REDUCING CO_2 EMISSIONS THROUGH INDUSTRIAL SYMBIOSIS: A SIMULTANEOUS HEAT AND MASS INTEGRATION APPROACH

A Thesis

by

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ABSTRACT

CO_2 emissions have a harmful effect on the environment as CO_2 is the most significant contributor to global climate change. In 2015, representatives from countries around the globe met at the Paris Climate Conference to discuss the status of the global carbon budget and climate change. There, it was agreed to make a global effort to reduce greenhouse gas emissions. It is expected intergovernmental mandates will be implemented to limit CO_2 emissions in effort to cap the global temperature rise at 2°C above pre-industrial temperatures.

Reduction of CO_2 emissions is one of the most important strategies in addressing global climate change. About half of all CO_2 emissions come from industry and power plants. Therefore, these stationary sources are logical starting points for consideration. A commonly proposed solution to reducing CO_2 emissions is Carbon Capture, Utilization and Sequestration (CCUS). This strategy presents the opportunity to simultaneously reduce CO_2 emissions and create valuable products from waste material, generating profit for companies without the need to overhaul the energy infrastructure. However, despite the promise of CCUS, the chemical properties of CO_2 have rendered many developments in this area to be cost prohibitive.

The objective of this work is to demonstrate that by applying the principles of heat and mass integration through an industrial-symbiosis approach, CO_2 utilization processes can be integrated into eco-industrial parks to yield value-added chemicals in a cost-effective manner while offering enhanced CO_2 fixation. A hierarchical approach and an optimization formulation have been developed to screen the alternatives and to provide conceptual designs of the promising pathways and integration strategies.

A case study was solved to illustrate the merits of the proposed approach. Preliminary screening shows that, when integrated with a typical hydrocarbon processing industrial city, urea, methanol, formic acid, acetic acid and ethylene glycol are viable candidates for production from CO_2. Various configurations of these processes show a positive net fixation of CO_2 while generating a profit. The overall reduction of CO_2 emissions, however, is limited to around 16% due to capacity constraints on the new processes.

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Contributors

Part 1, faculty committee recognition

This work was supervised by a thesis committee consisting of Professor Mahmoud El-Halwagi, Professor M. Sam Mannan of the Artie McFerrin Department of Chemical Engineering and Professor Hisham Nasr-El-Din of the Harold Vance Department of Petroleum Engineering.

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All work for the thesis was completed independently by the student.

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NOMENCLATURE

SETS

CN	New process cold streams
COM	components
CP	cold streams to be heated
HN	New process hot streams
HP	hot streams to be cooled
IN	inlet ports
INT	interceptors (separators mixers splitters etc.)
j	all process streams
NEW	sinks (new processes to be added to EIP)
OLD	source streams (existing processes with known properites)
OUT	outlet ports
U_IN	interceptor inlet ports
U_OUT	interceptor outlet ports
V_IN	sink inlet ports
z	heat exchange interval (starting from 0) | ord(k)>=2 corresponds

to z >=1

PARAMETERS

AC_feed	associated carbon dioxide - stoichiometric by-product from reaction to generate COM (mol CO_2 mol f^-1)
C_CU	$ per MMBtu
C_HU	$ per MMBtu
C_interceptor	cost per kmol of interceptor INT
C_source	cost (100000 $ per 100000 tons)
deltaH	specific enthalpy of stream j (MMBtu per ton)
deltaT_min	
F_available	available quantity (100000 tons per year) of stream j
F_in_max	maximum inlet mole flow rate to sink NEW
F_in_min	minimum inlet mole flow rate to sink j
max_CO_2	maximum annual CO_2 emissions (100000 tons per year)
N_max_new_proc	
phi	natural gas emissions factor (ton CO_2 per MMBtu)
P_Sell	selling price of each product (100000 $ per 100000 tons)

r_in_max	minimum inlet ratio of component COM and COM_STAR
r_in_min	minimum inlet ratio of component COM and COM_STAR
Supply	total available mole flow rate from source i (100000 tons per year)
T_cold	cold scale temperature leaving interval z
T_hot	hot scale temperature leaving interval z
T_supply	supply temperature of stream j
W_in_max	maximum inlet mole flow rate to interceptor INT (100000 tons per year)
W_in_min	minimum inlet mole flow rate to interceptor INT (100000 tons per year)
x	mass fraction of component c in source i
y_in_max	maximum inlet composition to interceptor INT
y_in_min	minimum inlet composition to interceptor INT
z_in_max	maximum inlet composition to sink NEW
z_in_min	minimum inlet composition to sink NEW
z_out	outlet composition of the product stream leaving unit NEW

z_stream	parameter indicating if stream j belongs to process k

VARIABLES

C_utilities	total cost of utilities
delta_CO_2	net CO_2 sequestration or emission
F	total mole flow rate from interceptor INT to sink NEW
F_in	inlet mole flow rate to sink NEW
F_out	outlet mole flow rate to sink NEW
F_used	how much of steam j (HP and CP) is used in the HEN
G_in	mole flow rate from source i to interceptor INT
G_used	mole flow rate from source i used in EIP
G_waste	mole flow rate from source i discharged from EIP
HCU	exchangeable load (how much heat it can accept) of cold utility (100000 MMBtu)
HC_new_proc	exchangeable load (how much heat it can accept) of stream j in interval z (100000 MMBtu)
HHU	exchangeable load (how much heat it can give up) of hot utility (100000 MMBtu)

HH_new_proc	exchangeable load (how much heat it can give up) of stream j in interval z (100000 MMBtu)
profit	total annualized profit
r	residual enthalpy leaving each interval
W_in	inlet mole flow rate to interceptor INT
W_out	outlet mole flow rate from interceptor INT
y_in	mass fraction of component c enterting interceptor INT
y_out	mass fraction of component c leaving interceptor INT
z_in	mass fraction of component c enterting sink NEW
z_new_proc	binary variable indicating which process has been selected

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1 INTRODUCTION

1.1 What is the carbon cycle

The surface of the earth and the oceans exchange carbon with the atmosphere in various forms: the primary currency of exchange between these media is carbon dioxide. Through the works of Antoine Lavoisier, J.J. Ebelmen, and various other scientists, the concept of the carbon cycle emerged in the early 19th century as a method to describe the exchanges amongst these media [1]. This method has evolved significantly over the years, but in principal it describes the relationships between various processes which emit carbon dioxide into the atmosphere (CO_2 sources) and processes which remove carbon dioxide from the atmosphere and fix it into another form (CO_2 sinks) [2]. Sources and sinks come in many forms; however, they can be divided into two categories:

1) Natural sources and sinks: animals, CO_2 wells, etc. (sources) and vegetation, dissolved CO_2 in oceans, weathering by silicate rocks, etc. (sinks)
2) Anthropogenic sources and sinks: any emissions and sinks that result from human behavior, primarily fossil fuels burned to supply power to residential and industrial processes as well vehicles for transportation

Without human intervention, natural sources and sinks tend to remain in balance. This is evidenced by the relatively stable atmospheric CO_2 concentration prior to the industrial revolution, when humans were not able to significantly impact the carbon cycle. Since the industrial revolution, the creation of anthropogenic sources has outpaced the creation of anthropogenic sinks. The result has been a shift in the natural of the balance carbon cycle to favor sources, leading to significant increases in atmospheric carbon dioxide concentration. [2]

1.2 Why is this important

There are two main consequences to disturbing the balance of the carbon cycle:

1) There is a limited supply of fossil carbon sources; therefore if it is being converted to CO_2 at a higher rate than CO_2 is converted to other forms of carbon, the limited supply of useful carbon will become depleted
2) The increase in atmospheric carbon dioxide contributes to global climate change through the intensification of the greenhouse effect

The second point is of high concern as this may contribute to irreversible damage to eco-systems as well as significant loss of social, economic and food security. The term “greenhouse effect” describes the process by which radiation from the sun is trapped in the earth’s atmosphere to warm the surface of the earth to a temperature above what it would be without the atmosphere. Gasses such as carbon dioxide, water vapor, methane, and others (collectively referred to as greenhouse gasses of GHGs), which absorb infrared radiation are the primary driving force behind this phenomenon. [3] Since the industrial revolution of the mid-18th century, there has been a measurable and significant change in the atmospheric CO_2 concentration. Historical CO_2 levels were measured by the analysis of ice cores, and these data revealed that CO_2 concentrations varied between 180 ppm (glacial maximum) and 300 ppm (warm interglacial periods) over the last 650,000 years. Furthermore, in the 10,000 years prior to the industrial revolution, the levels remained stable between 260 and 280 ppm. [4] In 2013, the atmospheric concentration of CO_2 exceeded 400 ppm for the first time in recorded history, and has continued to increase in recent years. Figure 1 shows how the atmospheric concentration has mirrored the global CO_2 emissions.

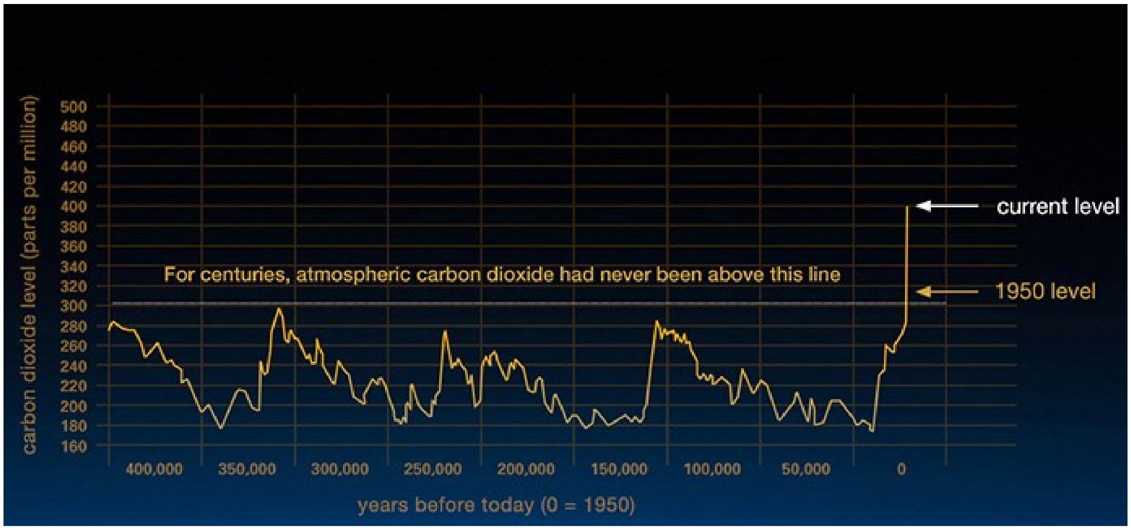

Figure 1: CO_2 Concentration Over Time, reprinted from [5]

This has been accompanied by a measurable and significant increase in the average temperature on the surface of the earth. The continuation of this phenomenon poses a significant threat to human life and other ecological systems. It is therefore important to develop strategies and implement technologies to actively manage the balance of anthropogenic sources and sinks.

1.3 Where do most emissions come from

The EIA gives a full breakdown of anthropogenic sources of carbon dioxide. Figure 2 below shows a proportional breakdown of these various sources from US emissions data in 2014.

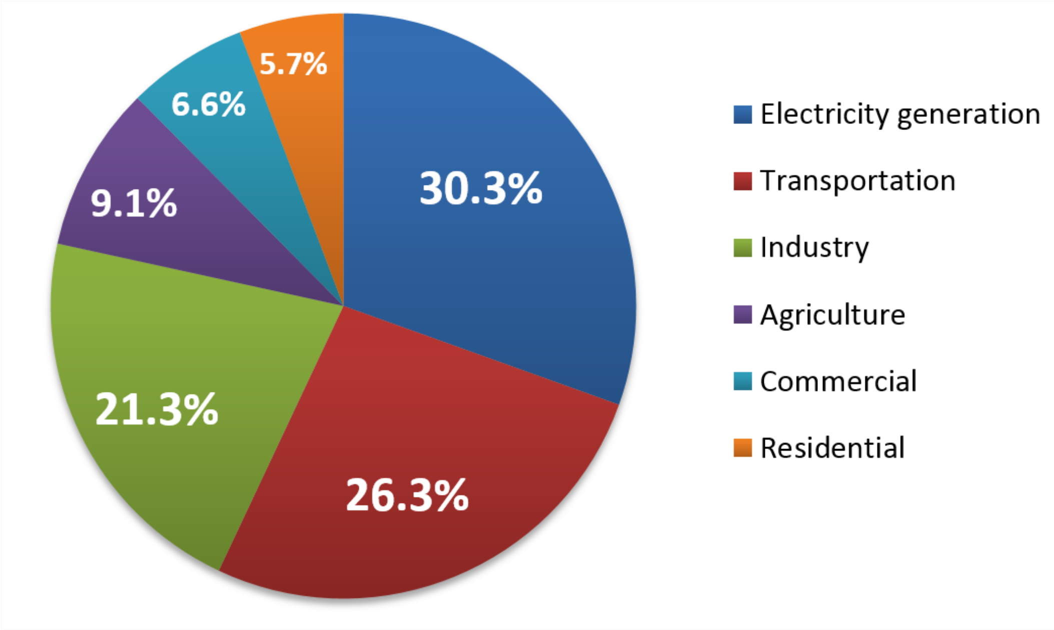

Figure 2: 2014 US CO2 Emissions by Sector, adapted from [6]

From the above figure, the majority (~78%) of anthropogenic sources can be grouped into 3 categories: fossil fired power plants for electricity generation, hydrocarbon fuels used for transportation and industrial facilities energy usage. Power plants and industrial facilities are considered stationary or point sources as these facilities do not change locations. The emissions associated with the transportation industry are considered to be mobile emission sources as cars, busses, trains, planes, ships and other vehicles are constantly moving during operation. This is an important distinction as the strategies for addressing a particular source will depend on whether it is a stationary source or a mobile source. The focus of this thesis is stationary sources.

The primary sink for CO_2 is the atmosphere – the increase in atmospheric CO_2 concentration is a measurable consequence of the disproportionate development and implementation of anthropogenic CO_2 emission sources without commensurate development of anthropogenic sinks.

1.4 What are the strategies for balancing emissions with sinks

Two strategies emerge when considering a solution to this balance:

1) Increase the capacity of existing sinks or develop new anthropogenic sinks
2) Reduce emissions of active anthropogenic sources

Although the high level strategies are very obvious, the implementation of these strategies is difficult.

Efforts to fulfil the first strategic objective are typically classified as carbon capture utilization and sequestration (CCUS) strategies. The carbon capture portion of CCUS typically involves physically capturing the streams containing CO_2, separating the CO_2 from other components, compressing the CO_2 and transporting it to site where it can be utilized or sequestered. [7] Utilization and sequestration strategies are wide ranging and include: geological sequestration, chemical sequestration, biological sequestration, conversion of CO_2 to useful chemicals, conversion of CO_2 to fuels and utilization of CO_2 as a solvent.

Efforts to fulfil the second strategic objective include 1) utilizing carbon resources more efficiently and 2) substituting or supplementing carbon based energy sources with carbon neutral energy sources. Strategies to improve efficiency include: reducing excess utilization of carbon based resources, exchanging heat within processes to minimize the need for carbon based heating and cooling utilities (heat integration), exchanging material among processes to minimize the need to carbon based feedstocks (mass integration) and to exchanging heat and material among nearby facilities to reduce carbon based heating, cooling and feedstocks (eco-industrial parks).

2 BACKGROUND

The central focus of this work is sustainable design. In his famous 1987 reportn, Brundtland [8] described sustainable development with the following:

> *"Humanity has the ability to make development sustainable to ensure that it meets the needs of the present without compromising the ability of future generations to meet their own needs".*

This is an important definition as excessive carbon dioxide emissions have the potential to impede the ability of future generations to meet their own needs. It is therefore imperative to embark upon sustainable design with respect to carbon dioxide. As discussed in the introduction, process integration and CCUS are two areas in which sustainable design can be implemented. In the remainder of this section the state of the art in process integration and CCUS will be described and the gaps in the literature as it pertains to the nexus of these two topics will be illustrated.

