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Review

The Potential Role of Ammonia for Hydrogen Storage and Transport: A Critical Review of Challenges and Opportunities

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Abstract: Hydrogen is being included in several decarbonization strategies as a potential contributor in some hard-to-abate applications. Among other challenges, hydrogen storage represents a critical aspect to be addressed, either for stationary storage or for transporting hydrogen over long distances. Ammonia is being proposed as a potential solution for hydrogen storage, as it allows storing hydrogen as a liquid chemical component at mild conditions. Nevertheless, the use of ammonia instead of pure hydrogen faces some challenges, including the health and environmental issues of handling ammonia and the competition with other markets, such as the fertilizer market. In addition, the technical and economic efficiency of single steps, such as ammonia production by means of the Haber–Bosch process, ammonia distribution and storage, and possibly the ammonia cracking process to hydrogen, affects the overall supply chain. The main purpose of this review paper is to shed light on the main aspects related to the use of ammonia as a hydrogen energy carrier, discussing technical, economic and environmental perspectives, with the aim of supporting the international debate on the potential role of ammonia in supporting the development of hydrogen pathways. The analysis also compares ammonia with alternative solutions for the long-distance transport of hydrogen, including liquefied hydrogen and other liquid organic carriers such as methanol.

Keywords: ammonia; hydrogen; storage; shipping; pipeline; energy conversion; transport; energy conversion

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1. Introduction

Anthropic activities have unequivocally and globally led to changes in ecosystems, with an increase in temperatures, a loss of biodiversity, sea level rise and extreme events such as heat waves, heavy rainfall, droughts and tropical cyclones [1]. Therefore, urgent measures must be applied to limit greenhouse gas (GHG) emissions that contribute to climate change, among which is the replacement of fossil fuels with alternative ones.

The European Union supports low- or zero-carbon energy production pathways to enable a target of carbon neutrality by 2050, in full coherence with the 2015 Paris Agreement, by means of the implementation of the "Clean energy for all Europeans package" adopted in 2019 [2], and subsequent initiatives, such as the REPowerEU plan [3]. The ambitious goal of REPowerEU is twofold: on the one hand, to reduce the EU's dependence on fossil fuels, and on the other, to combat climate change. The REPowerEU plan and the EU green hydrogen strategy aim to support the production, distribution and storage of renewable and low-carbon hydrogen. Green hydrogen could play a crucial role in reaching a climate-neutral continent by 2050, especially in hard-to-abate sectors, such as maritime transport, steel making and fertilizer production.

The EU Council and Parliament have reached a provisional deal on the update of the Renewable Energy Directive (RED III) [4], including some specific targets on renewable energy use in transport. Among the different transport targets, the EU has set a minimum requirement of 1% of renewable fuels of non-biological origin (RFNBOs) in the share of renewable energy supplied to the transport sector in 2030. These fuels will require a share of green hydrogen for their production.

Hydrogen is currently used in several applications, mostly as an intermediate for chemicals production and in refineries. Other potential applications include its use as input in the steel-making process, as an energy carrier for transport and in heat and power production [5]. Some scholars have highlighted that the European Union and UK could see a hydrogen demand of up to 2300 TWh by 2050 in the highest penetration scenarios, corresponding to 20–25% of their final energy consumption by 2050 [6]. However, in 2022, hydrogen contributed to less than 2% of total energy consumption, and was mainly used to produce fertilizers and plastics, and mostly from fossil fuels [7]. Furthermore, in Europe, around 2.5 Mt of hydrogen is used annually as a feedstock to produce ammonia, accounting for almost a third of the total current hydrogen consumption. Since most of the hydrogen is produced on-site, the ammonia industry is both the largest producer and consumer of hydrogen, after oil refining [8].

The current global demand for hydrogen is estimated to be around 90 Mt [9]. Almost all of it is produced from fossil fuels (mainly natural gas and coal), and the electrolysis process contributes to only 2% of the total, due to the historical maturity of gasification and reforming processes, and their lower costs. However, given the potential of low-carbon hydrogen generation via electrolysis when coupled with renewable power generation, the installed capacity of electrolyzers is expected to quickly grow to meet decarbonization targets, from 300 MW in 2020 to 54–96 GW in 2030 [10]. However, this capacity would not even match the current global hydrogen demand, as Mucci et al. [5] estimated that an installed capacity of around 550 GW would be required.

