TOWARDS CARBON NEUTRAL INDUSTRIAL PARKS

An Undergraduate Research Scholars Thesis

by

FARAH RAMADAN, ELIZABETH ABRAHAM, and TAHA KUBBAR

Submitted to the Undergraduate Research Scholars program at
Texas A&M University
in partial fulfillment of the requirements for the designation as an

UNDERGRADUATE RESEARCH SCHOLAR

Approved by Research Advisors: Dr. Dhabia Al-Mohannadi
Dr. Patrick Linke

May 2020

Major: Chemical Engineering

TABLE OF CONTENTS

ABSTRACT

Towards Carbon Neutral Industrial Parks

Farah Ramadan, Elizabeth Abraham, and Taha Kubbar
Department of Chemical Engineering
Texas A&M University

Research Advisor: Dr. Dhabia Al-Mohannadi
Department of Chemical Engineering
Texas A&M University

Research Advisor: Dr. Patrick Linke
Department of Chemical Engineering
Texas A&M University

CO_2 emissions from industrial processes adversely affect the environment, with significant contributions to climate change. Therefore, there is a global need to reduce CO_2 emissions into the atmosphere. Through this work, a tool that optimizes energy reuse while reducing emissions and maximizing profit was applied to an industrial cluster made up of several plants and/or processes producing several different products. There has been a recent focus on carbon capture utilization and storage solutions that integrate natural gas, energy, and other key materials like CO_2. This work introduces an integration approach to design a carbon neutral industrial park from resources such as natural gas, water, air, emissions, and energy as heat and power, to produce value-added products. The approach applies a Linear Program (LP) that can be applied to various combinations of plants, to find the optimum configuration for a set target. An illustrative example that explores different target scenarios and combinations was investigated to verify the approach.

DEDICATION

We dedicate this thesis to our families for their unfaltering encouragement and support of our work. We also dedicate our work to our faculty advisors, Dr. Dhabia Al-Mohannadi and Dr. Patrick Linke, for their continuous guidance throughout the duration of this research and the URS program.

ACKNOWLEDGMENTS

We would like to extend our gratitude to our faculty advisors, Dr. Dhabia Al-Mohannadi and Dr. Patrick Linke, for generously providing us with the help and direction we needed to complete this thesis. Without their support, this would not have been possible. We would also like to thank Shaza Shehab and Razan Ahmed, as it was their optimization model that was used to obtain results. We thank them for taking the time to explain the model to us and assisting us in running it.

Furthermore, we thank Texas A&M University and Texas A&M University at Qatar for making this opportunity possible. We also appreciate the LAUNCH: UGR staff who organized the URS program and guided us throughout its duration.

CHAPTER I

INTRODUCTION

CO_2 emissions from anthropogenic activities have dramatically increased in recent years. There is an ambitious universal need to reduce these emissions. Carbon capture utilization and storage (CCUS) systems that utilize and convert raw material, CO_2, into value added products present the immediate solution to this ongoing emission crisis. Globally, stationary sources are responsible for about 60% of carbon release of the total fossil fuel footprint.[1] This can be applied to industries such as Qatar's, where two-thirds of emissions come from industrial parks where most heavy industrial activities take place.[2] This provides a unique opportunity to capture large amounts of CO_2 from nearby sources and has the potential to apply CCUS.[3]

One way to model CO_2 conversion is to develop a source-sink representation between several plants that involve CO_2 as raw material, waste, or by-product. This can be done through an eco-industrial park (EIP), which is defined as a group of plants/processes that exchange energy, water, and material with one another to minimize waste, while remaining economically competitive and sustainable.[4] An EIP can optimize one resource (e.g. water integration) or several resources, some of which are referred to in Boix et al.[5] Furthermore, these plants would be located in proximity to one another for ease of material exchange. For an industrial park with a diversity of plants, an EIP could provide substantial improvements in resource management and emissions reduction. The challenge, however, is that designing an EIP requires the collection of a vast amount of data. This data is needed to tackle the numerous possible interactions that can co-exist in an industrial park.

Several works have attempted to design carbon-neutral industrial parks. Block et al[6] gave some examples of real applications of low-carbon industrial parks, and Fujii et al looked into deploying symbiosis to reduce emissions from urban Asian cities.[7] A review of other attempts can be found in Geng et al.[8] However, the aforementioned designs were reached in an ad-hoc manner, focusing only on one element of integration to reduce emissions and reach carbon neutrality, so they may overlook opportunities for savings and increased production. In the field of process systems, there has been a recent increase in the optimization of individual industrial processes through energy and mass integration that aim to have cleaner and more economical industrial plants. The use of CCUS systems and optimization of individual processes indicates that the integration of these systems along with multiple industrial plants will thereby create eco-industrial parks or clusters. There have been many approaches aimed at creating these green clusters with reduced carbon footprints. Some of these include work by Manan et al, which provides a review on the advances in integration aimed at CO_2 emission reduction through the use of Pinch Analysis,[9] Al-Mohannadi and Linke[10], whose work only looked into CO_2 conversion processes, and Hassiba et al, who incorporated waste heat exchange in their work.[11] These approaches, however, only looked into the integration of hydrocarbon streams without addressing the energy requirements for these plants.[12]

This project will assess the potential benefits of utilizing resources such as natural gas, water, air, emissions, and energy as heat and power to produce various value-added products. The approach described in this work enables one to integrate and optimize not only materials but also energy such as heat and power, reducing emissions without compromising other demands. It also provides the opportunity to incorporate renewable energy resources, further reducing emissions and use carbon capture and sequestration.[13] This will be with the objective of creating carbon-neutral industrial parks.

The economic attractiveness of the project will also be assessed. Energy requirements will also be accounted for in a way that ensures energy resources will not be costly or environmentally damaging. Hence, this project presents a tempting initiative to undertake in the near future as a means to reduce its carbon footprint.

Objectives

This project will aim to develop a carbon-neutral industrial park by using a systematic optimization approach. It will be applied to assess the potential benefits of integrating natural gas, water, air, emissions, and energy as heat and power to produce value-added products. This will involve mapping various industrial processes that can be integrated in an industrial park.

Literature Review

Al-Mohannadi and Linke developed an optimization-based approach to the systematic design of carbon integration networks for industrial parks. The approach involved an integrated analysis of sources, utilization, storage, capture, separation, compression, and transmission. Thus, integration was applied across various carbon emitting streams (sources) and utilization possibilities (sinks). The goal of this approach was to identify the carbon integration configuration at the lowest cost for a specified footprint reduction target. While previous work in energy and mass integration considered carbon capture and storage (CCS) as the only sink, Al-Mohannadi and Linke's approach systematically considered multiple sinks, studying carbon management synergies at a deeper level. The overall approach can be summarized into a series of four steps: data acquisition for the industrial park, identification of sinks, data acquisition for treatment and transmission, and optimal design of carbon integration networks. A Mixed Integer Non-Linear

Program (MINLP) formulation was used in this work and was solved using “What’sBest! 12.0” Lindo Global solver for MS-Excel 2010. The solver was used for net carbon reduction targets of 3%, 10%, 20%, 30%, 40%, and 50%. Specific costs depended on net carbon captured after power supply, inefficiencies, and heat demand were considered.[10]

Lovelady and El-Halwagi presented an optimization-based approach to the design and integration of water in an eco-industrial park (EIP). Possible configurations were described by a source-interception-sink structural representation. The problem was then framed as an optimization program with the goal of identifying recycle and separation strategies and minimizing costs of the interception devices, fresh water, and waste treatment. This systems integration approach was an improvement from the stand-alone processing model that was used at the time. A Non-Linear Program (NLP) or Mixed Integer Non-Linear Program (MINLP) formulation was solved using LINGO Global Software based on inception modeling and cost functions. The solver was used to decide on the EIP design, streams entering and exiting the system, freshwater distribution, and wastewater discharge while considering process and environmental constraints.[14]

Zero liquid discharge is a method in which a process that uses water does not release a wastewater stream back to the environment. For example, in a seawater desalination plant, the byproduct of this process is a brine that is highly concentrated with water. Instead of returning the water into the sea, there is a possibility to recover even more water for the industrial process and have a solid salt sludge that has no negative effects on the environment.[15] The paper presents a mathematical programing approach to water integration, specifically with brine management. The model was made by first considering the economic objective to minimize the total cost, coupled with a set of mass balances in order to describe the system. The model was then solved by LINDO Global Solver in Microsoft Excel 2013.[15]

Circular Economy (CE) is defined by Avraamidou et al as "an economic system that replaces the end-of-life concept with reducing, alternatively reusing, recycling and recovering materials in production/distribution and consumption processes." Operating at three distinct levels, namely the micro-level (products, companies, and consumers), meso-level (eco-industrial parks) and macro-level (city, region, nation, and beyond), this system aims to accomplish sustainable development by simultaneously creating environmental quality, economic prosperity, and social equity for present and future generations.[16] There are five key characteristics for a CE. The first characteristic is the reduction of material losses or residuals, which is the minimization of waste and pollutants through the recovery and recycle of materials and products. Reduction of input and use of natural resources is the characteristic whereby stresses posed on natural resources are reduced through the efficient use of natural resources like water, land, and raw materials. The replacement of non-renewable resources with renewable ones limits the use of virgin materials and also allows for an increase of the share in renewables. The reduction of emission levels from direct and indirect emissions or pollutants is another important characteristic. Finally, increasing the value durability of a product is the characteristic that allows the extension of its lifetime through product redesign and recycling.[16] Avraamidou et al lists the process systems engineering (PSE) approaches that can facilitate the transition towards CE and identifies the gap areas with great potential that PSE community can explore for this transition.[16]

A valuable and viable industrial procedure for targeting and planning the reduction of energy costs and emissions at the factory site level was developed through the collaboration of a number of educational institutes. The procedure also incorporates the environmental costs and other possible regulatory actions. This newly developed approach was then applied to continuous, semi-continuous, and batch operations in order to conduct a case study, which emphasized energy and water minimization. Methodologies were then developed at the total site level, which incorporates the overall economic impact of process modification, and were applied to case studies to validate the claim. A prototype software was developed for the multi-objective optimization of a design and control strategy for total sites which can be delivered to industry. A final case study was performed with the aim of reducing energy and water consumption on a paper mill.[17]

Traditional pinch analysis was used to assess the minimum practical energy needs for a process using five steps. Plant data is first collected, after which minimum practical energy needs are set as targets. The process changes are then examined to identify the ones that contribute to meeting the target by using composite curves. A minimum energy design that achieves the target is then obtained by integrating various processes, after which optimization is performed by trading-off energy costs against capital costs.[17]

The industry aims to conserve material to minimize the operating costs of processes. Until El-Halwagi et al introduced a systematic, single-staged graphical method to target the minimum usage of fresh material through recycling techniques to solve reuse or recycle problems for source or sink systems, most techniques to achieve this consisted of iterative, nonsystematic techniques. El-Halwagi et al presents a set of algebraic linear equations based on a mass balance of fresh feed and contaminants for the source sink system. The objective of this is to minimize the required fresh feed. The set of linear equations is solved globally in order to match the sources to the sinks. These linear equations are converted into lines on a graph that follows a set of rules, placing the contamination load on the y-axis and the flowrate of the source on the x-axis. Through following the set of rules, it is possible to identify the source and sinks as well as the minimum required fresh feed and the minimum waste generated in mass integration problems.[18]

The next chapter will use process systems method to create carbon-neutral industrial parks.