2.1 Process Integration and Eco-Industrial Parks

Process integration is a holistic approach to process design, optimization, retrofitting and operation that emphasizes unity of the process which exploits the strong interactions among process units, streams and resources in order to achieve sustainable design. [9, 10] Process integration is a relatively young field with the first major work coming in 1982 from Linnhoff et.al. [11] Over the past 3 decades many methodologies and tools have been developed to extend the principals of process integration: including El-Halwagi and Manousioutakis introducing a methodology for the automatic design of mass exchange networks [12], Wang and Smith introducing a methodology for wastewater minimization [13], El-Halwagi introducing a methodology for material recycle networks [14], and El-Halwagi et. al. introducing methodologies for property based integration [15]. In general, process integration includes the following activities [16]:

1. Task identification: for example maximizing profit or minimizing the emissions of a particular component
2. Targeting: the identification of performance benchmarks prior to detailed design
3. Generation of alternatives: enumerate the various configurations which meet the targeted benchmarks
4. Selection of alternatives: identify the optimum solution within the search space defined in (3)
5. Analysis of selected alternative(s): analysis of detailed process design decisions

Generally speaking, the activities described above can be applied to a single chemical process to achieve some objective. However, there is no reason these activities should be limited to a single facility. More recently, the concept of industrial symbiosis was born out of this. Chertow describes industrial symbiosis as [17]:

> *“Industrial symbiosis engages traditionally separate industries in a collective approach to competitive advantage* ***involving physical exchange of materials, energy, water, and/or by-products****. The keys to industrial symbiosis are collaboration and the synergistic possibilities offered by geographic proximity.”*

An eco-industrial park is a name given to collection of industrial facilities engaging in industrial symbiosis. Lovelady and El-Halwagi [18] first presented a framework for the design and integration of eco-industrial parks for managing water resources. Alnouri et. al. [19] followed up this work with more sophisticated methods involving water treatment. Noureldin and El-Halwagi [20] followed this up with a generalized approach to the design of symbiosis networks limited to components containing carbon, hydrogen and oxygen atoms. It is worth noting that industrial symbiosis is not simply an academic concept, but rather a realistic design methodology which has been implemented on an full scale. The Kalundborg Symbiosis park in Kalundbog, Denmark is the first such implementation of this concept. At its center is a 1500 MW power plant which exchanges low grade heat with nearby residential homes, mid grade heat with a nearby fishery, and high grade heat with a nearby refinery. In addition to the heat, it also exchanges material with nearby facilities including fly ash for cement production and gypsum to a drywall manufacturer. [21] A few key savings include economic savings of \$15 million/year and CO_2 emissions reduction of 65,000 tons/year.

2.2 Carbon Capture, Sequestration and Utilization (CCUS)

While reducing emissions and improving profit through process integration is a great start, there is much room for improvement in regards to CO_2 emissions reduction. CCUS is the generalized term for separating carbon dioxide from a material stream and then using that CO_2 for some other purpose. In order to evaluate a CO_2 utilization process, one must consider the full supply chain of the utilization process. In general, a CCUS supply chain includes the following activities shown in Figure 3:

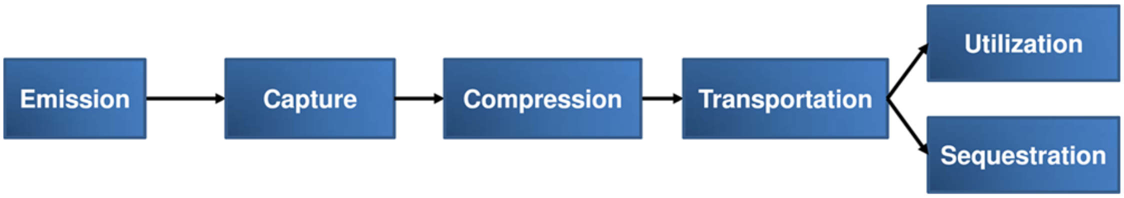

Figure 3: CCUS Supply Chain, reprinted from [7]

Generally speaking, utilization describes the process of using the captured CO_2 to add value to some activity such as enhanced oil recovery or use as a solvent, while sequestration broadly describes any activity whose primary objective is long term storage of CO_2.

2.2.1 Emission

The first link in the supply chain is the emission event. The emission event is very important as various event characteristics dictate the types of strategies which can be used to mitigate those emissions. The most important distinction to be made is whether the emission source is a mobile source or a stationary source. In addition to this distinction, quantity, composition and geographic location are also very important factors to consider.

2.2.1.1 Mobile sources

The majority of mobile emission sources are in the transportation sector: road transport, rail transport, air transport and water transport. Gas + diesel emissions (1,105 and 440 million metric tons, respectively) account for 83% of total US transportation sector and 29% of total US energy related CO_2 emissions [22]. Although mobile emissions constitute a significant portion of CO_2 emissions, there are not many technologies dedicated to mobile capture. The majority of strategies for mitigating mobile emissions operate analogously to artificial trees, where some device captures CO_2 from the atmosphere in an amount equal to the emissions for the area. [23, 24]

2.2.1.2 Stationary sources

Stationary emission sources comprise the remaining ~65% of CO_2 emissions. This number can be further broken down by economic sector. Excluding the mobile sources from the data presented in figure 1, the emissions are as follows: Electricity generation (41%), industry (29%), agriculture (12%), commercial (9%), residential (8%) and US territories (1%). The electricity generation sector is dominated by fossil fired power plants. As the single largest producer of CO_2 emissions, this is a very logical starting point for investigation. However, the flue gasses coming off of power plants cannot be utilized directly. The CO_2 must be separated from the nitrogen, water, NO_x, SO_x, H_2S and other trace compounds. Industry is the second largest producer or CO_2. The majority of industrial CO_2 is also generated by fossil fuel combustion for heating and power usage. However, in addition to fossil fuel combustion, CO_2 is also produced as a by-product in many processes. This CO_2 is sometimes of high purity (such as the by-product of hydrogen production by methane steam reforming) and may therefore be of interest.

2.2.2 Capture and Compression

There has been extensive research in the area of CO_2 capture, particularly CO_2 capture from power plants. The main strategies including: post combustion capture, pre combustion capture, oxy-combustion capture and chemical looping. [23, 25]

2.2.2.1 Post Combustion Capture

Post-combustion capture involves purifying CO_2 from flue gases created during fuel combustion with air. The most popular technologies in this area are absorption, adsorption, membrane separations and cryogenic methods.

2.2.2.2 Pre Combustion Capture

Pre-combustion capture involves separating CO_2 from a synthesis gas before fuel combustion.

2.2.2.3 Oxy Combustion Capture

Oxy-combustion capture involves combusting fuels with pure oxygen so that the fuel gas is high purity CO_2 and water.

2.2.2.4 Chemical Looping

Chemical looping combustion involves using alternate materials to transport the oxygen for combustion. Typically this is a metal oxide such that the products of combustion are: metal, water, CO_2. In this way, the water can be condensed and high purity CO_2 can then be obtained. Each of these strategies have unique advantages as well as challenges.

2.2.2.5 General Remarks on Capture from Power Plants

However, all of these strategies are expensive as they increase the electricity demand on a plant by as much as 85%. [26] And with a lack of economic incentive (lack of CO_2 taxes, few profitable routes to utilize CO_2), these processes remain to be adopted mainstream.

2.2.3 Transportation

CO_2 is generally transported from the sources to sinks as a supercritical fluid in pipelines. A typical state of this fluid could be 70°F and 2000 psia. Transportation is a relatively small cost for short distances. According to [27], the cost of transportation is approximately \$2-\$4 per 100km. In general, 80% or more of the costs of capture, compression, transportation and sequestration are incurred during the capture and compression phases. [28, 29] In the case of an eco-industrial park, the transportation costs are relatively inconsequential to the overall solution of the problem.

2.2.4 Utilization

Utilization activities include: CO_2 conversion to chemicals, CO_2 conversion to fuels, CO_2 as a process fluid (solvent, fracking fluid, enhanced oil recovery, etc.) and commercial use (dry ice, carbonated beverages, fire extinguishers, etc.). However, in the scope of reducing CO_2 emissions, utilization activities should be focused on applications which fix CO_2 long term rather than immediately re-release it to the atmosphere. Thermodynamics gives light into the nature of the challenge in chemically converting CO_2. The carbon in CO_2 is at the highest oxidation state, which means any conversion is energetically uphill. In some cases, such as dry reforming of methane ($CH_4 + CO_2 \rightarrow 2CO + 2H_2 \;\; \Delta H^{o}_{rxn} = +247\ kJ/mol$) [30], the C=O bond must be broken. This step is very energy intensive ($CO_2 \rightarrow CO + \frac{1}{2}O_2 \;\; \Delta H^{o}_{rxn} = +283\ kJ/mol$) [24], leading to large enthalpy changes in these reactions. In other cases, such as carbonyl chemistry, large amounts of energy must still be supplied.

2.3 Unaddressed Gaps

While each of the aforementioned methodologies and technologies have significant merit, there is still a question of how these various technologies and methodologies can work together from a systems perspective to efficiently reduce CO_2 emissions while still providing an economic benefit.

3 PROBLEM STATEMENT

This thesis screens CO_2 utilization processes to determine which process is best suited to be added to an eco-industrial park. Processes are screened based on the formation of symbiotic relationships driven by mass and energy demands. The problem can be stated as follows:

Given is a set of existing processing facilities in close proximity to one another with known material and energy inputs and outputs. In addition to the products that they sell, these facilities produce waste materials which may be useful as feedstocks to new processes. This set of material streams $OLD|OLD \in \{1,2,\dots,N_{OLD}\}$ has known flow rates $G_{OLD}^{available}$ and compositions $x_{COM,OLD}$. The processes also have heating and cooling demands which can be satisfied either by utilities or by integration with new processes. The set of hot streams to be cooled ($HP|j \in \{1,2,\dots,N_{HP}\}$) and cold streams to be heated ($CP|j \in \{N_{HP}+1, N_{HP}+2,\dots,N_{HP}+N_{CP}\}$) each have an available flow rate ($F_j^{available}$) and a known specific enthalpy change within each temperature interval ($\Delta H_{j,z} = C_{p_j}(T_z - T_{z+1})$). The total enthalpy contribution of the stream ($HH_{j,z}$) is an optimization variable to be determined.

Some of the material streams available for integration are not directly suitable as feedstocks to new processes. Therefore, a set of interception processes $INT|INT \in \{1,2,\dots,N_{INT}\}$ are available for service to mix or segregate streams or separate components in order to bring the material stream up to a desirable specification. The inclusion of an interceptor in the network and the operating conditions of the interceptor are optimization variables to be determined.

Lastly, a set of new processes $NEW|NEW \in \{1,2,\dots,N_{NEW}\}$ are available for service to utilize CO_2. Each process has unknown material demands ($F_{v^{in}}^{in}$ and $z_{COM,v^{in}}^{in}$) and energy demands ($HH_{j,z}^{new\ proc}$ and $HC_{j,z}^{new\ proc}$) subject to optimization. Product revenues from the new processes will vary based on which processes are selected and the production capacity determined in the optimization.

The costs incurred include the cost of operating the interceptors, the cost of utilities and the cost of purchases raw materials. While CO_2 is consumed by the processes, some emissions occur due to energy usage and unreacted CO_2 leaving the processes. There are two objective functions for this problem:

1. maximize profit (revenue minus the sum of the costs)
2. maximize the net fixation of CO_2 (CO_2 in – CO_2 out)

The combined objective is to observe the tradeoffs between maximizing profit and maximizing net CO_2 fixation (minimizing net CO_2 emissions) for various configurations of new processes added to the network.

4 METHODOLOGY

The two key aspects in the selection of a new process are the implications of heat integration and mass integration. In order to simultaneously screen the alternatives an optimization approach is employed to determine the best options subject to a number of chemical, logical and economic constraints.

4.1 Optimization formulation

The overall objective is to screen CO_2 utilization process which utilize waste heat and waste materials from existing processing facilities. The mass and heat integration will follow the flow chart in Figure 4 below.

The orange blocks represent known data inputs. The first set of data is the set of existing facilities in close proximity to one another with excess heat and material available for integration. The important data points here are the available quantity of material (tons/year), composition of waste streams, excess heating capacity (MMBtu/year) and its temperature, and excess cooling capacity and its temperature. The next set of data is the integration constraints. The heat integration constraints are a modified version of the set of constraints outlined in the transshipment model presented by Papoulias and Grossman [31]. The mass integration constraints are based on the set of constraints presented in the C-H-O Symbiosis Network development model proposed by Noureldin and El-Halwagi [20]. In addition to the constraints mentioned above, constraints were added to account for the addition of new processes to the EIP, rather than simply integrating existing processes. The last set of data is the set of new, CO_2 utilization processes to be added to the EIP. The key information here is the minimum and maximum plant capacities, required inlet composition, and the necessary process heating and cooling duties.

The blue blocks represent optimization processes. The heat integration, mass integration and selection of new processes are carried out simultaneously with two unified objective functions: maximize profit and maximize net CO_2 fixation (minimize net emissions). In order to account for the two objective functions, each objective is maximized with no regard for the other in order to determine the boundaries of the Pareto surface. Then, while maximizing the profit, the maximum allowable CO_2 emissions is gradually reduced until the maximum fixation is reached. The green blocks represent the optimization results with the final output being a Pareto optimal set of solutions.

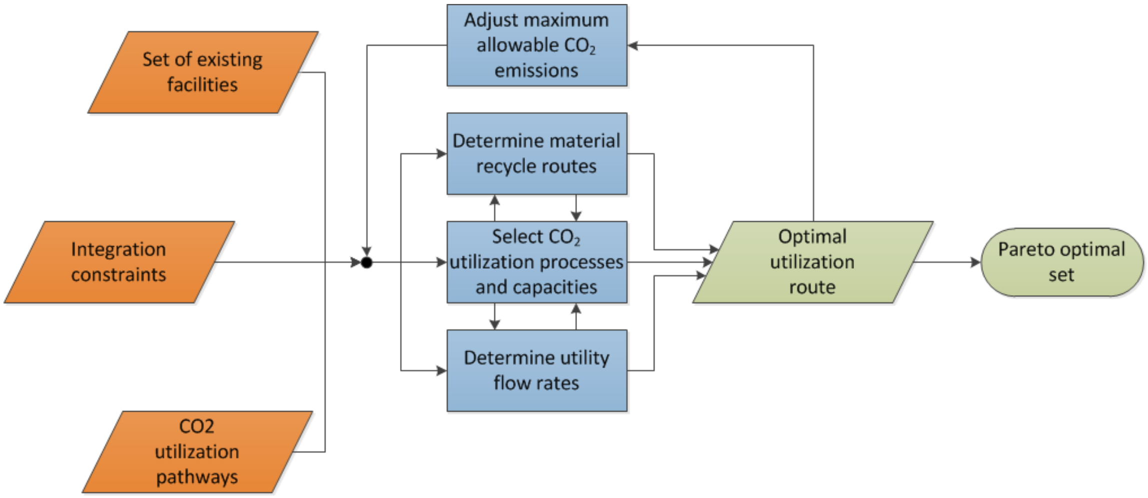

Figure 4: Solution Methodology

4.1.1 Select New Processes

4.1.1.1 Description

The first portion of the integration is to select the new processes to be added to the EIP while the process capacities will be optimized in the heat exchange network and mass exchange network sub problem.

4.1.1.2 Constraints

As numerous processes may be profitable at this level of analysis, the number of processes added to EIP may optionally be limited. In order to limit the number of processes, the following constraint must hold:

$$\sum_{NEW} z_{NEW}^{new\ proc} \leq N^{max,new\ proc}$$

If the process is selected to be included in the EIP, the capacity must be constrained. In order to do this, the throughput of the new processes must either equal zero if the process is not selected, or fall within the acceptable limits if it is selected:

$$F_{v^{in}}^{in} \leq z_{NEW}^{new\ proc} F_{v^{in}}^{max}; \forall\ v^{in}$$

$$F_{v^{in}}^{total} \geq z_{NEW}^{new\ proc} F_{v^{in}}^{min}; \forall\ v^{in}$$

4.1.2 Determine Utility Flow Rates

4.1.2.1 Description

The next step is to determine which existing processes will donate/accept heat and fix the utility flow rates needed to meet energy demands. This optimization takes place concurrently with the mass integration (*described in next section*). In order to account for undetermined flow rates of new processes, new sets, parameters, variables and constraints are added to the transshipment model.

New sets are included to represent the set of candidate new process streams: new process hot streams (HN) and new process cold streams (CN), and represented by the index (j). An additional new set is included to represent the set of candidate process (NEW) and represented by the index (k).

A new parameter will be included to represent the upper bound on the number of new processes added to the EIP ($N^{max,new\ proc}$).