The EU has developed an official hydrogen strategy aiming at producing up to 10 million tons of renewable hydrogen by 2030 and importing an additional 10 million tons by the same year [11]. Since there is currently no international hydrogen trade, the scale-up of imported volumes of green hydrogen to reach those targets is significant, and governments are sustaining efforts in order to support international hydrogen markets and bilateral agreements.

However, despite all the hype surrounding green hydrogen, at present, there are concerns about the techno-economic feasibility of these targets, including investment and operational costs for its production, distribution and storage [12]. Another important point is how to couple electrolysis and power generation from RESs in an effective and coherent way, since the low average capacity factors of solar and wind power lead to higher costs for the operation of electrolyzers [13]. The Clean Energy Group [14] has found that there are several reasons to be concerned about its use, particularly in power plants, namely: the generation of NO_X if the hydrogen is burned (up to six times higher than methane); the hydrogen embrittlement process when hydrogen is stored and transported with existing infrastructure; and energy losses in the electrolysis process and more generally in the entire hydrogen supply chain. Amin et al. [15] clearly stated that, for the successful utilization of hydrogen, the issues of production, separation and storage should be resolved. Tashie-Lewis and Nnabuife [16] highlighted practical limitations to a current hydrogen widespread use, encompassing low volumetric energy density in the gaseous state and high well-to-wheel costs in comparison with fossil fuel production and distribution, requiring further research to overcome these issues.

Hydrogen storage and transport remain important aspects to be addressed, in particular by limiting energy losses and costs associated with these steps of the supply chain. In addition to directly storing hydrogen in compressed or liquid form, alternative options include the production of other chemicals, such as ammonia or methanol (that will be addressed in this analysis), and the absorption-based storage of hydrogen in metal hydrides [17].

The main focus of this review is to investigate the most recent research literature on the use of ammonia as a chemical storage for hydrogen, highlighting opportunities of and barriers to this solution. Ammonia can be compressed and liquefied with reduced operation cost due to its mature production technology and well-developed infrastructure in comparison with hydrogen. However, there are some critical issues, mainly due to the energy losses, the handling, the cost associated with its storage and its competition with the fertilizers market, that require careful considerations. This paper provides a detailed description related not only to technological and economic aspects related to the ammonia production phase, but also to the transportation, storage and final utilization steps, that can affect the efficiency of the overall supply chain (Figure 1).

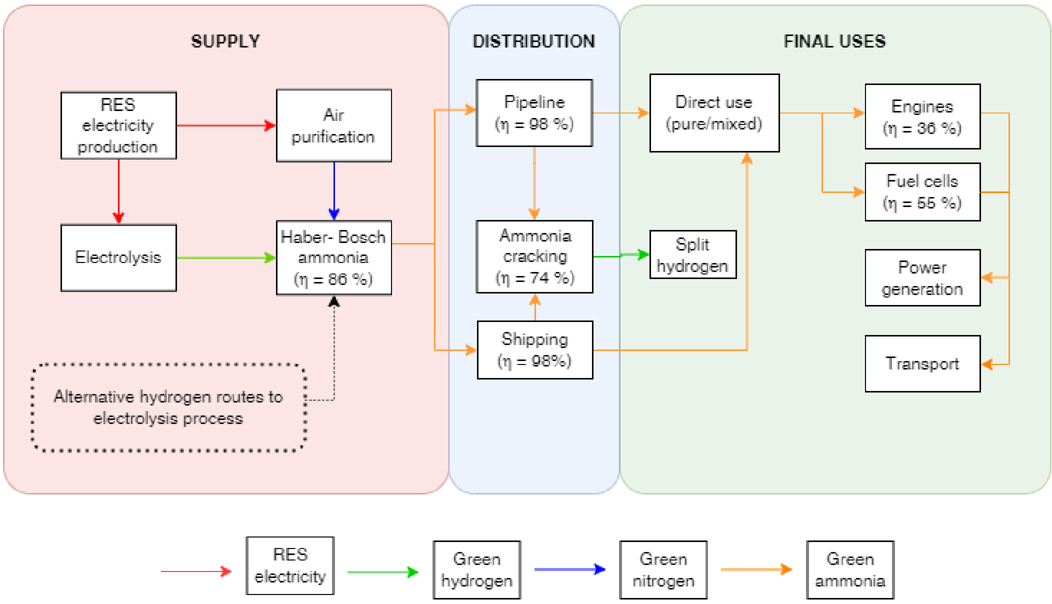

Figure 1. Ammonia pathways considered in this study. Energy efficiency process data from [18–20].

