The effect of location and inter-cluster networks on the optimal decarbonization of ammonia production

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Abstract

Ammonia is a key platform chemical, especially for the synthesis of fertilizers, and an important energy vector in net-zero energy systems. Yet, it faces environmental challenges due to its energy-intensive production and substantial greenhouse gas emissions. As such, prioritizing the decarbonization of the ammonia production process is crucial. In this study, we employ mixed integer linear programming optimization to assess different decarbonization strategies for low-carbon ammonia production. As a case study, we consider two existing production sites in the Netherlands, which allows us to investigate the influence of site-specific factors and the advantages of inter-cluster networks. Results show, that retrofitting plants with carbon capture achieves an 83-97.3 % cost-effective emission reduction. We also show, that achieving an early net-zero ammonia industry via H2O electrolysis presents challenges due to the availability of green electricity and the CO2 intensity of the electricity grid.

**Keywords**: Ammonia production, decarbonization, MILP, location, inter-cluster networks

* 1. Introduction

Ammonia is a vital platform chemical used in various products, primarily serving as a key component in 70 % of the world's nitrogen fertilizer production, which is essential for supporting global food production. Traditionally relying on energy-intensive grey hydrogen derived from natural gas-based steam reforming, the ammonia industry currently accounts for 2 % of global energy consumption and contributes 1.3 % of greenhouse gas emissions (IEA, 2021; IRENA and IEA, 2022). As such, prioritizing the decarbonization of the ammonia production process is crucial.

More sustainable, alternative routes for ammonia production include hydrogen production with carbon capture, electrified steam methane reforming, and electrolysis. These rely on the availability of low-carbon electricity and/or long-term CO2 storage. The accessibility of these resources across production site locations might vary, adding significant complexity to identifying the most efficient decarbonization route.

Here, we employ a mixed-integer linear program (MILP) model to determine the optimal decarbonization configurations – considering both sizing and operation – for ammonia production at two existing locations in the Netherlands. The analysis considers three alternative production routes and the impact of inter-cluster connections involving electricity, CO­2, and hydrogen. A full-year, hourly resolution is adopted to incorporate seasonal and hourly energy variations in energy prices and renewables availability.

* 1. Method
		1. MILP modeling framework

The decision variables that are optimized within the MILP model include design variables (i.e. selection and size of technologies) and operational variables (i.e. energy and material flows and storage levels). The framework uses hourly resolved input data on weather conditions, prices, and demand data together with a set of available technologies and the corresponding cost and performance coefficients. The objective function of the problem is to minimize the total annualized system cost, $J$, that is the sum of the technology and infrastructure cost, $J\_{c}$, and the operating cost, $J\_{o}$. The annualized cost is defined as

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| $$J\_{c}=\sum\_{i\in M}^{}\left(1+ψ\_{i}\right)λ\_{i}S\_{i}a\_{i}$$ | (1) |

where $λ\_{i}$ is the size-dependent cost parameter of technology/infrastructure $i$ and the annuity factor $a\_{i}$ is used to compute the annualized capital costs for each $i\in M$. The maintenance cost is included as fraction of the annual capital costs $ψ\_{i}$. The operating cost of the system is determined by the annual amount electricity and methane import, and the annual amount of CO2 that is exported and stored, which is expressed as

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| $$J\_{o}=\sum\_{t=1}^{T}\left(u\_{j,t}U\_{j,t}+v\_{CO\_{2}}V\_{CO\_{2},t}\right)$$ | (2) |

where $U\_{j,t}$ is the import and $u\_{j,t}$ the hourly price at hour $t$ of each imported carrier $j\in N$ (only methane and electricity in this work) and $V\_{CO\_{2},t}$ is the export of CO2 to an offshore storage with the costs $v\_{CO\_{2}}$. The total emissions include indirect emissions from the import of electricity and direct emissions from the ammonia/hydrogen production processes, and are calculated as

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| --- | --- |
| $$e\_{CO\_{2}}=\sum\_{t=1}^{T}\left[\left.ε\_{elec, t}U\_{elec,t}\right.+\sum\_{i\in M}^{}ϵ\_{i}F\_{input,i,t}\right]$$ | (3) |

where $ε\_{elec, t}$ is the carbon intensity of the electricity grid, $ϵ\_{i}$ is the emission factor of the technology per unit of main input carrier. It is assumed that all pure CO2 that is not supplied to the demand or transported and stored is emitted. There are no CO2 emission costs included in this work.

