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The Role of Ammonia in Decarbonization: A Techno-economic Assessment of NH_3 as H_2 Carrier and NH_3 as Energy Vector

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NH_3 is increasingly recognized as a versatile and promising energy vector in the transition towards a sustainable energy future. By utilizing renewable electricity to power the Haber-Bosch process for ammonia synthesis, green ammonia production eliminates or significantly reduces greenhouse gas emissions compared to conventional fossil-based NH_3 production pathways. As a clean and sustainable alternative to conventional ammonia, green NH_3 offers multiple benefits, including serving as a carbon-free fuel for transportation, providing a means of storing and transporting renewable energy, and enabling the production of carbon-neutral fertilizers and chemicals. In this framework, this work discusses the potential of NH_3 as both H_2 carrier and energy vector through a detailed techno-economic assessment. For each stage of the value chain, both fixed and operating costs are highlighted, to understand where to focus research efforts for future process intensification.

1. Introduction

Green ammonia, produced using renewable energy sources and sustainable production pathways, is emerging as a key ally to decarbonize various sectors, particularly the transportation, power generation and industry. As H_2 carrier, ammonia offers the advantages of high H_2 density (121 kg/m^3), ease of storage and transport, and compatibility with existing infrastructure, making it an attractive option for various energy applications.
NH_3 value chain as hydrogen carrier is represented in Figure 1.

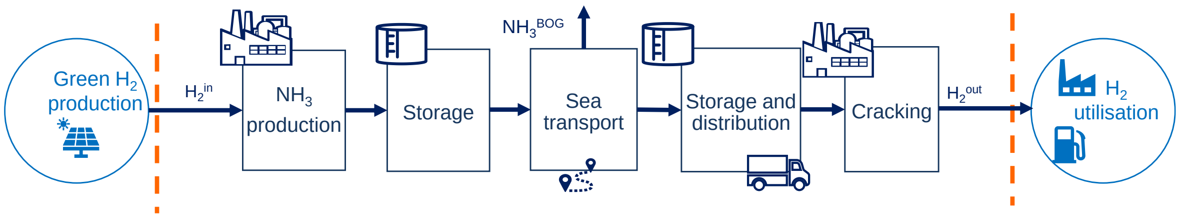

Figure 1. Green NH_3 value chain as H_2 carrier.

Typically, green NH_3 production sites are located in areas abundant in renewable energy, while importing H_2 regions are countries with high demand but limited green energy sources.
Electrolysis was initially embraced in the early 20th century as green NH_3 synthesis process, but was then abandoned because of the subsequent decline in natural gas costs (IRENA and AEA, 2022). More recently, several companies, including Siemens, Yara, Topsoe, ThyssenKrupp, Casale, KBR, Tsubame and Starfire Energy, are working on the Haber-Bosch process intensification to enable CO_2-free ammonia synthesis. By 2022, over 60 projects for renewable ammonia plants had been announced, targeting an annual production capacity of 71 million tons by 2040 (IRENA and AEA, 2022). Figure 2 illustrates the projected increase in annual global green ammonia capacity, depicting the start-up year and capacity of the announced plants.

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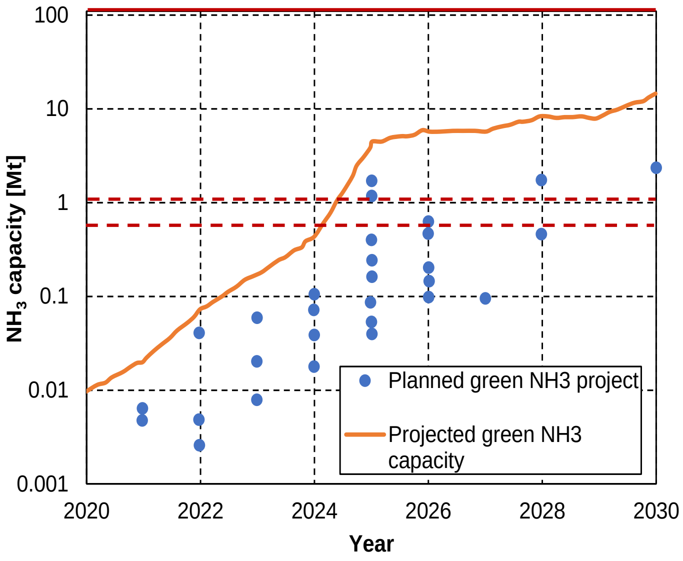


Figure 2. Projected renewable ammonia capacity (orange solid line) and planned green NH_3 projects (blue points) as a function of time. Dashed red lines stand for natural gas based NH_3 plant capacity, while solid red line is the global NH_3 demand (IRENA and AEA, 2022).

