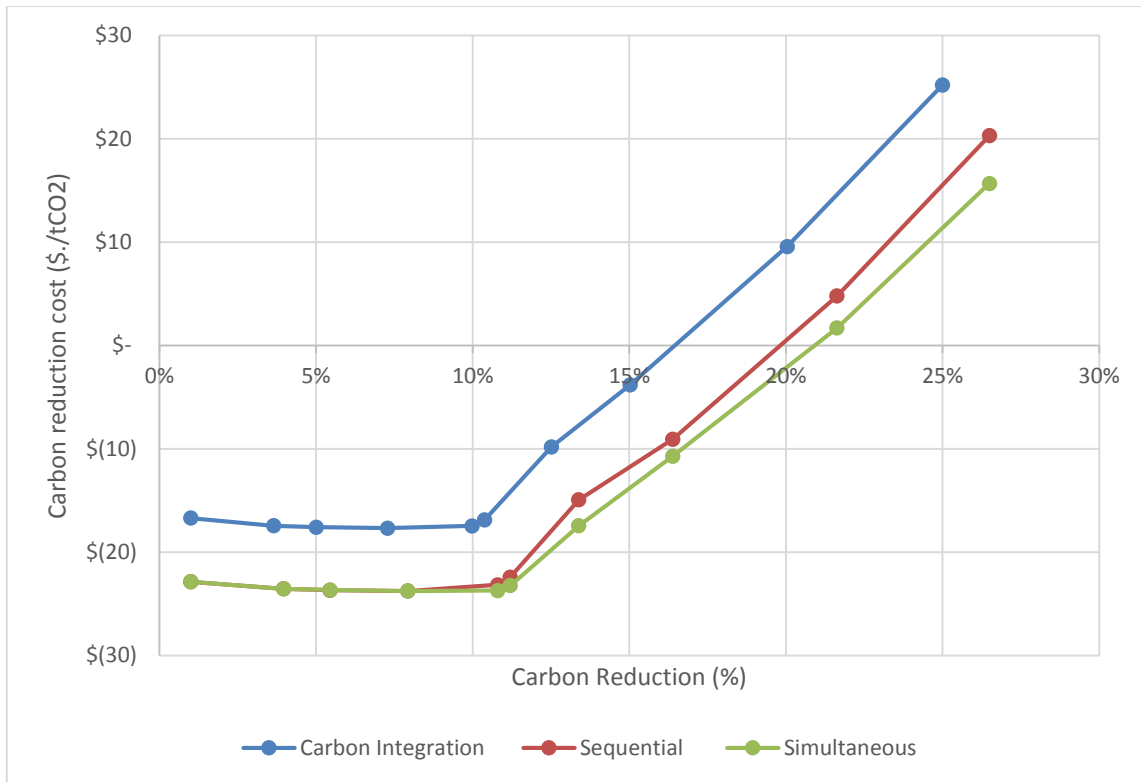


Figure 20: Carbon avoided cost per metric ton

6.6 Conclusion

This section presented a mathematical programming model to explore the potential of simultaneously combining energy and carbon integration. The model was used to solve a case study at different carbon reduction cuts. The cost of various networks and the cost of carbon avoided per metric ton were calculated and plotted for different carbon reduction cuts. The simultaneous approach aids in designing the utility system, while achieving minimum carbon emissions. Additionally, the results obtained from this approach are either equal to or outperformed the results obtained from the sequential approach. This is due to the fact that in the sequential approach the method improve the existing the network

that was obtained from carbon integration, which imposes a constraint on the search for better configuration to account for the available energy. However, the simultaneous approach incorporates the excess waste heat while searching for the optimum solution.

7. CONCLUSION

In this work, the synergy between energy and carbon integration was explored via different approaches. The developed approaches are applicable in an industrial city that is served by a common utility system. This work combined the TSA, utility system model and the carbon integration model to enhance energy efficiency, reduce carbon dioxide emissions, and design better carbon integration networks. The proposed methods solve the energy and carbon problem either through sequential approach or simultaneous approach.