The following sections will address the different steps of the supply chain presented in Figure 1. Section 1.1 presents a description of the main characteristics of hydrogen and ammonia, to provide a context for the following analysis. Section 2 includes a discussion of the main aspects related to ammonia production, dealing with energy consumption, carbon emissions, and the investment and operational costs of the different technologies. Ammonia transport and distribution is addressed in Section 3, with a comparison of shipping and pipelines for long-distance transport, and an analysis of the technical and economic indicators for ammonia and other hydrogen carriers. Section 4 is devoted to final energy uses of ammonia, including engine applications, fuel cells and other possible conversion technologies. Finally, Section 5 will summarize the main open issues that remain to be addressed for a successful use of ammonia as a hydrogen carrier, including health and safety issues, environmental impacts and additional potential hurdles. The main conclusions of this analysis are then presented in Section 6.

1.1. Hydrogen and Ammonia Characteristics

Hydrogen is a non-toxic compound, characterized by a high mass energy content and a low heating value (LHV) of 119.9 MJ kg^{-1} that is 2.4, 2.8 and 4 times higher than methane, gasoline and coal, respectively [21]. However, its density at ambient conditions is low (0.089 kg/m^3), with a very low boiling point (−252.7 °C), and it is highly explosive due to the wide explosion limit in air. Therefore, the large-scale distribution and storage of hydrogen, in terms of technical and economic feasibility, inextricably plays a crucial role for the development of the hydrogen-based economy.

In addition to underground storage, hydrogen can be stored directly by increasing its energy density (compression at 700 bar (4.5 GJ/m^3), liquefaction (8.5 GJ/m^3), transformed in organic liquids via chemical reactions (10 GJ/m^3) [22] or absorbed in the form of hydride metals (15 GJ/m^3) [23].

These limitations related to hydrogen storage motivate its conversion to energy carriers with higher volumetric energy density, ideally suitable for the existing infrastructure, such as ammonia and methanol. In the perspective of power-to-fuel, the renewable hydrogen production involves the use of electricity derived from renewable energy (mainly produced by wind or solar) to operate the electrolysis process, which converts water into hydrogen, having oxygen as a by-product. Furthermore, green hydrogen can react with nitrogen produced from air either via a reforming step or by an air separation process for the production of renewable ammonia, that can be considered an "e-fuel" if used for transport in different segments (aerial, maritime and terrestrial).

Hydrogen can be combined with nitrogen to generate ammonia, which can be stored at milder conditions (in comparison with hydrogen), and further dissociated back to hydrogen, if required. Ammonia is an excellent source of hydrogen in its liquid form, containing twice as much hydrogen as liquid hydrogen by volume, and it can be used either directly (as a feedstock for chemicals or as a fuel for power generation and maritime transportation) or reconverted to hydrogen. However, the dissociation process back to hydrogen and nitrogen is a catalytic process at high temperatures that requires a significant amount of energy. In addition, ammonia is hazardous to handle and the health risks associated with ammonia exposure must be taken into account.

In standard conditions, ammonia is a gas. At atmospheric pressure, ammonia is liquid at temperatures below −33.3 °C, while at 10 bar the condensation/boiling point is 25 °C. Thus, ammonia is liquid at room temperature if a slight compression is performed. Moreover, due to its chemical properties, ammonia contains a high volume of hydrogen and can be used as a hydrogen storage molecule due to its high energy density. Both in the form of gas or liquid, ammonia shows a higher density than hydrogen, that is reflected into a higher LHV and HHV per unit of volume. Additionally, ammonia has a narrower flammability range in air in comparison with hydrogen, respectively, 15–28% against 4–75%. Table 1 summarizes the main physical and chemical properties of hydrogen and ammonia [24].

Table 1. This table summarizes the chemical properties for hydrogen and ammonia [24].