Australia is slated to host 1/3 of the planned plants, capitalizing on its abundant wind and solar energy resources, facilitating high production capacities. The largest plant, boasting an announced ammonia capacity of 20,000 kt/y, is set to be constructed in Western Australia (The Royal Society, 2022).

Once produced, NH_3 is typically stored as a liquid in refrigerated, pressurized, or semi-refrigerated tanks and then transported to the utilization hub. Long distance NH_3 transport can exploit either pipelines (in Russia and the United States of America the transmission networks span over 2500 km) or seaborne transport. In this respect, it is worth noticing that the maritime sector views ammonia as a green fuel for shipping. MAN Energy Solutions aims to commercialize a two-stroke NH_3-based engine by 2024, while the Norwegian consortium led by Wärtsilä is developing a four-stroke NH_3 engine.

On the other hand, cargo trucks are typically employed for the short-distance delivery of ammonia due to their relatively high transportation costs per kilometre compared to other methods (Hinkley, 2021).

When arrived at the unloading terminal, ammonia has to be decomposed to favour H_2 release. The process of NH_3 decomposition to H_2 and N_2 (*i.e.*, NH_3 cracking) is commercially available for small-scale applications in the metallurgical industry (Ishimoto et al., 2020). The sole large-scale ammonia cracking process, situated in Argentina at the Arroyito heavy water production plant, has been non-operational since 2017 (Sadler et al., 2018). IRENA reports two ongoing large-scale cracking projects, both located in Europe. One, announced in the Netherlands by Transhydrogen Alliance, is set to start operations in 2024, fulfilling one-third of the current H_2 demand in the Netherlands. The second project is planned at the port of Wilhelmshaven in Germany and is expected to be operational by 2030, meeting 10% of Germany's projected hydrogen consumption.

Commercial small-scale ammonia crackers operate using a Ni-based catalyst at temperatures exceeding 850 °C, with the necessary heat supplied electrically. However, large-scale ammonia crackers are less likely to be electrically heated due to the substantial energy demand of the process. As an alternative, fuel combustion is responsible for providing the necessary heat for the decomposition reaction (Rouwenhorst et al., 2019).

Concerns regarding environmental impact arise from the fuel used in large-scale crackers. To mitigate CO_2 emissions, either a portion of the produced H_2 or part of the inlet NH_3 can be burned, although this approach reduces the process efficiency and the H_2 yield (Ashcroft and Goddin, 2022).

Complete NH_3 decomposition can be avoided at the utilization hub if NH_3 is used as an energy vector, as shown in Figure 3.

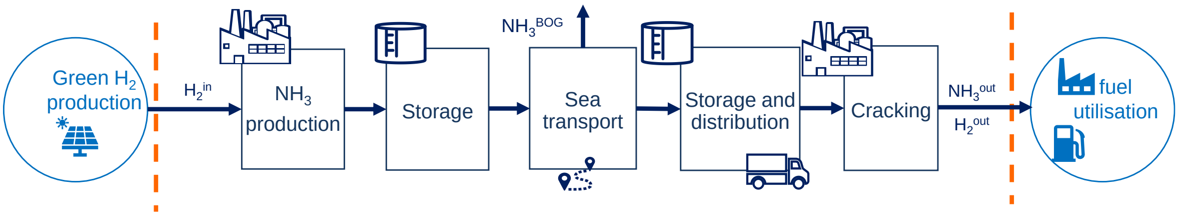


Figure 3. Green NH_3 value chain as energy vector. NH_3 cracking could be not needed.

