SYSTEMATIC DESIGN OF NATURAL GAS AND CO_2 UTILIZATION NETWORKS IN INDUSTRIAL CLUSTER

An Undergraduate Research Scholars Thesis

by

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ABSTRACT

Systematic Design of Natural Gas and CO_2 Utilization Networks in Industrial Cluster

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In the past decades, carbon dioxide (CO_2) emissions have been increasing alongside their negative effects on the environment. The most notable harm is the increase in global average surface temperatures. Governmental efforts, such as the Kyoto Protocol and the Paris Agreement, have been regulated, since 1997, to aid in the reduction of emissions. Carbon emissions can be reduced in several ways, including renewables and Carbon Capture, Utilization, and Storage (CCUS). CCUS is a sustainable and cost-effective way to reduce emissions from highly polluting industries such as cement, steel, and the chemical processing sector. Capturing and treating CO_2 emissions is a crucial step in carbon integration in which CO_2 is captured and used as a feedstock with natural gas to produce many hydrocarbon-based products such as methanol, ammonia, and hydrogen production. In this paper, a systematic approach on how to allocate and monetize natural gas networks sustainably will be explored. The allocation will be

done on an operational basis using a multi-integer nonlinear program to reduce CO_2 emissions from industrial clusters to mitigate climate change. Furthermore, carbon capture utilization including emerging technologies, such as the electrochemical carbon dioxide reduction, will be further investigated as methods to reduce carbon dioxide emissions. Renewable energy sources, such as solar energy, have been widely considered as the next step towards a decarbonized world. As a result, this paper will also explore the effect of integrating part of the power grid with renewable energy sources to reduce the emissions from natural gas fired power plants. Multi-period analysis will also be implemented to explore strategies to reduce CO_2 emissions from the cluster.

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1. INTRODUCTION

Global warming poses a serious concern due to the increase in the greenhouse effect. The greenhouse effect occurs when greenhouse gases, such as carbon dioxide and methane, absorb infrared radiation and reradiate it back to earth, which increases the overall global average surface temperature.[1] The industrial sector is to blame for the increase in these emissions as carbon dioxide is a major byproduct of many processes including the combustion of fossil fuels.[2] In order to reduce carbon dioxide emissions in the atmosphere, renewable sources such as solar, wind, and hydro energy can be used instead of combusting fossil fuels to generate electricity.[3] In addition, industries are transitioning into using natural gas instead of other conventional fossil fuels. Natural gas is an emerging fossil fuel due its low carbon dioxide footprint (0.2 kg CO_2/kWh)[4] compared to oil (0.25 kg CO_2/kWh) and bituminous coal (0.32 kg CO_2/kWh)[5]. Many processes and plants are dependent on natural gas as a feedstock and/or fuel. With significant technological advancements in hydraulic fracking, countries with significant reserves of shale gas, such as China, Argentina, and the United states, can now economically boost their production of shale gas. With an increase in natural gas processing, it can serve as a transition fuel towards a low carbon emission future. Qatar has the third largest proven natural gas reserve after Russia and Iran with its economy being highly dependent on it.[6] In Qatar, most plants depend on natural gas that is processed into several value-added products such as methanol, urea, ammonia, Gas-To-Liquid (GTL), Liquified Natural Gas (LNG), etc. The hydrocarbon derived products account for 91% of the country's export earnings.[7] Governments have been trying to mitigate emissions using multiple tools from policy making to the deployment of emerging new technology, such as Carbon Capture, Utilization, and Sequestration (CCUS). Despite these contributions, the carbon levels kept on growing, "In 1980, emissions were 330 million tons and grew to 360 million tons in 2014".[8] Carbon dioxide can be reduced in two ways: conversion and non-conversion methods. Carbon dioxide from fossil fuel, biomass, air, etc. would go through a conversion method to form fuels, chemicals, and materials such as cement and concrete.[9] Carbon dioxide can go through a non-conversion method where it gets used in yield boosting such as in greenhouses, as a solvent, heat transfer fluid, and many other uses such as in food and beverages.[9] For this reason, our research is aimed at reducing emissions for natural gas by using mass integration and carbon dioxide utilization. The outcomes of this model will help policymakers build new plants that will be resilient to possible future changes such as climate change.

This research distinguishes itself from previous work by focusing on multi-period analysis and carbon integration that previous research did not consider before. In the literature[10,11], certain papers discussed monetizing natural gas to GTL and LNG using small mobile plants built mostly for stranded gas. The work did not consider integration nor carbon dioxide reduction and does not account for price changes. Another report[12] investigated building natural gas networks in multiperiod form to see what the optimal network is to build with keeping the terrain in mind but multiperiod here only concerns building the pipeline infrastructure. On the other hand, another paper[13] analyzed multiperiod CO_2 emissions in building power plants. There are reports that looked into multiperiod power generation for the UAE with cost minimization and whether to increase imports of electricity.[14] These works only provide a partial picture of the system. More recently, a paper [15] focused on minimizing the cost of purchasing natural gas and CO_2 storage. Their crucial decision variable is the nomination value of natural gas. They use a term called "Industrial Gas" that is produced from natural gas. Their multiperiod component is to forecast demand from different customers and plant nodes without specifying what the plant nodes are and what the customers want.

The previous work analyzes parts of the problem – allocating natural gas or carbon reduction. The multiperiod models try to predict scenarios but lack evaluation of climate targets and the role of new technology. This work will address both of those aspects. One technology we aim to assess is electrochemical carbon dioxide reduction. This method would use an electrolysis cell to convert carbon dioxide to value-added products with electricity as a form of energy.[16] Carbon dioxide would first get captured; then, it enters the electrolyzer and leaves as a product that does not contain carbon dioxide.[16] Some products that can be made using this process include formaldehyde, methane, methanol, and ethylene. This technology is currently under development and is at the lab stage. A review was done and it found that the technology will reach the pilot level in ten years.[17] Using our method, we hope to explore this element to evaluate emerging technology potential in carbon dioxide reduction while continuing to utilize natural gas. This research focuses on predicting future outcomes (emissions, profit, production capacities, etc.) on a multi-period basis through building a multi-integer nonlinear program. This method aims to sustainably monetize natural gas while reducing CO_2 emissions using various emerging technologies. The model being developed is a merged version of the model proposed by Al-Mohannadi and Linke.[18–20]

2. METHODS

2.1 Approach description

Given an available industrial cluster, with an existing infrastructure to distribute methane, ethane, and power. The methane and ethane provided are already separated and are of pure quality ready to be processed into value added products. Such processes include but are not limited to: Methanol Synthesis, Natural Gas Liquidation, Ethane Cracking, etc. The industrial cluster is also equipped with gas fired power plants and available land to install renewable energy sources, such as solar energy. The main goal is to find the cost optimal network that also reduces the overall CO_2 emitted from the cluster. The plants will act as a sink for natural gas and are sources of chemical products (commodities) and CO_2. The commodities can either be sold outside of the cluster or transferred to another plant for further processing. As for the CO_2, it either be emitted into the atmosphere or allocated into a CO_2 sink. Certain CO_2 sources will need further treatment before being allocated into a CO_2 sink. Therefore, CO_2 treatment units, such as amine absorption, might be installed if needed. An illustrative industrial cluster is shown below in **Error! Reference source not found.**2.1 alongside a multi-period illustration in Figure 2.2

