CHEMICAL ENGINEERING TRANSACTIONS

VOL. 94, 2022

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Petar S. Varbanov, Yee Van Fan, Jiří J. Klemeš, Sandro Nižetić

ISBN 978-88-95608-93-8; **ISSN** 2283-9216

DOI: 10.3303/CET2294223

Design and Analysis of Ammonia Synthesis and Utilization Networks

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Ammonia is a fundamental commodity that boosts a well-established supply chain optimized for over a century. Produced primarily by the Haber-Bosch process, ammonia production has become more efficient over time through many technological advancements. However, it entails a significant carbon footprint due to its use of hydrogen obtained from fossil fuels. The need to address these sustainability challenges raised by the demand for fossil fuel and subsequent greenhouse gas emissions paved the way for several renewable production routes. As more sustainable means of production were developed, the range of ammonia's applicability also expanded. While ammonia continues to be a vital fertilizer and raw material for various commodity chemicals globally, its potential as a critical energy carrier presently takes center stage. Primarily seen as a hydrogen carrier, ammonia's decomposition into hydrogen and nitrogen was deemed necessary and led to the recent advancements for its direct application as a fuel. Thus, ammonia has several sustainable synthesis and utilization routes that must be carefully analyzed to explore synergies that further promote circularity. This work enables the design of profitable ammonia synthesis and utilization networks from a set of extensive processes with emission constraints through a robust multi-resource integration model. The optimization determined carbon-negative solutions under specified distribution scenarios that integrated green ammonia synthesis with carbon capture and utilization, renewable energy, and negative emissions technologies, achieving net removals of 652,000 and 350,936 t of carbon dioxide annually, while respectively generating profits of 573 and 263 M$/y.

1. Introduction

The discoveries made by Haber and Bosch over a century ago paved the way for the ammonia industry with its expansive production, transportation, and storage infrastructure that primarily boosts the production of fertilizers and other nitrogen-containing chemicals, materials, and pharmaceuticals. The commercial production of ammonia however contributes to almost 1 % of global CO_2 emissions (Kobayashi et al., 2019) due to its dependence on natural gas. Its sustainable production that utilizes renewable hydrogen and energy coupled with carbon capture utilization and storage has thus gained significant traction in R&D. By addressing its role in the ongoing climate crisis, ammonia will essentially become a more sustainable commodity. Since ammonia is relatively easy to store and transport by nature, sustainably produced ammonia will also likely have an extensive global supply chain (Cesaro et al., 2021). Additionally, when coupled with ammonia's low saturated vapor pressure at room temperature and high hydrogen content, the extensive logistics network makes it a promising carbon-free hydrogen carrier (Lin et al., 2022). In this context, the need to convert ammonia into hydrogen at its delivery point opened paths to explore its direct use as fuel (MacFarlane et al., 2020). This new perspective has recently garnered the interest of organizations such as the International Energy Agency, for applications particularly in the power and transportation industries (Guteša Božo et al., 2021). Technological progress in these industries has been extensively reviewed by works such as that of Valera-Medina et al. (2018), who outlines the utilization of ammonia as a viable energy vector along with its challenges in implementation and commercial deployment for power applications, and Ashirbad and Agarwal (2022) who explores its potential as a transport fuel in different engines. Summarily, while ammonia can be used in power generators, turbines, direct ammonia fuel cells, and even as fuel for marine and land transportation, presently, its carbon-based combustion has become a pressing matter to be addressed due to its adverse impact on the environment

Paper Received: 16 April 2022; Revised: 06 June 2022; Accepted: 01 August 2022
Please cite this article as: Abraham E.J., Al-Mohannadi D.M., 2022, Design and Analysis of Ammonia Synthesis and Utilization Networks, Chemical Engineering Transactions, 94, 1339-1344 DOI:10.3303/CET2294223