As a matter of fact, the ammonia heat of combustion (18.6 MJ/kg) suggests its potential use as a fuel source. Ammonia's use in internal combustion engines dates back to the Second World War in Belgium, where it was employed for buses due to fossil fuel shortages. Although this solution was abandoned after the fuel shortage ended, it underscored ammonia's potential as a viable fuel source. Researchers are actively developing methods to enhance ammonia combustion properties and design suitable burners. These efforts include blending ammonia with other fuels, as coal or H_2. Experimental findings indicate that a 28% blend of cracked NH_3 achieves performance comparable to fossil fuels (Verkamp et al., 1967).
To assess the opportunity of NH_3 as both H_2 carrier and energy vector, a detailed techno-economic assessment is carried out considering the green NH3 value chains of Figure 1 and Figure 3. The methodology for the techno-economic assessment is explained in section 2. Results are critically discussed in section 3, in view of NH_3 application to achieve the decarbonization target.

2. Methodology for techno-economic assessment

For each step of the value chains detailed in Figure 1 and Figure 3, an in-depth techno-economic assessment is carried out. Orange dashed lines of Figure 1 and Figure 3 identify system's boundaries. A flat green H_2 production of 43 t/d is assumed at the system's boundary. Harbour-to-harbour H_2 transport is considered, covering a distance of 2500 km. At the unloading terminal, different scenarios are taken into account:

1. scenario 1: NH_3 is cracked to H_2 and N_2 and is conveyed to the H_2 valley for electric energy production. H_2 is produced at 30 bar with a purity of 99.9 mol%, suitable for its industrial applications. In this case, variable utility cost is considered: the present one, referred to the year 2022, and the future one, which accounts for a cost reduction of electricity, particularly, in the next 5 years;
2. scenario 2: NH_3 is partially (28%) cracked to H_2 and N_2 for its application as a fuel. A mixture of H_2 and NH_3 is delivered at the battery limits.
3. scenario 3: NH_3 is not cracked at all. It is used directly as a fuel at the battery limits.

For each scenario discussed, the cost driving processes of the whole value-chain (*i.e.*, NH_3 synthesis and cracking, when needed), are modelled with Aspen Plus V11® process simulators (Restelli et al., 2024; Restelli et al., 2023). From simulation results, both fixed and operating costs (*i.e.*, CAPEX and OPEX) are estimated with the Turton methodology (Turton et al., 2012). As regards storage, sea transport and distribution, both fixed and operating costs are retrieved from literature (Restelli et al., 2024). From the evaluation of CAPEX and OPEX of each stage of Figure 1, the key performance indicator for NH_3 value chain as H_2 carrier (C_{H2}) is defined by Eq(1) and denotes the expense [€] of transporting 1 kg of H_2 to the end user.

$$C_{H_2}\left[\frac{€}{kg_{H_2}}\right]=\frac{\dfrac{CAPEX}{y_{payback}}+OPEX}{\dot{m}_{H_2}^{end\,user}} \quad (1)$$

In Eq(1), a ten-year payback period ($y_{payback}$) is assumed; while $\dot{m}_{H_2}^{end\,user}$ is retrieved from process simulations.

On the other hand, for the NH_3 value chain as an energy vector, the key performance indicator is the cost of energy (C_E) as defined by **Errore. L'origine riferimento non è stata trovata.**, representing the cost [€] of supplying 1 MWh of energy to the end user.

$$C_E\left[\frac{€}{MWh}\right]=\frac{\dfrac{CAPEX}{y_{payback}}+OPEX}{\dot{m}_{fuel}^{end}\cdot LHV_{fuel}} \quad (2)$$

In Eq**Errore. L'origine riferimento non è stata trovata.**, $\dot{m}_{fuel}^{end}$ is the fuel flow rate at the end of the value chain, computed by the technical analysis, while LHV_{fuel} is the lower heating value of the fuel considered.

3. Results and discussion

Results of the technical evaluation of the NH_3 value chain for H_2 transport is illustrated in Figure 4, with blue arrows indicating the process streams, namely NH_3 and H_2, while filled arrows representing utilities (orange), fuels (red), and CO_2 emissions (grey). NO_x emissions are neglected due to their minimal impact.