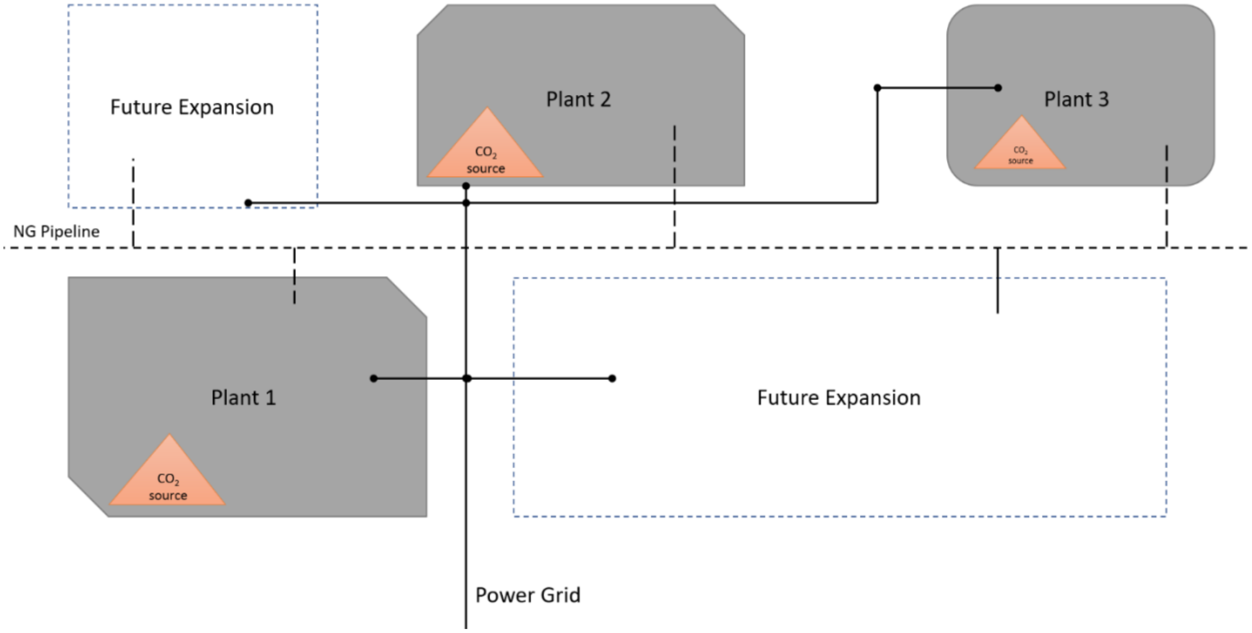

Figure 2.1*: Illustrative industrial cluster in a single period*

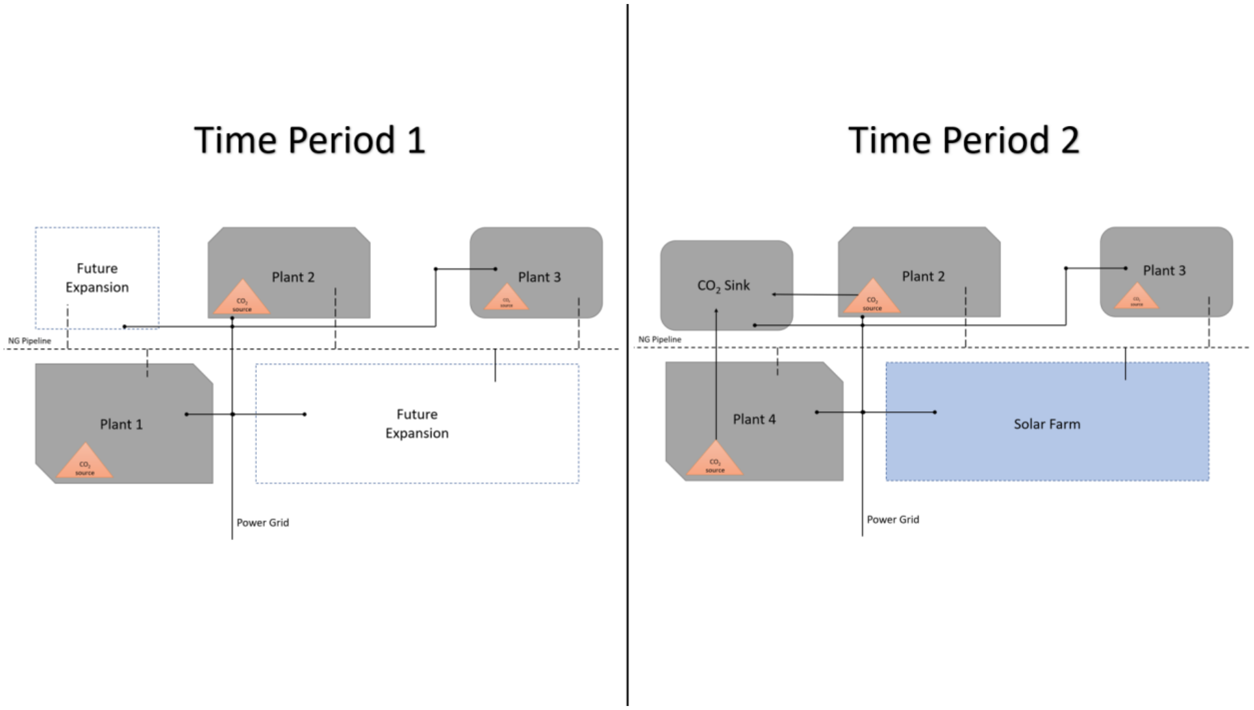

Figure 2.2*: Illustrative figure of an industrial cluster in a multi-period analysis*

2.2 Model Description

The following sets will be used:

C{c|c=1, 2, 3,…,$N_{commodities}$| C is a set of commodities}

T{t|t=1, 2, 3,…,T_{max}| T is a set of time periods}

P{p|p=1, 2, 3,…,P_{plants}| P is a set of chemical plants}

K{k|k=1, 2, 3,…,N_{sinks}| K is a set of carbon sinks}

2.2.1 Plant Module

The product flow from the plant is given as:

$$L^{c}{}_{t,p} \leq F^{c}{}_{t,p} \leq M^{c}{}_{t,p} \tag{2.1}$$

In Equation (2.1), ${F_{t,p}}^{c}$ corresponds to the flow of product c from plant p between a specified lower and upper bound, which are $L^{c}{}_{t,p}$ and $M^{c}{}_{t,p}$, respectively in a given time period.

For methane allocation, the methane intake to a plant to produce a certain commodity is shown below

$$F_{M,p,t} = \Sigma F^{c}{}_{t,p} \varphi^{c}{}_{p,M} \tag{2.2}$$

where $\varphi^{c}{}_{p,M}$ is a parameter, which corresponds to the methane that is required per product c in plant p.

$$\sum F_{M,p,t} = F_{M,t} \qquad 2.3)$$

In Equation 2.3), $F_{M,t}$ is the total amount of methane entering the industrial cluster in time period t.

$$L_{M,t} \leq F_{M,t} \leq M_{M,t} \tag{2.4}$$

In Equation (2.4), $L_{M,t}$ and $M_{M,t}$ are the specified lower and upper bound of methane entering the industrial cluster in time period t, respectively.

For ethane allocation, the ethane intake to a plant to produce a product is shown below

$$F_{E,p,t} = \Sigma F^{c}{}_{t,p} \varphi^{c}{}_{p,E} \tag{2.5}$$

where $\varphi^{c}{}_{p,E}$ is a parameter, which corresponds to the ethane that is required per product c in plant p.

$$\sum F_{E,p,t} = F_{E,t} \qquad 2.6)$$

In Equation 2.6), $F_{E,t}$ is the total amount of ethane entering the industrial cluster in time period t.

$$L_{E,t} \leq F_{E,t} \leq M_{E,t} \qquad 2.7)$$

In Equation 2.7), $L_{E,t}$ and $M_{E,t}$ are the lower and upper limit of ethane entering the industrial cluster in time period t, respectively.

2.2.2 Power Module

The power balance for the industrial cluster is given below

$$NGPP_t + S_t = Req_t \qquad 2.8)$$

In Equation 2.8), $NGPP_t$ and S_t correspond to the power produced by the gas fired plant and the solar cells in time period t, respectively. As for Req_t, it corresponds to the total power requirement of the industrial cluster in time period t.

The total requirement of the industrial cluster is given as

$$Req_t = \sum F^c{}_{t,p} \varphi^c{}_{p,POWER} + \sum F_{CO_2,k} \, \varphi^{CO_2}{}_{k,POWER} \tag{2.9)}$$

where Req_t is the total power requirement and $\varphi^c{}_{p,POWER}$ is the power parameter of product c from plant p.

Due to grid instability, solar power is confined between a lower and upper bound as given below.

$$SMIN_t \leq S_t \leq \alpha Req_t \tag{2.10)}$$

In Equation 2.10), the power produced by solar energy can be as low as $Smin_t$. The upper limit is the product of a constant, α, and the total power requirement in time period t. The constant is typically assumed to be 20% but can be varied.

2.2.3 Network Superstructure

The carbon emission from the industrial cluster is allocated between a lower and upper limit in time period t as shown below

$$L_{CO_2,t} \leq E_{CO_2,,t} \leq M_{CO_2,t} \tag{2.11)}$$

where $E_{CO_2,t}$ is the emitted CO2 from the cluster in time period t. $L_{CO_2}$and M_{CO_2} are the lower and maximum limits on CO2 emissions from the cluster in time period t.

The total emissions from the cluster is the sum of the emission from all the sources and sinks

$$E_{CO_2,t} = \sum F^c{}_{t,p} \varphi^c{}_{p,CO_2} y_{p,CO_2} - \sum F_{CO_2,k,t} + \sum F_{CO_2,fugitive,k,t} \tag{2.12)}$$

In Equation 2.12), $\varphi^c{}_{p,CO_2}$ is the CO2 parameter for commodity c in plant p, and y_{p,CO_2} is the purity of the CO2 emitted from plant p, $F_{CO_2,k,t}$ is the flow of CO2 into the carbon sink k in time period t, and $F_{CO_2,fugitive,t}$ is the flow of fugitive CO2 from sink k in time period t.

As for the carbon sinks, the allocation is given between a lower and upper bound

$$L_{CO_2,k,t} \le F_{CO_2,k,t} \le M_{CO_2,k,t} \tag{2.13)}$$

where $L_{CO_2,k,t}$ and $M_{CO_2,k,t}$ correspond to the lower and upper flow of CO_2 into sink k in time period t, respectively.

The mass balance around each sink is shown below

$$F_{CO_2,k,t} = \sum F_{CO_2,p,t} \tag{2.14)}$$

where $F_{CO_2,k,t}$ is the actual CO_2 flow into sink k in time period t and $F_{CO_2,p,t}$ is the allocated CO_2 from plant p in time period t.

For any source, it can be connected to any sink. However, the allocated CO_2 from any plant should not exceed the sink flow requirement, ${G_{k,p,t}}^{max}$, as described below

$$F_{CO_2,p,t} \le {G_{k,p,t}}^{max} \tag{2.15)}$$

2.2.4 Economics

The costing of the methane is given below

$$Cost^M{}_t = F_{M,t}P^M{}_t \tag{2.16)}$$

In Equation 2.16), $Cost^M{}_t$ corresponds to the cost of purchasing methane in time period t. As for $P^M{}_t$, it corresponds to the price of methane in time period t.

The costing of ethane in time period t is given below

$$Cost_t{}^E = F_{E,t}P^E{}_t \tag{2.17)}$$

In Equation 2.17), $P^E{}_t$ corresponds to the price of ethane in time period t.

The capital cost calculation for plant p in time period t is given below

$$CAPEX_{p,t} = F^{c}{}_{1,p}\varphi^{c}{}_{p,t,CAPEX} \qquad 2.18)$$

where $F_{1,p}{}^{c}$ corresponds to the flow of product c from plant p in the first time period, and $\varphi^{c}{}_{p,CAPEX}$ corresponds to the capital cost parameter of commodity c in plant p in time period t.

The operational cost calculation for plant p in time period t is given below

$$OPEX_{t,p} = F^{c}{}_{t,p}\varphi^{c}{}_{p,t,OPEX} \qquad 2.19)$$

where $\varphi^{c}{}_{p,OPEX}$ corresponds to the operational cost parameter of commodity c in plant p in time period t.

The capital cost of the gas fired power plant in time period t is given as

$$CAPEX^{NGPP}{}_{t} = NGPP_{t}\varphi^{p}{}_{NGPP,t,CAPEX} \qquad 2.20)$$

where $\varphi^{p}{}_{NGPP,t,CAPEX}$ is the CAPEX parameter of the gas fired power plant in time period t.

The capital cost of the renewable source in time period t is similar and is given as

$$CAPEX^{S}{}_{t} = S_{t}\varphi^{p}{}_{S,t,CAPEX} \qquad 2.21)$$

where $\varphi^{p}{}_{S,CAPEX}$ is the CAPEX parameter of the renewable source in time period t.

All the sinks in the industrial cluster are only allowed to take in pure CO_2. However, not all the sources of CO_2 in the cluster are pure and require treatment if they would need allocation to a given sink. Therefore, it is important to also specify the CAPEX and OPEX of the treatment. The treatment unit used in this work will be an amine absorption unit. For the $CAPEX^{treamtent}{}_{t}$, correlations found from the literature[21] will be used to cost the absorption units. As for the OPEX, it will just be costed as the electricity required to power the absorption units.

2.2.5 *Objective Function*

The objective of the industrial cluster is to yield the configuration that yields the maximum profit from the available natural gas. The profit in time period t can be calculated using Equation 2.22).

$$Profit_t = REV^c{}_t + REV^{CO_2}{}_t - (Cost^M{}_t + CAPEX_{1,p} + OPEX_{t,p} + Cost^E{}_t + CAPEX^{NGPP}{}_t + CAPEX^S{}_t + CAPEX^{treatment}{}_t) \tag{2.22)}$$

The revenue from all the products in time period t, $REV^c{}_t$, is given as

$$REV^c{}_t = \Sigma F^c{}_{t,p} C^c{}_{c,t} \tag{2.23)}$$

where $C^c{}_{c,t}$ is the price paid for commodity c in time period t.