New positive continuous variables will be included to represent enthalpy contribution of new process streams ($HH_j^{new\ proc}$ and $HC_j^{new\ proc}$). New binary variables will be included to determine whether or not a new process is included in the EIP ($z_k^{new\ proc} | z_k^{new\ proc} = 1\ if\ the\ process\ is\ included\ in\ the\ EIP, otherwise\ z_k^{new\ proc} = 0$).

In order to determine utility flow rates, a cascade diagram is constructed based on the transshipment model. However, there is no need to calculate minimum heating and cooling as all flowrates are unknown; therefore, only the modified cascade diagram is constructed. For each existing process, the supply and target temperatures ($T_j^{supply}$and T_j^{target}) are known. Additionally, a minimum temperature driving force (ΔT^{min}) is established to ensure feasible heat transfer within all exchangers. The temperature intervals for the cascade diagram can be determined by adding the ΔT^{min} to all cold stream supply and target temperatures, combining this set with the set of all hot stream supply and target temperatures, removing duplicate values from the set and then ordering the set from largest to smallest. This will result in a set of N_z temperatures, corresponding to N_z intervals (where z is the set of intervals and N_z is the cardinal of the set). Interval temperatures are noted as T_z^{hot} (hot scale temperature in interval z) and T_z^{cold} (cold scale temperature in interval z). $z = 0$ is a fictitious interval thus $T_{z=0}$ is undefined; however, practically speaking this temperature corresponds to the temperature of the hot utility as it is added prior to stage one. Therefore, the temperature of the hot utility should be $T^{HU} \geq T_{z=0} + \Delta T^{min}$.

4.1.2.2 Constraints

The exchangeable load from the existing hot streams ($HH_{j \in HP,z}$) and existing cold streams ($HC_{j \in CP,z}$) is the product of the mass flow rate (F_j^{used}) and the change in enthalpy of the stream in the interval of interest ($\Delta H_{j,z}$):

$$HH_{j,z} = F_j^{used} \Delta H_{j,z}; \forall\, j \in HP$$

$$HC_{j,z} = F_j^{used} \Delta H_{j,z}; \forall\, j \in CP$$

The exchangeable load from the new hot streams ($HH_{j \in HN}^{new\ proc}$) and new cold streams ($HC_{j \in CN}^{new\ proc}$) is the product of the flow rate of the process stream ($F_{v^{in}}^{in}$) and the change in enthalpy of the stream ($\Delta H_{j,v^{in},z}$) for streams existing in a given process. The following equations describe the exchangeable load for each stream:

$$HH_{j,z}^{new\ proc} = \sum_{v^{in}} F_{v^{in}}^{in} \Delta H_{j,v^{in},z}\,; \forall\, z, j \in HN$$

$$HC_{j,z}^{new\ proc} = \sum_{v^{in}} F_{v^{in}}^{in} \Delta H_{j,v^{in},z}\ ; \forall\ z, j \in CN$$

Including the new processes, the general energy balance around each interval becomes:

$$r_{z-1} + \sum_{j \in HP} HH_{j,z} + \sum_{NEW} \sum_{v_{NEW}^{in}} \sum_{j \in HN} HH_{j,v_{NEW}^{in},z}^{new\ proc}$$
$$= r_z + \sum_{j \in CP} HC_{j,z} + \sum_{NEW} \sum_{v_{NEW}^{in}} \sum_{j \in CN} HC_{j,v_{NEW}^{in},z}^{new\ proc}$$

The general energy balance is represented graphically in Figure 5 below:

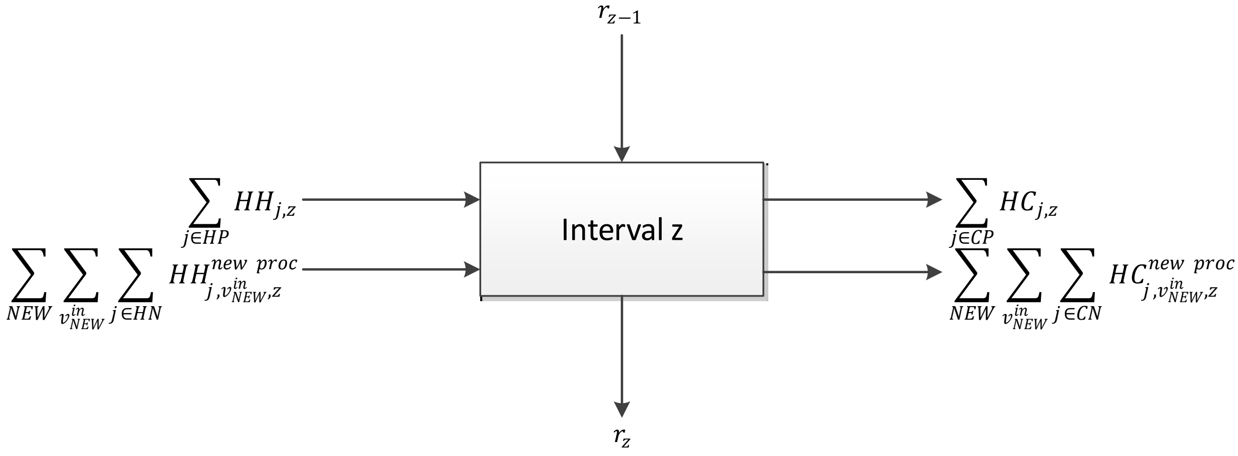

Figure 5: Heat Balance Around Interval z

The heating utility is added before the first interval. Therefore, the balance around the first interval is:

$$HHU + \sum_{j \in HP} HH_{j,z=1} + \sum_{NEW} \sum_{v_{NEW}^{in}} \sum_{j \in HN} HH_{j,v_{NEW}^{in},z=1}^{new\ proc}$$
$$= r_z + \sum_{j \in CP} HC_{j,z=1} + \sum_{NEW} \sum_{v_{NEW}^{in}} \sum_{j \in CN} HC_{j,v_{NEW}^{in},z=1}^{new\ proc}$$

This can be stated alternatively in terms of the general stage balance by adding an additional constraint around $r_{z=0}$:

$$r_{z=0} = HHU$$

The first stage energy balance is represented graphically in Figure 6 below:

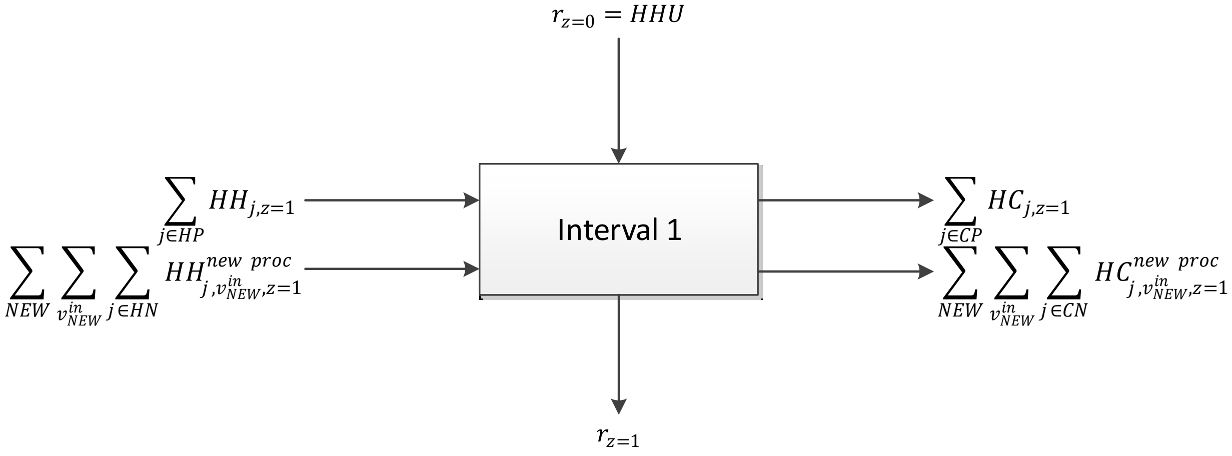

Figure 6: Heat Balance Around Interval z=1

The cooling utility is added only after the last interval. Therefore, the balance around the last interval becomes:

$$r_{z=N_z-1} + \sum_{j \in HP} HH_{j,z=N_z} + \sum_{NEW} \sum_{v_{NEW}^{in}} \sum_{j \in HN} HH_{j,v_{NEW}^{in},z=N_z}^{new\,proc}$$

$$= HCU + \sum_{j \in CP} HC_{j,z=N_z} + \sum_{NEW} \sum_{v_{NEW}^{in}} \sum_{j \in CN} HC_{j,v_{NEW}^{in},z=N_z}^{new\,proc}$$

This can be stated alternatively in terms of the general stage balance by adding an additional constraint around $r_{z=N_z}$:

$$r_{z=N_z} = HCU$$

The final stage energy balance is represented graphically in Figure 7 below:

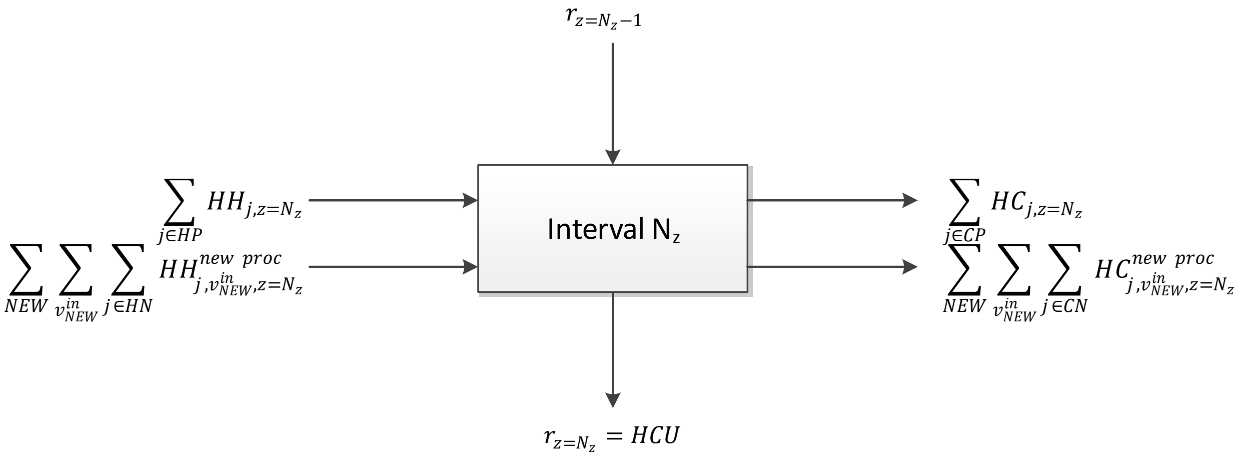

Figure 7: Heat Balance Around Interval z=N_z

4.1.2.3 *Objective variables*

The cost of utilities will be included along with the material demand and other costs in a profitability objective function. The total cost of utilities is given below:

$$C^{utilities} = HHU \times C^{HU} + HCU \times \ C^{HU}$$

The total CO_2 emitted as a result of utility usage will be included along with CO_2 emissions from process by-products in a CO_2 fixation objective function. The total CO_2 emissions dues to utilities can be calculated as follows:

$$E^{CO_2,utilities} = HHU \times \phi$$

where ϕ is an emissions factor based on burning natural gas.

The expressions for these variables can be substituted directly into the objective functions.

4.1.3 *Determine Material Recycle Routes*

4.1.3.1 Description

In addition to the heat exchange described in the sections above, the participants of the EIP can also exchange material in order to reduce the relative consumption of fresh resources. Although advanced atomic balance methods for material exchange have been proposed, a simpler material exchange network will be implemented following the framework presented in [20] based only on existing molecular species with CO_2 separation from flue gasses. Furthermore, many processes will emit relatively pure material streams which can be inexpensively purified. These streams will be considered in this methodology.

4.1.3.2 Constraints

Each source (OLD) can be divided to supply material to any number of interceptors. The mass balance around this first node, therefore, is as follows:

$$G_{OLD}^{used} = \sum_{INT} \sum_{u_{INT}^{in}} G_{OLD,u_{INT}^{in}}^{in}$$

Where G_{OLD}^{used} is the flow rate of material taken from source OLD. It is therefore subject to the additional constraint to ensure availability:

$$G_{OLD}^{used} \leq G_{OLD}^{available}$$

Whatever portion of $G_{OLD}^{available}$ is not used goes to waste. Therefore, the following constraint must also hold:

$$G_{OLD}^{used} + G_{OLD}^{waste} = G_{OLD}^{available}$$

Where G_{OLD}^{waste} is the unused supply of material from source OLD.

Each interceptor (INT) can accept material from any number of sources. Therefore, the overall mass balance around the inlet ports of the interceptors is as follows:

$$W_{u_{INT}^{in}}^{in} = \sum_{OLD} G_{OLD,u_{INT}^{in}}^{in}$$

Additionally, the component level mass balance around each interceptor inlet port is as follows:

$$W_{u_{INT}^{in}}^{in} y_{COM,u_{INT}^{in}}^{in} = \sum_{OLD} G_{OLD,u_{INT}^{in}}^{in} x_{COM,OLD}$$

Where $W_{u_{INT}^{in}}^{in}$ is the total mass flow rate into port u_{INT}^{in}, and $y_{COM,u_{INT}^{in}}^{in}$ is the mass fraction of component COM entering port u_{INT}^{in}. $x_{COM,OLD}$ is the mass fraction of component COM in source stream OLD.

Each interceptor may have constraints on the material compositions and flow rates which it may accept. In that case, the following constraints must hold:

$$y_{COM,u_{INT}^{in}}^{in,min} \leq y_{COM,u_{INT}^{in}}^{in} \leq y_{COM,u_{INT}^{in}}^{in,max}$$

$$W_{u_{INT}^{in}}^{in,min} \leq W_{u_{INT}^{in}}^{in} \leq W_{u_{INT}^{in}}^{in,max}$$

Interceptors can be any process unit including mixers, splitters, separators or reactors. Each type of interceptor will have a unique set of modeling equations. In general, this set of equations can be included as follows:

$$\Phi_{INT}\left(W_{u_{INT}^{in}}^{out}, y_{u_{INT}^{in}}^{out}, W_{u_{INT}^{in}}^{in}, y_{u_{INT}^{in}}^{in}, D_{INT}, O_{INT}, S_{INT}\right) = 0$$

$$\Xi_{INT}\left(W_{u_{INT}^{in}}^{out}, y_{u_{INT}^{in}}^{out}, W_{u_{INT}^{in}}^{in}, y_{u_{INT}^{in}}^{in}, D_{INT}, O_{INT}, S_{INT}\right) \leq 0$$

Where Φ_{INT} and Ξ_{INT} are, respectively, the vectors of modeling equations and inequalities governing the interceptors. While D_{INT}, O_{INT} and S_{INT} are design, operating and state variables of the interceptor.

Each interceptor can pass material to any number of sinks. The overall mass balances around the outlet ports of the interceptors are as follows:

$$W_{u_{INT}^{out}}^{out} = \sum_{NEW} \sum_{v_{NEW}^{in}} F_{u_{INT}^{out}, v_{NEW}^{in}}$$

Where $W_{u_{INT}^{out}}^{out}$ is the mass flow rate of material leaving port u_{INT}^{out} and $F_{u_{INT}^{out}, v_{NEW}^{in}}$ is the mass flow rate of material leaving interceptor port u_{INT}^{out} and entering sink port v_{NEW}^{in}.

As each sink may accept material from multiple interceptors, the following overall and component mass balances must hold:

$$F^{in}_{v^{in}_{NEW}} = \sum_{INT} \sum_{u^{out}_{INT}} F_{u^{out}_{INT}, v^{in}_{NEW}}$$

$$F^{in}_{v^{in}_{NEW}} z^{in}_{COM, v^{in}_{NEW}} = \sum_{INT} \sum_{u^{out}_{INT}} F_{u^{out}_{INT}, v^{in}_{NEW}} y^{out}_{u^{out}_{INT}}$$

Each sink may have constraints on the material compositions and flow rates which it may accept. In that case, the following constraints must hold:

$$z^{in,min}_{COM, v^{in}_{INT}} \leq z^{in}_{COM, v^{in}_{INT}} \leq z^{in,max}_{COM, v^{in}_{INT}}$$

$$F^{in,min}_{v^{in}_{INT}} \leq F^{in}_{v^{in}_{INT}} \leq F^{in,max}_{v^{in}_{INT}}$$

Similar to the interceptors, sinks can be a variety of process units. Each sink will have a unique set of modeling equations. In general, this set of equations can be included as follows:

$$\Psi_{NEW}\left(F^{out}_{v^{out}_{NEW}}, z^{out}_{v^{out}_{NEW}}, F^{in}_{v^{in}_{NEW}}, z^{in}_{v^{in}_{NEW}}, D_{NEW}, O_{NEW}, S_{NEW}\right) = 0$$

$$\Omega_{NEW}\left(F^{out}_{v^{out}_{NEW}}, z^{out}_{v^{out}_{NEW}}, F^{in}_{v^{in}_{NEW}}, z^{in}_{v^{in}_{NEW}}, D_{NEW}, O_{NEW}, S_{NEW}\right) \leq 0$$

Where Ψ_{NEW} and Ω_{NEW} are, respectively, the vectors of modeling equations and inequalities governing the sinks. While D_{NEW}, O_{NEW} and S_{NEW} are design, operating and state variables of the sink.