	Hydrogen	**Ammonia**
Boiling point [°C]	−252.7	−33.34
Melting point [°C]	−259	−77.73
Gas density [kg/m^3]	0.089	0.769
Liquid density [kg/L]	0.071	0.6819
LHV [MJ/kg]	119.9	18.6
LHV as liquid [MJ/L]	8.5	12.7
HHV [MJ/kg]	141.9	22.5
HHV as liquid [MJ/L]	10.1	15.3
Auto ignition [°C]	585	651
Flammability/air [-]	4–75%	15–28%

2. Ammonia Production

The production of ammonia requires hydrogen and nitrogen as inputs, and the former represents the highest part of energy consumption, emissions and costs.

2.1. Energy and Emissions

Given its current fossil-based technology, large-scale ammonia production generates GHG emissions more than other chemical processes [25]. Considering CO_2 emissions, the current global ammonia production causes around 450 Mt of direct emissions and 170 Mt of indirect emissions [26]. With a carbon footprint of 2.4 Mt of direct emissions per each tonne of ammonia, it is one of the most emission-intensive commodities produced by heavy industry (twice the level of steel and four times the level of cement). Thus, a decrease in the current emission intensity would already be an important step towards the decarbonization of energy systems. To meet the environmental challenges, ammonia production from renewable energy sources, called 'green ammonia', could be a promising pathway.

The production of green ammonia requires an electrolyzer for renewable hydrogen generation, an air separation unit for nitrogen and a Haber–Bosch process at around 400–600 °C and 200–400 atm for the combination of hydrogen and nitrogen into ammonia. However, the most energy-intensive process remains the electrolysis: to produce 100 kWh of hydrogen, 138 kWh of electricity from renewable energy sources is needed for the water electrolysis in the best conditions [24]. If we consider the overall ammonia synthesis process, most of the electricity (95%) is used for hydrogen production, with the remaining 5% used to power the air separation and Haber–Bosch synthesis unit [26]. The electrolysis process is, hence, highly electricity-demanding with an efficiency of 65–72% on a lower heating value basis for the electrolyzer [24,27]. It is worth to mention that the production of one tonne of ammonia requires around 180 kg of hydrogen.

The most diffused technologies for water electrolysis include alkaline, proton-exchange membrane and solid oxides electrolyzers, with different levels of maturity, conversion efficiencies, current densities, operating temperatures and investment costs [28]. An additional important point, especially for some technologies, is the need for noble metals as electrocatalysts (including Pt, Au, Ru and Ag), which may limit the deployment of electrolyzers at scale. For this reason, research studies are evaluating other potential materials to substitute these metals [29,30]. Electrolysis also requires a steady supply of (renewable) electricity and water as input, and, for this reason, appropriate sites may be preferred. In some areas, water desalination may be needed if freshwater is not available.

An additional potential route for the production of renewable hydrogen is its generation from biomass sources, which can be obtained through different thermochemical or biological routes [31]. Some pathways are still at low technology readiness level, while others are ready for an immediate market uptake and could constitute a complementing option to electrolysis. Nevertheless, given the limited availability of feedstock, especially considering other potential biomass uses, this solution is expected to contribute to a limited extent to the total green hydrogen supply.

The global average energy intensity of ammonia production today is around 41 GJ/t on a net basis—accounting for the generation of excess steam in modern process arrangements—compared with best available technology (BAT) energy performance levels of 28 GJ/t for natural gas-based production and 36 GJ/t for coal-based production (please refer to Table 2 for additional details). The adoption of BAT, in combination with technological improvements and a structural shift in the overall chain, could achieve a reduction of around 25% in the average energy intensity of ammonia production by 2050 in the Sustainable Development Scenario and the Net Zero Emissions by 2050 Scenario [26].

Table 2. This table shows the energy demand required for the production of 1 tonne of ammonia, and CO_2 direct emissions by means of alternative routes exploiting BAT [26]. SMR = Steam methane reforming, ATR = auto-thermal reforming, CCS = carbon capture and storage.