The revenue from the sinks, $\mathrm{REV}^{\mathrm{CO_2}}{}_{\mathrm{t}}$ is given as

$$REV^{CO_2}{}_t = \Sigma F_{CO_2,k,t} C^{CO_2}{}_{k,t} \tag{2.24)}$$

where $C^{CO_2}{}_{k,t}$ is the price paid for CO_2 to produce products within sink k in time period t.

2.3 Economic Description

Previous work as well as Qatar's sustainability reports will be referred to for data collection for clusters that use natural gas as feedstock. The data collected include mass balances, plant capacities, economics data such as CAPEX and OPEX, etc. The data will be scaled up to Qatar's capacity. To find the fixed capital investment (FCI) for Qatar's plants, Equation 2.25) is used.

$$FCI_B = FCI_A \left(\frac{Capacity_B}{Capacity_A}\right)^x \tag{2.25)}$$

Where FCI_B is Qatar's fixed capital investment, FCI_A is the literature fixed capital investment, $Capacity_B$ is Qatar's capacity, $Capacity_A$ is the literature's capacity, and x is an exponent. The exponent is usually 0.6, which is why it is called the sixth-tenths rule.

To find FCI at time 2, the below equation is used.[22]

$$FCI_{t2} = FCI_{t1}(\frac{Cost\ index\ at\ time\ t2}{Cost\ index\ at\ time\ t1}) \qquad 2.26)$$

Where FCI_{t2} is the fixed capital investment at the time of interest, FCI_{t1} is the year mentioned in the literature to be adjusted, $Cost\ index\ at\ time\ t2$ is the Chemical Engineering Plant Cost Index (CEPCI) at the time of interest, and $Cost\ index\ at\ time\ t1$ is the CEPCI at the year mentioned in the literature to be adjusted. A sample calculation of the economic adjustment of a single plant as well as the unscaled economic information used is found below in the appendix.

3. CASE STUDY

The method presented above in the previous section using Equations 2.1-25 have been applied on the following industrial cluster presented below. The conventional plants that will be used will be based upon the plants described by Alfadala and El-Halwagi.[23] The industrial cluster that will be used for this case study is reproduced in the following figures below.

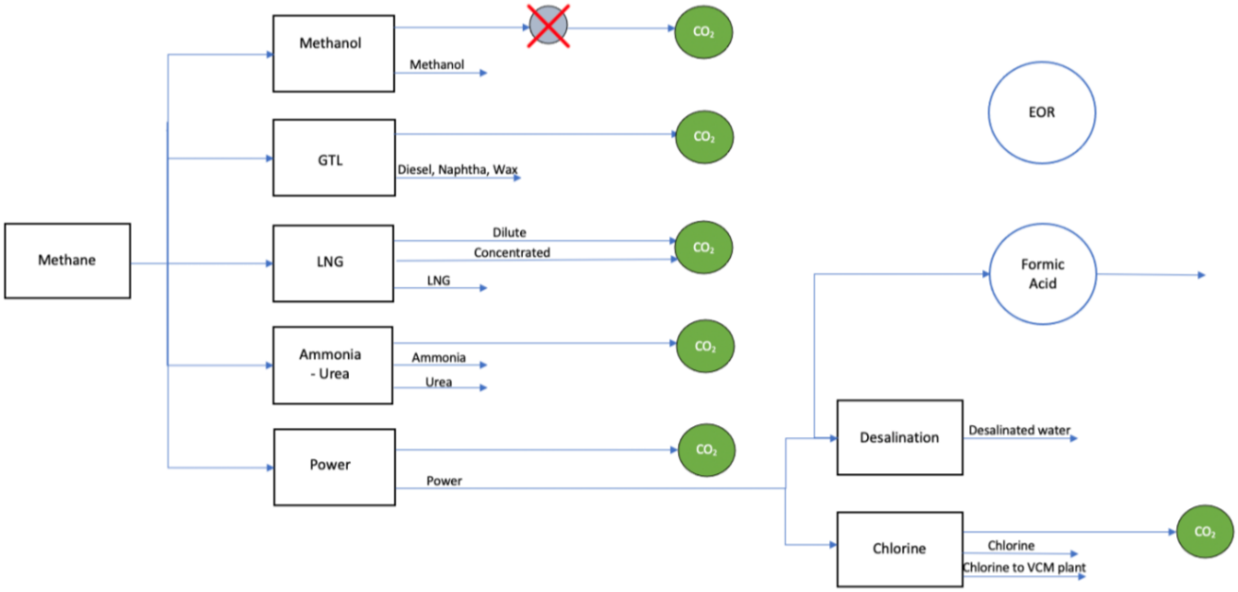

***Figure 3.1**: Methane allocation for general case study*

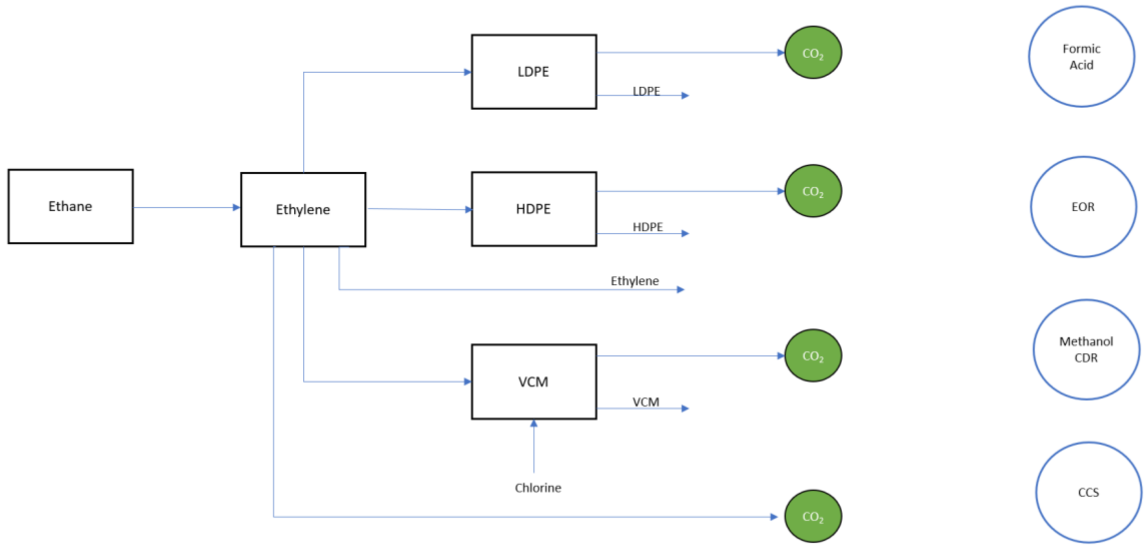

***Figure 3.2**: Ethane allocation for general case study*

3.1 Conventional Plants

This work focuses on industrial clusters that are found in Qatar that utilize a form of natural gas as the primary feedstock. All the plants will receive a limitless supply of natural gas from a common distributor to satisfy their production needs. The clusters included have sites available that could capture, treat, and manage the CO_2 emissions of the cluster. When it comes to the total CO_2 emission from the cluster, it will be comprised of all the individual plant emissions and will be constrained based on any reduction target. As a base case, the cluster will contain a variety of natural gas converting plants such as a gas to fuel or chemicals processes. Each plant has an associated CO_2 emission, which will need to be reduced in the future by given emission targets imposed by a governing entity. The CO_2 emission will be reduced by converting or sequestrating the emissions through carbon capture utilization and storage (CCUS) or reducing the production rate of the plants to decrease their emission. However, decreasing production will be the last resort as the goal is to still maximize economic return on the gas utilized within the cluster. Allocation of resources is based on an optimization approach that systematically enables the identification of the most profitable configuration that meets the CO_2 emission constraints. In Table 3.1, the processes are named alongside their main feedstock and main products.

Table 3.1*: Included plants in the industrial cluster*

Plant	Process name	Feedstock	Main products
VCM	Vinnolit Process	Ethylene	VCM – EDC – HCl
Chlorine	Chloro-Alkali	Salt + Water	Chlorine – Caustic Soda
Methanol	Methanol Synthesis	Natural Gas	Methanol
Ethylene	Ethylene Cracking	Ethane	Ethylene
Power	Electro-mechanical generator	Natural gas	Electricity
Ammonia	Haber Bosch	Natural gas	Ammonia
Urea	Urea Synthesis	Ammonia - CO_2	Urea
GTL	ATR	Natural gas	Kerosene – Diesel – Wax – Naphtha
LNG	Liquification	Natural gas	LNG
Desalination	Reverse Osmosis	Sea water	Treated water – brine
HDPE	Polymerization	Ethylene	HDPE
LDPE	Polymerization	Ethylene	LDPE

3.1.1 Vinyl Chloride Monomer (VCM) Plant

Vinyl chloride monomer (VCM) is exclusively produced (>95%) to be turned into polyvinyl chloride (PVC)[24] homopolymer and copolymer resins.[25] The rest of the produced VCM is used to manufacture chlorinated solvents and ethylene diamine.[26] The demand for VCM is highly dependent on the demand of the construction sector, as it consumes three-quarters of all the output of PVC. The natural gas input into the plant is ethylene. To produce a ton of VCM, 0.459 tons of ethylene, 0.575 tons of chlorine, as well as 0.139 tons of oxygen are required. Along with a ton of VCM, 0.513 tons of ethylene dichloride and 0.32 tons of CO_2.[27][28] In Qatar, Qatar Vinyl Company (QVC), a subsidiary of Qatar Petrochemical Company (QAPCO), is the company that produces VCM in Qatar. In 2016, QVC produced 355,000 MTPA of VCM.[29] QVC uses the Vinnolit Process to produce VCM from ethylene. To produce VCM, EDC must be produced first as an intermediate from ethylene. The production of EDC proceeds via two routes, oxychlorination and direct chlorination of ethylene. The two reactions are shown below.[28]

Direct chlorination:

$$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2 \quad \Delta H = -218\frac{kJ}{mol} \tag{3.1}$$

Oxychlorination:

$$C_2H_4 + 2HCl + \frac{1}{2}O_2 \rightarrow C_2H_4Cl_2 + H_2O \quad \Delta H = -238\frac{kJ}{mol} \tag{3.2}$$

To produce VCM from EDC, it is sent to a cracking unit. Any EDC produced from the direct chlorination is sent directly to the cracking unit. However, any EDC produced via the oxychlorination route must be sent to a purification process before cracking.[28]

$$C_2H_4Cl_2 \rightarrow C_2H_3Cl + HCl \quad \Delta H = 71\frac{kJ}{mol} \tag{3.3}$$

As can be seen from the equation above, the cracking of EDC co-produces HCl. HCl can be recovered and separated from the VCM and fed back into the oxychlorination process. This leads to a complete usage of the chlorine that enters the process.[28]