4.1.3.3 Objective Variables

The key objective variables in this section are the net profit (revenue from sales minus cost of fresh materials and cost of the interception network (primarily CO_2 separation)) and the net CO_2 emissions (unused CO_2 emitted from processes and CO_2 associated with procuring feedstocks minus the CO_2 fed to the processes). The net profit from materials sales and costs is given below:

$$profit = \sum_{COM}\sum_{NEW} F_{NEW}^{out} z_{COM,NEW}^{out} P_{COM}^{sell} - \sum_{OLD} G_{OLD}^{used} C_{OLD}^{source}$$

$$-\sum_{INT}\sum_{v_{INT}^{in}} W_{v_{INT}^{in}}^{in} C_{v_{INT}^{in}}^{interceptor}$$

The net CO_2 emissions is given below:

$$net\ emissions = F_{waste}^{in} z_{CO_2,waste}^{in} + \sum_{OLD} G_{OLD}^{used} AC_{OLD}^{feed} - \sum_{OLD} G_{OLD}^{used} x_{CO_2,OLD}$$

The expressions for these variables can be substituted directly into the objective functions.

4.1.4 Objective Functions

The two overall objective functions are the net profit and the net CO_2 emissions. Combining the objective variables from section 4.4.2.4 and 4.4.3.4 the following objective functions are obtained.

4.1.4.1 Objective 1: Maximize Annual Profit

$$profit = \sum_{COM} \sum_{NEW} F_{NEW}^{out} z_{COM,NEW}^{out} P_{COM}^{sell} - \sum_{OLD} G_{OLD}^{used} C_{OLD}^{source}$$

$$- \sum_{INT} \sum_{v_{INT}^{in}} W_{v_{INT}^{in}}^{in} C_{v_{INT}^{in}}^{interceptor} - HHU \times C^{HU} + HCU \times \ C^{HU}$$

4.1.4.2 Objective 2: Maximize CO_2 Fixation Rate

$$net\ emissions$$

$$= F_{waste}^{in} z_{CO_2,waste}^{in} + \sum_{OLD} G_{OLD}^{used} AC_{OLD}^{feed} + HHU \times \phi - \sum_{OLD} G_{OLD}^{used} x_{CO_2,OLD}$$

5 CASE STUDY

This case study involves a set of industrial processing facilities located in close proximity to one another. It is determined that they collectively want to reduce their carbon footprint by exchanging excess material and energy among each other as long as there is some economic benefit. In addition to heat and mass exchange, some members may elect to build a new processing facility to take advantage of excess materials. In order to limit the number of processes which are being considered, the candidate processes are limited to processes which utilize CO_2 as a raw material.

Each process will be assumed to have two streams: one hot stream and one cold stream. This is based on the assumption that heat integration has already been carried out for each process and only the excess heating and cooling capacities are available for integration.

In terms of the new processes, the energy demand and material inputs and outputs are estimated based on available information.

5.1 Existing Processes

The following facilities, shown in Table 1, exist in close proximity to one another. These are all well established industrial processes for which the material and energy inputs and outputs are already fixed and known. The following subsections of section 5.1 describe each of these processes in further details.

Table 1: Existing Case Study Plants

Existing Plant	Capacity	Product	Source
GTL plant (SMR)	2,210,540 tons/year	Liquid transportation fuels	[32]
Power plant	600 MW	Electricity	[33-35]
Ethylene plant	238,000 tons/year	Ethylene	[36, 37]
Ammonia plant	346,760 tons/year	Ammonia	[38, 39]
VAM plant	110,471 tons/year	Vinyl acetate monomer	[40]
MTP plant	568,000 ton/year	Propylene	[41, 42]

5.1.1 GTL Plant

Fischer-Tropsh (FT) based gas to liquids (GTL) processes are attractive liquefaction techniques used to convert natural gas into sulfur free, high cetane number transportation fuels. In order to convert natural gas (methane) into liquids, GTL process follows three main steps [32]:

1. Syngas production
    1. Reforming technology

$$CH_4 + H_2O \rightarrow CO + 3H_2$$ Steam Reforming (SMR)

or

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2$$ Partial Oxidation (POx)

or

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2$$ Dry Reforming (DRM)

    2. Adjust H_2/CO ratio

$$CO + H_2O \rightarrow CO_2 + H_2$$ Water Gas Shift (WGS)

2. Syncrude production

$$(2n+1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O$$

3. Syncrude refining

Step 1 involves sulfur removal, natural gas reforming (steam reforming, partial oxidation, dry reforming or some combination of these) and syngas conditioning (H_2/CO ratio adjustments via water gas shift, CO_2 removal) [32]. In this case study, the selected reforming technology is steam reforming (SMR) and the CO_2 removed from the syngas is made available for integration within the eco-industrial park.

5.1.2 Power plant with Post Combustion Capture

General emissions data for a natural gas fired power plant are given in Table 2 below [33]:

Table 2: Emissions Data for NG Power Plant

Factor	Value	Units
CO_2 emissions factor	116.999	lb CO_2/MMBtu
Heat rate	10,156	Btu heat/kWh power
Plant emissions	1.22	lb CO_2/kWh power
On stream factor	0.95	time on stream/total time

For 600 MW plant:

$$annual\ emissions = 600\ MW \times 1000\frac{kW}{MW} \times 365\frac{days}{yr} \times 24\frac{hours}{day} \times 0.95 \times 1.22\frac{lb\ CO_2}{kWh} \times \frac{1\ ton}{2000\ lbs} = 3{,}045{,}852\frac{tons\ CO_2}{year}$$

5.1.3 CO_2 Capture

Flue gas generated in power plants contains components in addition to CO_2. A typical power plant flue gas is a majority N_2 (~70%), CO_2 (14%) and water vapor (15%) with small compositions of NO_x, SO_x, H_2S, and other sulfur species and particulates. In order to utilize this CO_2 it must be separated from the other components. The most mature and cost effective method for carrying out this separation is a monoethanolamine (MEA) absorption cycle. [7, 34, 35] Cost and energy correlations for absorber operating costs are available in literature. Detailed calculations can be found in the appendix.

Cost correlations given by [7] yield the following:

$$CAPEX = 8.86\frac{10^6\$}{year};\ OPEX = 38.32\frac{10^6\$}{year}$$

$$total\ annualized\ cost = 47.18\frac{10^6\ \$}{year}$$

$$total\ annualized\ cost = \frac{47.18\frac{10^6\ \$}{year}}{3{,}045{,}852\ \frac{tons\ CO_2}{year}} = 15.49\frac{\$}{ton\ CO_2}$$

5.1.4 Ethane cracker

Since the shale boom, ethylene has grown in popularity as a replacement for naphtha in many petro-chemical plants. Steam cracking is the most widely used technology for producing ethylene. Over 85% of ethylene is produced through the dehydrogenation of ethane gas at high temperatures (750-850°C) and low pressures (1.5-3.5 bar). [36] At these conditions, a number of side reactions also take place as described by [37] with typical product yields of 0.85 mol C_2H_4/mol C_2H_6. For this case study, however, it will be assumed that only 3 primary reactions preside:

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

$$2C_2H_6 \rightarrow C_3H_8 + CH_4$$

$$C_3H_8 \rightarrow C_2H_4CH_4$$

Based on the 85% yield reported in literature, the overall reaction can be given as follows:

$$C_2H_6 \rightarrow 0.85C_2H_4 + 0.7H_2 + 0.3CH_4$$

In a typical ethylene plant, a series of compressors, coolers, and separation technologies follow the cracker. High purity hydrogen coming off the cooling train is in part used to hydrogenate by-product acetylene to ethylene while the remainder of this hydrogen is sent to utility. High purity methane is also separated from the product stream in a demethanizer unit and sent to utility.

5.1.5 Ammonia production

Ammonia is an important chemical in agriculture and has been produced for over 100 years. The main reactions in this process are as follows:

1. Primary reforming

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

2. Secondary reforming

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

3. Ammonia production

$$0.5N_2 + 1.5H_2 \rightarrow NH_3$$

The first step uses steam to reform the methane into CO and H_2. The resultant syngas is mixed with air and fed to a second reforming, followed by a water gas shift reactor. After the CO_2 is removed from this syngas, the 3:1 H_2/N_2 stream is fed to the ammonia synthesis loop where the ammonia reaction presides. The overall reaction can be given as:

$$0.8825\ CH_4 + 1.235\ H_2O + 0.265\ O_2 + N_2 \rightarrow 2\ NH_3 + 0.8825\ CO_2$$

5.1.6 Vinyl Acetate Monomer

Vinyl acetate monomer (VAM) is a commodity chemical used in manufacture of polyvinyl acetate and polyvinyl alcohol. Polyvinyl acetate is used in myriad applications ranging including water soluble acrylic paints, coatings for textile and paper industries, laminated safety glass, and automotive fuel tanks and acrylic fibers. [40] The most popular route for producing VAM includes acetic acid, ethylene and oxygen. The reaction takes place in the gas phase and follows the below chemistry:

$$CH_3COOH + C_2H_4 + 0.5O_2 \rightarrow H_2CCHOCOCH_3 + H_2O$$

The combustion of ethylene to CO_2 is an undesirable side reaction which takes place in small quantities (≈0.06 mol of the below reaction):

$$C_2H_4 + 3O_3 \rightarrow 2CO_2 + 2H_2O$$

5.1.7 Methanol to Propylene

Propylene is among the most important basic petrochemicals as it is used to produce plastics, fibers and other chemicals. Most propylene is produced by a steam cracking process; however, this process is very energy intensive so there is a lot of interest in producing light olefins through C_1 routes. Methanol to propylene (MTP) is one such implementation of a C_1 route. The primary reactions in this route are as follows [42]:

$$CH_3OH \rightarrow H_3COCH_3 + H_2O$$

$$H_3COCH_3 \rightarrow C_3H_6 + H_2O$$

However, in addition to the above reactions, many side reactions take place yielding a mix of hydrocarbons (gasoline) as an additional side product. The overall propylene yield compared to methanol is 46%, while the yield of gasoline is about 20%. [42]

5.1.8 Fresh Resources

In addition to the recycled resources available from existing plants in the EIP, a number of fresh resources are available for use in the new processes.

5.1.8.1 Raw Materials

Fresh resources may be needed to make up deficits in availability from waste streams. Available fresh resources include: natural gas, hydrogen, ethylene oxide, benzene, propylene oxide and ammonia. Costs for these resources are listed in Table 3 below:

Table 3: Feedstock Prices

Resource	Price (\$/ton)
Natural Gas	145
Hydrogen	637
Ethylene Oxide	844
Benzene	1,400
Propylene Oxide	1,250
Ammonia	424

In addition to the cost of the raw materials, there are carbon dioxide emissions associated with procuring some of these. These associated emissions are found in Table 4 below:

Table 4: Associated Emissions for Feedstock Procurement

Resource	Associated Emissions $\left(\frac{mol\ CO_2}{mol\ resource}\right)$
Hydrogen	0.25
Ammonia	0.75
Ethylene Oxide	0.33

5.1.8.2 Utilities

Hot utility is natural gas. EIA [33] gives a CO_2 emission factor for natural gas as 116.999 lb CO_2/MMBtu for natural gas. Therefore, the emissions factor: $\phi =$

$\frac{116.999}{2000}\frac{ton\ CO_2}{MMBtu}$. In addition to emissions, the purchase cost of utilities are important. The costs of utilities are found in Table 5 below:

Table 5: Utility Costs

Resource	Cost ($/MMBtu)
Heating	3.00
Cooling	0.50

5.2 *New Processes*

Many processes have been reported in literature to utilize CO_2 as a reactant. An incomprehensive list of these reactions is found in Table 6 below.

Table 6: Candidate Processes for Inclusion in EIP

Product	Stoichiometry	$\boldsymbol{\Delta H^{o}_{rxn}}$ [= kJ/mol]	Typical Capacity [=1000 tons/year]	Source
Methanol	$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$	-48.97	609	[43, 44]
Urea	$CO_2 + 2NH_3 \leftrightarrow CH_4N_2O + H_2O$	49.73	766	[45, 46]
Acetic Acid (CH_4)	$CO_2 + CH_4 \rightarrow CH_3COOH$	35.37	237	[47, 48]
Acetic Acid (H_2)	$2CO_2 + 4H_2 \rightarrow CH_3COOH + 2H_2O$	-129.6	237	
Formic Acid	$CO_2 + H_2 \rightarrow HCOOH$	-31.48		[49-51]
Ethylene Glycol	$\begin{cases} CO_2 + C_2H_4O \rightarrow C_2H_4CO_3 \\ C_2H_4CO_3 + 3H_2 \rightarrow C_2H_4(OH)_2 + CH_3O \end{cases}$	-144.74 148.41	298	[52, 53]
Propylene Carbonate	$CO_2 + C_3H_6O \rightarrow C_3H_6CO_3$	-75.5		[52]
Phenol	$CO_2 + C_6H_6 \rightarrow C_6H_5OH + CO$	35.06	243	[54]

Table 6 Continued

Product	Stoichiometry	$\boldsymbol{\Delta H^{o}_{rxn}}$ [= kJ/mol]	Typical Capacity [=1000 tons/year]	Source
Benzoic Acid	$CO_2 + C_6H_6 \rightarrow C_6H_5COOH$	-74.61	2.175	[54]
Acrylic Acid	$CO_2 + C_2H_4 \rightarrow C_2H_3COOH$	10.54		[55]
Toluene	$CO_2 + 3H_2 + C_6H_6 \rightarrow C_6H_5CH_3 + 2H_2O$	-161.05	417	[56]
Salicylic Acid	$CO_2 + C_6H_5OH \rightarrow C_6H_4OHCOOH$	-7.84	90	[46]

All ΔH^{o}_{rxn} were calculated using the ΔH^{o}_{f} values for the products and reactants according to:

$$\Delta H^{o}_{rxn} = \sum_{products} v_p \times \Delta H^{o}_{f,p} - \sum_{reactants} v_r \times \Delta H^{o}_{f,r}$$

Plant capacities were calculated as a percentage of total annual demand.

6 RESULTS AND CONCLUSIONS

6.1 Base Case: EIP with no heat integration

The first step in analysis was solving a base case scenario in which material integration was conducted with no heat integration within the eco industrial park. The results of this analysis show that material integration presents an attractive case economically. It is worth noting the relatively small contribution utility costs have on the overall economics of the process. However, utility usage does still have a significant impact on the overall CO_2 emissions, where there is still room for improvement. Figure 8 below shows the breakdown of product revenues and Figure 9 shows the breakdown of CO_2 usage for the two objective functions: maximize profit and maximize CO_2 fixation.