(MacFarlane et al., 2020). As a first step in achieving the sustainability needed, ammonia production was coupled with renewable energy, for which, optimization approaches were essential. Demirhan et al. (2019), for instance, developed a process synthesis and global optimization framework that determines an optimal ammonia production route using multiple competing technologies and renewable resources. However, such works solely focused on ammonia production. For ammonia to truly become a supporting pillar of a zero-carbon energy transition, further analysis of its combined sustainable production and utilization is required. Palys et al. (2021) reinforces this vision by describing the role of systems engineering in achieving synergies between synthesis and utilization. By managing the various material and energy resources involved in such combined ammonia networks enabled through process integration, greater circularity can be achieved in the integrated system which takes the form of an industrial park. Such integration in ammonia systems has been analyzed by Aziz et al. (2017), who proposed an energy-saving system that incorporates nitrogen and ammonia synthesis with power generation, and Samaroo et al. (2020) who developed an eco-industrial park that considers various utilization pathways for ammonia produced from natural gas. However, the designs analyzed in these works were predetermined, which leaves several other possibilities open for consideration. In this work, ammonia synthesis and utilization networks are designed through an optimization approach that considers multiple processes and resources simultaneously. The production and utilization of green ammonia is specifically analyzed here, making it the first of its kind to analyze optimization-based synthesis of green ammonia networks. The approach determines the optimal network for a set objective while meeting constraints placed on the resources involved, allowing policymakers and park authorities to develop industrial parks that achieve specific economic and environmental targets. The following sections will briefly describe the approach used, the case study used to illustrate the approach, and the conclusions drawn from this work.

2. Method

The mathematical formulation used in this work adopts the mixed integer linear program (MILP) developed by Ahmed et al. (2020). Each of the processes considered for the optimization has certain material and energy resources associated with it, where a resource simply refers to a feed, output, byproduct, intermediate, or even wastes and emissions. Every resource has a unique specification for its temperature, pressure, and purity. In this way, all the resources considered in the network can be exchanged regardless of their type, provided, the supplying and receiving processes have identical resource specifications. Of all the resources associated with a process, one resource, typically the primary output of the process, is chosen to be its reference product (RP), where the flowrate of this resource represents the capacity of that process. Other resources associated with a process are then defined using process parameters which represents these resources in terms of the RP. Additionally, each process has CAPEX cost parameters defined in terms of the RP that determines the capital costs incurred, while operating costs and revenues are determined using cost parameters and the flow of input and output resources to and from the network. The MILP identifies the existence of a process along with its capacity from a given set of processes as well as the flow of resources into, within, and from the network. In this work, distribution costs are additionally considered for the resources sold from the park, where it is assumed that the distribution incurs no loss in mass. Equality constraints are placed on resource balances while inequality constraints are placed on process capacities and resource flows to ensure non-negative operations. In this work, the model specifically determines the optimal green ammonia synthesis and utilization network, that achieves maximum economic profit as given by Eq(1). The MILP in this study was solved in a matter of seconds using the “What’sBest!17.0” solver in Microsoft Excel.

$$\text{Maximize Profit} = \text{Revenue} - \text{Capital costs} - \text{Operating costs} - \text{Distribution costs} \quad (1)$$

$$\text{Subject to} \quad \text{Equality constraints } h(x1, x2, \ldots Xn) = 0 \quad (2)$$

$$\text{Inequality constraints } g(x1, x2, \ldots Xn) \leq 0 \quad (3)$$

3. Case study

A hypothetical ammonia synthesis and utilization industrial park aimed at achieving maximum economic profit is considered in this study. Green ammonia is synthesized using nitrogen separated from air and hydrogen obtained from water splitting. The ammonia produced can then be utilized to manufacture nitric acid, urea, and electricity in an ammonia power plant, where urea production has a capture unit with 90 % efficiency. Power required by the park is supplied from either a photovoltaic system with solar panels, a negative emissions technology that produces bioenergy using biomass and atmospheric carbon dioxide, or the ammonia power plant, while all other utilities are imported. The feeds allowed into this park include air, water, biomass, cooling water and low-pressure (LP) steam, while emissions such as carbon dioxide from urea production and NOx from ammonia combustion are mitigated by constraints placed on their output flows. All the processes considered for the network are assumed to have a useful life of 20 y and are listed in Table 1 along with their reference products, maximum operational capacities, and annualized CAPEX parameters.

Table 1: Processes considered for the ammonia synthesis and utilization network

Process	Reference Product (RP unit)	Maximum Capacity (RP unit/y)	CAPEX Parameter ($/RP unit)
Ammonia production (AMM)	Ammonia (t NH_3)	1,000,000	11.397
Ammonia power plant (APP)	Ammonia (t NH_3)	1,000,000	20.184
Air separation unit (ASU)	Oxygen (t O_2)	1,000,000	7.095
Bioenergy carbon capture (BECC)	Carbon dioxide (t CO_2)	35,000,000	104.057
Nitric acid production (NAC)	Nitric acid (t HNO_3)	1,000,000	2.732
Photovoltaic system (PV)	Electricity (kWh)	20,000,000,000	0.001
Urea capture unit (URC)	Carbon dioxide (t CO_2)	1,000,000	6.850
Urea production (URP)	Urea (t CH_4N_2O)	1,000,000	9.307
Water splitting electrolyser (WSE)	Hydrogen (t H_2)	1,000,000	304.357

The process parameters used to define the flow of resources to and from each process is given in Table 2, where the negative and positive signs indicate that a resource is a process input and output.

