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# Multi-period Resource Integration in Carbon Dioxide Converting Networks

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Industrial symbiosis coupled with emission footprint minimization and resource conservation strategies is a highly acclaimed means of sustainably tackling global concerns of environmental pollution and depleting resources. Setting carbon reduction targets is the primary means policymakers employ to reduce emissions. The reduction is achieved by many pathways which include energy efficiency, fuel switching, carbon capture utilization and storage (CCUS), renewable energy (RE) and more recently, negative emission technologies (NETs). An eco-industrial park (EIP) incorporates industrial symbiosis to implement these solutions by synergistically exchanging resources between its entities. While many works have integrated a single resource in EIPs, the integration of multiple resources is an emerging area with remarkable potential to achieve sustainable benefits. This work introduces an extension to multiple resource integration by allowing it to translate over a time horizon. Policies are designed to achieve a target over a specified time horizon. The emerging reduction pathways will therefore change over time either by adapting to a policy or by modifying itself to improve performance, thereby making policies critical to an EIP's design during its lifetime. The proposed method will employ a mixed-integer linear programming model to optimize network configurations and planning strategies for a set of objectives over multiple time periods. The model will also assess the network's economic and environmental benefits to allow stakeholders to assess and implement changes in their facilities. The model is illustrated by developing a $CO_2$ converting network that maximizes total profit and minimizes emissions while simultaneously adapting to systematic changes in environmental policies.

## 1. Introduction

The industrial sector strives to achieve sustainability amid the rampant increase in $CO_2$ emissions globally owing to an increasing population and industrialization. In response to this challenge, eco-industrial parks, through their shared infrastructure and concentrated industrial activities, have emerged to achieve economic and environmental benefits through process integration, industrial ecology, and circular economy. Individual processes are coupled with $CO_2$ reduction pathways and optimized through process integration to develop green clusters capable of converting $CO_2$ into value-added products. While integration of single resources has been extensively studied, integration of multiple resources is a more recent focus, and include works such as the simultaneous integration of water and energy by Leong et al. (2017), and the integration of an unlimited number of resources, both material and energy, by Ahmed et al. (2020). Therefore, industrial parks can become effective strategies for policymakers who seek to incorporate sustainable economic development within their jurisdiction. The two primary instruments employed by policymakers to achieve emission reduction are the carbon tax and the cap-and-trade system (Goulder and Schein, 2013). The regulatory authority sets the price of $CO_2$ emissions under the carbon tax and thereby offers price certainty; in contrast, the authorities set the overall allowable quantities of emissions under the cap-and-trade system, offering benefit certainty (Avi-Yonah and Uhlmann, n.d.). While both strategies provide benefits in their own regard, these benefits are only visible in future periods. Hence, implementing these strategies in industrial $CO_2$ converting networks must be explored over time to assess emission reduction potential. Previous works look into integration of limited resources across periods such as the design of cost-effective clusters that integrated utility and $CO_2$ mitigation strategies like carbon capture and storage, and carbon credits trading (Ahn and Han, 2018), and the optimization of carbon networks with policy implementation to achieve specified footprints and enable transition planning through both non-linear

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(Al-Mohannadi et al., 2016) and linear programming models (Al-Mohannadi et al., 2020). Some other works include the design of low cost inter-plant hydrogen networks that can remain optimally operable with regeneration by Shehata et al. (2018) and the synthesis and retrofitting of optimal water networks based on variabilities in operation by Sotelo-Pichardo et al., (2014) over the considered time horizon. Integration of multiple resources simultaneously can pave the way for creating more circularity within the system. Therefore, a systematic approach that optimizes a network while integrating multiple resources over a time horizon is presented through this work. Analysis over time enables better planning and comprehension of the system's response to various policies, thereby assisting policymakers in drafting these reduction schemes and allowing cluster stakeholders to assess its economic and environmental performance when the policies come into effect. The following section outlines the approach, after which an illustrative example demonstrates its use.

## 2. Approach

The approach described in this work allows for the design and integration of a given set of plants in an industrial cluster over multiple periods to achieve specific economic and environmental targets. The cluster converts a given amount of $CO_2$ and restricts the level of emissions released, through carbon caps and taxes defined by the user. The objective of this work is to design integration networks that achieves the set targets while attaining the maximum profit possible over all specified periods by integrating both material and energy resources.