Production Route	**Energy Intensity (GJ/t)**						**t CO_2/t**
	Feedstock	**Fuel**	**Electricity**	**Steam**	**Gross**	**Net**	
Natural gas SMR	21.0	11.1	0.3	−4.8	32.4	27.6	1.8
Natural gas ATR	25.8	2.1	1.0	0.0	28.9	28.9	1.6
Coal gasification	18.6	15.1	3.7	−1.3	37.4	36.1	3.2
SMR with CCS	21.0	11.1	1.0	−3.1	33.1	30.0	0.1
ATR with CCS	25.8	2.1	1.5	0.0	29.4	29.4	0.1
Coal with CCS	18.6	15.1	4.9	2.6	38.6	41.2	0.2
Electrolysis	0.0	0.0	36.0	−1.6	36.0	34.4	0.0
Biomass gasification	18.6	16.5	1.4	0.0	36.5	36.5	0.0
Methane pyrolysis	40.5	0.0	8.4	−1.6	48.9	47.3	0.0

2.2. Economic Aspects

The production of ammonia requires additional costs, both energetic and economic, due to the conversion of hydrogen, in comparison with the hydrogen production itself. As far as green ammonia is concerned, the additional costs of the Haber–Bosch synthesis account for around 15% of the total ammonia production costs, while renewable electricity represents the biggest cost element, accounting for 30–40% of the total ammonia production costs [9]. In [26], the simplified levelized cost of ammonia (LCOA) production is reported for commercial processes and near-zero-emission production routes in 2020, including the contributions for CAPEX, fixed OPEX, fuel, feedstock and carbon capture and storage (CSS), if present. The lower simplified levelized cost is attributed to steam methane reforming (less than 500 USD/t_{NH_3}), while for the electrolysis routes, both grid-connected and with a dedicated renewable energy plant, it is around 900 USD/t_{NH_3}. More specifically, in the case of electrolysis with a dedicated renewable energy plant, the main contribution is related to CAPEX cost.

However, the green ammonia production cost strongly depends on the price of renewable electricity that is expected to fall, as technologies improve in efficiency and benefit from increased economies of scale. According to [32] by 2050, around two-thirds of the total energy supply is expected to be generated by RESs, and mainly by solar energy. For instance, ref. [33] reported that green ammonia could be available in many locations for less than 400 USD/t_{NH_3} in 2040 with the potential to be reduced to below 300 USD/t_{NH_3} if electrolyzers achieve optimistic cost reductions, or when more favorable renewable resources are used to supply a global green ammonia market.

The intermittency and unpredictability related to renewable sources poorly combine with the Haber–Bosch process, which requires steady-state operation mode—especially for avoiding the eventual damage of the catalyst—and, hence, the use either of an energy storage system or a hydrogen buffer. In [34], the combination of photovoltaic (PV) energy and a battery system was found to be the most optimal plant entailing 6 MW of PV coupled to 11 MWh of battery capacity with an LCOA of 774 USD/t_{NH_3}. In this case, the major contributors are economically attributed to the battery, the PV plant and electrolyzer, respectively, with 39%, 33% and 22% of total costs. Additionally, they found out that a competitive ammonia production cost below 500 USD/t_{NH_3} can only be achieved with a 50% reduction in the CAPEX of battery storage. Finally, this configuration is predicted to have a potential cost reduction down to 250 USD/t_{NH_3} in 2050, and could be feasible economical in 2030, compared with the conventional fossil-fuel-based processes.

Finally, the IRENA report [35] assessed that the production costs of green ammonia are expected to be between USD 67–114/MWh by 2050, mainly due to the fallen cost of hydrogen production.

3. Ammonia Transport and Distribution

The transport infrastructure will represent a pivotal aspect for the economic and technical viability of ammonia trade, and two routes are feasible: shipping and a pipeline network. If the imported ammonia is used directly without re-conversion to hydrogen, the current infrastructure for the trade is well-established, although it may require to be extended for ensuring more flexibility and account for an upscale of the current global ammonia trade.

3.1. Shipping Transport

There are around 170 ships worldwide that are able to carry ammonia as a product, and 40 of them are currently doing that exclusively [36]. Thus, some experts argue that it should be relatively easy to scale-up the existing infrastructure to transport ammonia in global markets. At the same time, around 200 ports worldwide are already equipped with the required infrastructure to transport ammonia [26], although in some cases the available capacities may not be enough for the expected increase in traded volumes.

One of the countries that sees an important role for ammonia is Japan, which is evaluating the possibility of adding ammonia in the fuel mix of existing coal-fired power plants, to decrease emissions through co-firing. Thanks to pilot projects and agreements with Australia, Norway and the Middle East, Japan is aiming at developing a supply chain of 3 Mt per year of ammonia by 2030 [37]. However, Japan is also investing in other potential options, such as importing liquefied hydrogen produced from coal gasification in Australia [38].