In the sequential approach, the problem is solved stepwise. The first step is to solve the energy problem using TSA and optimize the utility system, and then perform carbon integration. Afterwards, the excess waste heat available, which was not utilized in the energy problem, is used to fully or partially offset the energy and power demand required by the carbon integration. Consequently, the overall cost of the network is decreased and the carbon emission reduction is increased.

In the simultaneous approach, a MINLP model is developed to obtain the optimal network. The energy and the carbon problem are linked together via the utility model and solved simultaneously. This approach accounts for the change in the utility system and power plant emissions to meet the carbon integration problem heat and power demand. Also, the model accounts for the nonlinear relationship between heat, power and carbon dioxide.

While the sequential approach provides a quick estimate on the potential gain, the approach does not propose alternative networks compared to the one proposed by the

carbon integration. However, it calculates the saving obtained from the current network. Also, the approach calculates the reduced cost of the favored network and the new carbon emission cut. In addition, the sequential approach does not consider treating and allocating the carbon dioxide emitted to meet the carbon integration network energy demand. This limits the model from proposing network to meet large carbon footprint reduction.

On the other hand, the simultaneous approach addresses these issues. Firstly, the simultaneous approach searches for different network configurations, while incorporating the excess waste heat to identify the optimum network. Thus, a revenue generating sink that has a high treatment cost might not be selected in the first approach; however, it will be selected in this approach. In addition, the model considers treating the additional emissions resulting from the utility system and power plant to meet the carbon network demand, which offers two advantages:

- 1- Reflect the actual carbon sources (utility system and power plant) size, which gives the ability to capture large carbon cuts, given enough sink sizes.
- 2- If a high concentration carbon source flow increases, this source will be selected over low concentration source, which would've been selected otherwise.

A case study has been generated and solved to show the importance of utilizing waste heat. Also, the case study demonstrated the benefits of developing an optimization based approach compared to a step-by-step approach. The case study showed that the simultaneous optimization model was able to identify optimal networks that was not

identified otherwise. Also, the optimization-based method have the capability to propose networks for large reductions.

Recommendations for future work include:

- 1- Exploring the opportunities of incorporating renewable energy to reduce emissions from the utility system and power plant to meet the carbon integration energy and power demand.
- 2- Fuel switching and utilizing different type of fuels (coal, oil, and natural gas)
- 3- Optimizing the utility system configuration to meet the additional power and steam demand at minimum cost and emissions.
- 4- The use of different post-combustion capturing technologies
- 5- Combining post-combustion, pre-combustion, and oxy-fuels options.

REFERENCES

- [1] European Commission, The 2020 climate and energy package 2015. http://ec.europa.eu/clima/policies/strategies/2020/index_en.htm (accessed August 4, 2015).
- [2] Metz B, Davidson O, Conick H de, Loos M, Meyer L, editors. IPCC Special Report on: Carbon Dioxide capture and Storage: Prepared by Working Group III of the Intergovernmental Panel on Climate Change. Cambridge: Cambridge University Press; 2005.
- [3] International Energy Agency. World Balance. IEA Sankey Diagram 2015. <http://www.iea.org/Sankey> (accessed December 10, 2015).
- [4] Olivier J, Muntean M. Trends in Global CO₂ Emissions: 2014 Report. PBL Netherlands Environmental Assessment Agency. The Hague: PBL Publisher; 2014.
- [5] International Energy Agency. Tracking Industrial Energy Efficiency and CO₂ Emissions. Paris: Stedi Media; 2007.
- [6] Klemeš JJ, Kravanja Z. Forty years of heat integration: Pinch Analysis (PA) and Mathematical Programming (MP). *Curr Opin Chem Eng* 2013;2:461–74. doi:10.1016/j.coche.2013.10.003.
- [7] Al-Mohannadi DM, Linke P. On the systematic carbon integration of industrial parks for climate footprint reduction. *J Clean Prod* 2016;112:4053–64. doi:10.1016/j.jclepro.2015.05.094.