3.1.2 Chlorine Plant

Chlorine has a variety of uses. It is used to disinfect water and is part of the sanitation process for sewage and industrial waste. During the production of paper and cloth, chlorine is used as a bleaching agent. It is also used in cleaning products, including household bleach which is chlorine dissolved in water. Chlorine is used in the preparation of chlorides, chlorinated solvents, pesticides, polymers, synthetic rubbers, and refrigerants.[30] Chlorine is produced via the electrolysis of an aqueous solution of sodium chloride. There is no input of natural gas into the chlorine plant as the only feedstock is water and sea salt. However, the process requires a power input and the power is produced via natural gas power plants. Chlorine is produced via the Chloro-Alkali process. The dominant reaction in the electrolysis of aqueous sodium chloride solution is found below.[31]

$$2NaCl + 2H_2O \rightarrow Cl_2 + H_2 + 2NaOH \tag{3.4}$$

The Chlor-Alkali process uses three types of electrolytic processes: diaphragm cell, mercury cell, and membrane cell processes. Currently, membrane cell processes are the most popular among the three as they consume the least amount of electricity and steam compared to the other.[31] To produce a ton of chlorine, 2800 kWh of electricity, 1.63 tons of water, and 1.65 tons of water are required. Alongside one ton of chlorine, 2.25 tons of 50 wt% caustic solution, 28 kg of hydrogen gas, and 1.2 kg of CO_2 are produced as well.[32] Most of the emissions that come from the Chlor-Alkali process are due to the intensive power requirement of the process. In Qatar, QVC produced 180,000 MTPA of chlorine in 2016.[29]

3.1.3 Methanol Plant

Methanol is widely used as a building block for many chemical processes such as the production of acetic acid, dimethyl ether and hydrogen.[33] Methanol is synthesized using natural gas as the feedstock. This is used to make many products for example, plastics, paints and fuel.[34] The capacity of methanol in Qatar is 1,182,10 tons/year.[35] It consumes 0.683 tons of methane per ton of methanol produced. Moreover, it produces 0.5 tons of CO_2 per ton of methanol produced.[20]

3.1.4 Ethylene Plant

Ethylene is one of the most important chemicals in the chemical industry. It is used as a raw material to produce polyethylene, polyethylene terephthalate, polyvinyl chloride, and polystyrene. The largest consumer of ethylene, around 60% of all the total produced ethylene, goes into producing polyethylene. The second largest outlet of ethylene is to produce ethylene oxide.[36] Ethylene is traditionally produced via the steam cracking of ethane. This process uses high pressure steam to crack ethane into ethylene. In Qatar, QAPCO uses ethylene crackers to produce 830 ktpa of ethylene in the year 2016.[29]

3.1.5 Power Plant

In this system, a power plant in the form of solar photovoltaic (PV) cells convert sunlight into electricity using the photovoltaic effect. Photovoltaic power is an environmentally friendly form of energy and works in cloudy and rainy days. This form of energy can be easily integrated into systems. Using solar energy based power plants instead of instead of natural gas fired power plants will reduce GHG emissions and hence mitigate climate change.[37] PV power plants are only used for 20% of the system while the 80% is natural gas powered plants. With regards to the capital cost of the solar plants, 920$/ kW of energy produced is for the panels, while 1600 $/kWh of energy produced is for the Balance of System (BoS).[38] For the gas fired power plants, it consumes 0.00011 ton/kWh of methane and produces 0.00054 ton/kWh of carbon dioxide. The capital cost of this power plant is $614/kW.[39]

3.1.6 Ammonia Plant

Ammonia NH_3 is a chemical compound that is composed of hydrogen and nitrogen. It also uses natural gas as primary feedstock to its process. Qatar Fertilizer company (QAFCO) is the main producer of NH_3 in Qatar with the production of 3,289,491 tons/yr in 2016.[40] Ammonia production requires 0.68 tons CH_4/ton NH_3, and it produces 0.55 tons CO_2/ ton NH_3.[41] Ammonia is used as an intermediate product to nitrogen containing fertilizers, such as ammonium sulphate and ammonium phosphate, as well as a primary feedstock to produce Urea.[41]

The Haber-Bosch process is used to generate NH_3. This process directly combines nitrogen from air with hydrogen under high temperatures ($400^oC – 650^oC$) and very high pressure (200 – 400 atm) with the use of an iron-based catalyst.[42]

3.1.7 Urea Plant

Urea is generated from the reaction of NH_3 with CO_2 under high pressure. Urea is mainly used as a fertilizer, due to its 46% nitrogen content, and the production of Urea-Formaldehyde resins.[41] This compound is also produced through QAFCO in Qatar with the capacity of 5,657,925 tons/yr.[40] Urea production requires 1.17 tons CH_4/ton Urea, and it produces 0.95 tons CO_2/ ton Urea.[41] The use of Urea as a fertilizer comes with many benefits, like its high nitrogen content which reduces application costs and it is absorbed by the soil in the form of ammonium which is more resistant to leaching than in the form of nitrate.[41]

3.1.8 GTL Plant

The Gas-To-Liquid process takes natural gas as a main feedstock to produce value added products such as Kerosene, Diesel, Wax, and Naphtha. This process can undergo three possible routes: Auto-thermal reforming (ATR), patrial oxidation and catalytic reforming, or partial oxidation (PO). This paper focuses on Oryx GTL's production that utilizes ATR. ATR is a process that generates synthesis gas (syngas) which is composed of hydrogen and carbon monoxide through the partial oxidation of natural gas with oxygen and steam.[43] The plant is mainly composed of three units: a reformer that generates syngas, Fischer-Tropsch reactor, and a hydrocracking/cracking unit that produces that main products of GTL; Kerosene, Diesel, Wax, and Naphtha. Oryx GTL process's production is estimated to be 1,514,700 tons/yr.[23,44] To produce 1 ton of GTL, the process requires 1.62 tons of CH_4. the production of 1 ton of GTL produces 0.99 tons CO_2.[20]

3.1.9 LNG Plant

Liquefied natural gas (LNG) is a process that liquifies natural gas which is the cooling of natural gas till it turns into liquid. The main purpose of natural gas liquification is the ease of transport to customers which then gets converted to gas for commercial.[45] LNG is used widely in many applications mainly as a fuel source. The sector that uses natural gas the most in the United States is the energy sector as of 2019, as it accounts for 36% of the total natural gas consumption. Next comes the industrial sector where 33% of the natural gas consumption is used in the industry such as a heating source or as a feedstock in many processes. It is also used in the commercial and residential sectors as an energy source to heat buildings and water.[46] Currently, Qatar's LNG capacity is 79.2 MTPA. The process consists of 14 LNG trains, six of which are mega-trains. In this process, sulphur compounds, carbon dioxide and water are removed then the gas undergoes a refrigeration process in which the gas is chilled. Next, the heavy hydrocarbons are separated into liquified petroleum gas and plant condensation. Then, the gas is liquified as it cools to -150ºC. Lastly, the pressure is reduced to zero and the temperature to -162ºC, the nitrogen is removed, and LNG is transported to a storage tank to be placed in an LNG vessel. For our purposes, a capacity of 58.9 MTPA will be assumed. When it comes to production, LNG requires 1.046 ton CH_4/ton LNG and produces 0.2 ton CO_2/ton LNG.[20]

3.1.10 Desalination Plant

Desalination is the removal of salts from sea water to achieve high concentration of salts in one stream and pure water in the second stream for domestic and industrial use.[47] Water production capacity in Qatar is 626,472,361 tons/yr.[48] To achieve this separation, energy is required. Electricity is used as the source of energy from the combustion of natural gas. The power parameter for desalination is 0.71kWh/ton product.[49] Reverse Osmosis (RO) is used for the desalination process to purify (deionize/demineralize) water by passing it through a semi-permeable RO membrane under pressure from high areas of concentration to low areas of concentration.[47]

3.1.11 High-Density Polyethylene Plant

High-density polyethylene (HDPE) is a type of polyethylene that has no side branches, which makes it stiff and rigid.[50] HDPE is used as packaging for many chemicals as it is chemical resistant to acids, bases, and detergents. In addition, it is also used in film applications such as food packages and wrappers.[51] In Qatar, its HDPE capacity is 803 KTPA.[52] To produce a ton of HDPE, 1.027 tons of ethylene are needed.[50] Moreover, 1.8 tons of CO_2 are also produced per ton of HDPE produced.[53]

3.1.12 Low-Density Polyethylene Plant

Low-density polyethylene (LDPE) is a type of polyethylene that is produced in a high-pressure process. LDPE consists of highly branched molecular structures which makes soft, hard and elastic.[50] LDPE is used a mostly as a film application for packaging uses accounting for 55% of the worldwide consumption. Examples of applications of food and non-food packaging include:

poultry and meat wrapping, commercial bags and produce bags.[50] With regards to Qatar, its capacity for LDPE is 795 KTPA.[29] Ethylene gets converted to low-density polyethylene through polymerization.[50] It consumes 1.018 tons of ethylene per ton of LDPE produced.[50] Moreover, it produces 1.57 tons of CO_2 per ton of LDPE produced.[53]

All the plants found in the cluster will require a certain CAPEX and OPEX to operate. The non-adjusted linearized CAPEX and OPEX parameter used are found in Appendix B. To modify the parameters to Qatar's capacity in 2016, Equations 25 and 26 will be used to adjust for the time value of money and the economies of scale effect.

Table 3.2: *CAPEX and OPEX parameters used in the approach*

Plant/Commodity	Fixed Capital Investment ($/(ton product*year))	Operating Cost ($/(ton product*year))
VCM	27.12	60
Chlorine	48.9	394.06
Methanol	23	20
Ethylene	15.7	22.72
Ammonia-Urea	104	177.63
GTL	70.45	141
LNG	66.77	37.99
Desalination	0.006	0.08
HDPE	21.4745	1136.58
LDPE	22.5845	1138.28

3.2 Nonconventional Plant

The non-conventional plants used in the cluster are in the form of CO_2 sinks. The sinks that are used in the cluster are found in Table 3.3.3.

***Table 3.3**: CO_2 sinks available within the cluster*

Plant	Process	Feedstock	Main Products
CCS	CCS	CO_2	Stored CO_2
EOR	EOR	CO_2	Oil
Methanol CDR	CO2 hydrogenation	CO_2	Methanol - H_2O
Formic Acid	Electrochemical Reduction	CO_2	Formic Acid

3.2.1 Formic Acid via Electrochemical Reduction of CO_2

Rather than emitting carbon dioxide into the atmosphere, it is possible to convert it to value-added products such as formic acid using electrochemical reduction. This process is a hydrogenation reaction which is carried out in an electrolysis cell. The electrolysis system consists of three main parts: two electrodes, electrolyte and a catalyst. The carbon dioxide that is fed into this system must be pure, thus a capturing process can be implemented by feeding carbon dioxide into separating columns to separate the pure carbon dioxide from a gaseous mixture. The maximum flow of carbon dioxide in the electrochemical reduction of carbon dioxide system is 330,000 ton of CO_2 per year.[54] To account for the 50% conversion of the process, 660,000 tons of CO_2 are needed.