On the supply side, low-carbon ammonia shipments from the Middle East have recently being sent to Japan [39], Korea [40] and Germany [41] in the last months. This low-carbon ammonia is produced from natural gas with carbon dioxide capture and utilization in some downstream processes. Some industrial sites have been the first in the world to be certified by an independent company to produce a share of zero-carbon ammonia, thanks to carbon dioxide capture rates of 6–41%. The captured CO_2 is used to produce methanol and urea, and the corresponding share of ammonia is certified as blue ammonia with virtually no CO_2 emissions [42,43].

The most common method for ammonia storage and transportation is the use of tanks in liquid or gaseous forms, and, therefore, with different energy densities. Storage and transportation are technically feasible even in large quantities in liquid form under mild conditions. For instance, the equipment employed for ammonia transportation and storage is similar to that used for propane. According to [44], ammonia is a very good candidate for a transportation fuel, with a global cost of 261 $\text{EUR/MWh}_{\text{NH}_3}$. In the case of power to ammonia to power, Diaz et al. [24] estimated that the cost for the storage system is in the range 160–203 $\text{EUR/MWh}_{\text{NH}_3}$.

In general, no or low losses of cargo are generated during ammonia transportation in ships [45]. Considering a typical 30-day shipping duration, including the loading and unloading phase, the estimated ammonia boil-off remains below 1%, which is lower than a corresponding 5% figure for LNG [46]. However, a part of these losses could be potentially recovered if the ships are fuelled with the very same fuel they are transporting (both for ammonia and LNG).

Nevertheless, if the transport of hydrogen occurs via shipping, energy losses are to be expected along the chain, and their value depends on the choice of the selected energy carrier. The most common options that are being studied are liquid hydrogen, ammonia and liquid organic hydrogen carrier (LOHC). The IEA [18] has evaluated the energy available after the conversion and transport chain as a hydrogen equivalent for the 2030 scenarios, establishing the following routes:

- Liquid hydrogen: In this case, the hydrogen is liquefied, transported via shipping and regasified. The residual energy content of hydrogen along the chain compared to the initial amount is estimated at around 73–79%. The phase with the highest energy loss is the liquefaction process.
- Ammonia carrier: In this case, the hydrogen is sent to the Haber–Bosch process for the production of ammonia, which is then transported via shipment and subjected to the cracking process. The final energy content of hydrogen is estimated to be around 63–64% of the initial amount. The phase with the highest energy loss is the ammonia cracking process.
- Liquid organic hydrogen carrier (LOHC): Hydrogen is used for the production of LOHC, which is then shipped and dehydrogenated back to hydrogen. In this case, the final energy content of hydrogen is estimated to be around 57–59%. The phase with the highest energy loss is the dehydrogenation process back to hydrogen.

Based on these values, if the desired final form is pure hydrogen, the supply chain with the least energy losses appears to be liquid hydrogen transport. Alternatively, if we consider only the supply chain up to transportation, and no further conversions back to hydrogen, both ammonia and LOHC carriers are preferable to liquid hydrogen, but LOHC carriers show slightly better performance; the residual energy content of hydrogen along the chain compared to its initial value results in 92–95% for LOHC, against 85–86% for ammonia.

As far as the economic aspects are concerned in the case of shipping, since hydrogen gas must be liquefied or converted into other energy carriers, an additional cost must be applied to the cost of transmission and storage, and quantified as about 1 USD/kg_{H_2} for hydrogen liquefaction, about 0.5 USD/kg_{H_2} for LOHC conversion and about 1 USD/kg_{H_2} for NH_3 conversion. In [9], the total shipping cost for 3000 km (including conversion and transportation) is about 0.7 USD/kg_{H_2} in the case of LOHC, 1.3 USD/kg_{H_2} for ammonia and 2.4 USD/kg_{H_2} for liquid hydrogen, taking advantage of longer distances that reduce the impact of the additional cost of conversion or liquefaction processes. In case the split form is required for the final application, an additional cost of around 2.4 USD/kg_{H_2} and around 0.8 USD/kg_{H_2} is required, for the hydrogen conversion of LOHC and NH_3, respectively.

A comparison of cost estimations for conversion, long-distance transport via ships and reconversion from different sources is illustrated in Figure 2. The variability between minimum and maximum values is related to the specific assumptions of each study, including the size of plants, the year of the analysis (either 2020 or 2030), or the centralized or distributed reconversion facilities. This chart only presents the costs related to long-distance transport, and no hydrogen production costs nor further distribution to final users have been included in the total values.