- [8] Abdul Manaf N, Cousins A, Feron P, Abbas A. Dynamic modelling, identification and preliminary control analysis of an amine-based post-combustion CO₂ capture pilot plant. *J Clean Prod* 2015;113:635–53. doi:10.1016/j.jclepro.2015.11.054.
- [9] Chapel DG, Mariz CL. Recovery of CO₂ from flue gases : commercial trends. *Can Soc Chem Eng* 1999.
- [10] Abu-Zahra MRM, Schneiders LHJ, Niederer JPM, Feron PHM, Versteeg GF. CO₂ capture from power plants part I. A parametric study of the technical performance based on monoethanolamine. *Int J Greenh Gas Control* 2007;1:37–46. doi:10.1016/S1750-5836(06)00007-7.
- [11] Khan AA, Halder GN, Saha AK. Carbon dioxide capture characteristics from flue gas using aqueous 2-amino-2-methyl-1-propanol (AMP) and monoethanolamine (MEA) solutions in packed bed absorption and regeneration columns. *Int J Greenh Gas Control* 2015;32:15–23. doi:10.1016/j.ijggc.2014.10.009.
- [12] Luis P. Use of monoethanolamine (MEA) for CO₂ capture in a global scenario: Consequences and alternatives. *Desalination* 2016;380:93–99. doi:10.1016/j.desal.2015.08.004.
- [13] Geng Y, Zhang P, Ulgiati S, Sarkis J. Emergy analysis of an industrial park: the case of Dalian, China. *Sci Total Environ* 2010;408:5273–83. doi:10.1016/j.scitotenv.2010.07.081.
- [14] Hackl R, Harvey S, Andersson E. Total Site Analysis (TSA) Stenungsund Report. Chalmers University of Technology. Gothenburg: 2010.

- [15] Hackl R, Andersson E, Harvey S. Targeting for energy efficiency and improved energy collaboration between different companies using total site analysis (TSA). *Energy* 2011;36:4609–15. doi:10.1016/j.energy.2011.03.023.
- [16] Rubio-Castro E, Ponce-Ortega JM, Serna-González M, El-Halwagi MM. Optimal reconfiguration of multi-plant water networks into an eco-industrial park. *Comput Chem Eng* 2012;44:58–83. doi:10.1016/j.compchemeng.2012.05.004.
- [17] Cheng S-L, Chang C-T, Jiang D. A game-theory based optimization strategy to configure inter-plant heat integration schemes. *Chem Eng Sci* 2014. doi:10.1016/j.ces.2014.07.001.
- [18] Lowe EA. Creating by-product resource exchanges: Strategies for eco-industrial parks. *J Clean Prod* 1997;5:57–65. doi:10.1016/S0959-6526(97)00017-6.
- [19] Lovelady EM, El-Halwagi MM. Design and integration of eco-industrial parks for managing water resources. *Environ Prog* 2009;28:265–72. doi:10.1002/ep.
- [20] Boix M, Montastruc L, Azzaro-Pantel C, Domenech S. Optimization methods applied to the design of eco-industrial parks: a literature review. *J Clean Prod* 2015;87:303–17. doi:10.1016/j.jclepro.2014.09.032.
- [21] Dhole VR, Linnhoff B. Total site targets for fuel, co-generation, emissions, and cooling. *Comput Chem Eng* 1993;17:S101–9. doi:10.1016/0098-1354(93)80214-8.
- [22] Raissi K. Total Site Integration. PhD Thesis, UMIST, Manchester, UK, 1994.
- [23] Klemes J, Dhole VR, Raissi K, Perry SJ. Targeting and design methodology for