The balance for each material and energy carrier is formulated as:

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| --- | --- |
| $$\sum\_{i\in M}^{}\left(U\_{j,i,t}+P\_{j,i,t}-V\_{j,i,t}-F\_{j,i,t}\right)-D\_{j,t}=0$$ | (4) |

where $U\_{j,i,t}$ is import, $P\_{j,i,t}$ is the production, $V\_{j,i,t}$ is export, $F\_{j,i,t}$ is consumption and $D\_{j,t}$ is the demand of each carrier $j\in N$ at each hour $t$. The conversion performances of the technologies are described as

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| --- | --- |
| $$P\_{j^{'},t}=α\_{j^{'}}F\_{input,t}$$ | (5) |

and

|  |  |
| --- | --- |
| $$F\_{j^{''},t}=β\_{j^{''}}F\_{input,t}$$ | (6) |

where $α\_{j^{'}}$ and $β\_{j^{''}}$ represent the conversion efficiencies per unit of main input carrier of the outputs $j^{'}\in J^{'}⊂J$ and the ratio between inputs $j^{''}\in J^{''}⊂J$, respectively. The operation range of the technologies is expressed as

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| --- | --- |
| $$γ\_{i} S\_{i}\leq F\_{input,t}\leq S\_{i}$$ | (7) |

where $γ\_{i}$ is the minimum feasible operating point as a fraction of the installed capacity. Finally, the ramping rate (RR) is enforced by the following inequality constraints:

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| --- | --- |
| $$ - RR \leq F\_{input,t} - F\_{input,t-1} \leq RR$$ | (8) |

For a detailed description of the modeling of storage, the reader is referred to Gabrielli et al. (2018).

* + 1. Site data and boundary conditions

Our case study includes two ammonia production sites in the Netherlands, placed at the Chemelot industrial cluster and Sluiskil, respectively. The data for the respective sites is shown in Table 1. An hourly ammonia demand needs to be produced, which is based on the annual ammonia production capacity in 2017 (1819 kt for Sluiskil and 1184 kt for Chemelot) (Batool & Wetzels, 2019). As both sites also produce urea downstream of the ammonia plant, we include an hourly CO2 demand based on the annual urea production capacity (1300 kt/yr at Sluiskil, and 525 kt/yr at Chemelot) and a CO2 consumption of 0.75 t CO2/t Urea (Batool & Wetzels, 2019). The additional CO2 is either emitted or, in the case of the Sluiskil site, it can be transported and stored offshore for 54.56 €/t CO2 (IEA, 2022). Moreover, hydrogen and CO2 can be transported between the production sites, for which we assume the required hydrogen infrastructure exists. The overall length of the pipelines is assumed to be 155 km, including the distance between the two sites and a 10 % extra accounting for terrain factors (Roussanaly et al., 2013); the investment costs for the CO2 pipeline is 3.4 m€/km (Mikunda et al, 2011). Finally, we use a methane price of 35 €/MWh and electricity can be bought from the grid at both production sites for an hourly fluctuating price and CO2 intensity that reflects 2030 as the base year. For more information on the modeling of electricity prices and CO2 rates, the reader is referred to (Koirala et al., 2021).

* + 1. Ammonia production processes

The traditional ammonia production process relies on the energy-intensive steam reforming process to produce hydrogen from fossil fuels, mainly methane, which is used with nitrogen in the Haber-Bosch process. One of the most common production processes is the Kellogg, Brown and Root (KBR) process, which we consider as the baseline process. The following alternative hydrogen production technologies are evaluated: KBR with carbon capture (CC) from flue gas, electric steam methane reforming (eSMR), and alkaline electrolyzers (AEC). The technology cost and performance are shown in Table 2 and 3. In contrast to the KBR, where stoichiometric nitrogen for the Haber-Bosch process is added via the secondary autothermal reformer (ATR), the eSMR and the electrolyzers require a complementary ASU to produce the required nitrogen. Furthermore, we assume that the CO2 from the syngas in the KBR is always separated. Although conventional production is typically steady-state, the electric technologies allow for a more flexible production responding to the availability of renewables (Wismann et al., 2021), which is why ammonia and CO2 buffer storage is included in the analysis to deal with fluctuations in production.

Table 1: Site-specific input data for the Sluiskil and Chemelot ammonia production sites.

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| --- | --- | --- | --- | --- | --- |
| **Node** | **Hourly ammonia demand [t/h]** | **Hourly CO2 demand [t/h]** | **Offshore CO2 storage cost [€/t CO2]** | **Average electricity price [€/MWh]** | **Average electricity CO2 intensity [t/MWh]** |
| Sluiskil | 208 | 111 | 54.56 | 65.89 | 0.0636 |
| Chemelot | 135 | 45 | - | 91.02 | 0.0636 |

Table 2: Technology performance data for the conventional and alternative hydrogen production technologies, ammonia synthesis process and storage.