CHAPTER II

METHODS

There are many necessary steps that must be taken in order to achieve a profitable, carbon neutral industrial park. This park must be designed by using a bound set of inputs, which are air, CO_2, water, natural gas, and ethane, in order to produce a set of value-added products. The approach developed to achieve the objectives of this research consists of six phases, namely criteria selection, plant selection, database creation, ad-hoc plant cluster mapping, optimization through model application, and sensitivity analysis.

Criteria Selection

There are a number of different processes and products, each with its own set of inputs and outputs, that can be selected to be a part of an eco-industrial park. When designing an eco-industrial park, it is crucial to understand the components that are introduced, exchanged, and exiting. This can vary depending on the overall objective that the park is to achieve. The primary objective of this work is to design an eco-industrial park that is overall carbon neutral, or in other words, a park that consumes as much carbon dioxide as it releases. An eco-industrial park, by definition, enhances environmental and economic performance through resource management. This allows for carbon emissions produced by some processes to be utilized in others, which would not have been possible had they the processes been decoupled. Therefore, determining the processes that will be included is of fundamental importance. Three criteria have been identified to select the best suited processes to be placed in the park, namely reaction routes, interlinkage potential, and profitability. These criteria where developed from the understanding gained on the holistic approach to process integration and optimization. Table 1 summarizes the criteria that were identified and how they analyze each of the processes to identify the ideal candidates for the carbon neutral eco-industrial park.

Table 1: Selected criteria and their objectives

Selection Criteria	***Description***
Reaction Routes	Identifies if the process can utilize raw materials input into the park or products produced by other processes in the park
Interlinkage Potential	Analyzes the process in terms of the opportunities it allows for sharing of resources
Profitability	Evaluates the process in terms of profitability and market demand of end product

Plant Selection

The three criteria identified above are used in a stage-gate process, shown in Figure 1, to determine the processes to be selected with the objective of achieving overall carbon neutrality in the park. Firstly, a list of the most commonly known processes that utilize or produce CO_2 in them as a product, byproduct, raw material, or waste is developed. The first gate of the plant selection process is the reaction routes (identified through literature review) which establishes the processes that can utilize the products or produce the reactants of the initially identified CO_2 inclusive processes. Other routes can then be further used to identify more products that can be synthesized to or from the routes that prior processes pursue. All interlinkages between the plants are then made to analyze the possible connections or potential for sharing of resources at the second gate. Units are eliminated if they require more than two raw materials not available as natural resources such as air and water or resources produced from existing units. The third and final gate eliminates processes based on their profitability, assessed by analyzing market demand and growth, to determine the final set of plants that are to be included in the eco-industrial park.

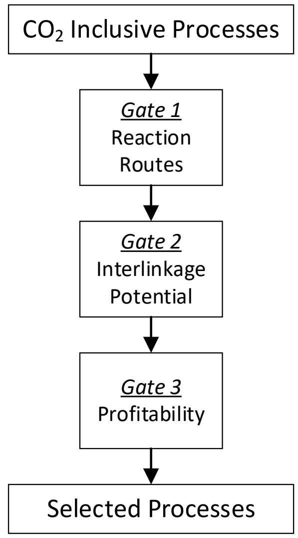


Figure 1: Stage-gate process for plant selection

Input and Output Analysis

Data on various process parameters was collected during this phase and summarized as shown below in a block diagram in Figure 2 for each of the ten candidates.

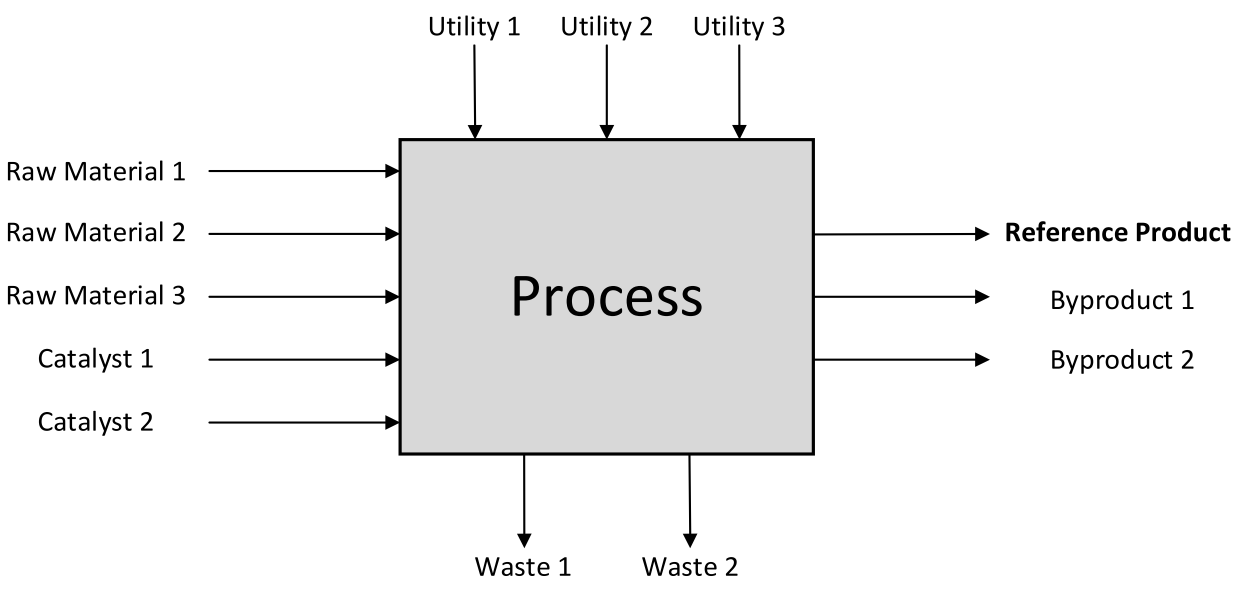


Figure 2: Process box diagram for data collection

Once all relevant information pertaining to Figure 2 has been found, tables that contain information on primary process inputs and outputs, the references of the sources they were identified from, and any comments that provide additional information for these resources, can be filled in the sample process data sheet shown in Appendix A. The process parameter, which is defined as the quantity of the said resource over that of the reference product, is the most important information that can be obtained from this table since it will serve as a basis for forming the inter-plant resource connections. These parameters will help determine the mass and energy quantities that are needed by a process to achieve a certain production capacity or vice-versa, where production capacity can be estimated from a known value of a resource. The parameter of the reference product for each process will always be 1, while that of the other resources may be greater or lesser than that of the reference product.

Design of Parks by Inspection

Design of parks by inspection looks at the candidate plants from a holistic view to draw out connections that would indicate the meaningful transfer of resource streams from one plant to another. To design these connections and eventually clusters, a plant representation is developed to allow for easy identification of what materials are relevant to which plant and to see the plants that have a possibility of forming connections between one another. The plant representation in Figure 3 has plants placed on the left and right-hand sides, while in between are headers that indicate the material streams. There are lines that are drawn from the header to the relevant plant to indicate that the stream is relevant to the plant. The arrow heads show whether the material is fed into the plant or is produced from the plant, which is the same when looking at the whole cluster of plants. From this information, it is possible to draw connections between plants, in essence, drawing the possible configurations for the industrial park. The industrial park does not need to have all the ten candidate plants selected and operating at the same time. In fact, an industrial park can have any number of plants on and operating at a time, depending upon the set objective of the cluster.

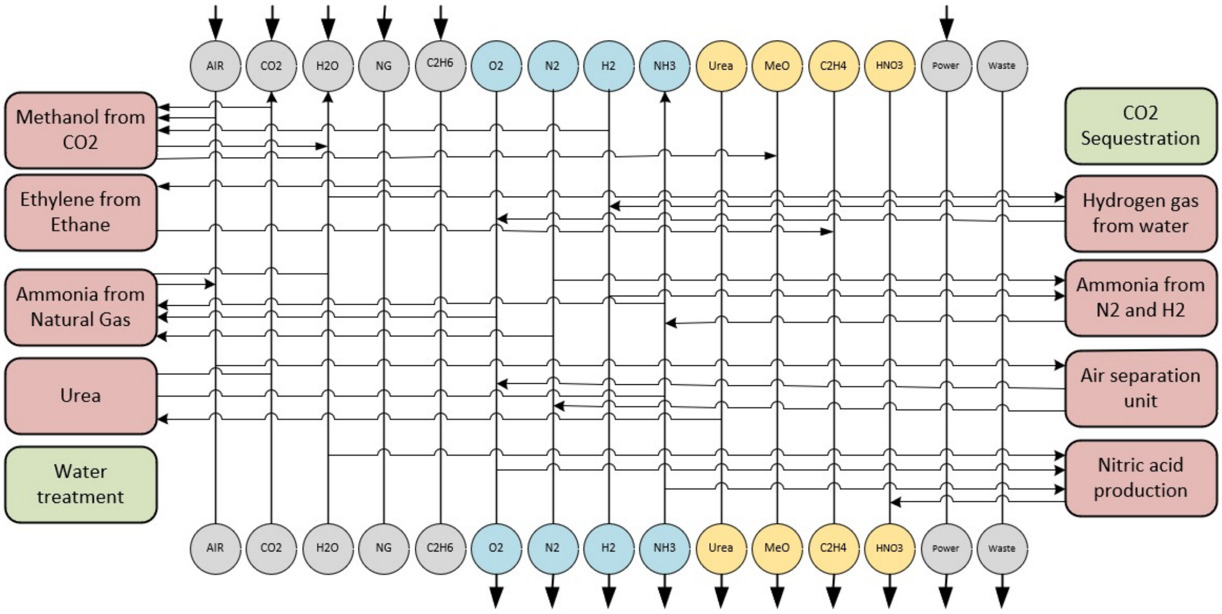


Figure 3: Resource line representation

Resource Integration and Model Optimization

The information collected in the database is to be fed into a model developed by Ahmed et al.[19] Since the data has information on the materials going in and out of each plant as well as the utilities used, it does complete the resource integration on its own.