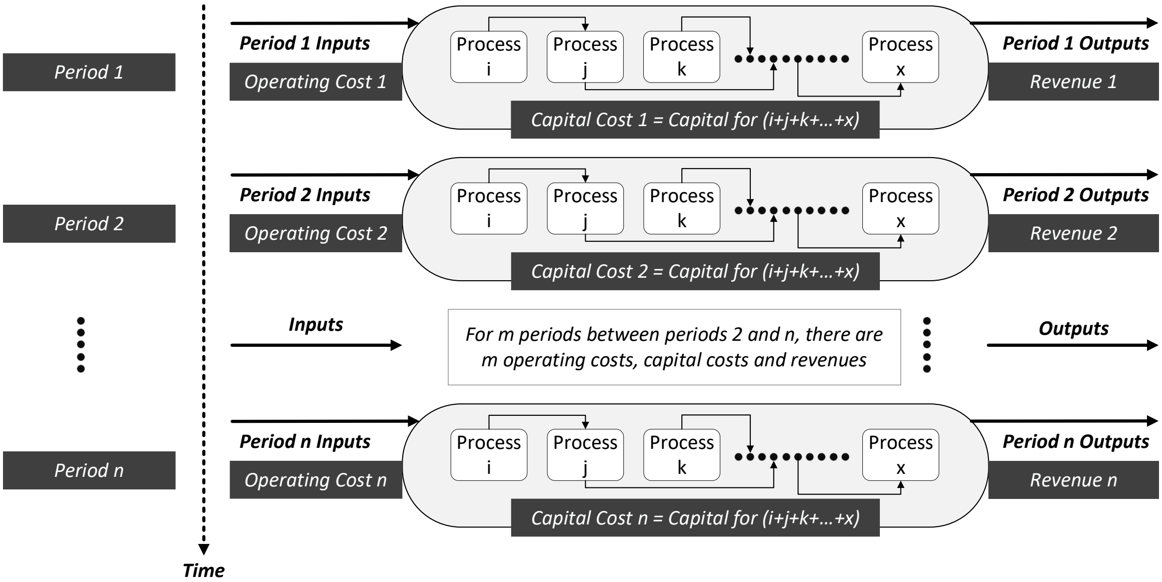

*Figure 1: General schematic of the cluster integration over periods*

The representation in Figure 1 shows an industrial cluster that consists of several processes, each having resources that can be integrated within a given period. A mixed integer linear programming (MILP) model is used to optimize the networks to achieve profitability across all periods. Equality and inequality constraints are placed on total resource balances, while non-negativity constraints check process capacities, resource inputs, and outputs. The optimization first identifies the process capacities for each period, after which the flows of the resources entering and leaving the cluster are determined for each period based on the corresponding process capacities. The maximum profit across all periods, which serves as the objective function is then determined.

$$Profit = \sum_{Period} \sum_{Process} Revenue - Operating\ Cost - Capital\ Cost \qquad (1)$$

Resources are integrated through piping systems and must meet the inlet specifications such as temperature, pressure, and quality conditions of the receiving process. Each process within the cluster has revenue, capital, and operating cost parameters associated with its resource parameters, determined at steady state operations, which define the process's material and energy demands and products. Each of these costs and resource related parameters can vary with time, and therefore independent calculations for profit are made for each period. The profit is determined after accounting for the capital and operating costs from the revenues. The sum of the profit for all periods, as shown in Eq(1), is optimized to maximize profit using the “What’sBest!16.0.2.6” solver in Microsoft Excel 2019 (Lindo Systems, 2021).

## 3. Case Study

To illustrate the approach, an industrial cluster with a set of nine given processes assessed the impact of carbon caps and taxes for meeting varying footprint constraints over time. The cluster designed should convert at least 600,000 t of $CO_2$ across all periods by converting a minimum of 200,000 t in each period. The case study analyses two scenarios considered over 3 periods, where each period has 5 years. The first scenario looks at decreasing carbon emission caps with increasing carbon tax rates, while the second scenario additionally incorporates capital cost reduction for developing technologies, which will be described further after the cluster and its constituent processes are defined. The processes investigated include air separation (AS), water splitting (WS), and the production of methanol (MP), ammonia (AP), and urea (UP). To tackle environmental pollution sequestration (SQ), water treatment (WT), and carbon capture units for methanol (MC) and urea (UC) production were also considered. Table 1 lists the processes with their reference products or the primary resource the process yields and its capital costs, which remain unchanged throughout the periods considered. The capital costs shown in the table below reflect the CAPEX parameter in Ahmed et al. (2020) annualized for an operational life of 15 years, where each process is assumed to have operational capacities between 10,000 and 60,000 tons per year (t/y).