Table 2: Process parameters given in terms of the reference product of the process (Unit/RP unit)

Resource (Unit)	AMM	APP	ASU	BECC	NAC	PV	URC	URP	WSE
Air (t)	-	-1,566	-4.33	-4.98	-4.48	-	-	-	-
Ammonia (t)	1	-1	-	-	-0.28	-	-	-0.57	-
AMM emissions (t)	0.03	-	-	-	-	-	-	-	-
APP emissions (t)	-	1,567	-	-	-	-	-	-	-
Argon (t)	-	-	0.06	-	-	-	-	-	-
Biomass (t)	-	-	-	-0.74	-	-	-	-	-
Carbon dioxide (t)	-	-	-	1	-	-	1	-0.73	-
Condensate (t)	-	-	-	-	-	-	-	1.10	-
Cooling water (t)	-	-	-	-1.20	-105	-	-	-75	-
Electricity (kWh)	-785	1,292	-245	574	-8.50	1	-27.30	-125	-54,000
Heat (kWh)	-	3,339	-	-	-	-	-	-	-
HP steam (t)	-	-	-	-	0.80	-	-	-	-
Hydrogen (t)	-0.18	-	-	-	-	-	-	-	1
LP steam (t)	-	-	-	-	-0.05	-	-1.21	-1.20	-
NAC emissions (t)	-	-	-	-	3.96	-	-	-	-
Nitric acid (t)	-	-	-	-	1	-	-	-	-
Nitrogen (t)	-0.85	-	3.27	-	-	-	-	-	-
Oxygen (t)	-	-	1	-	-	-	-	-	8
Urea (t)	-	-	-	-	-	-	-	1	-
URC emissions (t)	-	-	-	-	-	-	3.27	-	-
URP emissions (t)	-	-	-	-	-	-	-4.27	0.30	-
Water (t)	-	-0.40	-	-	-0.30	-	-	-	-9

The parameters used were either obtained or calculated from open literature that describes the respective process. The parameters for the AMM, ASU, NAC, PV, URC, URP, and WSE processes were obtained from Abraham et al. (2021), while those of the APP and BECC processes were obtained from Boero et al. (2021) and Bhave et al. (2017). Of the resources listed in Table 2, ammonia was assumed to be priced at 294.29 \$/t, hydrogen at 1177.68 \$/t, nitric acid at 496.30 \$/t, urea at 287.99 \$/t, water at 4.91 \$/t, biomass at 58.88 \$/t, and LP steam at 14.22 \$/t, while all other resources were obtained or priced at no cost. With ammonia being an alternative hydrogen carrier, distribution costs were considered only for the hydrogen and ammonia sold from the network to a hydrogen utilization facility. Hydrogen can be used as is at its delivery point, while ammonia must be converted back to hydrogen before use. The distribution costs for ammonia thus factors in the cost for its reconversion to hydrogen. Distribution costs of 400 \$/t hydrogen and 1,500 \$/t ammonia (IEA, 2019) are considered in this study, where it is assumed that these commodities are locally distributed over 500 km by truck. Four cases were analyzed in this study where the objective of the optimization is to achieve maximum profit. The operational capacities of the activated processes for each case is given in Table 3.

Table 3: Operational capacities of the four cases analysed

Process	Case 1	Case 2	Case 3	Case 4
Ammonia production (Mt/y NH_3)	1	0.850	0.836	1
Air separation unit (Mt/y O_2)	0.260	0.221	0.217	0.260
Bioenergy carbon capture (Mt/y CO_2)	-	0.660	-	0.351
Nitric acid production (Mt/y HNO_3)	1	1	1	1
Photovoltaic system (MWh/y)	20	8.832	8.929	20
Urea capture unit (Mt/y CO_2)	-	0.070	-	0.037
Urea production (Mt/y CH_4N_2O)	-	1	-	0.532
Water splitting electrolyser (Mt/y H_2)	0.354	0.155	0.152	0.357

In Case 1, the profit of the network is maximized without considering any distribution costs. The network produces ammonia using all the nitrogen and some of the hydrogen obtained from the air separation unit and electrolyser. Nitric acid is produced at its maximum allowed capacity using some of the ammonia produced, while all remaining ammonia and hydrogen are sold. The network takes on the structure shown in Figure 1 and incurs a capital cost of 144 M\$ while making a profit of 746 M\$/y.