Overview of Optimization

Optimization is the process of selecting the best (or optimum) solution from a number of possibilities. It applies to a mathematical model in which there is a degree of freedom, meaning there are multiple possible solutions that may satisfy the system. The process typically entails the maximization or minimization of an objective function subject to constraints. Optimization is particularly useful in providing a systematic solution to process integration problems. An optimization problem can be described by the types of constraints and the types of variables. The constraints determine whether the problem is a linear program (LP) or a non-linear program (NLP), while the variable determines whether it is an integer program (IP) or a mixed integer program (MIP). An MIP is one that uses real variables such as temperatures, pressures, and flow rates.[20]

The formulation of an optimization consists of four stages, namely the identification of an objective function, the development of a method to tackle the problem, the development of the constraints to be imposed, and improvement of the formulation. Amongst the benefits of using an optimization model is that it can efficiently solve interactive, large-scale problems that otherwise cannot be solved graphically or algebraically. The solution may then be used to develop a visual or algebraic solution. It is also possible, through optimization software, to easily conduct a sensitivity analysis and consider different scenarios. This allows for a better understanding of the system.[20]

Synthesis of Integrated Processing Clusters

The model developed by Ahmed et al presents a novel method for the synthesis of processing clusters. The representation allows for resources such as raw materials, intermediates, energy, emissions, and waste to be tracked across processes through “resource lines”. Input-output modules are used to interact with these resource lines and quantify material and energy conversions. This will allow us to exchange the resources effectively through the various plants. Each plant interacts with the resource lines by either consuming or producing that resource. This representation is able to identify all the possible interactions that can occur between the various plants within the industrial park. It allows for flexibility since it can be adjusted and applied to any problem involving configurations of multiple processes. To explore different configurations of a processing cluster and identify the most profitable configuration, a mixed-integer linear program (MILP) was introduced. It is a linear program because of the objective function, which is to maximize profit while ensuring a certain CO_2 conversion, and it is a mixed-integer since the variables used from the resources are mixed integers (pressures, temperatures, purities, flow rates, current, etc.). This compact model provides quick solutions to the optimization problem. It is designed on Microsoft Excel and uses the "What'sBest!" solver to solve the MILP to achieve maximum profitability while maintaining a low cost.[19]

Primary Model Equations

The model operates on the equations described by Ahmed et al which are detailed in this section with R, P, and C being a set of resources, processes, and components respectively, as shown below.[19]

$R = \{r_1, r_2, \ldots., r_n\}, n \in \mathbb{N}$

$P = \{p_1, p_2, \ldots., p_n\}, n \in \mathbb{N}$

$C = \{c_1, c_2, \ldots., c_n\}, n \in \mathbb{N}$

The resource line mass balance of each resource in the park is given by:

$$IF_r + \sum_p F_{r,p} - OF_r = 0 \qquad \forall\ r \in R \tag{1}$$

Where IF_r is the fresh feed of resource r to the cluster, $F_{r,p}$ is the flow of resource r to or from process p, and OF_r is the output of resource r from the cluster. The flow of resource r is related to the variable capacity of the process as follows through the parameter a_{rp}.

$$F_{r,p} - a_{r,p}\, C_p = 0 \qquad \forall\ (p \in P, r \in R) \tag{2}$$

Here, C_p is the capacity of process p. A reference product is specified for which $a_{r,p}$ is set to unity, while other resource parameters are normalized accordingly for each process. Practical process capacities are achieved by setting upper and lower limit restrictions as shown.

$$C_p^{min} I_p^C \le C_p \le C_p^{max} I_p^C \qquad \forall\ p \in P \tag{3}$$

Here, $C_p{}^{min}$ and $C_p{}^{max}$ are the minimum and maximum allowable capacities of process p, and $I_p{}^C$ is a binary variable which activates or deactivates the process. The fresh feed and the output of each resource to and from the clusters are defined with the following limits.

$$IF_r^{min} < IF_r < IF_r^{max} \qquad \forall\ r \in R \tag{4}$$

$OF_r^{min} < OF_r < OF_r^{max}$ ∀ r ∈ R (5)

Where IF^{min} and IF^{max} are the minimum and maximum fresh feed allowed. OF^{min} and OF^{max} are the allowed minimum and maximum output flows. Non-negativity constraints are applied on the fresh feed and output flows as follows.

$IF_r \geq 0$ ∀ r ∈ R (6)

$OF_r \geq 0$ ∀ r ∈ R (7)

The default objective adopted in this work is to achieve a carbon neutral park that is profitable for which the gross annual cluster profit, P, is given by:

$Max\ (P = TR - CAPEX - OPEX)$ (8)

The total revenue from resource sales, TR, the total annualized capital expenditure CAPEX, and the combined fixed and variable operating cost, OPEX, of the cluster are calculated as shown below, where β_r is the price of resource r, cc_p^{CAPEX} is the annualized capital cost parameter, and $ao^{variable}$ and ao^{fixed} are the fixed and variable operating costs for process p.

$TR = \sum_r OF_r\beta_r$ (9)

$CAPEX = cc_p^{CAPEX} C_p$ (10)

$OPEX = \sum_r IF_r\beta_r + \sum_p (ao_p^{variable} C_p + ao_p^{fixed})$ (11)

While the resource line is associated with a quality specification in terms of temperature, pressure, and purity, sometimes constraints may need to be applied on specific component flows in the resource. Examples of such constraints are allowable emissions or waste discharges from the cluster of certain components from the set of discharged components of interest, DC = {dc_1, dc_2, …., dc_n}, n ∈ ℕ. The component flows from the cluster can be established from:

$COF_{dc} = \sum_r x_{r,dc} OF_r$ ∀ dc ∈ DC (12)

Here, COF_{dc} is the total flow of component dc leaving the cluster, and $x_{r,dc}$ is the composition of component dc in the flow of resource r. Constraints can then be specified to limit components to allowable ranges.

$$COF_{dc}^{min} < COF_{dc} < COF_{dc}^{max} \qquad \forall \text{ dc} \in \text{DC} \qquad (13)$$

Here, COF^{min} and COF^{max} are the minimum and maximum allowable cluster output flows of component dc. Similarly, with a specified set of input components of interest IC = $\{ic_1, ic_2, \ldots, ic_n\}$, $n \in \mathbb{N}$, constraints on permissible component flows into the cluster can be included in the model.

$$CIF_{dc}^{min} < COF_{dc} < COF_{dc}^{max} \qquad \forall \text{ dc} \in \text{DC} \qquad (14)$$

$$CIF_{ic} = \sum_r x_{r,ic} IF_r \qquad \forall \text{ ic} \in \text{IC} \qquad (15)$$

$$CIF_{ic}^{min} < CIF_{ic} < CIF_{ic}^{max} \qquad \forall \text{ ic} \in \text{IC} \qquad (16)$$

Here, CIF^{min} and CIF^{max} are the minimum and maximum allowable component flows into the cluster and $x_{r,ic}$ is the composition of component ic in the flow of resource r. In some cases, the conversion of a component c to a certain extent is desired, for which the following constraint is added, where CV_c is the amount of component c that needs to be converted in the cluster.

$$CIF_c - COF_c \geq CV_c \qquad (17)$$

Using the equations detailed above and the "What'sBest!" plug in, different criteria or objectives can be placed based on the desired plant capacities and CO_2 conversion, for which the model will optimize a solution to achieve the highest profitability in Microsoft Excel. This may mean that some plants may not be operational if they do not assist in reaching the conversion goals or if the economics are unfavorable.

Sensitivity Analysis

A sensitivity analysis will be performed in order to determine the plant operations based on changes in product prices and utility costs. It will also be important to look beyond the industrial park if carbon neutrality is desired. In order to test for and understand full carbon neutrality, the cost and quantities of clean energy from renewable sources can be input into the model. There are multiple types of renewable energy that can be incorporated into the system such as solar energy, geothermal energy, and hydropower. The prices and efficiencies of the renewable energy would be different for different locations[21]. While renewable energy can be provided at low or zero carbon footprint, fossil fuel energy comes with CO_2 emissions that are incorporated into the balance. Furthermore, environmental protection policies such as carbon tax will be applied to the developed park to assess its compliance with a regulatory framework.

CHAPTER III

RESULTS

The design of a carbon neutral industrial city must be done by using a bounded set of inputs. The industrial city will be setup in a way that will produce both value-added products and the required intermediates ensuring a circular economy. The industrial city will operate at various plant capacities to maximize profit without hindering the carbon neutrality constraint. The carbon-neutral industrial park will mainly be powered by natural gas, which is primarily comprised of methane (95.39 mol%) amongst other gases. The composition of natural gas assumed is detailed in Table 2 below, obtained from Gabriel et al.[22]

Table 2: Natural gas composition and conditions

Component	***Composition (mol%)***
Methane	95.39
Ethane	3.91
Propane	0.03
Carbon Dioxide	0.59
Nitrogen	0.08
Temperature (°F)	79
Pressure (psia)	310

Plants Selected

Based on the criteria for plant selection, ten candidate plants were identified and determined to be feasible and have profit potential. It is these ten plants that will be arranged in various configurations to design a city that is profitable and carbon neutral. Each plant can be identified by its reference product. A reference product is the most desirable product of a plant. The parameter of the reference product is set to unity in material and energy balances, and all other resources are determined with respect to the reference product of the plant.[19] The plants and conversion processes are shown in Table 3.

Table 3: Description of selected candidate plants

Plant Number	***Reference Product***	***Process***
1	Ethylene	Steam cracking of ethane
2	Nitric Acid	Oxidation of ammonia (Ostwald Process)
3	Methanol	Hydrogenation of carbon dioxide
4	Urea	Synthesis from ammonia and carbon dioxide
5	Ammonia	Synthesis from hydrogen and nitrogen (Haber Process)
6	Ammonia	Steam reforming of natural gas
7	Oxygen	Fractional distillation of air (air separation)
8	Hydrogen	Electrolysis of water
9	Water	Treatment of wastewater
10	N/A	Sequestration of carbon dioxide

The input-output analysis and economic analysis of the candidate plants is presented in the database section.