*Table 1: Industrial cluster process specifics*

| Process | AS | WS | MP | AP | UP | MC | UC | SQ | WT |
|---|---|---|---|---|---|---|---|---|---|
| Reference Product | $O_2$ | $H_2$ | $CH_3OH$ | $NH_3$ | $CH_4N_2O$ | $CO_2$ | $CO_2$ | $CO_2$ | $H_2O$ |
| Capital Cost ($/t) | 24.21 | 1038.67 | 28.61 | 38.89 | 21.48 | 2.27 | 2.27 | 12.03 | 0.34 |

Resource parameters are obtained from mass and energy balances of a process, where the negative and positive sign for a parameter indicates if the resource is a process input or output respectively. A resource parameter is defined as the ratio of the quantities of a resource utilized or produced by a process to its reference product. Table 2 gives the resource parameters used for the study for each process. While these parameters can change with time due to changes in processes or improvements in process efficiency, it should be noted that the resource parameters do not change over the periods in this study.

*Table 2: Resource parameters given per unit of the reference product adopted from Ahmed et al. (2020).*

| Resource | AS (/t $O_2$) | WS (/t $H_2$) | MP (/t M) | AP (/t A) | UP (/t U) | MC (/t $CO_2$) | UC (/t $CO_2$) | SQ (/t $CO_2$) | WT (/t $H_2O$) |
|---|---|---|---|---|---|---|---|---|---|
| Air (t) | -4.33 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Oxygen (t) | 1.00 | 8.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Nitrogen (t) | 3.27 | 0.00 | 0.00 | -0.85 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Water (t) | 0.00 | -9.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 1.00 |
| Hydrogen (t) | 0.00 | 1.00 | -0.20 | -0.18 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Carbon dioxide (t) | 0.00 | 0.00 | -1.76 | 0.00 | -0.73 | 1.00 | 1.00 | -1.00 | 0.00 |
| Ammonia (t) | 0.00 | 0.00 | 0.00 | 1.00 | -0.57 | 0.00 | 0.00 | 0.00 | 0.00 |
| Methanol (t) | 0.00 | 0.00 | 1.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| MP emissions (t) | 0.00 | 0.00 | 0.40 | 0.00 | 0.00 | -3.90 | 0.00 | 0.00 | 0.00 |
| AP emissions (t) | 0.00 | 0.00 | 0.00 | 0.03 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Argon (t) | 0.06 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Waste water ($m^3$) | 0.00 | 0.00 | 0.56 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | -1.11 |
| UP emissions (t) | 0.00 | 0.00 | 0.00 | 0.00 | 0.30 | 0.00 | -4.27 | 0.00 | 0.00 |
| MC emissions (t) | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 2.90 | 0.00 | 0.00 | 0.00 |
| UC emissions (t) | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 3.27 | 0.00 | 0.00 |
| Urea (t) | 0.00 | 0.00 | 0.00 | 0.00 | 1.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Contaminants (t) | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.11 |
| Condensate (t) | 0.00 | 0.00 | 0.00 | 0.00 | 1.10 | 0.00 | 0.00 | 0.00 | 0.00 |
| Electricity (kWh) | -245 | -54000 | -169 | -785 | -125 | -27.30 | -27.30 | -95.30 | -5.00 |
| LP steam (t) | 0.00 | 0.00 | 0.00 | 0.00 | -1.20 | -1.21 | -1.21 | 0.00 | 0.00 |
| Cooling water ($m^3$) | 0.00 | 0.00 | -26.54 | 0.00 | -75.00 | 0.00 | 0.00 | 0.00 | 0.00 |

Table 3 shows the resources and their respective prices obtained from Ahmed et al. (2020). The cluster does not produce power, and hence power is imported at the cost specified in the table below, while the resources from Table 2 that are not specified here are assumed to be obtained free of charge. Furthermore, while resource prices can also vary based on market variables, it is assumed they do not change in this study over time.