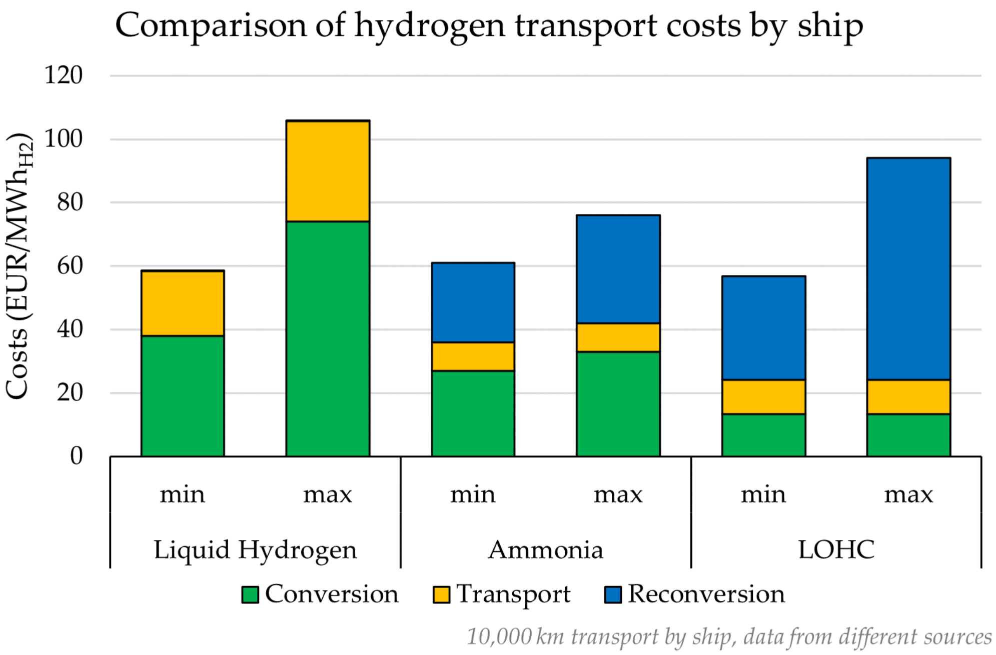

Figure 2. Comparison of hydrogen transport costs for different technologies, assuming 10,000 km transport by ship (data sources: [9,47–50]).

3.2. Pipeline Transport

Ammonia can also be transported over long distances by pipeline, and the technology is mature and has been in operation for decades. Ammonia pipelines in the U.S. currently connect eleven states, for a total of 4800 km in length, transporting around 2 million tonnes of ammonia per year [51]. Another notable example is the world's longest ammonia pipeline, with a length of about 2470 kilometres and in operation since 1981, connecting an ammonia production plant in Russia to a port in Odessa. The pipeline has been shut down since Moscow's invasion of Ukraine in February 2022 [52].

According to [26], long-distance transportation facilities still need to be developed, and the pipelines should be built where possible for a better cost-effective transportation. Furthermore, great interest is shown by governments, especially the European ones, for the conversion of the current LNG terminals to liquid hydrogen and ammonia. Ammonia may be a more suitable candidate than hydrogen because it requires less thermal insulation. In this case, the investment cost for the conversion of the terminal from LNG to ammonia would be decreased by 10–20 % compared to the construction of new ones [26]. In addition, building new pipelines for ammonia would be cheaper than new pipelines for pure hydrogen, especially considering also operating costs. However, given the lack of experience, the investment cost is uncertain.

The comparison between the shipping and pipeline strategies strongly depends on the distances and on the fluid that is transported [9].

4. Final Energy Uses of Ammonia

Ammonia could be used in different energy applications, directly or after being reconverted to hydrogen. Today, ammonia is being used as feedstock for different chemical industries, while its uses as an energy carrier are very limited. The current global production of ammonia is around 180 Mt (2019 data [53]), and it is produced mainly from natural gas (72%) and coal (26%), accounting for around 2% (8.6 EJ) of the total final energy consumption [26]. More than two-thirds of the global production is used for fertilizers, while other industrial applications include textiles, explosives, pharmaceuticals, polymers and commercial refrigeration and air conditioning. However, most of the ammonia is produced on-site, as the trade between countries represents only 20.6 Mt, around 12% of the global demand. In Europe, there are currently 32 ammonia facilities in operation, producing, at full capacity, around 17.7 Mt of ammonia per year, mainly located in Germany and the Netherlands [8].