Database

A database was developed consisting of the material and energy balances of candidate plants as well as their CAPEX parameters and prices. This data is summarized in Figure 4, Table

4, Table 5, and Table A2. The references used to calculate the data are compiled in Table A1, and the calculations for the CAPEX parameters in Table A2 in the appendix.

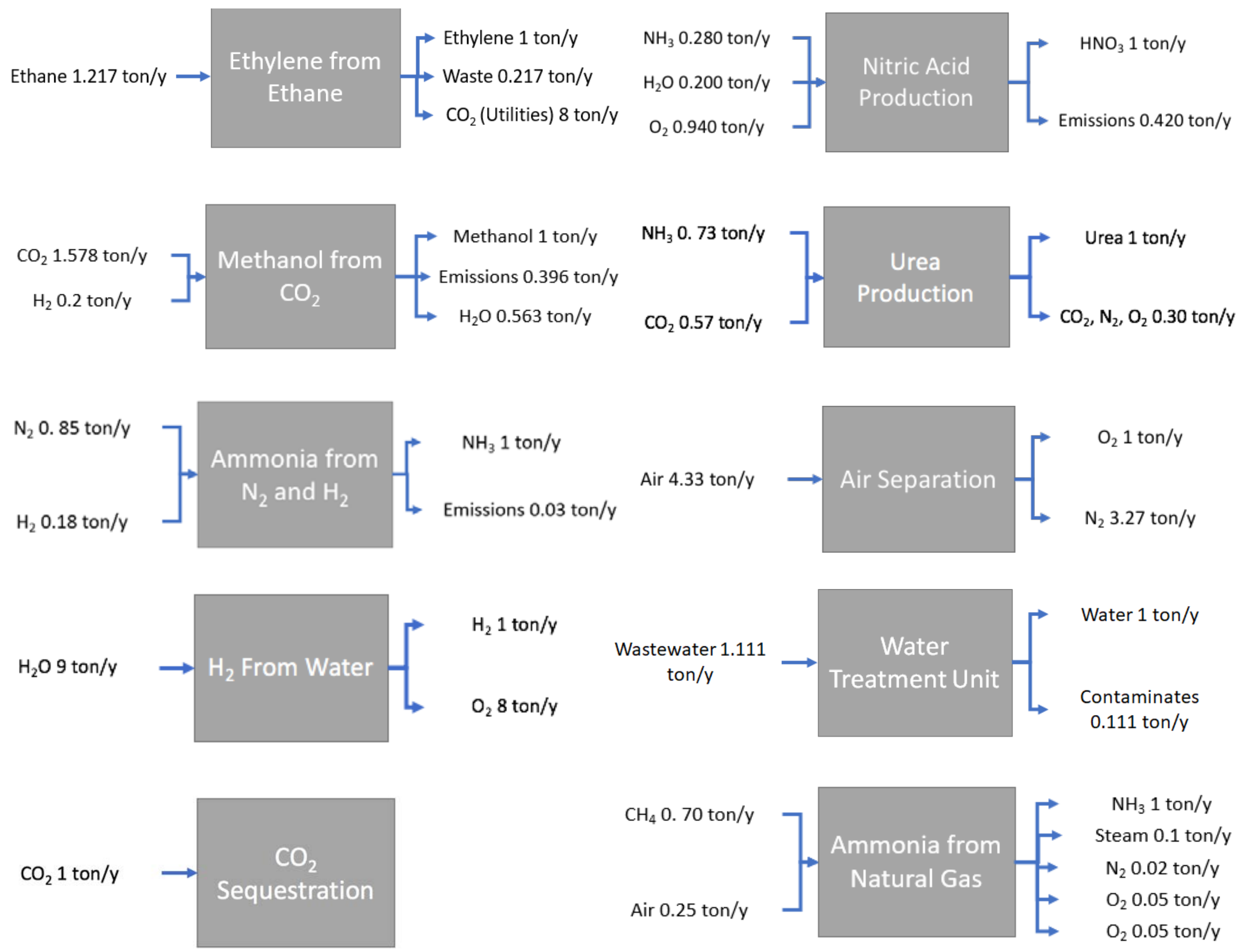


Figure 4: Material input and output of candidate plants

The ethylene plant oxidizes ethane to produce ethylene and CO_2. The nitric acid plant utilizes ammonia, water, and oxygen to produce nitric acid. The methanol plant hydrogenates CO_2 with hydrogen and air to produce methanol and water. The urea plant produces urea by reacting CO_2 with ammonia. Two types of ammonia plants are considered; the first uses nitrogen and hydrogen, while the second uses methane to produce ammonia. The air separation unit provides pure oxygen and nitrogen from air, while the hydrogen splitting plant provides pure oxygen and hydrogen from water. A wastewater treatment that purifies water using reverse osmosis and a carbon sequestration unit that stores CO_2 underground to prevent emissions are also considered. It should be noted that the carbon capture unit included at the end of Table 4 is usually an extension of a facility that produces emissions, and hence is not a standalone unit that should be considered separately. From the candidate plants selected, the ethylene, nitric acid, methanol, urea, and ammonia from natural gas plants will have a capture unit.

Table 4: CAPEX parameters of the candidate plants

Plant no.	***Plant Name***	***CAPEX Parameter ($/ton of reference product)***
1	Ethylene Production	76.05
2	Nitric Acid Production	11.52
3	Methanol Production	19.36
4	Urea Production	48.16
5	Ammonia from N_2 and H_2	26.96
6	Ammonia from Natural Gas	138.50
7	Air Separation	5.75
8	H_2 from Water Splitting	779
9	Water Treatment Unit	80.30
10	CO_2 Sequestration	90
11	Carbon Capture Unit	2

Table 5: Resource parameters of the candidate plants

Resource	***1***	***2***	***3***	***4***	***5***	***6***	***7***	***8***	***9***	***10***
Air	0	0	0	0	0	-0.246	-4.330	0	0	0
O_2	0	-0.940	0	0	0	0	1.000	8.000	0	0
N_2	0	0	0	0	-0.849	0	3.270	0	0	0
H_2O	0	-0.200	0	0	0	0	0	-9.000	1.000	0

Table 5 (Continued)

Resource	***1***	***2***	***3***	***4***	***5***	***6***	***7***	***8***	***9***	***10***
H_2	0	0	-0.200	0	-0.182	0	0	1.000	0	0
CO_2	0	0	-1.758	-0.733	0	0	0	0	0	-1.000
NH_3	0	-0.280	0	-0.567	1.000	1.000	0	0	0	0
Methanol	0	0	1.000	0	0	0	0	0	0	0
Methanol Plant Emissions	0	0	0.396	0	0	0	0	0	0	0
Ammonia from N_2 and H_2 Emissions	0	0	0	0	0.031	0	0	0	0	0
Ar	0	0	0	0	0	0	0.060	0	0	0
Wastewater	0	0	0.563	0	0	0	0	0	-1.111	0
CO_2, N_2, O_2 Emissions	0	0	0	0.300	0	0	0	0	0	0
Nitric Acid	0	1.000	0	0	0	0	0	0	0	0
Ammonia from NG Emissions	0	0	0	0	0	0.178	0	0	0	0
Urea	0	0	0	1.000	0	0	0	0	0	0
Water Contaminants	0	0	0	0	0	0	0	0	0.111	0
Ethane	-1.220	0	0	0	0	0	0	0	0	0
Ethylene	1.000	0	0	0	0	0	0	0	0	0
Butyne	0.030	0	0	0	0	0	0	0	0	0
Methane (NG)	0.050	0	0	0	0	-0.700	0	0	0	0
Ethylene Plant Emissions	0.140	0	0	0	0	0	0	0	0	0
Nitric Acid Emissions	0	0.420	0	0	0	0	0	0	0	0
HP Steam	0	0	0	0	0	-0.232	0	0	0	0
MP Steam	0.576	0.65	0	0	0	-4.365	0	0	0	0
LP Steam	0	0	0	0	0	-1.512	0	0	0	0
Cooling Water	0	0.05	0	-1.2	0	0	0	0	0	0
Electricity	-224	0	-26.47	-75	0	-157	0	0	0	0
Process water (Nitric Acid)	-0.028	-3.7	-169	-20	-785	-50	-245	-54000	-5.015	-1.370
Condensate	0	0.3	0	0	0	0	0	0	0	0
NG	0	0	0	1.084	0	0	0	0	0	0
SHP Steam	-0.224	0	0	0	0	-0.193	0	0	0	0

Design of Parks by Inspection

Attempt 1

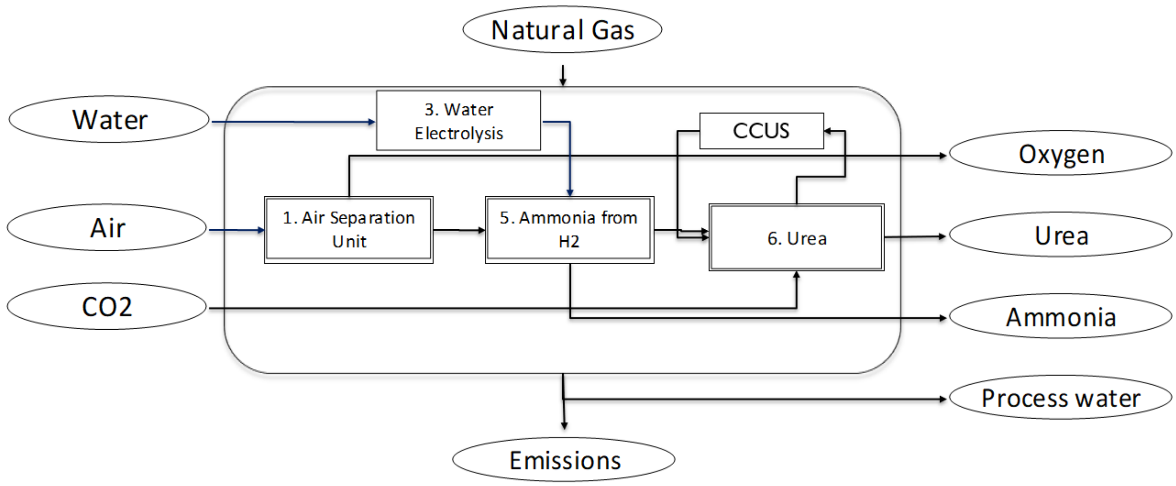


Figure 5: Industrial Park 1. First attempt at creating an industrial park

The first attempt at mapping out the industrial park was done using a total of four plants as seen in Figure 5. This park was designed in order to achieve the CO_2 objective as well as to aid us in understanding the process needed to do so. This could also be a possible solution that the model could produce if the remaining plants prove to be unprofitable based on the economics during the sensitivity analysis phase.