*Table 3: Resource prices across all periods*

| Resource | Price ($) | Unit |
|---|---|---|
| Oxygen | 79.00 | \$/t |
| Water | 5.00 | $\$/m^3$ |
| Hydrogen | 1,200.00 | \$/t |
| Carbon dioxide | 40.00 | \$/t |
| Ammonia | 415.00 | \$/t |
| Methanol | 320.00 | \$/t |
| Urea | 305.00 | \$/t |
| Electricity | 0.03 | \$/kWh |
| LP steam | 4.80 | \$/t |
| Cooling water | 0.03 | $\$/m^3$ |

The two scenarios analysed will be subject to the carbon cap and tax scheme as outlined in Table 4. The carbon cap is specified in such a way that it only allows a certain portion of the $CO_2$ entering the cluster to leave it, while the carbon tax penalizes any $CO_2$ emitted by setting a price on it. While the carbon cap has more recently started to gain traction in reducing emissions, the carbon tax is known to significantly reduce emissions with rates as low as 1 \$/t $CO_2$ and as high as 200 \$/t $CO_2$ (Hájek et al., 2019). The first scenario optimizes the cluster with the policy scheme in Table 4 in place. The second scenario differs from the first in that it additionally considers the potential cost savings in future periods from adopting developing technologies. Hydrogen production via electrolysis is an example of a developing technology that is anticipated to undergo a considerable reduction in its cost, specifically of its electrolyzers, following a learning rate model (Schmidt et al., 2017). Electrolysis was also identified to have the highest annualized capital cost in Table 1 of all the processes considered. Therefore, in the second scenario of the case study, a 10% capital cost reduction will be applied per period.

*Table 4: Policy scheme for both scenarios*

| Policy | Period 1 | Period 2 | Period 3 |
|---|---|---|---|
| Carbon Cap | 20% | 50% | 95% |
| Carbon Tax | 10 \$/t $CO_2$ | 50 \$/t $CO_2$ | 145 \$/t $CO_2$ |

For both scenarios, the first and second periods consume and emit 43,980 and 4,716 t $CO_2$/y by activating the air separation, water splitting, ammonia, and urea production processes. The third period with stricter reduction schemes in place additionally activates the sequestration process along with the previously activated processes to consume and emit 40,000 and 2,000 t $CO_2$/y. The operational capacities of the activated processes in tons of the reference product per period (t/period) are shown in Table 5, where Scenario 1 achieves an overall profit of \$19 M with a capital cost of \$227 M, and Scenario 2 achieves a profit of \$35 M with a capital cost of \$216 M.

*Table 5: Design capacities in t/period of the reference products*

| Process | Unit | Scenarios 1 & 2 (Periods 1 & 2) | Scenario 1 (Period 3) | Scenario 2 (Period 3) |
|---|---|---|---|---|
| Air Separation | t $O_2$/period | 300,000 | 300,000 | 300,000 |
| Water Splitting | t $H_2$/period | 50,000 | 50,000 | 54,576 |
| Urea Production | t $CH_4N_2O$/period | 300,000 | 127,226 | 127,226 |
| Ammonia Production | t $NH_3$/period | 274,833 | 274,833 | 299,989 |
| Sequestration | t $CO_2$/period | 0 | 106,743 | 106,743 |

The optimization designs the same cluster in the first and second periods for both scenarios as illustrated in Figure 2. In this design, urea production operates at its maximum capacity for both periods to utilize all the $CO_2$ entering the cluster. The production of urea also generates emissions, however, these fall below the specified carbon cap. To facilitate urea production, the ammonia production process was activated, while the air separation and water splitting processes were activated to supply the nitrogen and hydrogen needed for ammonia production. While the hydrogen produced was entirely utilized for ammonia production, only a part of the nitrogen produced was used. The rest of the nitrogen leaves the cluster as a waste stream, whereas the oxygen from the air separation and water splitting processes were sold along with the ammonia unused by urea production. Thus, the cluster generates revenues from ammonia, oxygen, and urea.