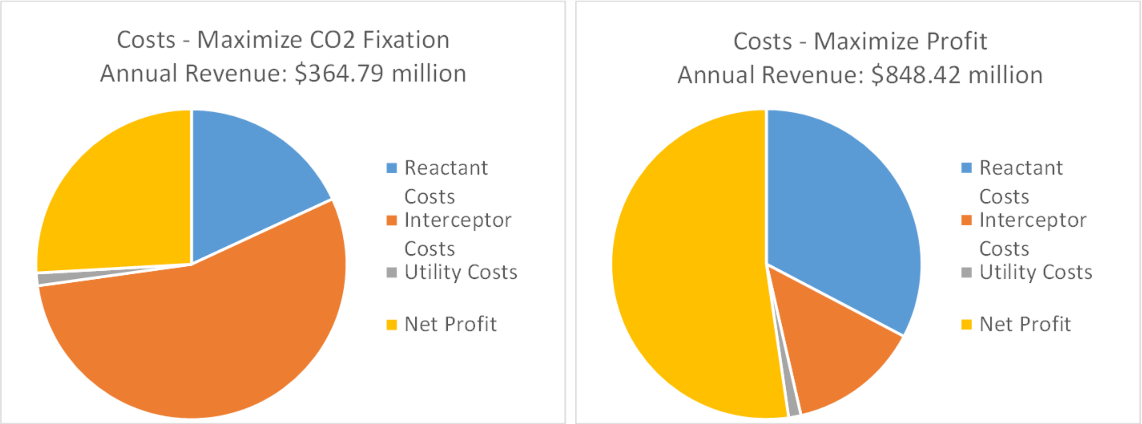

Figure 8: Breakdown of product revenue – No Heat Integration

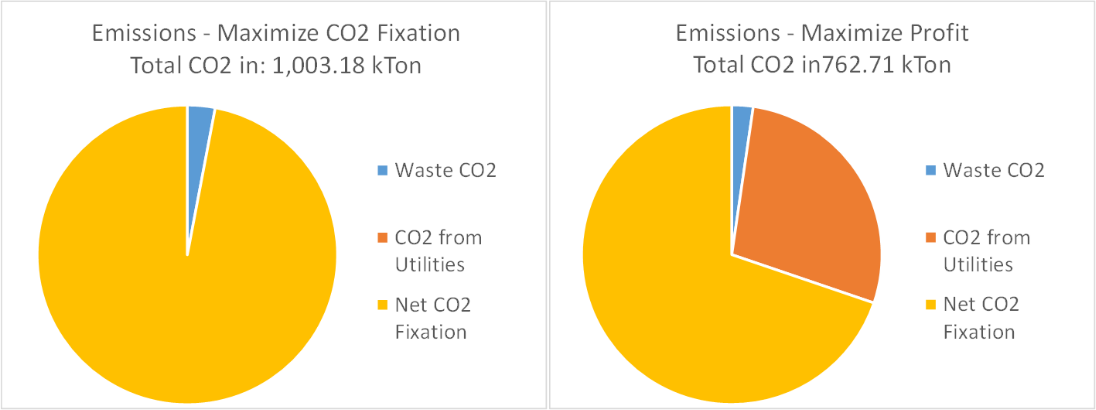

Figure 9: Breakdown of net CO_2 emitted/fixed – No Heat Integration

6.2 EIP with heat integration

After the base case was solved, the case study was solved again with heat integration. In this case, the overall economics were not significantly impacted; however, the net fixation of CO_2 increased significantly as seen in Figure 11. Figure 10 and Figure 11 show the results of the case study solved with simultaneous heat and mass integration.

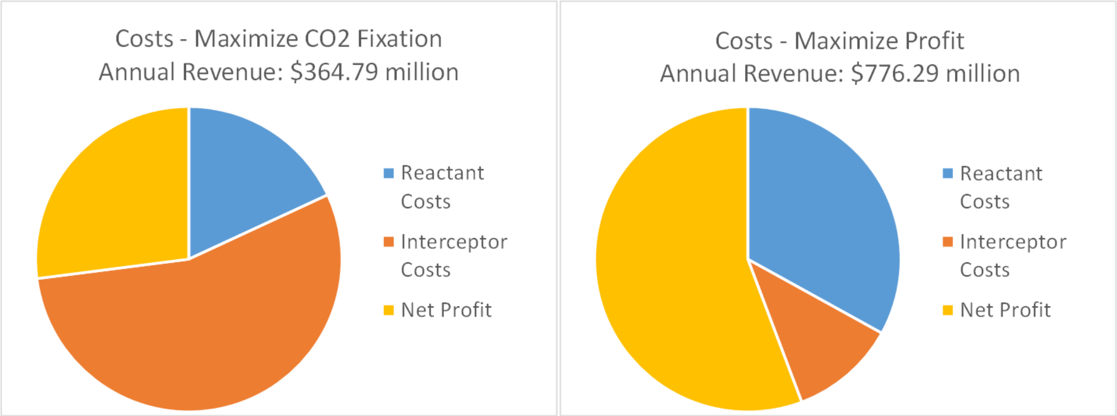

Figure 10: Breakdown of product revenue – With Heat Integration

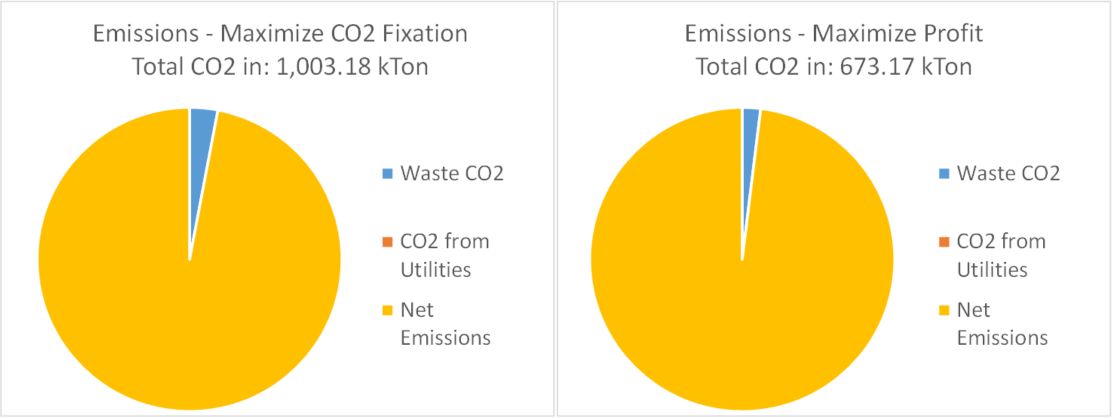

Figure 11: Breakdown of net CO_2 emitted/fixed – With Heat Integration

6.3 Pareto Optimal Results

The previous section describes the two extreme scenarios: 1) maximize profit with no regards to CO_2 fixation and 2) maximize CO_2 fixation with no regards to profitability. In order to explore the effects of trading off the two objectives various configurations were considered. Additionally, three different cases were simulated: a maximum of 1, 2 or 3 processes cold be added to the in the EIP. Figure 12 below shows the results of these simulations. All of the solutions in this set of simulations are optimal solutions subject to the constraints in that particular scenario.

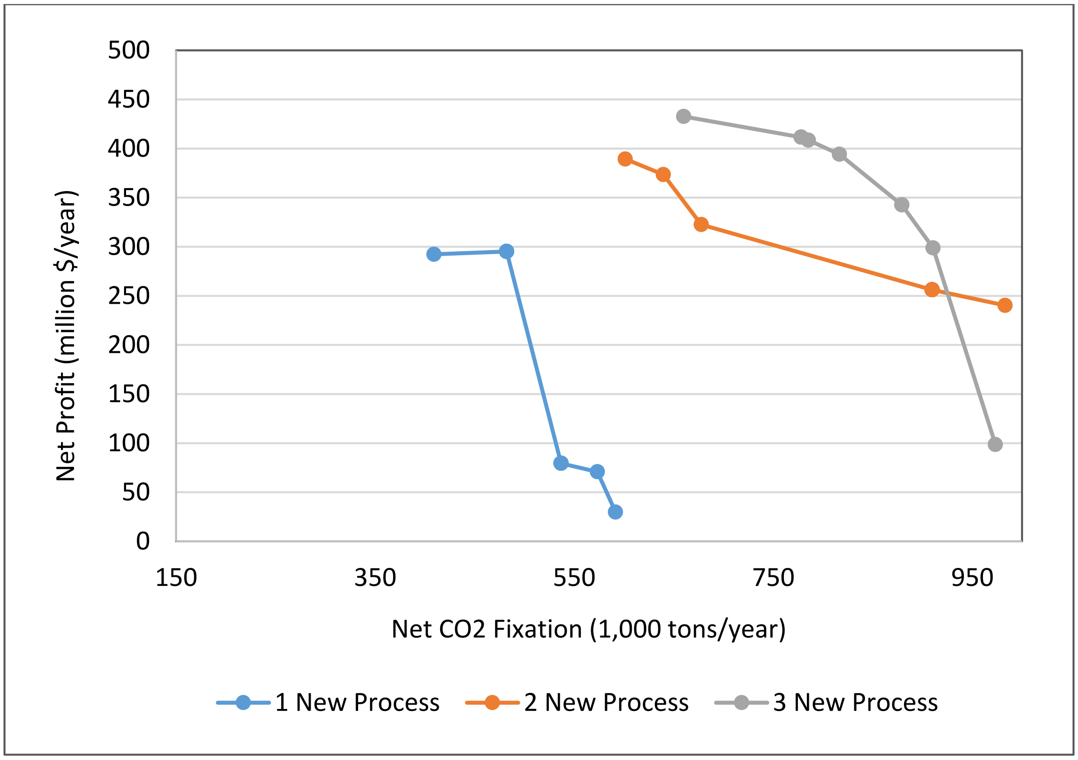

Figure 12: Net Profit vs Net CO_2 Fixation

6.4 Simulation Results

This section explores more detailed results of the various simulations. For each case, scenario 1 seeks to maximize the net CO_2 fixation with no regards to profit. Scenario 11 seeks to maximize the profit with no regards to CO_2 fixation. Scenarios 2-10 are cuts in between which target for CO_2 fixation while seeking to maximize the profit. Tables 7, 10 and 13 show the optimized flow rates of the processes which were selected to be added to the EIP for each scenario. This includes the processes which were selected from Table 6 as well as waste disposal. Tables 8, 11 and 14 show the flow rates of utilities and heat integration for the EIP for each scenario. Finally, Tables 9, 12 and 15 show the optimized flow rates of all material sources used in the EIP. This includes streams sourced from existing plants (referred to as recycled resources, regardless of whether or not the stream was treated by an interceptor) and fresh resources purchased from external sources.

6.4.1 One New Process

Table 7 below shows the optimized flow rates of the processes which were selected to be added to the EIP.

Table 7: Case 1 Selected Processes (all values in units of 1,000 tons/year)

Scenario #	Methanol	Urea	waste
1	670		1,627
2	670		2,087
3	670		2,087
4	642		1,855
5	642		1,855
6	642		1,855
7		843	735
8		843	735
9		843	735
10		843	735
11		764	

Table 8 shows the optimized flow rates of utilities and heat integration for the EIP.

Table 8: Case 1 Energy Sources (all values in units of MMBtu/year)

Scenario #	H1_GTL	H1_Ammonia	C1_GTL
1		346,750.00	182,800
2		346,750.00	182, 800
3		346,750.00	182, 800
4		346,750.00	175,500
5		346,750.00	175,500
6		346,750.00	175,500
7	255,400	346,750.00	
8	255,400	346,750.00	
9	255,400	346,750.00	
10	255,400	346,750.00	
11	230,600.00	346,750.00	

Table 9: Case 1 Source Material Flow Rates (all values in units of 1000 tons/year)

	Recycled Resources						Fresh Resources	
Scenario #	Power Plant Flue Gas	Ethylene Cracker H2	Ethylene Cracker CH4	Ammonia waste CO_2	VAM waste CO_2	GTL Flue Gas	Hydrogen	Ammonia
1				395	7	1,818	76	
2	1,050	14	48	395	7	1,176	62	
3	1,050	14	48	395	7	1,176	62	
4	1,070	14	48	395	7	905	59	
5	1,070	14	48	395	7	905	59	
6	1,070	14	48	395	7	905	59	
7	280			395	7	546		349
8	280			395	7	546		349
9	280			395	7	546		349
10	280			395	7	546		349
11	45			395	7			316

6.4.2 Two New Processes

Table 10: Case 2 Selected Processes (all values in units of 1,000 tons/year)

Scenario #	Methanol	Urea	Acetic Acid ($CH4 + CO_2$)	Formic Acid	waste
1	636	842			3,415
2	636	842			3,415
3	548	842			2,978
4	548	842			2,978
5	548	842			2,978
6	548	842			2,978
7	548	842			2,978
8	548	842			2,978
9		842	260		1,646
10		842		165	1,414
11		842		165	2,827

Table 11: Case 2 Energy Sources (all values in units of MMBtu/year)

Scenario #	H1_GTL	H1_Ammonia
1	200	347
2	200	347
3		5
4		5
5		5
6		5
7		5
8		5
9	331	347
10	200	347
11	200	347

Table 12: Case 2 Source Material Flow Rates (all values in units of 1000 tons/year)

	Recycled Resources								Fresh Resources	
Scenario #	Power Plant Flue Gas	Ethylene Cracker H2	Ethylene Cracker CH4	Ammonia waste CO_2	VAM treated waste water	VAM waste CO_2	GTL Flue Gas	GTL Treated waste water	Natural Gas	Hydrogen
1	4,070	14		395		7				59
2	4,070	14		395		7				59
3	3,555	14		395		7				48
4	3,555	14		395		7				48
5	3,555	14		395		7				48
6	3,555	14		395		7				48
7	3,555	14		395		7				48
8	3,555	14		395		7				48
9	8		48	395		7	1,923		18	
10	1,663	7		395		7				
11	2,252	14	48	395	26	7		743		

6.4.3 Three New Processes

Table 13: Case 3 Selected Processes (all values in units of 1,000 tons/year)

Scenario #	Methanol	Urea	Acetic Acid ($CH4 + CO_2$)	Acetic Acid ($H2 + CO_2$)	Formic Acid	Ethylene Glycol	Propylene Carbonate	waste
1	670			260	165			3416
3		843	260	260				3040
4		843		260	165			2857
5		843		260	165			2857
6		843	260			327		2460
7		843	260			327		2236
8		843	260			327		2184
9		843	260			327		2184
10		843	260			327		2184
11		826			165		165	1490

Table 14: Case 3 Energy Sources (all values in units of MMBtu/year)

Scenario #	H1_GTL	H1_Ammonia	C1_GTL	C1_Ammonia
1			302,865	
3	157,626	346,750		
4	147,627	346,750		346,750
5	147,627	346,750		346,750
6	331,209	346,750		
7	331,209	346,750		
8	331,209	346,750		
9	331,209	346,750		
10	331,209	346,750		
11	134,097	346,750		

Table 15: Case 3 Source Material Flow Rates (all values in units of 1000 tons/year)

	Recycled Resources						Fresh Resources				
Scenario #	Power Plant Flue Gas	Ethylene Cracker H2	Ethylene Cracker CH4	Ammonia waste CO_2	VAM waste CO_2	GTL Flue Gas	Natural Gas	Hydrogen	Ethylene Oxide	Propylene Oxide	Ammonia
1	4,004			395	7			104			
3	3,565	14	48	395	7		18	7			349
4	3,345	14		395	7			13			349
5	3,345	14		395	7			13			349
6	13	14	48	395	7	2,894	18	6	146		349
7	71	14	48	395	7	2,612	18	6	146		349
8	80	14	48	395	7	2,552	18	6	146		349
9	80	14	48	395	7	2,552	18	6	146		349
10	80	14	48	395	7	2,552	18	6	146		349
11	1,804	7		395	7					89	342

7 CONCLUSIONS

7.1 Overall Emissions Reduction

The primary goal of this implementation is to maximize the overall CO_2 emissions reduction while still manufacturing economically competitive products. Even with the favorable results presented above, the utilization of total CO_2 available in the EIP is limited. With huge sources like a power plant and GTL plant, total CO_2 emissions for the park are about 6,119,737 tons per year. The new processes, limited by production capacity, only have a maximum net fixation rate of about 983,100 tons per year, or just 16%. This can be addressed by increasing the capacity of the new processes, particularly methanol and urea, to accommodate the high influx of CO_2. Additionally, other strategies such as geological sequestration or other utilization routes such as syngas production through dry reforming or water electrolysis could also play a part in the overall emissions reduction.

7.2 Selected processes

The results of the simulation are commensurate with expected predictions: 1) adding more processes to the park yields both higher CO_2 fixation rates and profits and 2) as the CO_2 fixation rate is increased, the profits decrease.

With regards to which processes were selected for inclusion, MISR is not the best predictor of success in the integration. The highest MISR products aren't selected due to the small gross economic potential (volume*profit margin). Methanol and urea were among the most favorable processes in all scenarios although their MISR values were in the middle of the group. This is due to their moderate MISR values, high demand and exothermic process heat. Additionally, when more processes were allowed to be added, the products were selected with higher MISR values but lower demands such formic acid, acetic acid and ethylene glycol. This is due to the gross economic potential increasing as the demands for multiple products is additive.