Attempt 2

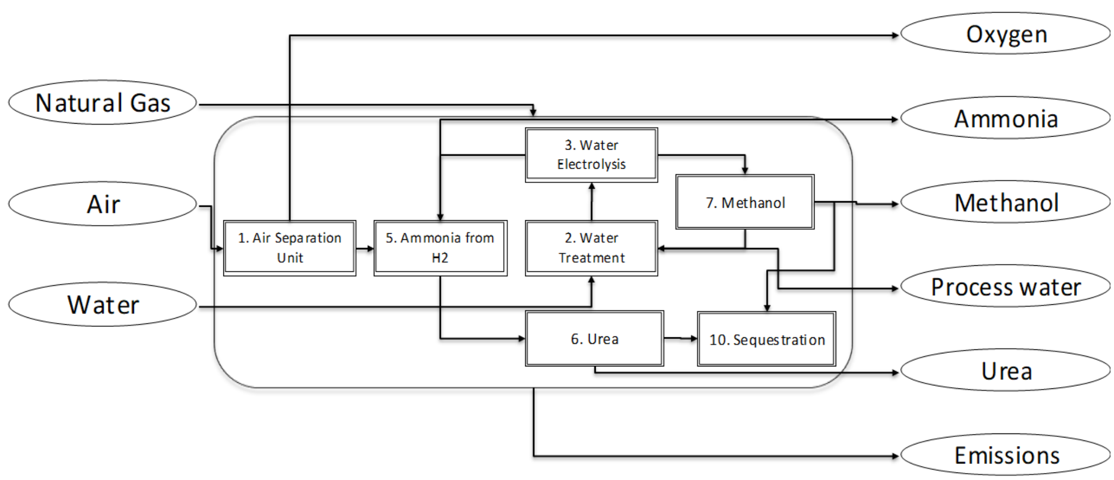


Figure 6: Industrial Park 2. Second attempt at creating an industrial park

The second attempt at resource integration was done manually as shown in Figure 6, based solely on material balances of eight different plants. Considering a basis of 1 ton/day of air input into the air separation unit and 3 ton/day of methanol produced from the methanol production plant, the park appears to be carbon negative, consuming air, carbon dioxide, and hydrogen to produce urea and methanol amongst other byproducts and waste. Based only on the material balances, the park would not require CO_2 sequestration. However, most of these conclusions are untrue due to the assumptions made. This attempt did consider emissions from burning fuel to fulfil power requirements, steam, water for cooling, or any resources not directly involved in the reactions. It is likely that resource integration considering the aforementioned emissions and resource consumption would yield very different results.

Attempt 3

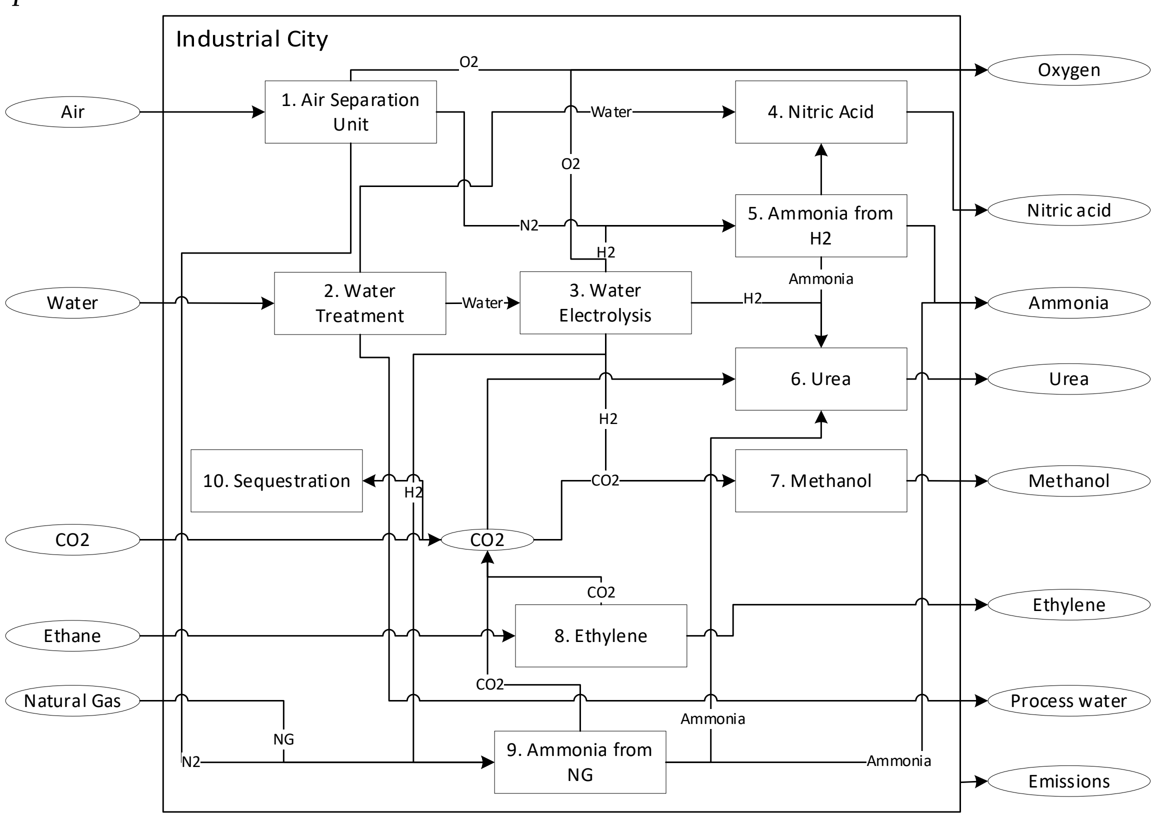


Figure 7: Industrial Park 3. Third attempt at creating an industrial park

A third attempt was completed considering the presence of all ten candidate plants, which can be seen in Figure 7. This gives a more general and descriptive view of the circular economy of the plants. All plants here are present and are interacting with each other either directly or indirectly ensuring that as much material is reused as possible with minimal waste produced. This city uses five feed stocks and can produce a variety of value-added products.

Optimized City

In order to understand the results obtained by the model, it is important to understand the model inputs. In addition to balance parameters, there are economic costs that determine the economical size and capacities of the various plants. The inputs to the base case can be seen in Table A3 as well as Table A4 in the appendix.

Based on the inputs, the model optimized the system and obtained an industrial park that satisfies the carbon dioxide conversion requirement in addition to maximizing the profit. The capacities for the optimized system can be seen in Table 6.

Table 6: Capacities for optimized base case

Plant Number	***Reference Product***	***Process (ton/year)***
1	Ethylene Production Plant	0
	Ethylene Carbon Capture Unit	0
2	Nitric Acid Production Plant	92,546
	Nitric Acid Carbon Capture Unit	0
3	Methanol Production Plant	0
	Methanol Carbon Capture Unit	0
4	Urea Production Plant	1771
	Urea Carbon Capture Unit	0

Table 6 (Continued)

Plant Number	***Reference Product***	***Process (ton/year)***
5	Ammonia Production from N_2 and H_2	0
6	Natural Gas Ammonia Production Plant	26,917
	Natural Gas Ammonia Carbon Capture Unit	1298
7	Air Separation Unit	100,000
8	Water Splitting Unit	0
9	Wastewater Treatment Unit	0
10	CO_2 Sequestration	120,000

The model optimized the capacity of each plant in a matter of seconds. This was done using What'sBest! Version 16 solver on a PC with 32 bits. The results have been summarized in Table 6. The optimization model only allowed the industrial park to operate six plants. The remainder of the plants' operations would hinder the economics of the industrial park. Methanol production is not profitable; therefore, the water splitting plant is shut down as there is no hydrogen requirement in the industrial park. Ammonia production from N_2 and H_2 was also shut down for similar reasons. There is an alternative ammonia production process that the optimization model deemed to be more profitable, and it is the production of ammonia from natural gas. There was also no need to open a water treatment plant, considering the plants that were already opened. Unfortunately, it was not possible to achieve complete 100% carbon reduction in the industrial city. The city produces 12,000 ton/year of CO_2 because not all emission streams containing carbon dioxide could be captured. Carbon dioxide from fugitive emissions and the CCU network inefficiencies are responsible for the emission losses in the city. This plant configuration for the set prices gave a yearly profit of $36,000,000 with an ROI of 11.05% of the initial investment every year. Hence, the city is profitable and economically attractive. Sample images of the optimization model's What'sBest! report in addition to images of the optimization model and its cost calculation table can be seen in Appendix B as Figure 8, Figure 9, and Figure 10.

Sensitivity Analysis

The sensitivity analysis was conducted for 5 scenarios. The costs of the utilities and raw materials and the prices of end user products were varied to analyze how the overall industrial park would fair in an ideal economy. They cases considered are as follows:

1. Electricity cost was set to a value of $0.02/kWh without varying other prices, and the sequestration plant was not operational, however a carbon tax was imposed on the model.
2. Electricity cost was set to a value of $0.04/kWh without varying other prices.
3. Electricity cost was set to a value of $0.08/kWh without varying other prices.
4. All resources were set to their highest prices in the last five years.
5. All resources were set to their lowest prices in the last five years.

In the table below, the first four cases considered a change in electricity price while the last three were determined by the market values of the materials that are going in and out of the system. The exact costs for these can be found in Table A2 and Table A3 in the Appendix. The results for the plant capacities are summarized in Table 7.

Table 7: Sensitivity analysis results

	Energy Costs ($/kWh)				***Material Costs***		
Sensitivity Analysis Conditions	0.02	0.04	0.06	0.08	Current	Highest	Lowest
Plants	***Capacities (ton/year)***						
Ethylene Production	100,000	0	0	0	0	0	0

Table 7 (Continued)

	Energy Costs ($/kWh)				***Material Costs***		
Sensitivity Analysis Conditions	0.02	0.04	0.06	0.08	Current	Highest	Lowest
Plants	***Capacities (ton/year)***						
Ethylene CCU	0	0	0	0	0	0	0
Nitric Acid Production	88,578	93,622	92,546	92,546	92,546	89,096	93,622
Nitric Acid CCU	0	0	0	0	0	0	0
Methanol Production	72,666	765	0	0	0	2920	765
Methanol CCU	7770	82	0	0	0	312	82
Urea Production	0	0	1771	1771	1771	0	0
Urea CCU	0	0	0	0	0	0	0
Ammonia Production from N_2 and H_2	24,802	0	0	0	0	0	0
Ammonia Production (NG)	0	26,214	26,917	26,917	26,917	100,000	26,214
Ammonia (NG) CCU	0	1264	1298	1298	1298	4822	1264
Air Separation	100,000	100,000	100,000	100,000	100,000	100,000	100,000
Hydrogen form Water Splitting	19,031	153	0	0	0	583	153
Water Treatment Unit	0	0	0	0	0	0	0
CO_2 Sequestration	0	120,000	120,000	120,000	120,000	120,000	120,000

The results summarized in Table 7 suggest that depending on the economics, there are various plant configurations that will result in the most profitable industrial park. The first noticeable result is that in the first case, the CO_2 sequestration unit is not operational. It is noticeable that this is also the only configuration where the ethylene plant is operational. In this case, it is more economically attractive to pay a carbon tax as opposed to adding a sequestration plant within the industrial park.