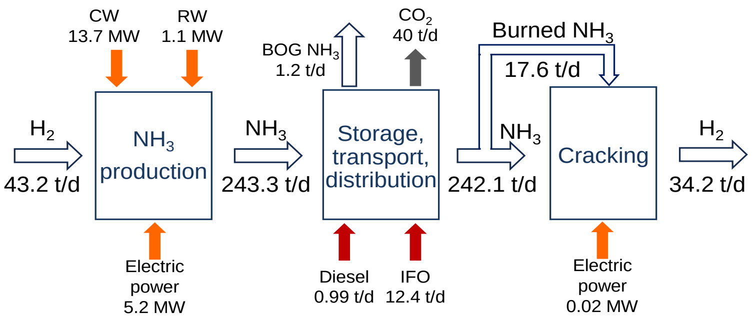
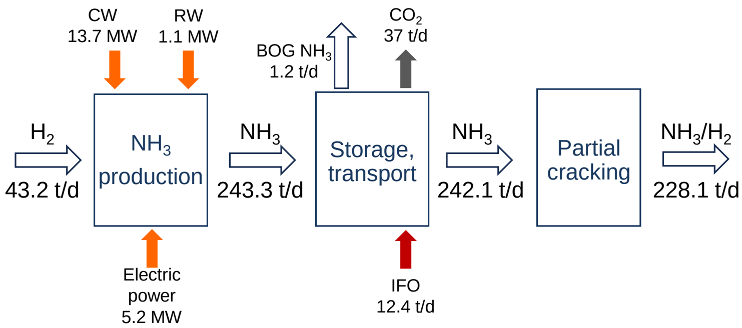


Figure 4. BFD of the green NH_3 value chain as H_2 carrier: scenario 1. CW: Cooling Water, RW: Refrigerated Water, IFO: Intermediate Fuel Oil, BOG: Boil Off Gas.

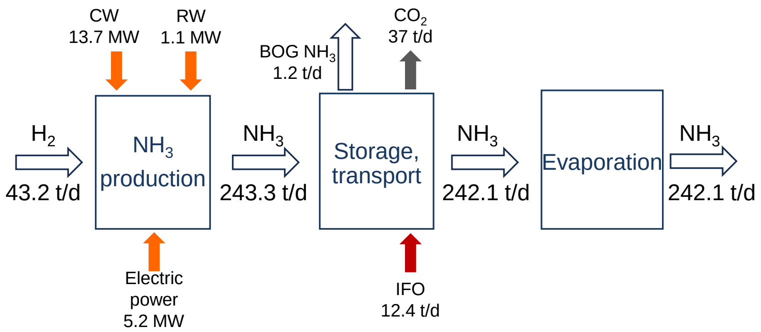
The technical evaluation reveals a significant difference in utility consumption among the cost-driving processes. NH_3 synthesis proves to be more energy-intensive if compared to ammonia cracking, primarily due to the electric power required by compression to 200 bar in the reaction section. Additionally, the ammonia synthesis process utilizes refrigerated and cooling water to cool gases between compression stages and facilitate separations in the ammonia purification section. A daily boil-off gas (BOG) rate of 0.1% during maritime transport is assigned (Al-Breiki and Bicer, 2020). Therefore, the amount of ammonia at the unloading terminal is evaluated considering the number of days required by the seaborne transport. At the unloading terminal, NH_3 cracking exhibits minimal external utility consumption owing to efficient process heat recovery. Notably, CO_2 emissions are primarily associated with transport steps, with maritime transport responsible for 92% of total emissions. Consequently, the development of sustainable alternatives to fossil fuels in the shipping industry is imperative for mitigating climate change. The heat duty required by the reaction is provided by the NH_3 – H_2 mixture combustion. For this reason, the amount of H_2 transported at the end of the value chain is lower than expected, due to the NH_3 utilization as a fuel.

On the other hand, Figure 6 summarizes the results of scenario 2 and scenario 3 for NH_3 application as energy vector. In each of the two configurations, the fuel production step does not require external utilities as the operating pressure aligns with that of the storage tanks, and internal heat recovery occurs between hot and cold streams in cracking processes. While pure ammonia fuel boasts the lowest Lower Heating Value (*LHV* = 18.6 MJ/kg for pure NH_3 against *LHV* = 19.4 MJ/kg for partially cracked NH_3) among the produced fuel mixtures, it achieves the highest productivity due to the absence of product losses during evaporation.



a)

Figure 5. BFD of the green NH_3 value chain as energy vector: a) scenario 2 and b) scenario 3. CW: Cooling Water, RW: Refrigerated Water, IFO: Intermediate Fuel Oil, BOG: Boil Off Gas.



b)

Figure 6. BFD of the green NH_3 value chain as energy vector: a) scenario 2 and b) scenario 3. CW: Cooling Water, RW: Refrigerated Water, IFO: Intermediate Fuel Oil, BOG: Boil Off Gas.