- reduction of fuel, power and CO₂ on total sites. *Appl Therm Eng* 1997;17:993–1003.
- [24] Stijepovic MZ, Linke P. Optimal waste heat recovery and reuse in industrial zones. *Energy* 2011;36:4019–31. doi:10.1016/j.energy.2011.04.048.
- [25] Stijepovic VZ, Linke P, Stijepovic MZ, Kijevčanin ML, Šerbanović S. Targeting and design of industrial zone waste heat reuse for combined heat and power generation. *Energy* 2012;47:302–13. doi:10.1016/j.energy.2012.09.018.
- [26] Mavromatis SP, Kokossis a. C. Conceptual optimisation of utility networks for operational variations - I. Targets and level optimisation. *Chem Eng Sci* 1998;53:1585–608. doi:10.1016/S0009-2509(97)00431-4.
- [27] Mavromatis SP, Kokossis a. C. Conceptual optimisation of utility networks for operational variations - II. Network development and optimisation. *Chem Eng Sci* 1998;53:1585–608. doi:10.1016/S0009-2509(97)00431-4.
- [28] Varbanov PS, Doyle S, Smith R. Modelling and optimization of utility systems. *Chem Eng Res Des* 2004;82:561–78. doi:http://dx.doi.org/10.1205/026387604323142603.
- [29] Varbanov P, Perry S, Makwana Y, Zhu XX, Smith R. Top-level analysis of site utility systems 2004;82:784–95.
- [30] Duran MA, Grossmann IE. Simultaneous optimization and heat integration of chemical processes. *AIChE J* 1986;32:123–38. doi:10.1002/aic.690320114.

- [31] Grossmann IE, Papoulias SA. A structural optimization approach process synthesis-I. *Comput Chem Eng* 1983;7:695–706.
- [32] Kobayashi S, Umeda T, Ichikawa A. Synthesis of optimal heat exchange systems - an approach by the optimal assignment problem in linear programming. *Chem Eng Sci* 1971;26:1367–80.
- [33] Hohmann EC. Optimum networks for heat exchange. PhD Thesis, University of Southern California, USA, 1971.
- [34] Umeda T. Synthesis of optimal processing system by an integrated approach. *Chem Eng Sci* 1972;27:795–804.
- [35] Linnhoff B, Hindmarsh E. The pinch design method for heat exchanger networks. *Chem Eng S* 1983;38:745–63.
- [36] Papoulias SA, Grossmann IE. A structural optimization approach to process synthesis-II. Heat recovery networks. *Comput Chem Eng* 1983;7:707–21.
- [37] Linnhoff B, Mason DR, Wardle I. Understanding heat exchanger networks. *Comput Chem Eng* 1979;3:295–302. doi:10.1016/0098-1354(79)80049-6.
- [38] Umeda T, Harada T, Shiroko K. A thermodynamic approach to the synthesis of heat integration systems in chemical processes. *Comput Chem Eng* 1979;3:273–82.
- [39] Linnhoff BOD, Flower JR. Synthesis of heat exchanger networks : i. systematic generation of energy optimal networks. *AIChE* 1978;24:633–42.

- [40] Flower JR, Linnhoff B. Thermodynamic analysis in the design of process networks. *Comput Chem Eng* 1979;3:283–91.
- [41] El-Halwagi MM. Pollution prevention through process integration: Systematic design tools. San Diego, USA: Academic Press; 1997.
- [42] Almutlaq AM, Kazantzi V, El-Halwagi MM. An algebraic approach to targeting waste discharge and impure fresh usage via material recycle/reuse networks. *Clean Technol Environ Policy* 2005;7:294–305. doi:10.1007/s10098-005-0005-8.
- [43] El-Halwagi MM, Gabriel F, Harell D. Rigorous graphical targeting for resource conservation via material recycle/reuse networks. *Ind Eng Chem Res* 2003;42:4319–28. doi:10.1021/ie030318a.
- [44] El-Halwagi MM, Manousiouthakis V. Synthesis of mass exchange networks. *AIChE J* 1989;35:1233–44. doi:10.1002/aic.690350802.
- [45] Wang YP, Smith R. Wastewater minimisation. *Chem Eng Sci* 1994;49:981–1006. doi:10.1016/0009-2509(94)80006-5.
- [46] Alva-Argáez A, Vallianatos A, Kokossis A. A multi-contaminant transshipment model for mass exchange networks and wastewater minimisation problems. *Comput Chem Eng* 1999;23:1439–53. doi:10.1016/S0098-1354(99)00303-8.
- [47] Alnouri SY, Linke P, El-Halwagi M. A synthesis approach for industrial city water reuse networks considering central and distributed treatment systems. *J Clean Prod* 2015;89:231–50. doi:10.1016/j.jclepro.2014.11.005.