Looking at the electricity cost, it is noted that the industrial city would look very different at the lower prices than at higher prices. When the electricity price is very low, CO_2 utilization sinks may be used as opposed to CO_2 sequestration. This is due to the high electricity requirement needed to operate the methanol and ammonia production (from N_2 and H_2) plants, which are not activated at high electricity prices. When the optimization model determines that it is most profitable to operate one of these plants, it will allow another energy intensive plant to operate as well: the hydrogen from water splitting plant. This is supported by the results, where these three plants begin to operate when electricity is priced at 0.02 and 0.04 $/kWh. The main difference between the two cases is that at 0.02 $/kWh, the hydrogen from water splitting plant can operate at a higher capacity, opening the ammonia production from N_2 and H_2 plant, while this plant remains closed 0.04 $/kWh. At the higher electricity costs, these plants fail to contribute to the profitability of the industrial park.

Material cost also play a significant role in the operational capacities of the industrial park. The current material costs present the lowest quantity of operational plants compared to the other two cases, as it is the only scenario that does not produce methanol. Since the methanol plant is non-operational for the current prices, the hydrogen from water splitting will also remain non-operational. The highest material costs case displays significantly larger capacities in the methanol and ammonia production (from N_2 and H_2) plants compared to the other two cases. This is driven by the high profitability of both of these plants at the specified conditions. This is mainly because the raw materials needed for these plants, CO_2, N_2, and water, have generally remained stable, with small changes in prices. However, at the highest material costs, all three products, hydrogen, ammonia, and methanol, have significantly higher prices, allowing for an economic attraction to operate these plants at higher capacities.

An economic analysis was also conducted on these plants, and the total profit and the return on investment were obtained. A return on investment is a measure of how much of the initial investment is recovered in an operational year and is calculated as follows:

$$ROI = \frac{Yearly\ revenue\left(\frac{\$}{yr}\right) - Yearly\ operational\ costs\left(\frac{\$}{yr}\right)}{Total\ capital\ cost\ (\$)} \times 100 \qquad (18)$$

The results for the economics are summarized in Table 8 for electricity prices and Table 9 for material costs.

Table 8: Economics of variation in electricity prices

Material Costs	***1***	***2***	***3***	***4***
Electricity Price ($/kWh)	0.02	0.04	0.06	0.08
Profit from Cluster ($/year)	44,343,142	36,540,308	35,911,871	35,384,109
ROI	12.00%	11.27%	11.05%	10.88%
Total CO_2 Emissions (ton/year)	12,000	12,000	12,000	12,000

Table 9: Economics of variation in prices

Material Costs	***Current Cost***	***Lowest Cost***	***Highest Cost***
Profit from Cluster ($/year)	35,911,871	42,919,900	46,014,982
ROI	11.05%	13.23%	8.60%
Total CO_2 Emissions (ton/year)	12,000	12,000	12,000

Each economic case studied in the sensitivity analysis has differences in the yearly profit from the industrial city. However, they all maintain a return on investment of around 10% as can be seen in Table 8 and Table 9. This means that every year, the industrial park will recover approximately 10% of the capital investment, meaning that in all cases, the park requires roughly 10 years of production to see enough materials to cover its initial investment.

Since the operational plant capacities are key indicators of the yearly profit for each case, it is expected that the most profitable plants will also be the largest plants. The electricity price variations have shown that at lower prices, the plants will operate at generally higher capacities. The data in Table 8 shows that this is linked to a higher annual profit.

Similar to the effect of electricity prices, it is expected that the effect of material costs should follow the same trend shown in the plant capacities. Table 9 displays that profitability is analogous to the operational capacities of the plants. This means that the cases with the highest material prices resulted in the largest yearly profits. On the contrary, these cases also exhibit the lowest return on investment. This is mainly due to the high capital cost of the ammonia from natural gas plant. Nevertheless, the model determined that this combination of plants increases profitability, which is supported by the highest yearly profit out of the results for the various material costs.

CHAPTER IV

CONCLUSION

The purpose of this work was to develop a carbon neutral industrial park by using a systematic optimization approach. Industrial clusters were analyzed through linear programming to find the optimal operating capacities of individual units within the cluster that would achieve overall carbon neutrality. Ten feasible candidate plants producing value-added products such as methanol, urea, ammonia, ethylene, and nitric acid, were solved to illustrate the method. Using an optimization model, it was shown that the most profitable, carbon-neutral combination of plants only involved six of the ten candidate plants. This work demonstrated the benefits of integrating natural gas, water, air, emissions, and energy as heat and power in an eco-industrial park as opposed to a traditional industrial city in which integration does not occur. A sensitivity analysis was conducted in order to understand the impact of changes in parameters such as energy and material costs on the plant capacities and profit obtained from the model. Furthermore, an economic analysis was conducted to determine total profit and return on investment. For the base case, the city made $36,000,000 in profit per year and had an ROI of 11.05%. Results showed that the city is profitable and demonstrates advantages of resource integration. The city used CO_2 as an input and had some fugitive emissions that could not be captured. Therefore, it is a carbon negative/ carbon reducing industrial park. This can be achieved with low cost, renewable energy for power and heat production. The application of this work has great profit potential and is environmentally friendly in comparison to existing carbon positive industrial parks.

REFERENCES

1. Metz B, Davidson O, de Coninck H, Loos M, Meyer L. *CARBON DIOXIDE CAPTURE AND STORAGE*. Cambridge; 2005.

2. *Qatar National Development Strategy 2011~2016*. Doha; 2011.

3. Al-Yaeeshi AA, Al-Ansari T, Govindan R. The potential for carbon dioxide capture and utilization within the State of Qatar. *Comput Aided Chem Eng*. 2018;43:1499-1504. https://doi.org/10.1016/B978-0-444-64235-6.50261-8.

4. Susur E, Hidalgo A, Chiaroni D. A strategic niche management perspective on transitions to eco-industrial park development: A systematic review of case studies. *Resour Conserv Recycl*. 2019;140:338-359. doi:10.1016/j.resconrec.2018.06.002

5. 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(1):303-317. doi:10.1016/j.jclepro.2014.09.032

6. Block C, Van Praet B, Windels T, et al. Toward a Carbon Dioxide Neutral Industrial Park: A Case Study. *J Ind Ecol*. 2011;15(4):584-596. doi:10.1111/j.1530-9290.2011.00355.x

7. Fujii M, Fujita T, Dong L, et al. Possibility of developing low-carbon industries through urban symbiosis in Asian cities. *J Clean Prod*. 2016;114:376-386. doi:10.1016/j.jclepro.2015.04.027

8. Geng Y, Fujita T, Park HS, Chiu ASF, Huisingh D. Recent progress on innovative eco-industrial development. *J Clean Prod*. 2016;114:1-10. doi:10.1016/j.jclepro.2015.09.051

9. Manan ZA, Mohd Nawi WNR, Wan Alwi SR, Klemeš JJ. Advances in Process Integration research for CO2 emission reduction – A review. *J Clean Prod*. 2018;167:1-13. doi:10.1016/j.jclepro.2017.08.138

10. Al-Mohannadi DM, Linke P. On the systematic carbon integration of industrial parks for climate footprint reduction. *J Clean Prod*. 2016;112:4053-4064. doi:10.1016/j.jclepro.2015.05.094

11. Hassiba RJ, Linke P. On the simultaneous integration of heat and carbon dioxide in industrial parks. *Appl Therm Eng*. 2017;127:81-94. doi:10.1016/j.applthermaleng.2017.07.157

12. Panu M, Topolski K, Abrash S, El-Halwagi MM. CO 2 footprint reduction via the optimal design of Carbon-Hydrogen-Oxygen SYmbiosis Networks (CHOSYNs). *Chem Eng Sci*. August 2019:1-11. doi:10.1016/j.ces.2019.03.066

13. Shehab S, Ahmad R, Al-Mohannadi D, Linke. Patrick. Resource Integration and CO2 Conversion in Industrial Clusters. *Chem Eng Trans*. 2019.

14. Lovelady EM, El-halwagi MM. Degradation of lignin in ionic liquid with HCl as catalyst. *Environ Prog Sustain Energy*. 2015;35(3):809-814. doi:10.1002/ep

15. Alnouri SY, Linke P, El-Halwagi MM. Accounting for central and distributed zero liquid discharge options in interplant water network design. *J Clean Prod*. 2018. doi:10.1016/j.jclepro.2017.09.236

16. Avraamidou S, Baratsas SG, Tian Y, Pistikopoulos EN. Circular Economy - A challenge and an opportunity for Process Systems Engineering. *Comput Chem Eng*. 2020;133:106629. doi:10.1016/j.compchemeng.2019.106629

17. Klemeš J, Dhole VR, Raissi K, Perry SJ, Puigjaner L. Targeting and design methodology for reduction of fuel, power and CO2 on total sites. *Appl Therm Eng*. 1997;17(8-10):993-1003. doi:10.1016/s1359-4311(96)00087-7

18. El-Halwagi MM, Gabriel F, Harell D. PROCESS DESIGN AND CONTROL Rigorous Graphical Targeting for Resource Conservation via Material Recycle/Reuse Networks. 2003. doi:10.1021/ie030318a

19. Ahmed R, Shehab S, Al-Mohannadi DM, Linke P. Synthesis of integrated processing clusters. 2020:1-37.

20. El-Halwagi MM. *Overview of Optimization*.; 2017. doi:10.1016/b978-0-12-809823-3.00011-4

21. Renewable energy auctions: Status and trends beyond price. */publications/2019/Dec/Renewable-energy-auctions-Status-and-trends-beyond-price*.