The energy costs associated with the two produced fuels are as follows: 134.5 €/MWh for pure ammonia, 163.1 €/MWh for partially cracked ammonia. The distribution of energy costs among the various blocks of the green NH_3 value chain as both H_2 carrier and energy vector is illustrated in Figure 7. In the case of NH_3 as energy vector, the costs evaluated pertain to the lower heating value of the fuel and do not encompass its utilization in a power generation plant, due to the absence of commercialized technologies. Consequently, the calculated energy costs serve as a foundation for future analyses, awaiting the availability of ongoing pilot projects on NH_3 combustion at large scale.

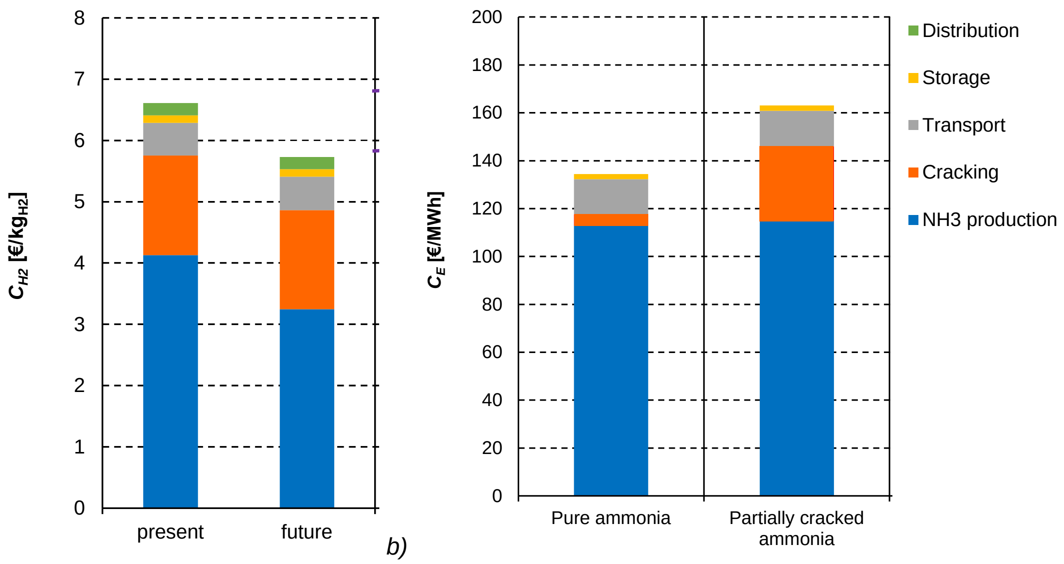


Figure 7. Detail of cost distribution of NH_3 value chain as a) H_2 carrier and b) energy vector.

4. Conclusions

This study examines the potential applications of NH_3 as both H_2 carrier and energy vector within the present markets. The present cost of hydrogen transport (C_{H2}) through NH_3 as H_2 carrier is 6.61 €/kg$_{H2}$. A cost reduction is expected in future, mainly because of the reduced electricity cost. NH_3 production emerges as the cost driver of the whole value chain: optimizing the Haber Bosh process on such a small scale is crucial for promoting NH_3 application as a H_2 carrier. While the NH_3 synthesis is designed referring to the standard Haber-Bosch process, it does not account for renewable energy source fluctuations. An analysis of the process performance with variable H_2 feed could be crucial in assessing the plant flexibility. Lower operating pressure for the NH_3 production could enhance the process flexibility. However, lower operating pressures of the reaction section result in reduced conversion per stage, prompting the investigation of potential alternatives to achieve higher NH_3 production, such as ammonia removal along the reactor (Spatolisano and Pellegrini, 2023).
Together with NH_3 synthesis, exploring cracking technologies operating at lower temperatures is thus of interest to reduce the energy consumption of the carrier decomposition stage.

The assessment of NH_3 as an energy vector involves analysing the costs associated with energy generation through fuel combustion obtained at the end of the value chain.
Further examination of the environmental impact of the ammonia value chain would be needed, in view of its application as a climate change mitigation solution. Life Cycle Assessment (LCA), specifically, could ascertain the ammonia's validity as a green hydrogen carrier and energy vector, enhancing the accuracy of techno-economic analysis in environmentally friendly process design.

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