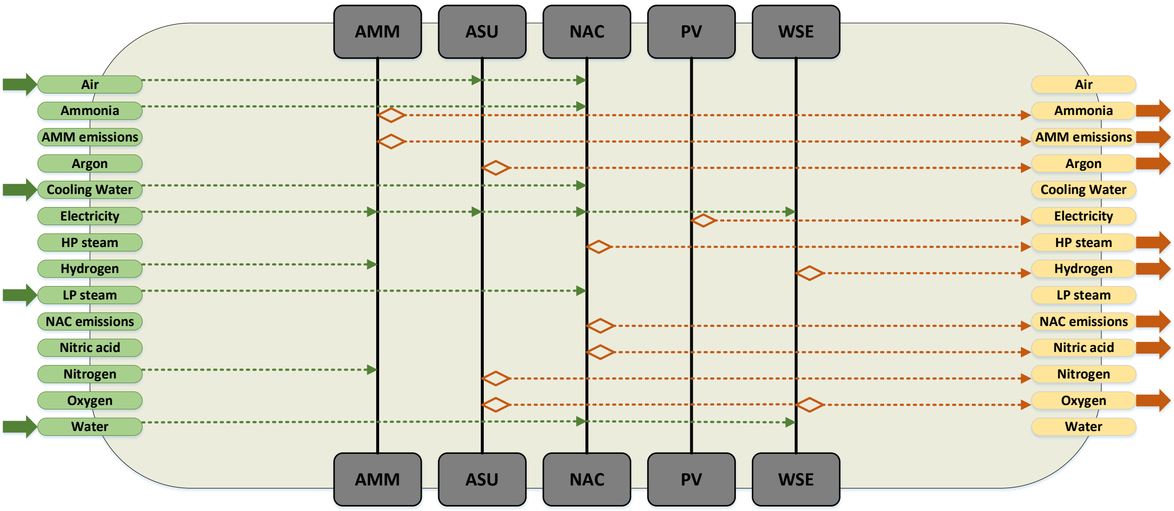

Figure 1: Network superstructure for Cases 1 and 3

For Case 2, distribution costs were factored into the optimization. In this case, the bioenergy and urea plants with its capture unit were additionally activated. No ammonia and hydrogen are sold from this network since they incur distribution costs, which led to the activation of the urea plant to generate revenues. To facilitate its operation, the bioenergy plant supplied the carbon dioxide required for urea production. The capture unit of the urea process was also activated to manage the emissions generated during its operation. The network generated a profit of 573 M$/y with a capital cost of 148 M$ and is illustrated by Figure 2.