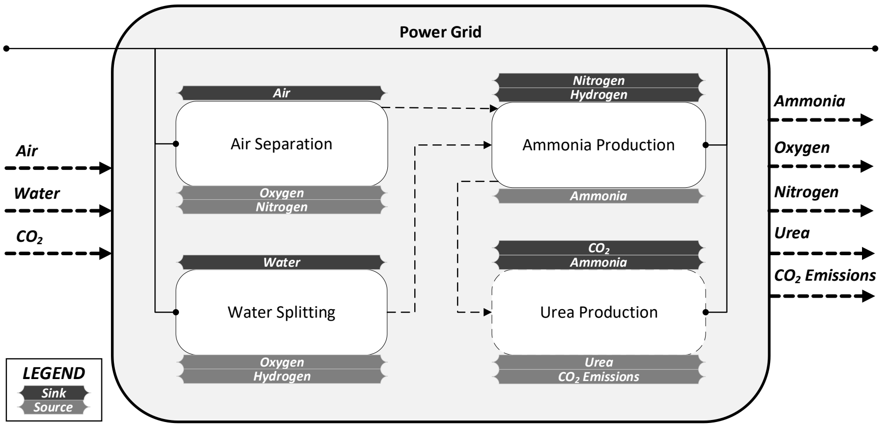

*Figure 2: Schematic of the cluster generated for periods 1 and 2*

The third period yields two designs for both scenarios that are structurally similar as illustrated in Figure 3, but have different operational capacities as shown in Table 5. The primary difference between the first two periods and the third is the activation of the sequestration process to meet the stringent $CO_2$ cap constraint and carbon tax. While revenues are still generated from ammonia, oxygen, and urea, the production of urea decreases by nearly 58%. The third period only permits 5% of the $CO_2$ entering the cluster to leave, and since urea production leads to the release of emissions, only smaller operational capacities with corresponding lower emission levels are feasible. The loss in revenue from this decrease is made up by ammonia, whose cluster output was nearly doubled as much less is utilized for urea production. The slightly increased production of hydrogen and ammonia in Scenario 2, when comparing the third periods of both scenarios, stems from reducing the capital cost associated with the electrolyzer, which allowed for greater hydrogen production, and subsequently greater ammonia production. The decrease in capital costs was applied to both the second and the third periods. However, the decrease only furthered these productions in the third period, where there was a 20% decrease from the first, and did not lead to any changes in the second period, indicating that significant reductions are necessary to vary the design.

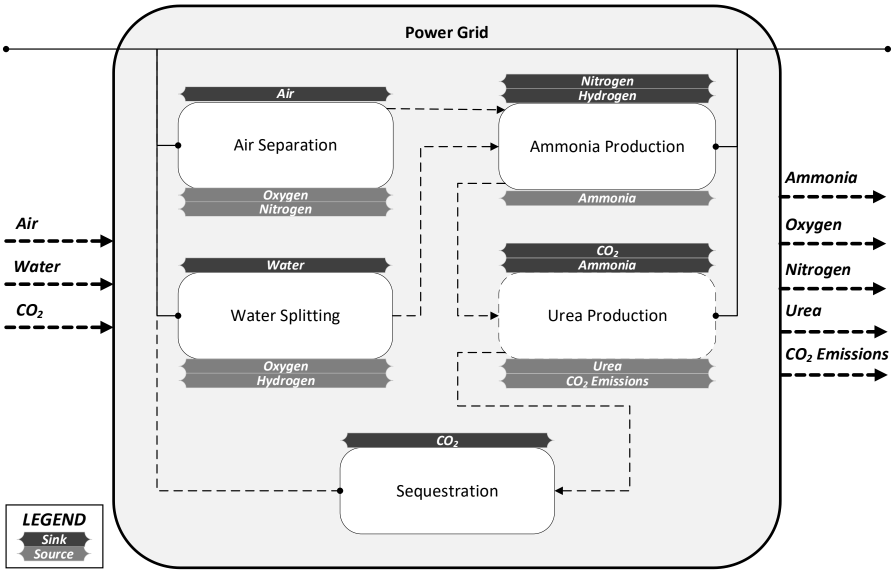

*Figure 3: Schematic of the cluster generated for period 3*

The methanol production process was not activated as a carbon sink in both scenarios owing to its high operating cost. Therefore, the case study emphasizes the importance of policy guidelines and cost efficiencies in the economic and environmental constraints of industrial clusters.

## 4. Conclusion

The integration of multiple resources over multiple periods has been investigated in carbon converting networks with policy frameworks to achieve overall footprint reductions. The optimization problem utilizes mixed integer linear programming to optimize for overall profit across the periods considered and generated carbon-negative designs. The case study highlights the significant impact of both policies and process efficiencies on design strategies of industrial clusters using two scenarios. The first investigated policy schemes solely, while the second additionally investigated capital cost reduction on a cluster that must convert a minimum specified amount of $CO_2$. The results indicate that stringent policy measures are necessary to elicit significant changes in designs of carbon converting networks. Furthermore, a significant reduction in investment costs is necessary for low-carbon energy systems like water electrolysis to generate profits. These observations imply that policy frameworks and process parameters must be simultaneously factored to allow policymakers to propose regulations and industrial park innovators to design clusters for the same objective.

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