3.2.2 Carbon Capture and Storage

Carbon capture and storage is a technology that captures carbon dioxide from a source such as plant emissions, transports it and stores it. This method aims to reduce greenhouse emissions and subsequently global warming. The three main steps of CCS are, first, the capture and separation of carbon dioxide from a flue gas stream then the concentrated carbon dioxide is compressed and transported through pipeline or vehicles to an appropriate site for geological storage. Then, carbon dioxide is injected into deep underground rock formations, one kilometer below the ground.[55] The maximum flow of carbon dioxide in the CCS system is 5,000,000 ton of CO_2 per Qatar announcements.[56] CCUS tackles the issue of industrial production by reducing around one-fifth of the industrial sector emissions.[57] Around 28 $GtCO_2$ is captured from processes until 2060, mainly from chemical subsectors, cement, and steel. This is crucial as the need for plastics, steel, and cement has increased by factors over ten, three, and seven over the years since 1971.[57] Industry is considered the second largest source of CO_2 emissions after the power sector accounting for 8 $GtCO_2$ of direct CO_2 emission in 2017 and adding the indirect CO_2 emissions makes it the cause of 40% overall CO_2 emissions. CCUS is a sufficient economical investment considering that it can help in reducing unit costs through economies of scale and provide means for CO_2 capture investment for existing and new industrial plants. In addition, the adoption of CCUS in cement, chemicals, and steel industries can aid in establishing sustainable markets around the world.[57] For this work, two carbon capture technologies have been identified that could be used in Qatar, membrane technology and amine absorption.

3.2.2.1 Membrane Technology

Membrane CO_2 capture technology is usually used for post-combustion CO_2 capture in which it needs certain properties to be deemed effective, such as high CO_2 selectivity, high CO_2 permeability, cost effectiveness, etc.[58] This technology is mostly used in oil refineries and the petrochemical industry.[59] Membrane separation units can also be used for recovery or purification of gas streams to generate value added products, like methane, syngas, and hydrogen.[58] The membrane unit consists of a treatment unit with filters and a heater which is adjusted based on the separation process.[58] Membranes act like filters that selectively allow components to permeate through them to separate certain components from other components. Membrane has already been used for water desalination and reverse osmosis around the world. This technology is less mature for gas separation in comparison to other technologies, like physical and chemical absorption.[60] Not only that, but it is also energy intensive and it has a trade-off between purity and selectivity as it cannot achieve a 99.9% recovery of CO_2.[61] It is worth noting that this process needs high operating pressures and is costly compared to other separation techniques.[62]

3.2.2.2 Physical Absorption

This separation technique depends on a chemical reaction between CO_2 and the solvent. The system's requirement consists of an absorber, stripper, a solvent, a reboiler, *and a condenser*. Nowadays, amine-based solvents, especially alkanolamines, are used in carbon capture systems due to their low corrosivity, low molecular, and availability.[62] In the absorber, the contact between the flue gas and the MEA-based sorbent occurs, allowing the CO_2 that is from the flue gas to dissolve in the sorbent. Majority of the absorbers are polymer packed columns that provide a larger interfacial area.[62] chemical absorption operates at regular temperature and pressure, it is preferable for CO_2 streams for flue gas from power plants, and it is a mature and commercially available technology in comparison to the membrane technology.[62]

3.2.3 Enhanced Oil Recovery

Enhanced Oil Recovery is a method of improving oil production through the utilization of CO_2. Carbon dioxide is injected in pre-existing oil reservoirs to increase the pressure of the oil field which forces the oil out, enhancing the production rate by allowing the oil to flow faster. Qatar Petroleum (QP) is currently considering the implementation of this technology. The maximum flow of carbon dioxide in the EOR system is 2,100,000 ton of CO_2 per year.[56]

3.2.4 Methanol from CO_2 feedstock

Rather than releasing CO_2 into the atmosphere, methanol plants can utilize their CO_2 emissions to produce even more ethanol using the CO_2 hydrogenation reaction. In this reaction, pure hydrogen and CO_2 are reacted together at 70 bar and 250°C to yield methanol and water.[29] QAFAC currently captures 500 tons of CO_2 and utilizes it in their process to yield more methanol. The maximum flow of carbon dioxide in the methanol B system is 165,000 ton of CO_2 per year.[63] Even though the maximum flow of carbon dioxide is 165,000 tons, 181,318 tons of CO_2 are required to account for a sink efficiency of 91%.

4. RESULTS

The case study was solved using What’sBest! 17.0 – Excel Add-In for Linear, Nonlinear, and Integer Modeling and Optimization by Lindo[64]. The software was run using a laptop with Intel Core i7, 16 GB RAM, and 64-bit operating system. Four cases were studied in the single-period analysis which was followed by a case for multi-period analysis.

4.1 Single-Period Analysis

4.1.1 Case 1: No Restrictions or Carbon Capture

When no CO_2 emissions were captured by the industrial cluster, the software ran all the plants at their maximum capacity for maximum profit. The cluster resulted in a profit of $1.523*10^{10}$ \$/yr and 15.8 mega tons of CO_2 emitted per year. It was also noticed that the power production complex only activated the natural gas power plants to supply all the power that is required by the plants, which amounts to $1.53*10^{9}$ kWh/yr. The software chose not to activate the solar power option as it was more profitable to burn methane to meet the power demand. The results of the allocation of methane and ethane are shown in the figures below.