- [48] Chew IML, Thillaivararna SL, Tan RR, Foo DCY. Analysis of inter-plant water integration with indirect integration schemes through game theory approach: Pareto optimal solution with interventions. *Clean Technol Environ Policy* 2010;13:49–62. doi:10.1007/s10098-010-0280-x.
- [49] Yoo C, Lee TY, Kim J, Moon I, Jung JH, Han C, et al. Integrated water resource management through water reuse network design for clean production technology: State of the art. *Korean J Chem Eng* 2007;24:567–76. doi:10.1007/s11814-007-0004-z.
- [50] Aresta M, Dibenedetto A. Utilisation of CO₂ as a chemical feedstock: opportunities and challenges. *Dalton Trans* 2007:2975–92. doi:10.1039/b700658f.
- [51] Turk GA, Cobb TB, Jankowski DJ, Wolsky AM, Sparrow FT. CO₂ transport : a new application of the assignment problem. *Energy* 1987;12:123–30.
- [52] Tapia JFD, Lee J-Y, Ooi REH, Foo DCY, Tan RR. CO₂ Allocation for scheduling Enhanced Oil Recovery (EOR) operations with geological sequestration using discrete-time optimization. *Energy Procedia* 2014;61:595–8. doi:10.1016/j.egypro.2014.11.1189.
- [53] Hornafius KY, Hornafius JS. Carbon negative oil: A pathway for CO₂ emission reduction goals. *Int J Greenh Gas Control* 2015;37:492–503. doi:10.1016/j.ijggc.2015.04.007.
- [54] Middleton RS, Bielicki JM. A scalable infrastructure model for carbon capture and storage: SimCCS. *Energy Policy* 2009;37:1052–60.

doi:10.1016/j.enpol.2008.09.049.

- [55] Hasan MMF, First EL, Boukouvala F, Floudas CA. A multi-scale framework for CO₂ capture, utilization, and sequestration: CCUS and CCU. *Comput Chem Eng* 2015;81:2–21. doi:10.1016/j.compchemeng.2015.04.034.
- [56] Pena M a., Gómez JP, Fierro JLG. New catalytic routes for syngas and hydrogen production. *Appl Catal A Gen* 1996;144:7–57. doi:10.1016/0926-860X(96)00108-1.
- [57] Tan RR, Foo DCY. Pinch analysis approach to carbon-constrained energy sector planning. *Energy* 2007;32:1422–9. doi:10.1016/j.energy.2006.09.018.
- [58] Pękala ŁM, Tan RR, Foo DCY, Jeżowski JM. Optimal energy planning models with carbon footprint constraints. *Appl Energy* 2010;87:1903–10. doi:10.1016/j.apenergy.2009.12.012.
- [59] Hasan MMF, Baliban RC, Elia JA, Floudas CA. Modeling , Simulation , and Optimization of Postcombustion CO₂ capture for variable feed concentration and flow rate . 1 . Chemical absorption and membrane processes. *Ind Eng Chem Res* 2012;51:15642-64.
- [60] Kunze C, Spliethoff H. Assessment of oxy-fuel, pre- and post-combustion-based carbon capture for future IGCC plants. *Appl Energy* 2012;94:109–16. doi:10.1016/j.apenergy.2012.01.013.
- [61] Jansen D, Gazzani M, Manzolini G, Dijk E Van, Carbo M. Pre-combustion CO₂