22. Gabriel KJ, Linke P, Jiménez-Gutiérrez A, Martínez DY, Noureldin M, El-Halwagi MM. Targeting of the Water-Energy Nexus in Gas-to-Liquid Processes: A Comparison of Syngas Technologies. *Ind Eng Chem Res*. 2014;53(17):7087-7102. doi:10.1021/ie4042998

APPENDIX

Appendix A

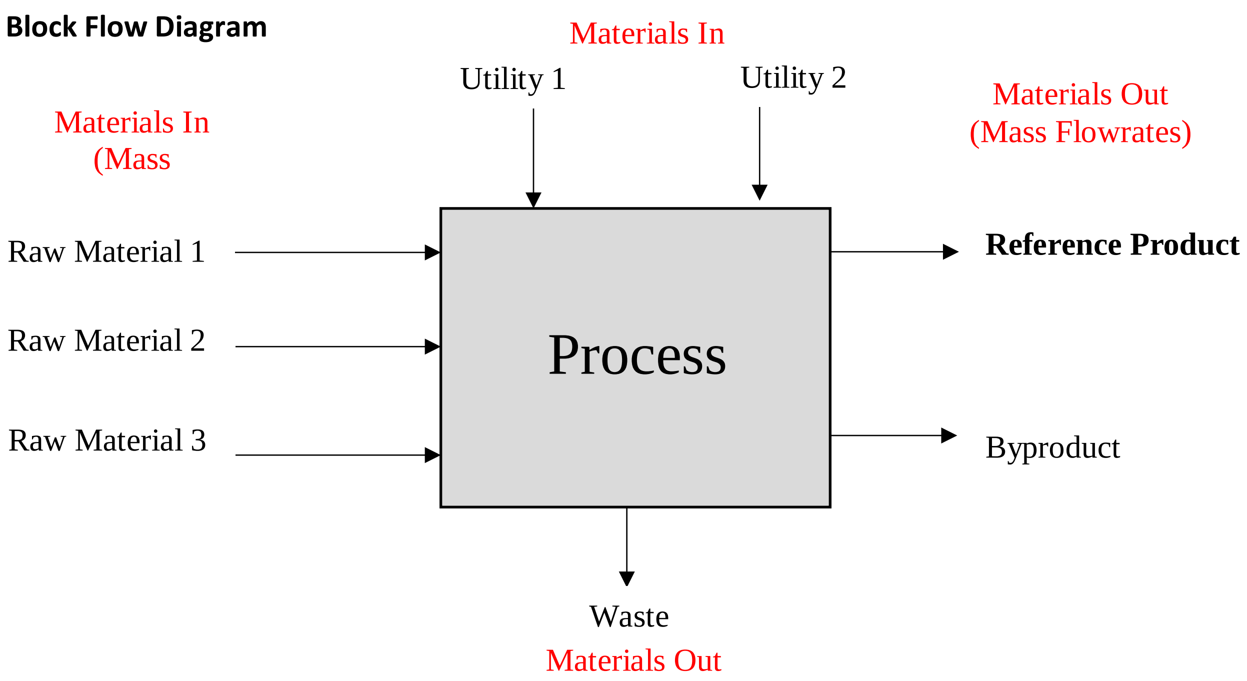
Data Sheet

Process Name: ____________________

Main Product and Quality: __________________________

Route: _____________________________

Block Flow Diagram



Resources Parameters

Process Input:

Resource	Unit	Parameter (UnitR/ton RefP)	Reference (no.)	Comments
Raw Material 1	ton			
Raw Material 1	ton			
Raw Material 1	ton			
Utility 1	MW			
Utility 2	ton			

Process Output:

Resource	Unit	Parameter (UnitR/ton RefP)	Reference (no.)	Comments
Reference Product	ton			
Byproduct	ton			
Waste	ton			

Reference Product: ___________________

Process Information Chemical Reactions

Dominant Chemical Reactions:

Information	Value	Reference no.	Comments
Process Selectivity			
Reactor Selectivity			
Catalyst Type			
Process Yield			
Process Conversion			
Heat of Reaction			
Reaction Temperature			

Information on Process Safety:

Has this plant been built before? Yes/ No

Capital Cost ($/tonP): ___________________________

Technology	Capacity (t/y)	Capital Cost (MM$)	Parameter ($/tonP/y)	Year	Reference (no.)

Note: Please add the above in terms of descending capacity.
Note: If capacity was found in ton/hr, then assume an operating year of 8000 hours. If ton/day, then just convert the previous value.
Note: M stands for a thousand and MM a million (i.e. $4 M = $4,000 & $1 MM = 1,000,000)
Note: The year which you found that specific Capital Cost for that plant. (i.e. From literature, it was found that the plant costs $7 MM when built in *2017*)

List of References:

Note: Please make sure the references are from verified reports, books, official documents, peer reviewed journals or verified fact-checked reputable news organizations.

Table A1: References used to calculate the various parameters specific to each plant

Plant	Resources
1	[1] H. Zimmerman and R. Walzl, "Ethylene," *Ullmann's Encyclopedia of Industrial Chemistry*. 2012. [2] P. Zhang, J. Tong, and K. Huang, "Role of CO 2 in Catalytic Ethane-to-Ethylene Conversion Using a High-Temperature CO 2 Transport Membrane Reactor," 2019. [3] W. Will, I. Emit, A. Contaminant, F. Wide, and E. Rate, "What You Need to Know about Shell's Petrochemical Facility," no. 15, pp. 1–4. [4] A. Kreisa, "Arenales Suspension Bridge Dow Gulfstream LHC-9 Ethylene Production Facility Copyright of ENR: Engineering News-Record is the property of BNP Media and its content may not be copied or emailed to multiple sites or posted to a listserv without the copyrig," 2017. [5] "Dow Ethylene Production Facility Freeport Texas." [Online]. Available: https://corporate.dow.com/en-us/news/press-releases/dow-ethylene-production-facility-freeport-texas.html. [Accessed: 17-Dec-2019]. [6] "Chevron Phillips Chemical starts up Baytown ethane cracker - Houston Business Journal." [Online]. Available: https://www.bizjournals.com/houston/news/2018/03/12/chevron-phillips-chemical-starts-up-baytown-ethane.html. [Accessed: 25-Dec-2019]. [7] "Ethylene Production via Cracking of Ethane-Propane - Chemical Engineering | Page 1." [Online]. Available: https://www.chemengonline.com/ethylene-production-via-cracking-ethane-propane/. [Accessed: 19-Jan-2020]. [8] O. Jackson, "Ethylene production," *Nature*, vol. 225, pp. 1019–1022, 1979.
2	[1] LSB Industries, Inc. In: *Imperial Capital Global Opportunities Conference*. New York: LSB Industries, Inc.; 2014. http://investors.lsbindustries.com/static-files/ac3efddd-aaea-46de-b06a-dd860bf866ed. [2] Lovochemie Nitric Acid Plant, Lovosice. Chemical Technology. https://www.chemicals-technology.com/projects/lovochemie/. Accessed December 19, 2019. [3] Nitric Acid Manufacture. *Journal of the Air Pollution Control Association*. 1964;14(3):91-93. doi:10.1080/00022470.1964.10468252.

Table A1 (Continued)

Plant	Resources
2	[4] thyssenkrupp Industrial Solutions AG. Nitric acid. https://d13qmi8c46i38w.cloudfront.net/media/UCPthyssenkruppBAIS/assets.files/products___services/fertilizer_plants/nitrate_plants/brochure-nitric-acid_scr.pdf. Accessed December 15, 2019. [5] Wiesenberger H. *State-of-the-Art for the Production of Nitric Acid with Regard to the IPPC Directive*. Umweltbundesamt GmbH; 2001. https://www.umweltbundesamt.at/fileadmin/site/publikationen/M150.pdf.
3	[1] M. Pérez-Fortes, J. C. Schöneberger, A. Boulamanti, and E. Tzimas, “Methanol synthesis using captured CO2 as raw material: Techno-economic and environmental assessment,” *Appl. Energy*, vol. 161, pp. 718–732, 2016. [2] É. S. Van-Dal and C. Bouallou, “Design and simulation of a methanol production plant from CO2 hydrogenation,” *J. Clean. Prod.*, vol. 57, pp. 38–45, 2013. [3] S. Alsayegh, J. R. Johnson, B. Ohs, and M. Wessling, “Methanol production via direct carbon dioxide hydrogenation using hydrogen from photocatalytic water splitting: Process development and techno-economic analysis,” *J. Clean. Prod.*, vol. 208, pp. 1446–1458, 2019. [4] F. Maréchal, G. Heyen, and B. Kalitventzeff, “Energy savings in methanol synthesis: Use of heat integration techniques and simulation tools,” *Comput. Chem. Eng.*, vol. 21, pp. S511–S516, 2003. [5] B. Anicic, P. Trop, and D. Goricanec, “Comparison between two methods of methanol production from carbon dioxide,” *Energy*, vol. 77, pp. 279–289, 2014. [6] D. Parigi, E. Giglio, A. Soto, and M. Santarelli, “Power-to-fuels through carbon dioxide Re-Utilization and high-temperature electrolysis: A technical and economical comparison between synthetic methanol and methane,” *J. Clean. Prod.*, vol. 226, pp. 679–691, 2019.
4	[1] D. Al-Mohannadi, “A Systematic Approach to Carbon Footprint Reduction Strategies In Industrial Parks,” no. December, 2014. [2] “Stamicarbon Urea Process Data,” vol. 3, p. 1, 2013. [3] J. Meessen, “Urea,” *Ullmann’s Encycl. Ind. Chem.*, no. Iv, pp. 9–11, 2012.