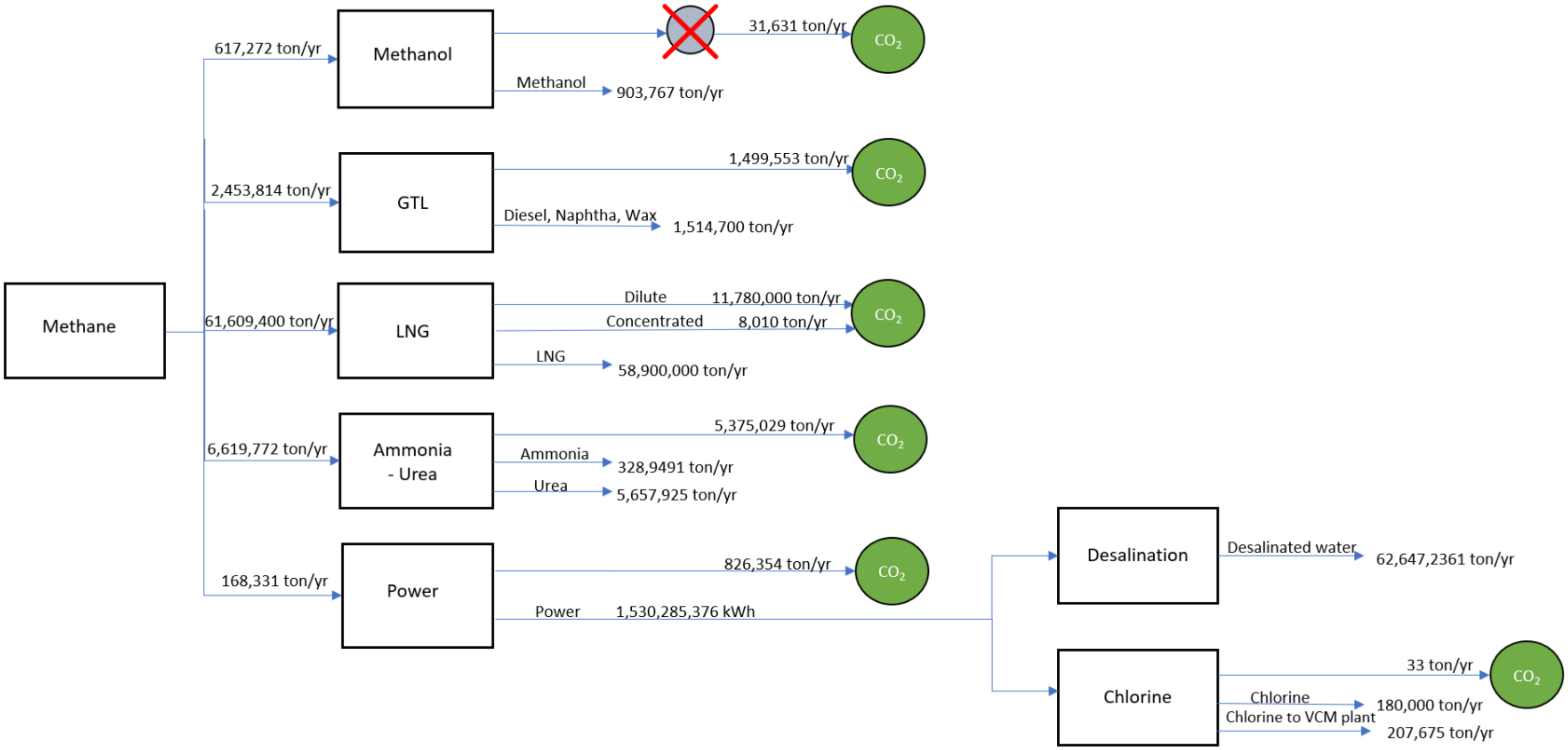

Figure 4.1*: Methane allocation for Case 1*

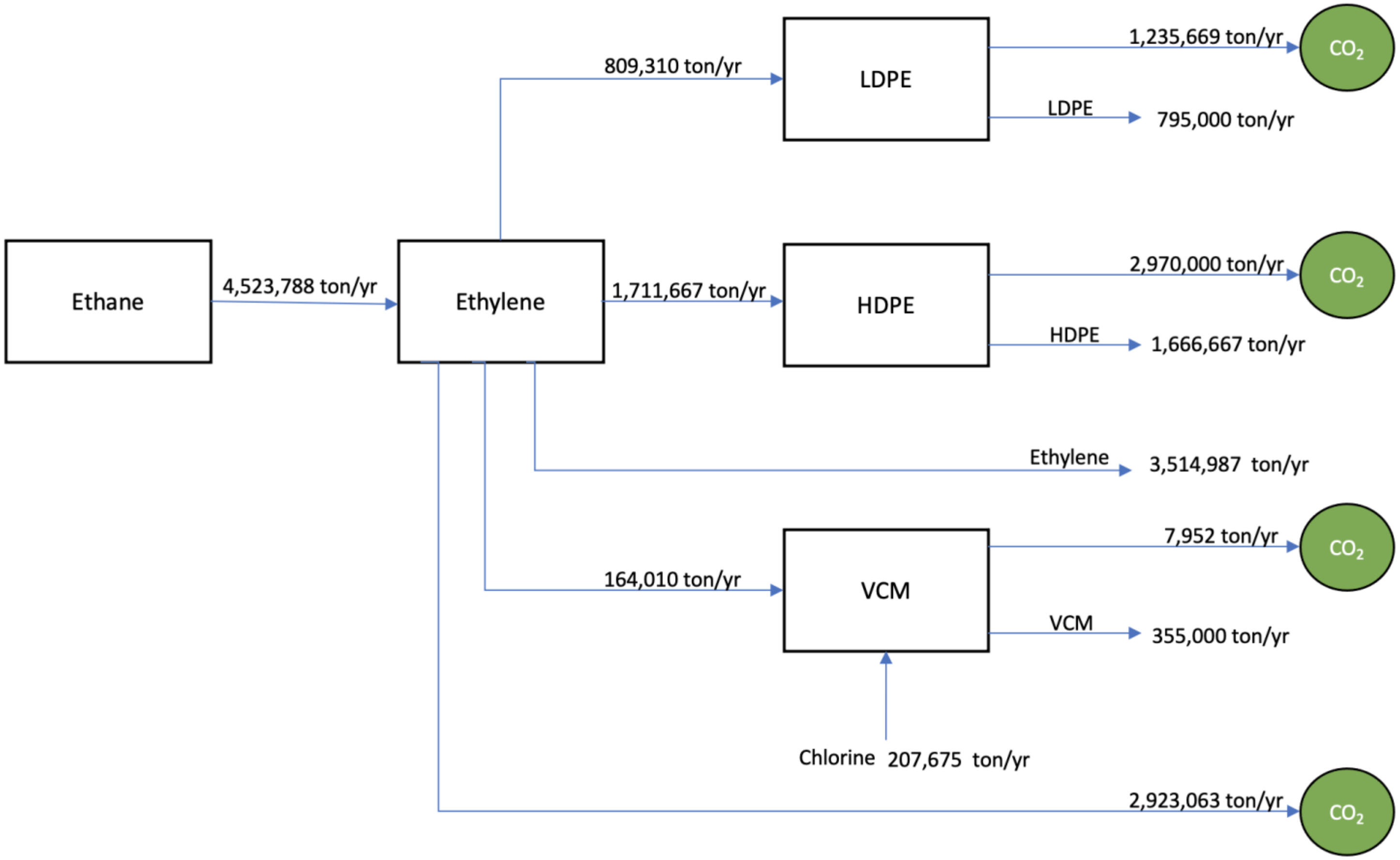

***Figure 4.2**: Ethane allocation for Case 1*

4.1.2 Case 2: Activation of Carbon Capture and Solar

The second case that was explored was when no restriction on emissions were imposed but the system is free to activate any of the carbon sinks. The cluster resulted in a profit of $1.549*10^{10}$ \$/yr and 14 mega tons of CO_2 emitted per year. The significant decrease in CO_2 emissions and the slight increase in profits is due to the activation of profitable CO_2 sinks. The approach activated and ran the formic acid plant, EOR, and Methanol CDR at maximum capacity while keeping carbon storage deactivated. It is important to note that the system chose to run methanol CDR to satisfy the methanol demand as it was more profitable to use exchanged CO_2 than to use more methane. The CO_2 was allocated from the Ethylene cracker, Ammonia-Urea plant, GTL plant, and both polyethylene plants. These plants were chosen over the other plants as it is cheaper to allocate pure CO_2 rather than treat the emissions from the nonpure sources such as from the LNG plant. 1,000,000 tons of CO_2 was from Ammonia-Urea and high-density polyethylene each and 100,000 tons of CO_2 from the GTL plant to EOR. As for the formic acid plant, 660,000 tons of CO_2 were allocated from the GTL plant. Finally, 181,318 tons of CO_2 were allocated to the methanol CDR from the high-density polyethylene plant. At first glance, the CO_2 seems to be overallocated to the formic acid plant and methanol CDR. However, the overallocation is due to the inefficiency of the sinks and the release fugitive CO_2 as a balance. The results of the methane, ethane, and CO_2 allocation are found in Figure **4.3**4.3 and Figure **4.4**4.4.