- capture. *Int J Greenh Gas Control* 2015;40:167–87. doi:10.1016/j.ijggc.2015.05.028.
- [62] Abu-Zahra MRM, Niederer JPM, Feron PHM, Versteeg GF. CO₂ capture from power plants part II. A parametric study of the economical performance based on mono-ethanolamine. *Int J Greenh Gas Control* 2007;1:135–42. doi:10.1016/S1750-5836(07)00032-1.
- [63] Van-Dal ÉS, Bouallou C. Design and simulation of a methanol production plant from CO₂ hydrogenation. *J Clean Prod* 2013;57:38–45. doi:10.1016/j.jclepro.2013.06.008.
- [64] Olah GA, Goepfert A, Prakash GKS. Chemical recycling of carbon dioxide to methanol and dimethyl ether: From greenhouse gas to renewable, environmentally carbon neutral fuels and synthetic hydrocarbons. *J Org Chem* 2009;74:487–98. doi:10.1021/jo801260f.
- [65] Gharaie M, Zhang N, Jobson M, Smith R, Panjeshahi MH. Simultaneous optimization of CO₂ emissions reduction strategies for effective carbon control in the process industries. *Chem Eng Res Des* 2013;91:1483–98. doi:10.1016/j.cherd.2013.06.006.
- [66] U.S. Energy Information Administration. How much carbon dioxide is produced per kilowatthour when generating electricity with fossil fuel? 2016. <https://www.eia.gov/tools/faqs/faq.cfm?id=74&t=11> (accessed January 1, 2016).
- [67] Natural Resources Canada. Canadian ammonia producers: benchmarking energy

efficiency and carbon dioxide emissions. Government of Canada Publications,
<http://publications.gc.ca/pub?id=9.690687&sl=0>; 2008.

- [68] Natural Resources Canada. Pinch analysis : for the efficient use of energy, water & hydrogen - nitrogen-based fertilizer industry. Government of Canada Publications,
<http://publications.gc.ca/pub?id=9.652442&sl=0>; 2012.

APPENDIX A

Appendix A. Steam cost and emission estimation

The cost of VHP steam generation is calculated based on the fuel cost. The following equation is used:

$$Q_{BF} = \frac{1}{\eta_{Blr}} * m_{stm} * \Delta h_{gen}$$

$$\eta_{Blr} = \frac{Q_{stm}}{Q_{BF}}$$

$$\text{Steam cost} = Q_{BF} * \text{Fuel Cost}$$

In this work, the cost of fuel was assumed to be 3.9 \$/MMBtu (3.7 \$/GJ), while the energy required to generate one ton of VHP steam is 3191.3 MJ/ton. Thus, the cost of generating one ton of steam per hour is:

$$Q_{BF} = \frac{1}{0.81} * 1 \frac{\text{ton}}{\text{hr}} * 3.19 \frac{\text{GJ}}{\text{ton}} = 3.93 \frac{\text{GJ}}{\text{ton*hr}}$$

$$\text{Steam cost} = 3.93 \frac{\text{GJ}}{\text{ton*hr}} * 3.7 \frac{\$}{\text{GJ}} = 14.55 \frac{\$}{\text{ton*hr}}$$

The emissions associated with generating one ton of steam from the boiler is estimated using the following equation:

$$\psi_{b,fuel} = \frac{1}{\Delta h_{combustion}} * \frac{MW_{CO_2}}{MW_{methane}}$$

$$F_{CO_2}^{VHP} = Q_{BF} * \psi_{b,fuel}$$

The heat of combustion of natural gas, which is assumed to be pure methane, is 50 MJ/ton. Also, the molecular weights of carbon dioxide and methane are 44 kg/kmol and 16 kg/kmol, respectively. Thus, the associated carbon dioxide is:

$$\psi_{b,fuel} = \frac{1}{50 \text{ GJ/ton}} * \frac{16}{44} = 0.055 \frac{tCO_2}{GJ}$$

$$F_{CO_2}^{VHP} = 3.93 \frac{GJ}{\text{ton VHP steam}} * 0.055 \frac{tCO_2}{GJ} = 0.22 \frac{tCO_2}{\text{ton VHP steam*hr}}$$

While the VHP steam can be calculated directly from the boiler data, the LP steam value and associated carbon dioxide emissions depends on the utility system. The utility system that is used for this problem is shown in the figure below.