7.3 Final Conclusions and Recommendations for Future Work

An optimization formulation for the integration of CO_2 utilization processes into eco-industrial parks has been presented. A case study was then solved to demonstrate the validity of the metholodgy. This work demonstrated that while profitability and net CO_2 fixation are indeed competing objectives, there do exist potential solutions to sequester CO_2 while making a profit. The primary challenge with converting CO_2 into useful chemicals is scale. Additional processes such as dry reforming and electrolysis should be included in future work to open up the market for synthetic fuels and other large demand commodity chemicals.

REFERENCES

1. Matthieu Emmanuel Galvez and Jérôme Gaillardet, *Historical constraints on the origins of the carbon cycle concept (Contraintes historiques sur les origines du concept de cycle du carbone).* Comptes Rendus Géoscience, 2012. **344**(Novembre 2012): p. 549-567.
2. Philippe Ciais, Christopher Sabine, Govindasamy Bala (India), Laurent Bopp (France), Victor Brovkin (Germany/Russian Federation), Josep Canadell (Australia), Abha Chhabra (India), Ruth DeFries (USA), James Galloway (USA), Martin Heimann (Germany), Christopher Jones (UK), Corinne Le Quéré (UK), Ranga B. Myneni (USA), Shilong Piao (China), and Peter Thornton (USA), *Carbon and Other Biochemical Cycles*, in *Climate Change 2013: The Physical Science Basis*. 2013, Intergovernmental Panel on Climate Change (IPCC).
3. H. Le Treut, R. Somerville, U. Cubasch, Y. Ding, C. Mauritzen, A. Mokssit, T. Peterson, and M. Prather, *2007: Historical Overview of Climate Change*, in *Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, S. Solomon, D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor and H.L. Miller, Editor. 2007, Intergovernmental Panel on Climate Change (IPCC): Cambridge, United Kingdom and New York, NY, USA.
4. K.L. Denman, G. Brasseur, A. Chidthaisong, P. Ciais, P.M. Cox, R.E. Dickinson, D. Hauglustaine, C. Heinze, E. Holland, D. Jacob, U. Lohmann, S

Ramachandran, P.L. da Silva Dias, S.C. Wofsy, and X. Zhang, *2007: Couplings Between Changes in the Climate System and Biogeochemistry*, in *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, S. Solomon, D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M.Tignor and H.L. Miller, Editor. 2007: Cambridge, United Kingdom and New York, NY, USA.

5. NASA. *Graphic: The relentless rise of carbon dioxide*. 2017; Available from: https://climate.nasa.gov/climate_resources/24/.
6. United States Environmental Protection Agency (EPA). *Greenhouse Gas Inventory Data Explorer*. 2015 April 30, 2015 [cited 2016 July 7]; Available from: https://www3.epa.gov/climatechange/ghgemissions/inventoryexplorer/.
7. M. M. Faruque Hasan, Fani Boukouvala, Eric L. First, and Christodoulos A. Floudas, *Nationwide, Regional, and Statewide CO2Capture, Utilization, and Sequestration Supply Chain Network Optimization.* Industrial & Engineering Chemistry Research, 2014. **53**(18): p. 7489-7506.
8. Gro Harlem Brundtland, *Report of the World Commission on Environment and Development: Our Common Future*. 1987: Oslo, Norway.
9. Mahmoud M El-Halwagi, *Pollution prevention through process integration: systematic design tools*. 1997: Academic press.

10. Mahmoud M El-Halwagi, *Sustainable design through process integration: fundamentals and applications to industrial pollution prevention, resource conservation, and profitability enhancement*. 2011: Elsevier.

11. Bodo Linnhoff, *A user guide on process integration for the efficient use of energy*. 1982: Institution of Chemical Engineers.

12. Mahmoud El-Halwagi and Vasilios Manousioutakis, *Automatic Synthesis of Mass Exchange Networks.* Chemical Engineering Science, 1989. **45**(9): p. 2813-2831.

13. YP Wang and Robin Smith, *Wastewater minimisation.* Chemical Engineering Science, 1994. **49**(7): p. 981-1006.

14. M. M. El-Halwagi, F. Gabriel, and D. Harell, *Rigorous Graphical Targeting for Resource Conservation via Material Recycle/Reuse Networks.* Industrial & Engineering Chemistry Research, 2003. **42**(9): p. 4319-4328.

15. Mahmoud M El-Halwagi, Ian M Glasgow, Xiaoyun Qin, and Mario R Eden, *Property integration: componentless design techniques and visualization tools.* AIChE Journal, 2004. **50**(8): p. 1854-1869.

16. Mahmoud M El-Halwagi, *Process integration*. Vol. 7. 2006: Academic Press.

17. Marian R Chertow, *Industrial symbiosis: literature and taxonomy.* Annual review of energy and the environment, 2000. **25**(1): p. 313-337.

18. Eva M. Lovelady and Mahmoud M. El-Halwagi, *Design and integration of eco-industrial parks for managing water resources.* Environmental Progress & Sustainable Energy, 2009. **28**(2): p. 265-272.

19. Sabla Y. Alnouri, Patrick Linke, and Mahmoud M. El-Halwagi, *Synthesis of industrial park water reuse networks considering treatment systems and merged connectivity options.* Computers & Chemical Engineering, 2016. **91**: p. 289-306.

20. Mohamed M. B. Noureldin and Mahmoud M. El-Halwagi, *Synthesis of C-H-O Symbiosis Networks.* AIChE Journal, 2015. **61**(4): p. 1242-1262.

21. John Ehrenfeld and Nicholas Gertler, *Industrial ecology in practice: the evolution of interdependence at Kalundborg.* Journal of industrial Ecology, 1997. **1**(1): p. 67-79.

22. U.S. Energy Information Administration. *FREQUENTLY ASKED QUESTIONS: How much carbon dioxide is produced by burning gasoline and diesel fuel?* 2016 [cited 2016 5/27/16]; Available from: http://www.eia.gov/tools/faqs/faq.cfm?id=307&t=10.

23. K. M. Yu, I. Curcic, J. Gabriel, and S. C. Tsang, *Recent advances in CO2 capture and utilization.* ChemSusChem, 2008. **1**(11): p. 893-9.

24. Christopher Graves, Sune D. Ebbesen, Mogens Mogensen, and Klaus S. Lackner, *Sustainable hydrocarbon fuels by recycling CO2 and H2O with renewable or nuclear energy.* Renewable and Sustainable Energy Reviews, 2011. **15**(1): p. 1-23.

25. Brett P. Spigarelli and S. Komar Kawatra, *Opportunities and challenges in carbon dioxide capture.* Journal of CO2 Utilization, 2013. **1**: p. 69-87.

26. Kartik Ramasubramanian, Yanan Zhao, and W. S. Winston Ho, *CO2capture and H2purification: Prospects for CO2-selective membrane processes.* AIChE Journal, 2013. **59**(4): p. 1033-1045.

27. Joshua D. Rhodes, Carey W. King, Gürcan Gulen, Sheila M. Olmstead, James S. Dyer, Robert E. Hebner, Fred C. Beach, Thomas F. Edgar, and Michael E. Webber, *A Geographically Resolved Method to Estimate Levelized Power Plant Costs with Environmental Externalities.* White Paper UTEI/2016-04-1, 2016.

28. Gabriel Alves da Costa Lima, *CO2 Capture And Storage In Mature Oil Reservoir: Physical Description, EOR And Economic Valuation Of A Case Of A Brazilian Mature Field*. Society of Petroleum Engineers.

29. M. Algharaib and N. Abu Al-Soof, *Economical Modeling of CO2 Capturing and Storage Projects*. Society of Petroleum Engineers.

30. Mohamed M. B. Noureldin, Nimir O. Elbashir, and Mahmoud M. El-Halwagi, *Optimization and Selection of Reforming Approaches for Syngas Generation from Natural/Shale Gas.* Industrial & Engineering Chemistry Research, 2014. **53**(5): p. 1841-1855.

31. Soterios A. Papoulias and Ignacio E. Grossmann, *A structural optimization approach in process synthesis—II.* Computers & Chemical Engineering, 1983. **7**(6): p. 707-721.

32. Kerron J. Gabriel, Patrick Linke, Arturo Jiménez-Gutiérrez, Diana Yered Martínez, Mohamed Noureldin, and Mahmoud M. El-Halwagi, *Targeting of the Water-Energy Nexus in Gas-to-Liquid Processes: A Comparison of Syngas*

Technologies. Industrial & Engineering Chemistry Research, 2014. **53**(17): p. 7087-7102.

33. U.S. Energy Information Administration (EIA). *FREQUENTLY ASKED QUESTIONS: How much carbon dioxide is produced per kilowatthour when generating electricity with fossil fuels?* 2016 2/20/2016]; Available from: https://www.eia.gov/tools/faqs/faq.cfm?id=74&t=11.

34. Zeinab Amrollahi, Paul Andreas Marchioro Ystad, Ivar S. Ertesvåg, and Olav Bolland, *Optimized process configurations of post-combustion CO2 capture for natural-gas-fired power plant – Power plant efficiency analysis.* International Journal of Greenhouse Gas Control, 2012. **8**: p. 1-11.

35. Patricia Luis, *Use of monoethanolamine (MEA) for CO2 capture in a global scenario: Consequences and alternatives.* Desalination, 2016. **380**: p. 93-99.

36. Preetha Thiruvenkataswamy, Fadwa T. Eljack, Nitin Roy, M. Sam Mannan, and Mahmoud M. El-Halwagi, *Safety and techno-economic analysis of ethylene technologies.* Journal of Loss Prevention in the Process Industries, 2015. **39**: p. 74-84.

37. Serveh Kamrava, Kerron J. Gabriel, Mahmoud M. El-Halwagi, and Fadwa T. Eljack, *Managing abnormal operation through process integration and cogeneration systems.* Clean Technologies and Environmental Policy, 2014. **17**(1): p. 119-128.

38. C. W. Hooper and J.R. Jennings (Ed.), *Catalytic Ammonia Synthesis: Fundamentals and Practice (Chapter 7: Ammonia Synthesis: Commercial Practice).* 1991, New York: Plenum Press.

39. Max Appl, *Ammonia, 3. Production Plants.* 2011.

40. Alexandre C. Dimian and Costin Sorin Bildea, *Chemical Process Design: Computer-Aided Case Studies*. 2008, Weinheim, Germany: WILEY-VCH Verlag GmbH & Co.

41. Sarah Jasper and Mahmoud El-Halwagi, *A Techno-Economic Comparison between Two Methanol-to-Propylene Processes.* Processes, 2015. **3**(3): p. 684-698.

42. T. Ren, M. Patel, and K. Blok, *Steam cracking and methane to olefins: Energy use, CO2 emissions and production costs.* Energy, 2008.

43. Daaniya Rahman, *Kinetic Modeling Of Methanol Synthesis From Carbon Monoxide, Carbon Dioxide, And Hydrogen Over A Cu/ZnO/Cr2O3 Catalyst*, in *Department of Chemical and Materials Engineering*. 2012, San José State University.

44. Jia-Lin Tao, Ki-Won Jun, and Kyu-Wan Lee, *Co-production of dimethyl ether and methanol from CO2 hydrogenation: development of astable hybrid catalyst.* APPLIED ORGANOMETALLIC CHEMISTRY, 2001. **15**: p. 105-108.

45. Mar Pérez-Fortes, Andrei Bocin-Dumitriu, and Evangelos Tzimas, *CO2 Utilization Pathways: Techno-Economic Assessment and Market Opportunities.* Energy Procedia, 2014. **63**: p. 7968-7975.

46. Michele Aresta, *Carbon dioxide as chemical feedstock*. 2010: John Wiley & Sons.

47. Esther M. Wilcox, George W. Roberts, and James J. Spivey, *Direct catalytic formation of acetic acid from CO2 and methane.* Catalysis Today, 2003. **88**(1-2): p. 83-90.

48. Yang Li, Chang-Jun Liu, Baldur Eliasson, and Yu Wang, *Synthesis of Oxygenates and Higher Hydrocarbons Directly from Methane and Carbon Dioxide Using Dielectric-Barrier Discharges: Product Distribution.* Energy & Fuels, 2002. **16**(4): p. 864-870.

49. S. Moret, P. J. Dyson, and G. Laurenczy, *Direct synthesis of formic acid from carbon dioxide by hydrogenation in acidic media.* Nat Commun, 2014. **5**: p. 4017.

50. Satish K. Kabra, Esa Turpeinen, Mika Huuhtanen, Riitta L. Keiski, and Ganapati D. Yadav, *Direct synthesis of formic acid from carbon dioxide and hydrogen: A thermodynamic and experimental study using poly-urea encapsulated catalysts.* Chemical Engineering Journal, 2016. **285**: p. 625-634.

51. Mar Pérez-Fortes, Jan C. Schöneberger, Aikaterini Boulamanti, Gillian Harrison, and Evangelos Tzimas, *Formic acid synthesis using CO2 as raw material: Techno-economic and environmental evaluation and market potential.* International Journal of Hydrogen Energy, 2016. **41**(37): p. 16444-16462.

52. Bhalchandra M Bhanage, *Transformation and utilization of carbon dioxide*. Springer.

53. J. Tamura, A. Ono, Y. Sugano, C. Huang, H. Nishizawa, and S. Mikoshiba, *Electrochemical reduction of CO2 to ethylene glycol on imidazolium ion-terminated self-assembly monolayer-modified Au electrodes in an aqueous solution.* Phys Chem Chem Phys, 2015. **17**(39): p. 26072-8.

54. F. Goettmann, A. Thomas, and M. Antonietti, *Metal-free activation of CO2 by mesoporous graphitic carbon nitride.* Angew Chem Int Ed Engl, 2007. **46**(15): p. 2717-20.

55. David C. Graham, Cassandra Mitchell, Michael I. Bruce, Gregory F. Metha, John H. Bowie, and Mark A. Buntine, *Production of Acrylic Acid through Nickel-Mediated Coupling of Ethylene and Carbon Dioxide—A DFT Study.* Organometallics, 2007. **26**(27): p. 6784-6792.

56. Y. Li, T. Yan, K. Junge, and M. Beller, *Catalytic methylation of C-H bonds using CO(2) and H(2).* Angew Chem Int Ed Engl, 2014. **53**(39): p. 10476-80.

APPENDIX 1: CO_2 CAPTURE ENERGY CALCULATIONS

The energy demand to capture 90% of the CO_2 from the flue gas estimated from [34] is below:

Description	Duty [= MJ/ton CO_2]
Power production penalty for solvent regeneration*	589.68
CO_2 compression work	299.38
Pumps, blower	226.80
Net power per ton CO_2	1,115.86

* the reboiler is integrated with the steam cycle, therefore the production penalty is given in units of power rather than units of heat.