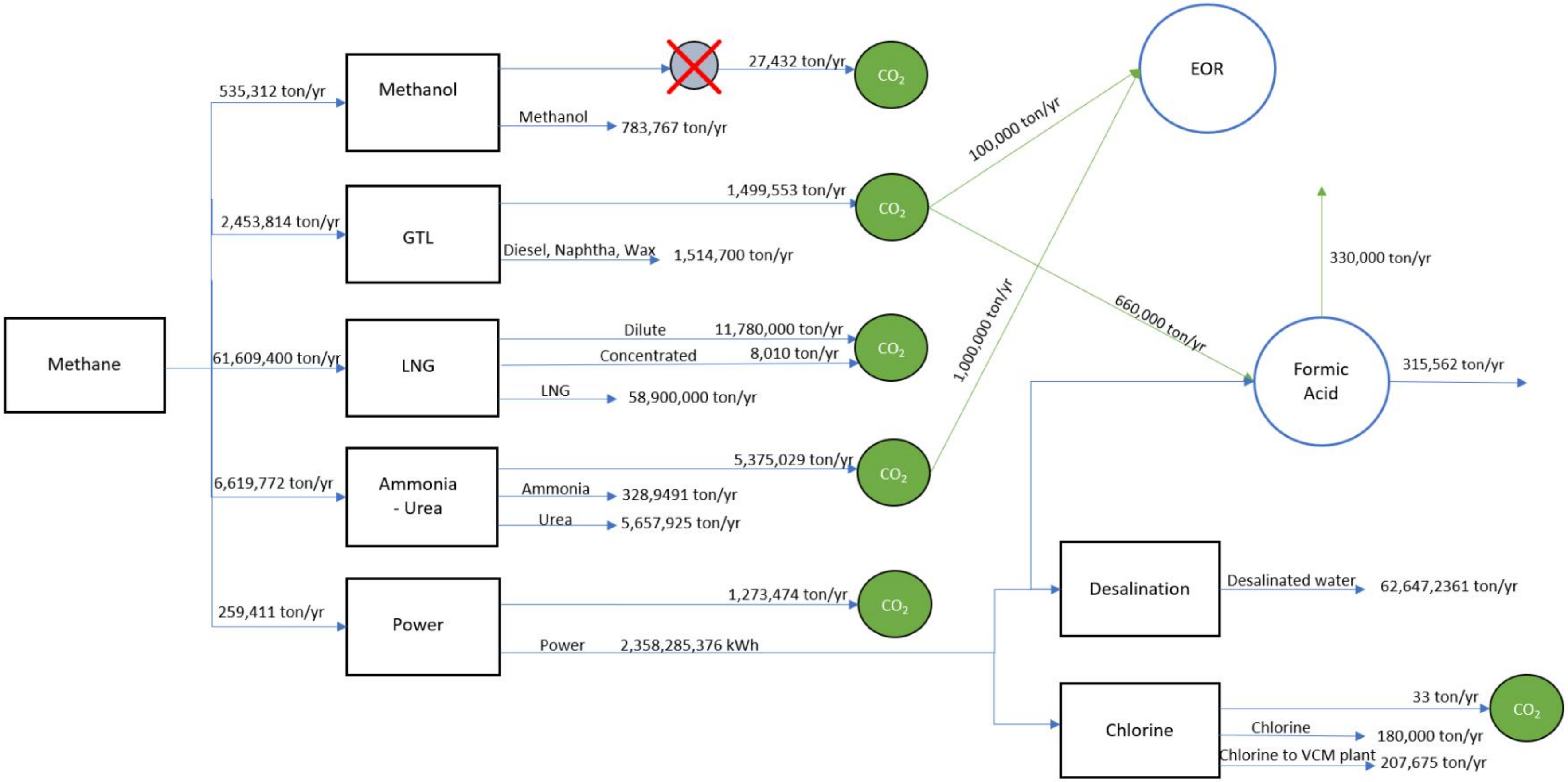

***Figure 4.3**: Methane and CO_2 allocation for Case 2*

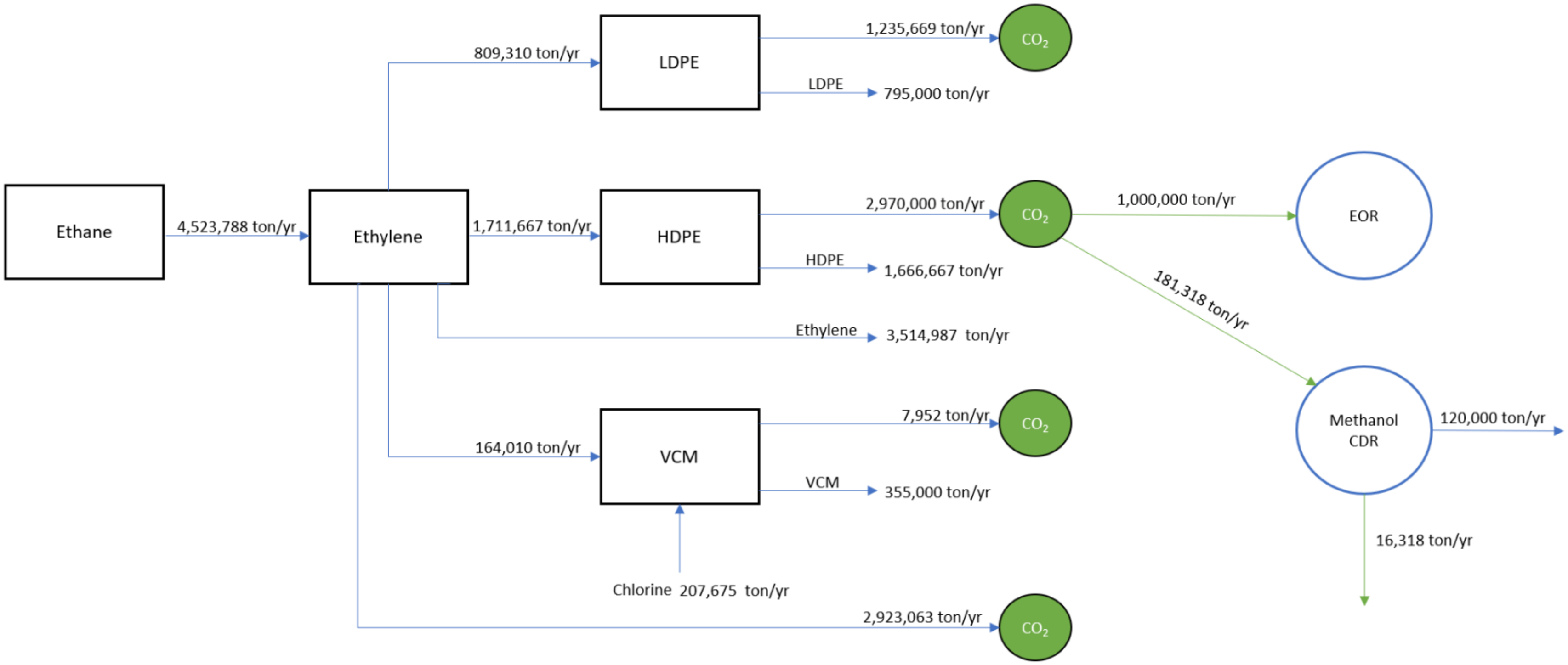

***Figure 4.4**: Ethane and CO_2 allocation for Case 2*

4.1.3 Case 3: 25% Reduction in Emissions

The third case that was explored was when a 25% reduction on emissions was imposed on the base case. The cluster resulted in a profit of $1.541*10^{10}$ \$/yr and 11.8 mega tons of CO_2 emitted per year. The decrease in profits is due to the activation of the solar power plant and the CO_2 storage sink. All commodity plants and profitable CO_2 sinks continued running at maximum capacity to maximize profits while allocating the excess CO_2 into storage to meet the CO_2 limit imposed on the cluster. The solar power plant was able to supply 20% of the clusters power need. Not only did the solar plant meet the power balance, but it mitigated the release of 254,695 tons of CO_2 if all the power was produced from burning methane. As for the CO_2 allocation, the approach chose not to allocate any of the dilute CO_2 sources into storage. This result was expected as it would have incurred an extra cost to activate the absorption process to capture the CO_2 from the dilute stream before allocating it. The approach chose to allocate CO_2 from the Ammonia-Urea, low-density polyethylene, high-density polyethylene, and ethylene plants. The choice of plants to allocate pure CO_2 from in Case 3 is different from Case 2. This result is acceptable as the approach is free to choose from any of the pure sources. Our results will vary if the distance of the CO_2 sinks from the sources and pressure requirements were included in the optimization. The results of the methane, ethane, and CO_2 allocation are found in the tables below.

***Table 4.1**: Methane and CO_2 allocation for Case 3*

Methane and Power Sink	Flow of Methane (ton/yr)	Power Requirement (kWh/yr)	Product Flow (ton/yr)	CO_2 Emissions (ton/yr)	CO_2 to EOR (ton/yr)	CO_2 to Storage (ton/yr)	CO_2 to Methanol CDR (ton/yr)	CO_2 to Formic Acid (ton/yr)
Methanol	535,312	-	783,767	27,431	-	-	-	-
LNG	61,609,400	-	58,900,000	824,600	-	-	-	-
GTL	2.453,814	-	1,514,700	1,499,553	100,000	866,699	-	-
Ammonia-Urea	6,619,772	-	5,657,925 U 3,289,491 A	5,375,028	-	1,000,000	169,07	84,954
Gas fired Power Plant	207,529	-	1,886,628,301 kWh	1,018,779	-	-	-	-
Desalination	-	444,795,376.31	626,472,361	-	-	-	-	-
Chlorine	-	1,085,490,000.00	180,000	-	-	-	-	-

***Table 4.2**: Ethane and CO_2 allocation for Case 3*

Ethane/Ethylene Sink	Ethane/Ethylene Intake (ton/yr)	Power requirement (kWh/yr)	Product Flow (ton/yr)	CO_2 Emissions (ton/yr)	CO_2 to EOR (ton/yr)	CO_2 to Storage (ton/yr)	CO_2 to Methanol CDR (ton/yr)	CO_2 to Formic Acid (ton/yr)
Ethylene	4,523,787	-	830,000	2,952,588	1,000,000	-	93,926	326,024
LD PolyE	809,310	-	795,000	1,248,150	-	-	-	-
HD PolyE	1,711,666	-	1,666,666	3,000,000	1,000,000	-	42,494	164,068
VCM	164,010	-	355,000	7952	-	-	-	-

***Table 4.3**: CO_2 flow into CO_2 sinks and treatment units for Case 3*

Sink/Treatment Unit	Flow Into Sink (ton/yr)	Product Stream (ton/yr)	Fugitive Emissions (ton/yr)	Power Requirement (kWh/yr)
EOR	2,100,000	-	-	-
Formic Acid	660,000	315,652	330,000	828,000,000
Storage	1,866,699	-	-	-
Methanol B	181,318	120,000	16,318	-
LNG Absorption	-	-	-	-
VCM Absorption	-	-	-	-
Methanol Absorption	-	-	-	-

4.1.4 Case 4: 75% Reduction in Emissions

The fourth case is an extreme case of Case 3 where the restrictions have increased to a 75% reduction in emissions. The cluster results in a profit of 1.398×10^{10} \$/yr and 3.9 mega tons of CO_2 emitted per year. To meet the CO_2 restriction, the approach chose to operate the Ammonia-Urea plant at 9% of its max capacity. It was not possible to operate the plant at its maximum capacity as all the CO_2 sinks were operating at their maximum capacity and could not accommodate any extra CO_2. It is important to question why the software chose to decrease the capacity of Ammonia-Urea as opposed to other plants such as GTL and high-density polyethylene with higher CO_2/(ton product) ratios. Even though GTL has a slightly higher ratio, 0.99 as opposed to 0.95 for Ammonia-Urea, the profit margin for the GTL plant is significantly higher. When factoring in the CAPEX, OPEX, and the price of the commodity, GTL produces a profit of \$676/(ton product) as opposed to \$442/(ton product) from Ammonia-Urea. Therefore, it is sound that the Ammonia-Urea plant's capacity was reduced. When looking at the high-density polyethylene plant, with a ratio of 1.8, multiple factors play a role. The profit margin of high-density polyethylene is almost half of the Ammonia-Urea process, with a profit margin of \$260/(ton product). However, it is much more profitable to produce high-density polyethylene as ethane is cheaper as a feedstock and is highly profitable in the ethylene cracker. Based on these results, it is safe to say that the results from the optimization are reliable. Moving on to the CO_2 allocation, the 75% reduction activated the absorption process for the dilute CO_2 source in the LNG plant. Even though it would have been more profitable to allocate CO_2 from pure sources, the assumption that all sources are only allowed to allocate 1,000,000 tons of CO_2 per year set a limit on how much the pure sources can be used. This assumption was set in place to consider that large allocations will incur extreme costs in terms of compression, purchase of compressors and pipes, and utility. On top of the capital cost of the absorption columns, an extra cost is incurred on the cluster to supply electricity to the absorption columns as part of its operating costs. This extra power requirement is also translated as extra costs to purchase extra methane in the power plant to supply the needed power. It is also important to note that the absorption process is not 100% efficient and releases fugitive CO_2. The results of the allocation of methane, ethane, and CO_2 are found in the tables below.

Table 4.4*: Methane and CO_2 allocation for Case 4*

Methane and Power Sink	Flow of Methane (ton/yr)	Power Requirement (kWh/yr)	Product Flow (ton/yr)	CO_2 Emissions (ton/yr)	CO_2 to EOR (ton/yr)	CO_2 to Storage (ton/yr)	CO_2 to Methanol CDR (ton/yr)	CO_2 to Formic Acid (ton/yr)
Methanol	535,312	-	783,767	27,431	-	-	-	-
LNG	61,609,400	-	58,900,000	824,600	-	497,158	-	-
GTL	2.453,814	-	1,514,700	1,499,553	499,553	1,000,000	-	-
Ammonia-Urea	619,249	-	529,273 U 307,717 A	502,809	-	502,809	-	-
Gas fired Power Plant	220,611	-	2,005,555,072 kWh	1,083,000	-	-	-	-
Desalination	-	444,795,376	626,472,361	-	-	-	-	-
Chlorine	-	1,085,490,000.00	180,000	-	-	-	-	-

Table 4.5*: Ethane and CO_2 allocation for Case 4*

Ethane/Ethylene Sink	Ethane/Ethylene Intake (ton/yr)	Power requirement (kWh/yr)	Product Flow (ton/yr)	CO_2 Emissions (ton/yr)	CO_2 to EOR (ton/yr)	CO_2 to Storage (ton/yr)	CO_2 to Methanol CDR (ton/yr)	CO_2 to Formic Acid (ton/yr)
Ethylene	4,523,787	-	830,000	2,952,588	352,297	1,000,000	181,318	660,000
LD PolyE	809,310	-	795,000	1,248,150	499,553	1,000,000	-	-
HD PolyE	1,711,666	-	1,666,666	3,000,000	1,000,000	1,000,000		
VCM	164,010	-	355,000	7952	-	-	-	-

Table 4.6*: CO_2 flow into CO_2 sinks and treatment units for Case 4*

Sink/Treatment Unit	Flow into Sink/Treatment (ton/yr)	Product Stream (ton/yr)	Fugitive Emissions (ton/yr)	Power Requirement (kWh/yr)
EOR	2,100,000	-	-	-
Formic Acid	660,000	315,652	330,000	828,000,000
Storage	5,000,000	-	-	-
Methanol B	181,318	120,000	16,318	-
LNG Absorption	543,498	-	54,350	148,658,465
VCM Absorption	-	-	-	-
Methanol Absorption	-	-	-	-

4.2 Multi-period Analysis

In the second part of the analysis, a multi-period study has been conducted on an existing industrial cluster. The overall goal of the cluster is to reduce its overall CO_2 emissions by 50% based on no carbon capture. All capital expenditure will be based on period 1 with no additional investments in the subsequent periods. In the first period, comprising of 5 years, no carbon tax will be imposed on the cluster. In the second period, also comprising of 5 years, a carbon tax of \$25/(ton CO_2 emitted) is imposed. The result of the analysis is shown below.