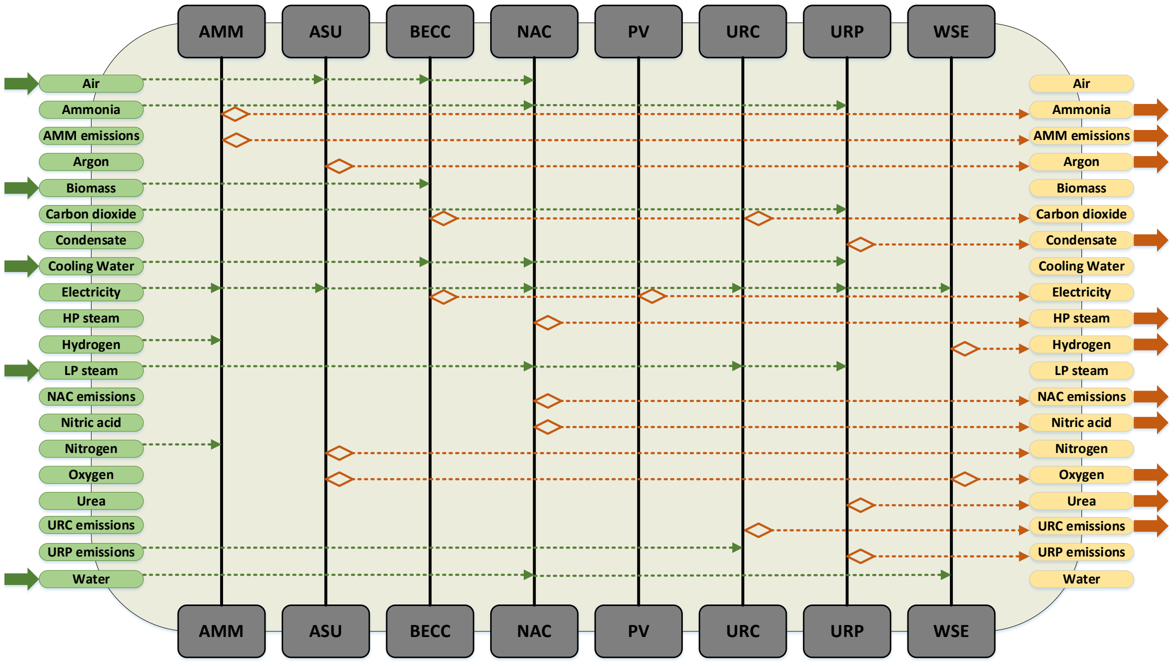

Figure 2: Network superstructure for Cases 2 and 4

As both green ammonia and hydrogen are considered future fuels for energy transition, their distribution from the network must be thoroughly investigated. Cases 3 and 4 were set up to ensure that at least 100,000 and 250,000 t of hydrogen were exported either as liquid hydrogen or as ammonia, while maximizing profit. The activated processes for Cases 3 and 4 are identical to those for Cases 1 and 2, with the only difference being the capacities at which the processes operate and the subsequent flow of resources throughout the park. The networks for Cases 3 and 4 are also illustrated in Figures 1 and 2. In Case 3, only ammonia is sold as a product of the network while only the hydrogen needed to maintain ammonia production is synthesized. Here, a profit of 428 M$/y is obtained with capital and distribution costs totaling 69 M$ and 150 M$/y. For Case 4, ammonia and hydrogen are exported from the cluster, with distributions costs totaling 480 M$/y. A profit of 263 M$/y is earned in this case with capital costs of 186 M$. The bioenergy and urea plants were activated to generate revenues which helped offset some of the network's hydrogen distribution costs. In other words, as more hydrogen distribution is enforced, greater revenues must be generated to balance the distribution costs incurred. The urea capture unit is also activated as in Case 2 to ensure that the emissions it generates are mitigated. When distribution is enforced and accounted for in the optimization, it is clear from these two cases that there is a direct decrease in the profits generated, which drives the network to explore other means of generating revenues such as through urea production in the fourth case.

4. Conclusions

Ammonia synthesis and utilization networks were explored in this work using a MILP optimization approach that integrates multiple resources simultaneously. The approach enables the design of networks based on the flow of its resources from economic and environmental perspectives defined by the user. More specifically for this study with the need to decarbonize the ammonia industry, this approach can identify the optimal networks that meet environmental objectives while generating profits. Four cases were analyzed to understand the impact of distribution costs on designing an ammonia synthesis and utilization network. The first case did not factor distribution costs into decision-making, resulting in a network that made profits from ammonia, hydrogen, and nitric acid sales. With the incorporation of distribution costs in the second case, urea production, which was previously absent, generated profits. At the same time, the network ceased to let ammonia and hydrogen leave as park outputs. In other words, when distribution was accounted for in the park's economics, the sale of commodities with a distribution cost was omitted. When distribution was enforced in the third case, there was a decrease in the profits generated by the park, whose design reverted to that in the first case without urea production. However, as the distribution demand for hydrogen was increased in the fourth case, activation of the urea plant was inevitable. Additionally, the networks with urea production were carbon-negative due to the activation of the bioenergy carbon capture plant, which achieved a net removal of 652,000 and 350,936 t of carbon dioxide in the second and fourth cases. It can be inferred from these four cases that an optimal combination of green technologies enables the synthesis of economically and environmentally feasible ammonia networks. The carbon-negative designs that earned profits even with additional expenditures such as distribution costs are especially significant since systems that remove atmospheric carbon dioxide are typically cost-ineffective. It is also imperative to note that the design was not forced to be carbon-negative but determined by the optimization to be that way in the given scenarios. The designs generated serve as motivation to encourage the incorporation of negative emissions technologies which have previously not been coupled with ammonia networks and effectively only focused on renewable energy and carbon capture utilization and storage. Thus, ammonia synthesis and utilization networks integrated with carbon capture and utilization, renewable energy, and negative emission technologies are undoubtedly a step towards creating a sustainably profitable system. Further analysis in this direction is necessary to better understand the consequences of such integrated systems while more technological options must also be investigated to explore greater synergistic opportunities.

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