For a power plant emitting 3,045,852 tons of CO_2 per year, the energy penalty is as follows:

$$total\ power = 1{,}115.86 \frac{MJ}{ton\ CO_2} \times 3{,}045{,}852\ \frac{tons\ CO_2}{year} = 3{,}398{,}732{,}229 \frac{MJ}{year}$$

$$= 107.8\ MW$$

APPENDIX 2: CO_2 CAPTURE COST CALCULATIONS

From the correlations given in [7]:

Variables:

$$F_{mass} = mass\ flow\ rate\ \left(\frac{tons}{year}\right)$$

$$F_{molar} = mole\ flow\ rate\ \left(\frac{mols}{s}\right)$$

$$= F_{mass} \times \frac{907{,}185\,\frac{g}{ton}}{44\,\frac{g}{mol}} \times 365\,\frac{days}{year} \times 24\,\frac{hr}{day} \times 3600\,\frac{s}{hr}$$

$$x = molar\ CO_2\ composition\ on\ a\ dry\ basis$$

Parameters:

$$CAPEX\text{:}\ \alpha = 7719, \beta = 67871, \gamma = 901.00, n = 0.660, m = 0.800$$

$$OPEX\text{:}\ \alpha = 0, \beta = 24088, \gamma = 0, n = 1.00, m = 1.00$$

Model:

$$CAPEX(\$/yr) = \alpha + \left(\beta x_{CO_2}^{n} + \gamma\right)(F_{molar})^{m}$$

$$OPEX(\$/yr) = \alpha + \left(\beta x_{CO_2}^{n} + \gamma\right)(F_{molar})^{m} + 10.22F_{mass}$$

$$total\ annualized\ cost = CAPEX + OPEX$$

For a power plant emitting 3,045,852 tons of CO_2 ($x_{CO_2} = 15\%$) per year, the costs are as follows:

$$F_{molar} = 3{,}045{,}852\,\frac{\text{tons}}{\text{year}} \times \frac{907{,}185\,\frac{g}{ton}}{44\ \frac{g}{mol}} \times 365\,\frac{days}{year} \times 24\,\frac{hr}{day} \times 3600\,\frac{s}{hr}$$

$$= 1991\,\frac{mols}{s}$$

$$CAPEX(\$/yr) = 7719 + \left((67871) \times (0.15)^{0.660} + 901.00\right)(1991)^{0.800} = 8.86\,\frac{10^6\$}{year}$$

$$OPEX(\$/yr) = 24088 \times 0.15 \times 1991 + 10.22 \times 3045852 = 38.32\,\frac{10^6\$}{year}$$

$$total\ annualized\ cost = 8.86 + 38.32 = 47.18\,\frac{10^6\ \$}{year}$$

$$total\ annualized\ cost = \frac{47.18\,\frac{10^6\ \$}{year}}{3{,}045{,}852\ \frac{tons\ CO_2}{year}} = 15.49\,\frac{\$}{ton\ CO_2}$$