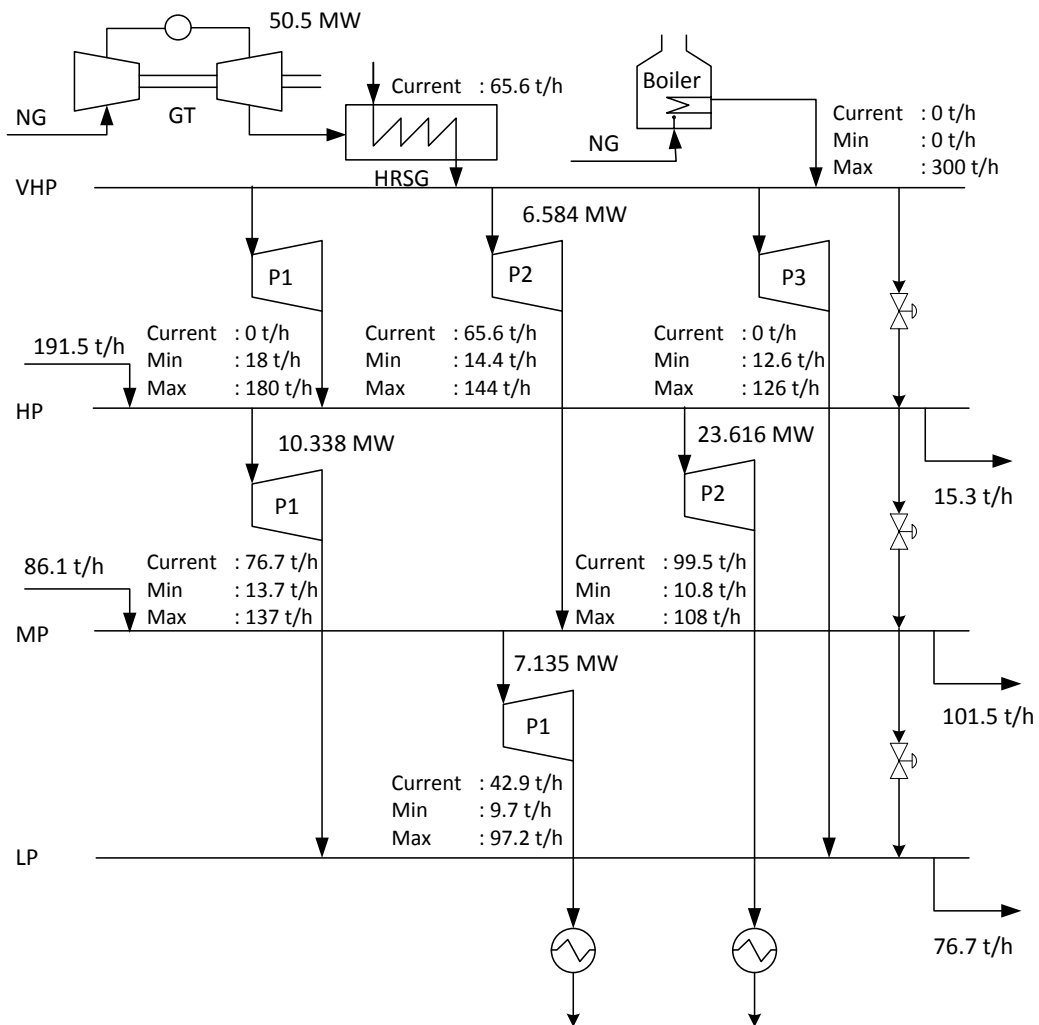


Figure 21: Optimized utility system

The value LP steam and the associated emissions depends on the power generated to expand VHP steam to LP steam. The steam is expanded from VHP to LP steam through VHP-P3. The following equations were used to determine the parameters for LP steam.

$$C_{LP} = C_{VHP} - C_{power} * W_{VHP-P3}$$

Willan's line is used to estimate the power of steam turbine with varying load, which is shown below. The parameters used in the equation are listed in Table 14. The power output of VHP-P3 is determined at 50% of the full capacity of the steam turbine. The maximum flowrate in the turbine is 126 t/h (i.e. 35 kg/s). The value for L is 0.05.