Table 4.7: *Methane and CO_2 allocation in period 1*

Methane and Power Sink	Flow of Methane (ton/yr)	Power Requirement (kWh/yr)	Product Flow (ton/yr)	CO_2 Emissions (ton/yr)	CO_2 to EOR (ton/yr)	CO_2 to Storage (ton/yr)	CO_2 to Methanol CDR (ton/yr)	CO_2 to Formic Acid (ton/yr)
Methanol	535,312	-	783,767	27,431	-	-	-	-
LNG	61,609,400	-	58,900,000	824,600	8,010	-	-	-
GTL	2.453,814	-	1,514,700	1,499,553	18,913	1,000,000	-	-
Ammonia-Urea	6,619,772	-	5,657,925 U 3,289,491 A	5,375,028	1,000,000	1,000,000	181,318	660,000
Gas Fired Power Plant	207,529	-	1,886,628,301 kWh	1,018,779	-	-	-	-
Desalination	-	444,795,376.31	626,472,361	-	-	-	-	-
Chlorine	-	1,085,490,000.00	180,000	-	-	-	-	-

Table 4.8: *Methane and CO_2 allocation in period 2*

Methane and Power Sink	Flow of Methane (ton/yr)	Power Requirement (kWh/yr)	Product Flow (ton/yr)	CO_2 Emissions (ton/yr)	CO_2 to EOR (ton/yr)	CO_2 to Storage (ton/yr)	CO_2 to Methanol CDR (ton/yr)	CO_2 to Formic Acid (ton/yr)
Methanol	535,312	-	783,767	27,431	-	-	-	-
LNG	61,609,400	-	58,900,000	824,600	8,010	-	-	-
GTL	2.453,814	-	1,514,700	1,499,553	499,553	1,000,000	-	-
Ammonia-Urea	4,862,448	-	4,155,939 U 2,416,243 A	3,948,142	1,000,000	1,000,000	-	660,000
Gas Fired Power Plant	207,529	-	1,886,628,301 kWh	1,018,779	-	-	-	-
Desalination	-	444,795,376.31	626,472,361	-	-	-	-	-
Chlorine	-	1,085,490,000.00	180,000	-	-	-	-	-

***Table 4.9**: Ethane and CO_2 allocation in period 1*

Ethane/Ethylene Sink	Ethane/Ethylene Intake (ton/yr)	Power requirement (kWh/yr)	Product Flow (ton/yr)	CO_2 Emissions (ton/yr)	CO_2 to EOR (ton/yr)	CO_2 to Storage (ton/yr)	CO_2 to Methanol CDR (ton/yr)	CO_2 to Formic Acid (ton/yr)
Ethylene	4,523,787	-	830,000	2,952,588	1,000,000	1,000,000	-	-
LD PolyE	809,310	-	795,000	1,248,150	73,077	1,000,000	-	-
HD PolyE	1,711,666	-	1,666,666	3,000,000	-	1,000,000	-	-
VCM	164,010	-	355,000	7952	-	-	-	-

Table 4.10: *Ethane and CO_2 allocation in period 2*

Ethane/Ethylene Sink	Ethane/Ethylene Intake (ton/yr)	Power requirement (kWh/yr)	Product Flow (ton/yr)	CO_2 Emissions (ton/yr)	CO_2 to EOR (ton/yr)	CO_2 to Storage (ton/yr)	CO_2 to Methanol CDR (ton/yr)	CO_2 to Formic Acid (ton/yr)
Ethylene	4,523,787	-	830,000	2,952,588	295,693	1,000,000	-	181,319
LD PolyE	809,310	-	795,000	1,248,150	36,466	1,000,000	-	-
HD PolyE	1,711,666	-	1,666,666	3,000,000	260,277	1,000,000	-	-
VCM	164,010	-	355,000	7952	-	-	-	-

***Table 4.11**: Flow of CO_2 into CO_2 sinks and treatment units in period 1*

Sink/Treatment Unit	Flow into Sink/Treatment (ton/yr)	Product Stream (ton/yr)	Fugitive Emissions (ton/yr)	Power Requirement (kWh/yr)
EOR	2,100,000	-	-	-
Formic Acid	660,000	315,652	330,000	828,000,000
Storage	5,000,000	-	-	-
Methanol B	181,318	120,000	16,318	-
LNG Absorption	-	-	-	-
VCM Absorption	-	-	-	-
Methanol Absorption	-	-	-	-

***Table 4.12**: Flow of CO_2 into CO_2 sinks and treatment units in period 2*

Sink/Treatment Unit	Flow into Sink/Treatment (ton/yr)	Product Stream (ton/yr)	Fugitive Emissions (ton/yr)	Power Requirement (kWh/yr)
EOR	2,100,000	-	-	-
Formic Acid	660,000	315,652	330,000	828,000,000
Storage	5,000,000	-	-	-
Methanol B	181,318	120,000	16,318	-
LNG Absorption				
VCM Absorption	-	-	-	-
Methanol Absorption	-	-	-	-

Over the 10 year period, the cluster generated a profit of \$1.495*10^{11} and emitted 80 mega tons of CO_2. In the first period, all the plants and CO_2 sinks operated at maximum capacity. The approach chose to do this to maximize profits generated by all the plants. However, the implementation of the carbon tax changed the profitability of the cluster in the second period. In the first period, the cluster generated a profit of 1.531*10^{10} \$/yr while the second period generated 1.458*10^{10} \$/yr. The decrease in profits in the second period is due to three factors. The most obvious factor is the implementation of the carbon tax. The industrial cluster in the second period emitted 7.3 mega tons of CO_2 per year, which is 83.6% of the CO_2 emitted from the first period. Due to these emissions, the carbon tax in the second period amounted to 1.82*10^{8} \$/yr. The second factor that contributed to the decrease in profits is the decrease in the capacity of the Ammonia-Urea plant. In the second period, the Ammonia-Urea plant operated at 73% of its maximum capacity. The reason for the decrease is identical to the logic used in Case 4 of the single-period study where ammonia and urea don’t bring enough profit as GTL nor high-density polyethylene. The final factor that lead to the decrease in profits is the costing of the Ammonia-Urea plant. In a single-period analysis, the approach is free to scale up or scale down the CAPEX and OPEX of any plant by using the technical factors. However, in a multi-period analysis, this logic does not apply. In a multi-period analysis, the CAPEX is fixed in all the periods as the same plant built in the first period will carry on to the second period while the OPEX can vary based on the production. The freezing of the CAPEX of the Ammonia-Urea plant at maximum capacity while also operating at 73% of the maximum capacity contributed to the loss in profit in the second period. When looking at the renewables, both periods used solar at 20% of the total power requirement to supply 471,657,075 kWh/yr. The use of solar contributed to savings of 7*10^{6} \$/yr in methane costs and 254,695 tons of CO_2 emitted per year. Another observation to be made is that the approach chose not to activate any of the CO_2 absorption units to allocate dilute sources of CO_2. This result is reasonable as it is more profitable to allocate pure sources to the sinks and decrease production as the treatment units incur extra unnecessary costs. These costs include the CAPEX of the treatment units as well as the extra methane to be burned to supply electricity to the treatment units. It will be counterproductive to burn more methane and emit more CO_2 for a unit to treat CO_2 sources that is also not 100% efficient.

5. CONCLUSION AND FUTURE WORK

The optimization approach that was used in this paper helped explore the relationship between allocating methane, ethane, CO_2, and power in an industrial cluster to maximize profitability while also decreasing emissions. The overall goal of this paper was to explore how the diversification of products from plants in Qatar were profitable but also explore strategies to reduce emissions when several restrictions were placed. Different case studies were presented in both single-period and multi-period analysis to showcase how an industrial cluster can be planned in the future. The approach was given numerous choices when it comes to product selection, source-sink allocation, as well as power source. Evidently from the data, the industrial cluster managed to profitably reduce emissions by using profitable CO_2 sinks. However, it was also observed that the approach always chooses to decrease production first before ever treating any dilute source of CO_2 and allocating to any of the sinks. This shows the need to develop more efficient technology and processes that could effectively utilize and treat CO_2 without generating excessive fugitive emissions. In the future, the role of direct air capture technology will be investigated. Additionally, renewable energy sources can be improved to integrate more of the power and heat into the analysis. With all these strategies combined, it will help future policy makers in drafting climate change strategies to profitably reduce emissions.

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APPENDIX A: SAMPLE CALCULATION

5.1 GTL Plant

5.1.1 CAPEX

$$FCI_B = FCI_A (\frac{Capacity_B}{Capacity_A})^x$$

$$\therefore FCI_B = \$347.6 \text{ MM} (\frac{34000}{5430})^{0.6} = \$1044.93 \text{ MM}$$

$$FCI_{t2} = FCI_{t1} (\frac{Cost\ index\ at\ time\ t2}{Cost\ index\ at\ time\ t1})$$

$$\therefore FCI_{t2} = \$1044.93 \text{ MM} \left(\frac{556.8}{607.5}\right) = \$957.72 \text{ MM}$$

Conversion barrels per day to dollars per year:

1 ton= 7.33 barrels

$$CAPEX\left(\frac{\$}{ton.yr}\right) = CAPEX(\$) \times \frac{1}{plant\ life\ (year)} \times \frac{1}{capacity\ (\frac{barrel}{day})} \times \frac{1}{operational\ days\ (day)} \times \frac{7.33\ barrels}{1\ ton}$$

$$\therefore CAPEX\left(\frac{\$}{ton.yr}\right) = \$957.72 \times 10^6 \times \frac{1}{20\ years} \times \frac{1}{34000\ \frac{barrel}{day}} \times \frac{1}{333\ day} \times \frac{7.33\ barrels}{1\ ton} = 31.28\ \frac{\$}{ton.yr}$$

5.1.2 OPEX

$$FCI_B = FCI_A (\frac{Capacity_B}{Capacity_A})^x$$

$$\therefore FCI_B = \$78.88\ \text{MM}(\frac{34000}{5430})^{0.6} = \$237.13\ \text{MM}$$

$$FCI_{t2} = FCI_{t1}(\frac{Cost\ index\ at\ time\ t2}{Cost\ index\ at\ time\ t1})$$

$$\therefore FCI_{t2} = \$237.13\ \text{MM}\left(\frac{556.8}{607.5}\right) = \$217.34\ \text{MM}$$

$$OPEX\left(\frac{\$}{ton}\right) = OPEX(\$) \times \frac{1}{capacity\ (\frac{barrel}{day})} \times \frac{1}{operational\ days\ (day)} \times \frac{7.33\ barrels}{1\ ton}$$

$$\therefore OPEX\left(\frac{\$}{ton}\right) = \$217.34 \times 10^6 \times \frac{1}{34000\ \frac{barrel}{day}} \times \frac{1}{333\ day} \times \frac{7.33\ barrels}{1\ ton} = 140.71\ \frac{\$}{ton}$$

APPENDIX B: RAW DATA

Table B. 1*: Literature capacity, CAPEX, OPEX, and commodity price*

Plant	**Capacity**	**CAPEX ($)**	**OPEX ($/yr)**	**Price of Commodity ($/ton)**
VCM	355,000 (tons/yr)	168,385,152[65]	21,300,000[65]	765
Chlorine	166,500 (tons/yr)	111,000,000[31]	22,500,000[31]	350
Methanol	1,665,000 (tons/yr)	41,975,000[20]	36,500,000[20]	442
Ethylene	830,000 (tons/yr)	551,852,90[50]	798,604,97[50]	1093
Power	N/A	614$/kw[39]	-	-
Ammonia	499,500 (ton/yr)	450,000,000[41]	88,726,185	550
Urea	432,900 (tons/yr)	6,974,019[41]	3,337,659[41]	405
GTL	34,000 (barrel/day)	347,600,000[66]	788,830,000[66]	850
LNG	2,920,000 (tons/yr)	730,000,000[20]	415,376,774[20]	370
Desalination	626,472,361 (tons/yr)	6,036,815	50,117,789	1.8
HDPE	200,000 (tons/yr)	108,000,000[50]	132,000,000[50]	1420
LDPE	300,000 (tons/yr)	141,000,000[50]	192,000,000[50]	1250