APPENDIX 3: GAMS CODE

```
$OnEOLCom
$EOLCom //
$OnSymList
$OffOrder

* define the input file where the data is housed
$onecho > inputFile.txt
  "C:\Users\panumm\Dropbox\TAMU\Coursework\CHEN 691 - Research\My Work\GAMS\CHOSYN\data.xls"
$offecho


$ontext

General Comments:
  this formulation differs from that described in the thesis as some of the
    parameters are calculated in the GAMS file and binary parameters are used
    to impose conditional bounds on variables

instances:
  Interval(j,z) - used to impose heat exchange interval bounds. i.e.,the model
    describes: F*deltaH(change within the interval, i.e. Cp*dT) > HH/HC_new_proc > 0
    but the gams file says: if interval(j,z) = 1 then HH/HC_new_proc.up = F*deltaH, otherwise
    HH/HC_new_proc.up = 0. Similar calculations for HH/HC parameters have been applied

changes:
  HH/HC_new_proc.up = F*DeltaH*Interval
  remove parameter HH_available
  add parameters deltaH_old, F_used
    deltaH_old = deltaH * interval
    F_used.up = F_available
  in equation stage_balance: change HH_available -> F_used * deltaH_old
```

```
  added parameter AC_feed

$offtext

* ******************************************************************************
* ==============================================================================
* ========================= Mass exchange network design =======================
* ==============================================================================
* ******************************************************************************

$ontext

  this represents the CHOSYN implementation program presented by Noureldin:
    Noureldin, M. M. B. and M. M. El-Halwagi (2015). "Synthesis of C-H-O Symbiosis Networks." AIChE
Journal 61(4): 1242-1262.

  this program is modified from that presented by Noureldin by excluding the
    temperature, pressure and component ratio constraints

  the data in this case is taken from excel
    simple test case: C:\Users\panumm\Dropbox\TAMU\Coursework\CHEN 691 - Research\My
Work\GAMS\CHOSYN\testData.xls
    MS thesis data: C:\Users\panumm\Dropbox\TAMU\Coursework\CHEN 691 - Research\My
Work\GAMS\CHOSYN\data.xls

  make sure to check the z_in limits to account for impurities (i.e. N2)

  this model will take forever to solve depending on the tolerance

$offtext


* ==============================================================================
```

```
* ============== DECLARE AND DEFINE SETS, VARIABLES AND PARAMETERS =============
* ==============================================================================

*                     ======================================
*                                  declare sets
*                     ======================================
sets
  OLD            source streams (existing processes with known properites)
  NEW            sinks (new processes to be added to EIP)
  INT            interceptors (separators mixers splitters etc.)
  IN             inlet ports
  OUT            outlet ports
  U_IN(IN,INT)   interceptor inlet ports
  U_OUT(OUT,INT) interceptor outlet ports
  V_IN(IN,NEW)   sink inlet ports
  COM            components
;

$Onecho > indata.txt
  dset=OLD  rng=Sets!N2   rdim=1
  dset=NEW  rng=Sets!M2   rdim=1
  dset=INT  rng=Sets!O2   rdim=1
  dset=IN   rng=Sets!P2   rdim=1
  dset=OUT  rng=Sets!Q2   rdim=1
  dset=COM  rng=Sets!A2   rdim=1

  set=U_IN  rng=Ports!A2 rdim=1 cdim=1
  set=U_OUT rng=Ports!A9 rdim=1 cdim=1
  set=V_IN  rng=Ports!A16 rdim=1 cdim=1
$Offecho

$CALL GDXXRW i=@inputFile.txt o=indata.gdx trace=3 @indata.txt
$GDXIN indata.gdx
```

```
$LOAD OLD NEW INT IN OUT COM U_IN U_OUT V_IN
$GDXIN

display OLD, NEW, INT, IN, OUT, COM, U_IN, U_OUT, V_IN;

  alias(COM, COM_STAR);


*                      ======================================
*                           declare and define parameters
*                      ======================================
parameters
* sources
  Supply(OLD) total available mole flow rate from source i (100000 tons per year)
  x(COM,OLD) mass fraction of component c in source i
  C_source(OLD) cost (100000 $ per 100000 tons)
  CO2_Tax cost (100000 $ per 100000 tons) of CO2 emitted
  P_Sell selling price of each product (100000 $ per 100000 tons)
  max_CO2 maximum annual CO2 emissions (100000 tons per year) / 100 /

* interceptors
  W_in_min(IN,INT)   minimum inlet mole flow rate to interceptor INT (100000 tons per year)
  W_in_max(IN,INT)   maximum inlet mole flow rate to interceptor INT (100000 tons per year)

  y_in_min(COM,IN,INT)   minimum inlet composition to interceptor INT
  y_in_max(COM,IN,INT)   maximum inlet composition to interceptor INT

  C_interceptor(IN,INT) cost per kmol of interceptor INT

* sinks
  F_in_min(IN,NEW)   minimum inlet mole flow rate to sink j
  F_in_max(IN,NEW)   maximum inlet mole flow rate to sink NEW
```

```
  z_in_min(COM,IN,NEW)   minimum inlet composition to sink NEW
  z_in_max(COM,IN,NEW)   maximum inlet composition to sink NEW

  r_in_min(COM,COM_STAR,IN,NEW) minimum inlet ratio of component COM and COM_STAR
  r_in_max(COM,COM_STAR,IN,NEW) minimum inlet ratio of component COM and COM_STAR

  z_out(COM, NEW) outlet composition of the product stream leaving unit NEW
;

$Onecho > indata.txt
  par=Supply         rng=Parms2!A1    rdim=1
  par=x              rng=Parms2!D1    rdim=2
  par=C_source       rng=Parms2!H1    rdim=1
  par=CO2_Tax        rng=Parms2!BG2   rdim=0
  par=P_Sell         rng=Parms2!BI2   rdim=1

  par=W_in_min       rng=Parms2!K1    rdim=2
  par=W_in_max       rng=Parms2!O1    rdim=2
  par=y_in_min       rng=Parms2!S1    rdim=3
  par=y_in_max       rng=Parms2!X1    rdim=3
  par=C_interceptor  rng=Parms2!BP2   rdim=2

  par=F_in_min       rng=Parms2!AC1   rdim=2
  par=F_in_max       rng=Parms2!AG1   rdim=2
  par=z_in_min       rng=Parms2!AK1   rdim=3
  par=z_in_max       rng=Parms2!AP1   rdim=3
  par=z_out          rng=Parms2!BL1   rdim=2
  par=r_in_min       rng=Parms2!AU1   rdim=4
  par=r_in_max       rng=Parms2!BA1   rdim=4
$Offecho

$CALL GDXXRW i=@inputFile.txt o=indata.gdx trace=3 @indata.txt
$GDXIN indata.gdx
```

```
$LOAD Supply x C_source CO2_Tax P_Sell
$LOAD W_in_min W_in_max y_in_min y_in_max C_interceptor
$LOAD F_in_min F_in_max z_in_min z_in_max z_out r_in_min r_in_max
$GDXIN

display y_in_max;

* default values in case something is unspecified
* including the zeros so that I don't get the error of symbols not being initialized
  W_in_min(U_IN)$(W_in_min(U_IN)=0) = 0;
  W_in_max(U_IN)$(W_in_max(U_IN)=0) = 1000;

  y_in_min(COM,U_IN)$(y_in_min(COM,U_IN)=0) = 0;
  y_in_max(COM,U_IN)$(y_in_max(COM,U_IN)=0) = 1;

* set up CO2 separation unit constraints
  y_in_max(COM,"1","CO2SeparationMEA") = 0;
  y_in_max("CO2","1","CO2SeparationMEA") = 0.2;
  y_in_max("N2","1","CO2SeparationMEA") = 0.9;

  C_interceptor(IN,INT)$(C_interceptor(IN,INT)=0) = 0;

  F_in_min(V_IN)$(F_in_min(V_IN)=0) = 0;
  F_in_max(V_IN)$(F_in_max(V_IN)=0) = 1000;

  z_in_min(COM,V_IN)$(z_in_min(COM,V_IN)=0) = 0;
  z_in_max(COM,V_IN)$(z_in_max(COM,V_IN)=0) = 0;
  z_in_max(COM,IN,"waste") = 1;

* allow for impurities into the sink
*  z_in_max("N2",V_IN) = 0.1;

display Supply, x, C_source, CO2_Tax, P_Sell
```

```
        W_in_min, W_in_max, y_in_min, y_in_max, C_interceptor
        F_in_min, F_in_max, z_in_min, z_in_max, z_out, r_in_min, r_in_max

*                     ======================================
*                                declare variables
*                     ======================================
positive variables
* sources
  G_used(OLD)   mole flow rate from source i used in EIP
  G_waste(OLD)  mole flow rate from source i discharged from EIP
  G_in(OLD,IN,INT)   mole flow rate from source i to interceptor INT

* interceptors
  W_in(IN,INT)   inlet mole flow rate to interceptor INT
  y_in(COM,IN,INT) mass fraction of component c enterting interceptor INT

  W_out(OUT,INT)   outlet mole flow rate from interceptor INT
  y_out(COM,OUT,INT) mass fraction of component c leaving interceptor INT

  F(OUT,INT,IN,NEW) total mole flow rate from interceptor INT to sink NEW

* sinks
  F_in(IN,NEW)   inlet mole flow rate to sink NEW
  z_in(COM,IN,NEW) mass fraction of component c enterting sink NEW
  F_out(NEW)   outlet mole flow rate to sink NEW
;

*                     ======================================
*                          apply domain bounds to variables
*                     ======================================

* only domain of viable ports should be eligible for optimization
* first set all bounds to 0
```

```
  G_in.fx(OLD,IN,INT) = 0;
  W_in.fx(IN,INT) = 0;
  y_in.fx(COM,IN,INT) = 0;
  W_out.fx(OUT,INT) = 0;
  y_out.fx(COM,OUT,INT) = 0;

  F.fx(OUT,INT,IN,NEW) = 0;
  F_in.fx(IN,NEW) = 0;
  z_in.fx(COM,IN,NEW) = 0;

* remove upper bounds if port exists
  W_out.up(U_OUT) = inf;
  F.up(OUT,INT,V_IN) = inf;

* logical constraints: if the min/max is specified, the variable must fall within those constraints
* sources
  G_waste.up(OLD) = Supply(OLD);
  G_used.up(OLD) = Supply(OLD);
  G_in.up(OLD,U_IN) = Supply(OLD);

*interceptors
  W_in.up(U_IN)$(W_in_max(U_IN)>0) = W_in_max(U_IN);
  W_in.lo(U_IN)$(W_in_min(U_IN)>0) = W_in_min(U_IN);
  y_in.up(COM,U_IN)$(y_in_max(COM,U_IN)>0) = y_in_max(COM,U_IN);
  y_in.lo(COM,U_IN)$(y_in_min(COM,U_IN)>0) = y_in_min(COM,U_IN);
  y_out.up(COM,U_OUT) = 1;

* sinks
  F_in.up(V_IN)$(F_in_max(V_IN)>0) = F_in_max(V_IN); // F_in lower bound is activated by binary
constratint
  z_in.up(COM,V_IN)$(z_in_max(COM,V_IN)>0) = z_in_max(COM,V_IN);
  z_in.up("N2",V_IN) = 1;
  z_in.lo(COM,V_IN)$(z_in_min(COM,V_IN)>0) = z_in_min(COM,V_IN);
```

```
display G_in.up, G_in.lo, G_used.up, G_used.lo, G_waste.up, G_waste.lo
        W_in.up, W_in.lo, y_in.up, y_in.lo
        W_out.up, W_out.lo, y_out.up, y_out.lo
        F.up, F.lo, F_in.up, F_in.lo, z_in.up, z_in.lo;

binary variables
  z_new_proc(IN,NEW) binary variable indicating which process has been selected
;

free variables
  delta_CO2 net CO2 sequestration or emission
  profit total annualized profit
;

* ==============================================================================
* ============================== DEFINE EQUATIONS ==============================
* ==============================================================================

*                     ======================================
*                               declare equations
*                     ======================================

equations
  source_splitting, source_used, source_waste

  interceptor_inlet_total, interceptor_inlet_component, interceptor_outlet_total

  interceptor_mass_balance, interceptor_component_balance //this will not hold true if there is a
chemical reaction
  CO2_Separator_fractional_recovery

  sink_inlet_total, sink_inlet_component, sink_composition
```

```
  sink_inlet_min, sink_inlet_max
*, sink_selection
  sink_r_in_max, sink_r_in_min

  sink_mass_balance

  objective, net_CO2_emissions, max_CO2_emissions
;

*                     ======================================
*                                     sources
*                     ======================================
* logical constraints
  source_waste(OLD).. G_used(OLD) + G_waste(OLD) =e= Supply(OLD);
  source_used(OLD).. G_used(OLD) =l= Supply(OLD);

* input output balance around source streams
*                         inlet           outlet
*                         ---------       ------------------------
  source_splitting(OLD).. G_used(OLD) =e= sum( U_IN , G_in(OLD,U_IN));
*G_in.fx("PowerPlant_CO2","1","CO2SeparationMEA") = 1;
*G_in.fx("Fresh_H2","1","bypass1") = 1;

*                     ======================================
*                       general interceptor mass balances
*                     ======================================
* input output balance around interceptor ports
*                                           input                                     output
*                                           ----------------------------              ---------------
--------------
  interceptor_inlet_total(U_IN)..           sum(OLD, G_in(OLD,U_IN))              =e= W_in(U_IN);
  interceptor_inlet_component(COM,U_IN)..   sum(OLD, G_in(OLD,U_IN) * x(COM,OLD)) =e= W_in(U_IN) *
y_in(COM,U_IN);
```

```
  interceptor_outlet_total(U_OUT)..         W_out(U_OUT)                          =e= sum(V_IN,
F(U_OUT,V_IN));

*                     ======================================
*                           interceptor unit modeling
*                     ======================================
* W_in and W_out, y_in, y_out, etc related through unit modeling equations
* overall input output balance around interceptors
*                                           input                                        output
*                                           ----------------------------                 ------------
-----------------
  interceptor_mass_balance(INT)..           sum(IN, W_in(IN,INT))                    =e= sum(OUT,
W_out(OUT,INT));
  interceptor_component_balance(COM,INT)..  sum(IN, W_in(IN,INT) * y_in(COM,IN,INT)) =e= sum(OUT,
W_out(OUT,INT) * y_out(COM,OUT,INT)) ;

* unit specific constraints
* outlet stream is 99% CO2, 1% impurity (N2)

   y_out.fx(COM,"1","CO2SeparationMEA") = 0;
   y_out.fx("CO2","1","CO2SeparationMEA") = 0.99;
   y_out.fx("N2","1","CO2SeparationMEA") = 0.01;

   y_out.fx(COM,"2","CO2SeparationMEA") = 0;
   y_out.up("CO2","2","CO2SeparationMEA") = 1;
   y_out.up("N2","2","CO2SeparationMEA") = 1;

* 95% of the CO2 is recovered in the product stream
   CO2_Separator_fractional_recovery.. W_in("1","CO2SeparationMEA") *
y_in("CO2","1","CO2SeparationMEA") * 0.95 =e= W_out("1","CO2SeparationMEA") *
y_out("CO2","1","CO2SeparationMEA");

*                     ======================================
```

```
*                            general sink mass balances
*                      ======================================
  sink_inlet_total(IN,NEW).. F_in(IN,NEW) =e= sum((OUT,INT), F(OUT,INT,IN,NEW));
  sink_inlet_component(COM,V_IN).. F_in(V_IN) * z_in(COM,V_IN) =e= sum(U_OUT, F(U_OUT,V_IN) *
y_out(COM,U_OUT));
  sink_composition(V_IN).. sum(COM, z_in(COM,V_IN)) =e= 1;

  sink_r_in_max(COM,COM_STAR,V_IN)$(abs(r_in_max(COM,COM_STAR,V_IN)) > 0).. z_in(COM,V_IN) =l=
r_in_max(COM,COM_STAR,V_IN) * z_in(COM_STAR,V_IN);
  sink_r_in_min(COM,COM_STAR,V_IN)$(abs(r_in_min(COM,COM_STAR,V_IN)) > 0).. z_in(COM,V_IN) =g=
r_in_min(COM,COM_STAR,V_IN) * z_in(COM_STAR,V_IN);

  sink_inlet_min(V_IN).. F_in(V_IN) =g= z_new_proc(V_IN) * F_in_min(V_IN);
  sink_inlet_max(V_IN).. F_in(V_IN) =l= z_new_proc(V_IN) * F_in_max(V_IN);

*  sink_selection.. sum(V_IN, z_new_proc(V_IN)) =g= 3;
*  z_new_proc.fx("1","Methanol") = 1;

*                      ======================================
*                                sink unit modeling
*                      ======================================
* F_in, F_out, z_in, z_out, etc related through unit modeling equations
  sink_mass_balance(NEW).. sum(IN, F_in(IN,NEW)) =e= F_out(NEW);




* ***************************************************************************
* ===========================================================================
* ========================= Heat exchange network design ======================
* ===========================================================================
* ***************************************************************************
```

```
$Ontext

  this  model is based on the transshipment model proposed in 1983 by Papoulias
    Grossmann:
        Papoulias, S. A. and I. E. Grossmann (1983). "A structural optimization approach
        in process synthesis—II." Computers & Chemical Engineering 7(6): 707-721.

  this model minimizes the cost of the HEN. Since the constraints are written to
    satisfy the energy needs of the new processes, the optimum solution is zero
    (the solution when all new processes selected to be zero). Therefore, in order
    to get a solution, you have to fix at least one new process to have a flow
    rate (i.e. z_new_proc.fx(NEW_PROCESS) = 1; )

  changes:
    F -> F_available
    HH/HC -> HH_available/HC_available

$Offtext

* ==============================================================================
* ============== DECLARE AND DEFINE SETS, VARIABLES AND PARAMETERS =============
* ==============================================================================

*                     ======================================
*                                  declare sets
*                     ======================================
set
  j all process streams

  HP(j) hot streams to be cooled
  CP(j) cold streams to be heated
  HN(j)  New process hot streams
```

```
  CN(j)  New process cold streams

  z heat exchange interval (starting from 0) | ord(k)>=2 corresponds to z >=1
;

$Onecho > indata.txt
  dset=j   rng=Sets!f2      rdim=1

  dset=HP  rng=Sets!g2      rdim=1
  dset=CP  rng=Sets!h2      rdim=1
  dset=HN  rng=Sets!i2      rdim=1
  dset=CN  rng=Sets!j2      rdim=1

  dset=z   rng=Sets!s2      rdim=1
$Offecho

$CALL GDXXRW i=@inputFile.txt o=indata.gdx trace=3 @indata.txt
$GDXIN indata.gdx
$LOAD j HP CP HN CN z
$GDXIN

display j, HP, CP, HN, CN, z;


*                     ======================================
*                               declare parameters
*                     ======================================

Parameters
  T_supply(j) supply temperature of stream j
  T_hot(z)  hot scale temperature leaving interval z
  T_cold(z) cold scale temperature leaving interval z
```

```
  Interval(j,z) binary parameter defining which interval(s) j belongs to

  AC_feed(OLD) associated carbon dioxide - stoichiometric by-product from reaction to generate COM
(mol CO2 mol f^-1)

  deltaH(j) specific enthalpy of stream j (MMBtu per ton)
  deltaH_OLD(j,z) specific enthalpy of stream j (MMBtu per ton)
  deltaH_NEW(j,NEW) specific enthalpy of stream j (MMBtu per ton)
  deltaT_min / 100 /

$ontext
changes:
  HH/HC_new_proc.up = F*DeltaH*Interval
  remove parameters HH/HC_available
  add parameters deltaH_OLD
    deltaH_old = deltaH * interval
  add variable F_used(OLD)
    F_used.up = F_available
  in equation stage_balance: change HH_available -> F_used * deltaH_old
$offtext

  F_available(j) available quantity (100000 tons per year) of stream j

  z_stream(j,NEW) parameter indicating if stream j belongs to process k
  C_HU "$ per MMBtu" / 3 /
  C_CU "$ per MMBtu" / 0.5 /
  phi natural gas emissions factor (ton CO2 per MMBtu) / 0.0585 /

  N_max_new_proc / 3 /
;

$Onecho > indata.txt
  par=T_supply     rng=Parms!e2    rdim=1
```

```
  par=AC_feed      rng=parms!ag2   rdim=1
  par=deltaH       rng=Parms!c2    rdim=1
  par=F_available  rng=Parms!a2    rdim=1
  par=T_hot        rng=Parms!h2    rdim=1
  par=z_stream     rng=Parms!p2    rdim=2
$Offecho

$CALL GDXXRW i=@inputFile.txt o=indata.gdx trace=3 @indata.txt
$GDXIN indata.gdx
$LOAD T_supply AC_feed deltaH F_available T_hot z_stream
$GDXIN

*                     ======================================
*                              calculate parameters
*                     ======================================

  T_cold(z)$(T_hot(z) > 0) = T_hot(z) - deltaT_min;

  Interval(HP,z)$(T_supply(HP) = T_hot(z) and T_supply(HP) > 0) = 1;
  Interval(CP,z)$(T_supply(CP) = T_cold(z) and T_supply(CP) > 0) = 1;
  Interval(HN,z)$(T_supply(HN) = T_hot(z) and T_supply(HN) > 0) = 1;
  Interval(CN,z)$(T_supply(CN) = T_cold(z) and T_supply(CN) > 0) = 1;

*  HH_available(HP,z) = F_available(HP) * deltaH(HP) * Interval(HP,z);
*  HC_available(CP,z) = F_available(CP) * deltaH(CP) * Interval(CP,z);

  deltaH_NEW(j,NEW) = deltaH(j) * z_stream(j,NEW);

  deltaH_OLD(j,z) = deltaH(j) * Interval(j,z);

* display T_supply, T_hot, T_cold, F, deltaH, Interval, HH_available, HC_available
display T_supply, AC_feed, T_hot, T_cold, deltaH_NEW, C_HU, C_CU
```

```
*                      =======================================
*                                declare variables
*                      =======================================
positive variables
  F_used(j) how much of steam j (HP and CP) is used in the HEN
  HH_new_proc(j,z) exchangeable load (how much heat it can give up) of stream j in interval z (100000
MMBtu)
  HC_new_proc(j,z) exchangeable load (how much heat it can accept) of stream j in interval z (100000
MMBtu)
  HHU              exchangeable load (how much heat it can give up) of hot utility (100000 MMBtu)
  HCU              exchangeable load (how much heat it can accept) of cold utility (100000 MMBtu)
;

* if Interval(HN/CN, z) = 1, then upper bound = F*deltaH, else upper bound = 0
  HH_new_proc.up(HN,z) = sum(NEW, F_in_max("1",NEW) * deltaH_NEW(HN,NEW) * Interval(HN,z));
  HC_new_proc.up(CN,z) = sum(NEW, F_in_max("1",NEW) * deltaH_NEW(CN,NEW) * Interval(CN,z));

* can only use up to the available quantity of stream j
  F_used.up(j) = F_available(j);

display HH_new_proc.up, HC_new_proc.up, F_used.up

free variables
  r(z) residual enthalpy leaving each interval
  C_utilities total cost of utilities
;



* ===============================================================================
* ============================== DEFINE EQUATIONS ===============================
* ===============================================================================
```

```
*                     ======================================
*                               declare equations
*                     ======================================

equations
  exchangeable_hot_load, exchangeable_cold_load
  stage_energy_balance, first_stage_residual, last_stage_residual
  max_new_proc
;

  exchangeable_hot_load(HN,z)$(Interval(HN,z)=1)..  HH_new_proc(HN,z) =e= sum(NEW, F_in("1",NEW) *
deltaH_NEW(HN,NEW) );
  exchangeable_cold_load(CN,z)$(Interval(CN,z)=1).. HC_new_proc(CN,z) =e= sum(NEW, F_in("1",NEW) *
deltaH_NEW(CN,NEW) );

  stage_energy_balance(z)$(ord(z)>=2).. r(z-1) + sum(HP, F_used(HP) * deltaH_OLD(HP,z)) + sum(HN,
HH_new_proc(HN,z)) =e=
                                        r(z) + sum(CP, F_used(CP) * deltaH_OLD(CP,z)) + sum(CN,
HC_new_proc(CN,z));

  first_stage_residual(z)$(ord(z) = 1)..      r(z) =e= HHU;
  last_stage_residual(z)$(ord(z) = card(z)).. r(z) =e= HCU;

  max_new_proc.. sum(NEW, z_new_proc("1",NEW)) =l= N_max_new_proc;

*                     ======================================
*                         heat + mass objective function
*                     ======================================
  objective.. profit =e= sum( (COM,NEW), F_out(NEW) * z_out(COM,NEW) * P_sell(COM))       // revenue
from sales
                       - sum(OLD, G_used(OLD) * C_source(OLD) )                           // material
costs
```

```
                       - sum( (IN,INT), W_in(IN,INT) * C_interceptor(IN,INT) )            //
interceptor costs
                       - HHU * C_HU - HCU * C_CU                                          //
utilities costs
;
*                       - sum(OLD, G_waste(OLD) * x("CO2",OLD)) * CO2_Tax                  // unused
CO2 cost
*                       - sum(U_OUT, F(U_OUT,"1","waste") * y_out("CO2",U_OUT)) * CO2_Tax  // unused
CO2 cost
   profit.lo = -30000;
   profit.up =  30000;

  net_CO2_emissions.. delta_CO2 =e= F_in("1","waste") * z_in("CO2","1","waste")  // waste CO2
                                  + sum(OLD, G_used(OLD) * AC_feed(OLD) )         // CO2 from
feedstocks
                                  + HHU * phi                                     // CO2 from heating
utilities
                                  - sum(OLD, G_used(OLD) * x("CO2",OLD) );       // CO2 fed to
processes

  delta_CO2.up = 20; delta_CO2.lo = -20;

  max_CO2_emissions.. delta_CO2 =l= max_CO2;

* ******************************************************************************
* ==============================================================================
* =============================== SOLVE THE MODEL ==============================
* ==============================================================================
* ******************************************************************************

model CHOSYN / all /;
option minlp=baron
       limrow = 330
```

```
       limcol = 330
       reslim = 1000;

set
  runs /1*11/;

Parameter
  Report(runs,*)
  SelectedProcesses(runs,IN,NEW)
  UsedProcessHeat(runs,j)
  UsedMaterial(runs,OLD)
  MaxCO2Cut, minEmissions, maxEmissions
;

* solve first to determine maximum CO2 utilizatoin
solve CHOSYN min delta_CO2 using minlp;
  minEmissions = delta_CO2.l;
  Report("11","Model Status") = CHOSYN.ModelStat;
         if(Report("11","Model Status") = 1 or Report("11","Model Status") = 8,

                  Report("11","Product Sales")     = sum( (COM,NEW), F_out.l(NEW) * z_out(COM,NEW) *
P_sell(COM));
                  Report("11","Reactant Costs")    = sum(OLD, G_used.l(OLD) * C_source(OLD) );
                  Report("11","Interceptor Costs") = sum( (IN,INT), W_in.l(IN,INT) *
C_interceptor(IN,INT) );
                  Report("11","Utility Costs")     = HHU.l * C_HU - HCU.l * C_CU;

                  Report("11","Net Profit") = profit.l;

                  Report("11","Utilized CO2")        = sum(OLD, G_used.l(OLD) * x("CO2",OLD) );
                  Report("11","Waste CO2")           = F_in.l("1","waste") *
z_in.l("CO2","1","waste");
*                  Report("11","CO2 from Feedstocks") = sum(OLD, G_used.l(OLD) * AC_feed(OLD) );
```

```
                  Report("11","CO2 from Utilities")  = HHU.l * phi;

                  Report("11","Max Emissions") = max_CO2;
                  Report("11","Net Emissions") = delta_CO2.l;

                  SelectedProcesses("11","1",NEW) = F_in.l("1",NEW);
                  UsedProcessHeat("11",j) = F_used.l(j);
                  UsedMaterial("11",OLD) = G_used.l(OLD);
           )

* solve next to determine maximum profit
solve CHOSYN max profit using minlp;
  maxEmissions = delta_CO2.l;
  Report("1","Model Status") = CHOSYN.ModelStat;

         if(Report("1","Model Status") = 1 or Report("1","Model Status") = 8,

                  Report("1","Product Sales")     = sum( (COM,NEW), F_out.l(NEW) * z_out(COM,NEW) *
P_sell(COM));
                  Report("1","Reactant Costs")    = sum(OLD, G_used.l(OLD) * C_source(OLD) );
                  Report("1","Interceptor Costs") = sum( (IN,INT), W_in.l(IN,INT) *
C_interceptor(IN,INT) );
                  Report("1","Utility Costs")     = HHU.l * C_HU - HCU.l * C_CU;

                  Report("1","Net Profit") = profit.l;

                  Report("1","Utilized CO2")        = sum(OLD, G_used.l(OLD) * x("CO2",OLD) );
                  Report("1","Waste CO2")           = F_in.l("1","waste") * z_in.l("CO2","1","waste");
*                  Report("1","CO2 from Feedstocks") = sum(OLD, G_used.l(OLD) * AC_feed(OLD) );
                  Report("1","CO2 from Utilities")  = HHU.l * phi;

                  Report("1","Max Emissions") = max_CO2;
                  Report("1","Net Emissions") = delta_CO2.l;
```

```
                  SelectedProcesses("1","1",NEW) = F_in.l("1",NEW);
                  UsedProcessHeat("1",j) = F_used.l(j);
                  UsedMaterial("1",OLD) = G_used.l(OLD);
           )
;

* determine the cut factor to reduce the maximum allowable CO2 emissions
  MaxCO2Cut = (maxEmissions - minEmissions)/10;
  max_CO2 = maxEmissions;

* loop through values of max CO2
loop(runs$(ord(runs) > 1 and ord(runs) < 11),

         max_CO2 = max_CO2 - MaxCO2Cut;

         solve CHOSYN max profit using minlp;

         Report(runs,"Model Status") = CHOSYN.ModelStat;

         if(Report(runs,"Model Status") = 1 or Report(runs,"Model Status") = 8,

                  Report(runs,"Product Sales")     = sum( (COM,NEW), F_out.l(NEW) * z_out(COM,NEW) *
P_sell(COM));
                  Report(runs,"Reactant Costs")    = sum(OLD, G_used.l(OLD) * C_source(OLD) );
                  Report(runs,"Interceptor Costs") = sum( (IN,INT), W_in.l(IN,INT) *
C_interceptor(IN,INT) );
                  Report(runs,"Utility Costs")     = HHU.l * C_HU - HCU.l * C_CU;

                  Report(runs,"Net Profit") = profit.l;

                  Report(runs,"Utilized CO2")        = sum(OLD, G_used.l(OLD) * x("CO2",OLD) );
```

```
                  Report(runs,"Waste CO2")           = F_in.l("1","waste") *
z_in.l("CO2","1","waste");
*                  Report(runs,"CO2 from Feedstocks") = sum(OLD, G_used.l(OLD) * AC_feed(OLD) );
                  Report(runs,"CO2 from Utilities")  = HHU.l * phi;

                  // the value for CO2 recycled to processes doesn't show up in the objective
function as it is accounted for in the fact that this CO2
                  // does not make it into CO2 waste (ie. CO2 waste = CO2 out - CO2 internal) so CO2
internal is not directly factored into the net emissions

                  Report(runs,"Max Emissions") = max_CO2;
                  Report(runs,"Net Emissions") = delta_CO2.l;

                  SelectedProcesses(runs,"1",NEW) = F_in.l("1",NEW);
                  UsedProcessHeat(runs,j) = F_used.l(j);
                  UsedMaterial(runs,OLD) = G_used.l(OLD);
           )
     )

display Report,SelectedProcesses,UsedProcessHeat,UsedMaterial;
```