Table A1 (Continued)

Plant	Resources
4	[4] E. Koohestanian, J. Sadeghi, D. Mohebbi-Kalhori, F. Shahraki, and A. Samimi, "A novel process for CO 2 capture from the flue gases to produce urea and ammonia," *Energy*, vol. 144, pp. 279–285, 2018. [5] D. Y. Murzin, "13.2.2 Urea from CO2 and Ammonia," *Chemical Reaction Technology*. De Gruyter, 2015. [6] A. Edrisi, Z. Mansoori, and B. Dabir, "Urea synthesis using chemical looping process - Techno-economic evaluation of a novel plant configuration for a green production," *Int. J. Greenh. Gas Control*, vol. 44, pp. 42–51, 2016. [7] A. Bose, K. Jana, D. Mitra, and S. De, "Co-production of power and urea from coal with CO2 capture: Performance assessment," *Clean Technol. Environ. Policy*, vol. 17, no. 5, pp. 1271–1280, 2015.
5	[1] T. Grundt and K. Christiansen, "HYDROGEN BY WATER ELECTROLYSIS AS BASIS FOR SMALL SCALE AMMONIA PRODUCTION. A COMPARISON WITH HYDROCARBON BASED TECHNOLOGIES," vol. 7, no. 3, pp. 247–257, 1982. [2] R. Nayak-Luke, R. Bañares-Alcántara, and I. Wilkinson, "'green' Ammonia: Impact of Renewable Energy Intermittency on Plant Sizing and Levelized Cost of Ammonia," *Ind. Eng. Chem. Res.*, vol. 57, no. 43, pp. 14607–14616, 2018.
6	[1] Ollerhead A. Ammonia Synthesis for Fertilizer Production Contents: 2018:1-59. https://web.wpi.edu/Pubs/E-project/Available/E-project-081915-125250/unrestricted/Ammonia_Paper_Final.pdf. [2] Santos S, Collodi G, Azzaro G, Ferrari N. Techno-Economic Evaluation of HYCO Plant Integrated to Ammonia / Urea or Methanol Production with CCS. February 2017. https://www.researchgate.net/publication/320766153_Techno-Economic_Evaluation_of_HYCO_Plant_Integrated_to_Ammonia_Urea_or_Methanol_Production_with_CCS
7	[1] D. Jones, D. Bhattacharyya, R. Turton, and S. E. Zitney, "Optimal design and integration of an air separation unit (ASU) for an integrated gasification combined cycle (IGCC) power plant with CO2 capture," *Fuel Process. Technol.*, vol. 92, no. 9, pp. 1685–1695, 2011.

Table A1 (Continued)

Plant	Resources
7	[2] A. Darde, R. Prabhakar, J. P. Tranier, and N. Perrin, "Air separation and flue gas compression and purification units for oxy-coal combustion systems," *Energy Procedia*, vol. 1, no. 1, pp. 527–534, 2009. [3] Y. A. Alsultanny and N. N. Al-Shammari, "Oxygen specific power consumption comparison for air separation units," *Eng. J.*, vol. 18, no. 2, pp. 67–80, 2014. [4] A. Ebrahimi, M. Meratizaman, H. A. Reyhani, O. Pourali, and M. Amidpour, "Energetic, exergetic and economic assessment of oxygen production from two columns cryogenic air separation unit," *Energy*, vol. 90, pp. 1298–1316, 2015. [5] P. C. Wankat and K. P. Kostroski, "Hybrid air separation processes for production of oxygen and nitrogen," *Sep. Sci. Technol.*, vol. 45, no. 9, pp. 1171–1185, 2010. [6] G. Subbaraman, "Final Report-Rev0 Emerging and Existing Oxygen Production Technology Scan and Evaluation," 2018.
8	[1] T. R. Ayodele and J. L. Munda, "Potential and economic viability of green hydrogen production by water electrolysis using wind energy resources in South Africa," *Int. J. Hydrogen Energy*, vol. 44, no. 33, pp. 17669–17687, 2019. [2] A. Gambhir, S. Few, J. Nelson, A. Hawkes, O. Schmidt, and I. Staffell, "Future cost and performance of water electrolysis: An expert elicitation study," *Int. J. Hydrogen Energy*, vol. 42, no. 52, pp. 30470–30492, 2017. [3] Guerra OJ. *Cost-Competitive Electrolysis-Based Hydrogen under Current U.S. Electric Utility Rates*. Pittsburgh, PA: 2018 AIChE Annual Meeting; 2018.
9	[1] S. Bhojwani, K. Topolski, R. Mukherjee, D. Sengupta, and M. M. El-Halwagi, "Technology review and data analysis for cost assessment of water treatment systems," *Sci. Total Environ.*, vol. 651, pp. 2749–2761, 2019.
10	-

Table A2: CAPEX parameter calculations

Plant Number	CAPEX from Literature ($)	Capacity from literature (MTPA)	Year	Adjusted Plant Capacity (MTPA)	Updated 2019 CAPEX for adjusted capacity	CAPEX Parameter in 2019 ($/ton Reference Product)
1	2,370,000,000	1,700,000	2015	100,000	152,106,047	76.05
2	45,000,000	300,000	2002	100,000	23,034,631	11.52
3	28,287,283	73,056	2019	100,000	38,720,000	19.36
4	3,760,370	3,856	2019	100,000	97,519,969	48.76
5	58,889,727	110,000	2018	100,000	53,926,696	26.96
6	307,000,000	110,834	2019	100,000	276,990,815	138.50
7	96,500,000	839,500	2019	100,000	11,494,937	5.75
8	32,562,200	2,090	2019	100,000	1,558,000,000	779.00
9	30,393,600	18,925	2019	100,000	160,600,264	80.30
10	25,288,718,400	14,049,288	2019	100,000	180,000,000	90.00

Table A3: Prices of all components in the model determined from Intratec

Material	Base Cost	Lowest Cost	Highest Cost
Air	0	0	0
O_2	66.12	61.03	66.12
N_2	65	65.29	65
H_2O	0.22	0.22	0.22
H_2	1200	522	2338
CO_2	51	30	63
NH_3	311	299.58	477.2
Methanol	286	225.67	393.17
Methanol Plant Emissions	0	0	0
Ammonia Emissions (N_2/H_2/ NH_3/Ar)	0	0	0
Ar	0	0	0
Wastewater	0	0	0
CO_2, N_2, O_2 Emissions	0	0	0
Nitric Acid	546	505.58	546
Ammonia from NG Emissions	0	0	0
Urea	301	237.67	329
Water Contaminants	0	0	0
Ethane	112	110	244
Ethylene	364	349.33	633
Butyne	0	0	0
Methane (NG)	176.84	166.5	199
Ethylene Plant Emissions	0	0	0
Nitric Acid Emissions	0	0	0
Steam (HP)	15.72	14.75	17.48

Table A4: Prices of utilities in the model determined from Intratec

Resource	***Base Cost***	***Lowest Cost***	***Highest Cost***
HP Steam	15.72	14.75	17.48
MP Steam (Parabolic Troughs - Solar)	14.56	13.66	16.18
LP Steam (Geothermal)	13.95	13.08	15.49
Cooling Water	0.04	0.04	0.04
Electricity	0.06	0.06	0.06
Process Water (Nitric Acid)	0.221	0.221	0.221
Condensate	0	0	0
NG	3.6	3.6	3.6
SHP Steam	20	20	20

Appendix B

```
What'sBest!® 16.0.2.2 (Mar 22, 2019) - Lib.:12.0.3977.144 - 64-bit - Status Report -
- Eval Use Only -

DATE GENERATED:                    Mar 30, 2020                         03:48 PM


MODEL INFORMATION:

  CLASSIFICATION DATA            Current   Capacity Limits
  ------------------------------------------------------
  Total Cells                       1770
    Numerics                        1641
      Adjustables                     76             300
        Continuous                    76
        Free                           0
        Integers/Binaries            0/0              30
      Constants                     1079
      Formulas                       486
    Strings                            0
    Constraints                      129             150
  Nonlinears                           0              30
  Coefficients                      1388

  Minimum coefficient value:        0.01224  on City Balance!N75
  Minimum coefficient in formula:   City Balance!D156
  Maximum coefficient value:        1.0000000000000e+013  on <RHS>
  Maximum coefficient in formula:   City Balance!Z35

MODEL TYPE:                        Linear (Linear Program)

SOLUTION STATUS:                   GLOBALLY OPTIMAL

OBJECTIVE VALUE:                   58,431,811.535664

BEST OBJECTIVE BOUND:              . . .

INFEASIBILITY:                     0.0

DIRECTION:                         Maximize

SOLVER TYPE:                       . . .

ITERATIONS:                        7.0

STEPS:                             . . .

ACTIVE:                            . . .

SOLUTION TIME:                     0 Hours  0 Minutes  0 Seconds

End of Report
```

Figure 8: What'sBest! Sample report

#1: Min and Max Capacities							
	Plant	Product	Minimum Capacity (tpy)	≤	Capacity (tpy)	≤	Maximum Capacity (tpy)
1	Air Separation	Oxygen and Nitrogen	0	<=	**100,000**	=<=	100,000
2	Hydrogen from Water Splitting	Hydrogen and Oxygen	0	=<=	**0**	<=	100,000
3	Methanol Production	Methanol	0	=<=	**0**	<=	100,000
4	Ammonia Production From N2 and H2	Ammonia	0	=<=	**0**	<=	100,000
5	Urea Production	Urea	0	<=	**1,771**	<=	100,000
6	Ethylene Production	Ethylene	0	=<=	**0**	<=	100,000
7	Nitric Acid Production	Nitric Acid	0	<=	**92,546**	<=	100,000
8	CO2 Sequestration	Treated CO2	0	<=	**120,000**	=<=	120,000
9	Water Treatment Unit	Treated Water	0	=<=	**0**	<=	100,000
10	Ammonia Production (NG)	Ammonia	0	<=	**26,917**	<=	100,000

Figure 9: Screenshot of capacity table in the optimization model

#15: Total Cost Calculations						
Plant	Capital Cost ($)	Operating Cost ($/yr)	Total Cost ($/yr)	Revenue ($/y)	Profit ($/y)	
Air Separation	$ 575,000	$ -	$ 575,000	$ 26,253,289	$ 25,678,289	
Hydrogen from Water Splitting	$ -	$ -	$ -	$ -	$ -	
Methanol Production	$ -	$ -	$ -	$ -	$ -	
Ammonia Production From N2 and H2	$ -	$ -	$ -	$ -	$ -	
Urea Production	$ 85,281	$ 413,407	$ 498,688	$ 533,005	$ 34,318	
Ethylene Production	$ -	$ -	$ -	$ -	$ -	
Nitric Acid Production	$ 1,066,135	$ 12,433,244	$ 13,499,379	$ 43,772,781	$ 30,273,402	
CO2 Sequestration	$ 10,800,000	$ 6,129,864	$ 16,929,864	$ -	$ -16,929,864	
Water Treatment Unit	$ -	$ -	$ -	$ -	$ -	
Ammonia Production (NG)	$ 3,728,010	$ 6,140,118	$ 9,868,127	$ 8,371,198	$ -1,496,929	
SUM	**$ 16,254,425**	**$ 25,356,613**	**$ 41,611,038**	**78,930,274**	**$ 37,559,216**	**#16: Overall Profit**
	Input-Output	$ 13,068,083	$ 29,322,508	65,234,475	$ 35,911,967	Total Profit of Overall Cluster
					11	ROI

Figure 10: Screenshot of cost calculations in the optimization model