$$W = n * m - W_{int}$$

$$W_{int} = \frac{L}{B} * (\Delta h_{is} * m_{max} - A)$$

$$n = \frac{L+1}{B} * (\Delta h_{is} - \frac{A}{m_{max}})$$

$$A = b_0 + b_1 * \Delta T_{sat}$$

$$B = b_2 + b_3 * \Delta T_{sat}$$

Table 15: Regression coefficients for used in the steam turbine model

	Back pressure turbines		Condensing turbines	
	$W_{max} < 2$ MW	$W_{max} > 2$ MW	$W_{max} < 2$ MW	$W_{max} > 2$ MW
b_0 (MW)	0	0	0	-0.463
b_1 (MW°C ⁻¹)	0.00108	0.00423	0.000662	0.00353
b_2	1.097	1.155	1.191	1.220
b_3 (°C ⁻¹)	0.00172	0.000538	0.000759	0.000148

$$A = 4.23 \left(\frac{kW}{c} \right) * (303 - 130) \quad C = 731.8 \text{ kW}$$

$$B = 1.155 + 0.000538 (303 - 130) \quad C = 1.24807$$

$$n = \frac{(1+0.05)}{1.24807} * \left(815.1 \frac{kJ}{kg} - \frac{731.8}{35 \left(\frac{kg}{s} \right)} \right) = 668.15$$

$$W_{int} = \frac{0.05}{1.24807} * \left(815.1 \frac{kJ}{kg} * 35 \left(\frac{kg}{s} \right) - 731.8 kW \right) = 1113.58 kW$$

$$W = 668.15 \frac{kJ}{kg} * 18 \frac{kg}{s} - 1113.58 kW = 10913.1 kW$$

$$W_{is} = 815.1 \frac{kJ}{kg} * 18 \frac{kg}{s} = 14671.8 kW$$

$$\eta_{is} = \frac{10913.1}{14671.8} = 74.4\%$$

The turbine efficiency at 50% capacity is estimated to be 75%. Thus, it can be calculated that one ton of VHP yields 168 kWh of electricity when expanded to LP steam. The value of electricity and the carbon emissions associated with it is 0.051 \$/kWh and 0.55 kg CO₂/kWh. Thus, the cost of LP steam and the emissions associated with it can be calculated as following:

$$C_{LP} = 14.55 \frac{\$}{tVHP} - 168 kWh * 0.051 \frac{\$}{kWh} = 5.95 \frac{\$}{tLP}$$

$$F_{CO_2}^{LP} = 0.22 \frac{tCO_2}{tVHP} - 168 kWh * 0.55 \frac{kg CO_2}{kWh} * 1 \frac{t}{1000 kg} = 0.12 \frac{tCO_2}{tLP steam}$$

APPENDIX B

Appendix B. Costing Parameters

The annualized capital cost for compressor is based on the following correlation [7]:

$$C_{s,k}^{compressor} = 158,902 \left(\frac{P^{comp} * (T_{s,k,t} + U_{s,k})}{224} \right)^{0.84} * CRF$$

where CRF is the capital recovery factor, which is assumed to be 0.15.

Following correlation was used to estimate the annualize capital cost of the pump:

$$C_{s,k}^{pump} = \left(1.11 * 10^6 * \frac{P^{pump} * (T_{s,k,t} + U_{s,k})}{1000} + 0.07 * 10^6 \right) * CRF$$

The pipe sizing and annualized cost are calculated based on the following:

$$D_{s,k}^C = \sqrt{\left(\frac{4}{\pi} \right) * 8.314 * \frac{T_s (\sum_{s \in S} \sum_{t \in T} T_{s,k,t} + \sum_{s \in S} U_s)}{v_{s,k} * m_s (\Delta P_{s,k} + \Delta P_{s,k}^{pipe})}}$$

$$C_{s,k}^{pipe} = (95,230 * (D_{s,k}^C) + 96904) * CRF$$

where $D_{s,k}^C$ is the pipeline diameter. $v_{s,k}$ is the velocity of the flow, in this case study it was assumed that the velocity is 20 m/s for all flows.