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| --- | --- | --- | --- | --- | --- | --- | --- |
| Technology | Inputs | Input ratio ($β\_{j^{''}}$) | Outputs | Output ratio ($α\_{j^{'}}$) | Emission factor (ϵ*i*) [t/input] | Minimum load ($γ\_{i}$) [%] | Ramping rate [unit/h] |
| *KBR* | {methane, electricity} | [1, 0.001] | {hydrogen, CO2, nitrogen} | [0.807, 0.171, 0.137] | 0.035 | 0.7 | 7 |
| *KBR with CC* | {methane, electricity} | [1, 0.015] | {hydrogen, CO2, nitrogen} | [0.807, 0.203, 0.137] | 0.003 | 0.7 | 7 |
| *eSMR* | {electricity, methane} | [1, 3.676] | {hydrogen, CO2} | [3.408, 0.739] | 0.01 | 0.3 | 70 |
| *Alkaline electrolyzer* | {electricity} | [1] | {hydrogen} | [0.665] | 0 | 0.2 | - |
| *Haber Bosch process* | {hydrogen, nitrogen} | [1, 0.139] | {ammonia} | [0.168] | 0 | 0.3 | 70 |
| *Air separation unit* | {electricity} | [1] | {nitrogen} | [4.000] | 0 | 0 | - |
| *Ammonia storage* | {ammonia, electricity} | [1, 0.01] | {ammonia} | [1] | 0 | - | - |
| *CO2 buffer storage* | {CO2} | [1] | {CO2} | [1] | 0 | - | - |

Table 3: Technology cost data for the conventional and alternative hydrogen production technologies, the ammonia synthesis process and storage.

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| --- | --- | --- | --- | --- | --- |
| Technology | CAPEX [€/unit] | Unit | OPEX [%] | Lifetime [y] | Discount rate |
| *KBR* | 800902 | MWth | 0.04 | 25 | 0.1 |
| *KBR with CC* | 949004 | MWth | 0.04 | 25 | 0.1 |
| *eSMR* | 2484888 | MWel | 0.02 | 25 | 0.1 |
| *Alkaline electrolyzer* | 1400000 | MWel | 0.02 | 30 | 0.1 |
| *Haber bosch process* | 460650 | MWth | 0 | 25 | 0.1 |
| *Air separation unit* | 3906200 | MWel | 0 | 20 | 0.1 |
| *Ammonia storage* | 1034 | tonne ammonia | 0 | 25 | 0.1 |
| *CO2 buffer storage* | 551 | tonne CO2 | 0.06 | 25 | 0.1 |

* 1. Results

To assess the impact of geographical location and inter-cluster networks on the decarbonization of the ammonia industry, we employed a two-step optimization approach: first an individual site optimization followed by the optimization of both sites simultaneously with interconnecting networks. Several optimizations were carried out minimizing costs for different (decreasing) emission limits, thus resulting in the Pareto fronts shown in Figure 1. Notably, our findings show that, across all three case studies, a net-zero ammonia process is not feasible considering the technologies portfolio adopted here. The reasons lie in two main factors; firstly, the demand for pure CO2 requires on-site production, often via technologies with less than 100 % capture rate, leading to direct emissions. Secondly, the carbon intensity associated with electricity consumption in the eSMR and AEC processes contributes to indirect emissions. The KBRCC is the most cost-effective technology due to the limited changes and the high CO2 capture ratio; electric technologies are more expensive and have higher indirect emissions from the electricity grid. In fact, 83.0 %, 97.1 %, and 97.3 % reductions can be achieved by installing only the KBRCC in the Chemelot, Sluiskil, and the combined case, respectively.

Our analysis shows how site-specific factors affect the optimal decarbonization strategy, as the Sluiskil site outperforms the Chemelot case by achieving lower emissions more cost-effectively. This advantage is attributed to several factors, including the accessibility of offshore CO2 transport and storage, and a higher on-site CO2 consumption. Moreover, our study underscores the potential synergies achievable through collaborative efforts among industrial clusters. The combined Chemelot and Sluiskil case exhibits similar minimum emissions compared to the stand-alone Sluiskil scenario, thus highlighting the benefits of inter-site cooperation in the pursuit of decarbonizing production processes within industrial clusters.



Figure 1: Pareto fronts for the two individual Chemelot and Sluiskil site optimizations and the simultaneous optimization of both sites.

* 1. Conclusions

In this study, we assessed how (i) different ammonia production processes, (ii) the location of production sites, and (iii) the integration of inter-cluster networks impact the emissions reduction strategies. Using a detailed MILP model with a full year, hourly resolution, we optimized the selection and size of technologies and their operation, while considering also fluctuations in electricity prices across seasons and hours. Our analysis shows that cost-effective CO2 reduction (up to 97.3 %) can be achieved by retrofitting traditional ammonia production plants with carbon capture. The results highlight the effect of site-specific factors, such as varying electricity prices and CO2 transport and storage costs, on the feasibility and cost-effectiveness of emission reduction efforts. Moreover, our findings demonstrating that similar specific costs and emissions can be achieved when both sites are optimized simultaneously, emphasizing the benefits of inter-cluster cooperation. To expand our understanding, we propose extending this approach beyond the ammonia industry to explore potential synergies across different production processes. Finally, we conclude that achieving a net-zero ammonia industry by 2030 presents significant challenges, as deep decarbonization must rely on a fully decarbonized electricity grid.

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