The first use of ammonia as fuel took place in 1822, when it was applied in a gas locomotive [54]. Then, during World War II, it was used as a replacement for conventional fossil fuels, due to their limited availability. Ammonia can be applied as a fuel in existing technologies, such as gas turbines [19], internal combustion engines, both compression ignition (CI) [55] and spark ignition (SI) [56,57] engines, and alkaline [58] and direct ammonia solid oxide (SO) [59] fuel cells (FCs).

4.1. Ammonia for Engine Applications

Ammonia, even though it has a lower energy density compared to gasoline, has a higher octane number, improving the SI engine performances. According to [20], at full load, the efficiency of the SI engine fuelled with pure ammonia was found similar to the methane engine used as a reference, with an indicated efficiency of about 36%. Instead, its high autoignition temperature, narrow flammability limits and low flame speed are disadvantages for CI engines, requiring high compression ratios to increase their competitiveness [54]. If used in both CI and SI combustion engines, ammonia should be mixed with significant amounts of ignition fuel (e.g., hydrogen, diesel or alcohols) in order to overcome ignition issues [60]. For instance, Morch at al. [56] stated that SI engines performances were higher if ammonia was mixed with 10% vol of hydrogen. The ignition of ammonia in aqueous solution was simulated in [61]; the compression ratio required for the combustion of pure ammonia is 24.8, while it was 26.7 in the case of 25% aqueous ammonia solution [62]. In the review work conducted in [63] regarding ammonia dual-fuel combustion, the ammonia addition can contribute to significant CO and CO_2 reduction, although causing NO_X and un-burnt NH_3 emissions. However, the authors found out that advanced injection strategies can limit these emissions.

Furthermore, similarly to hydrogen, there is no existing framework of regulations, rules and guidelines regarding the use of ammonia as fuel [64], and since current examples are missing, its uptake will require the development of specific safety standards. Furthermore, ammonia is corrosive on metals and this issue must be taken into account in the design of fuel systems, since it can also damage steel combustion equipment. Although it does not generate carbon dioxide, ammonia produces NO_X emissions, N_2O emissions and ammonia slip. These emissions can be mitigated by optimum combustion strategies and after-treatment systems, otherwise the resulting air pollution and climate impact would significantly reduce the benefits of adopting green ammonia as an energy carrier. Scholars reported that ratios of ammonia below 60% and 40% in dual-fuel engines reduce NO_C emissions [65,66], while the addition of ammonia to diesel can lead to an abatement of 80% [67].

In parallel, NO_X emissions could be reduced through the already existing and well-known NO_X reduction technologies used for fossil fuels, like the selective catalytic reduction (SCR) and exhaust gas recirculation (EGR). If ammonia is used for fuelling a vessel, it is possible to directly use onboard ammonia for the abatement units, instead of using urea as the SCR's reductant [68].

However, it is worth to mention that these end-of-pipe technologies, although having a significant environmental role, would also increase the cost and complexity of vessel design compared with vessels utilizing traditional fuels. For instance, Kim et al. [59] found out that an ammonia-based ship costs 3.5–5.2 times compared to a conventional ship, considering a total lifecycle perspective.

4.2. Ammonia for Fuel Cell Applications

An alternative to the combustion process is the use of fuel cell (FC) applications, that directly convert chemical potential energy into electrical energy. Ammonia can directly fuel alkaline, alkaline membrane and solid oxide fuel cells (SOFCs), or can be used as a hydrogen source in its split form for proton-exchange membrane (PEM) FCs [58]. FCs can potentially be a zero-emission energy system, but this depends on the energy carrier that is used and the source of electricity for its production. Being modular, they can be scaled up or down according to the energy needs. Among all of the different types of FCs, efficiency levels vary, on average, between 50% and 60%, but some FCs can achieve up to 85% overall efficiency if heat recovery is introduced into the system [69]. When ammonia is used directly in SOFCs, their slow dynamics during the transient operations require an energy storage system (ESS) that can also be used as cold start energy [59]. In their assessment, Kim at al. [59] also stated that the SOFC power system is the most eco-friendly alternative (up to 92.1%), even though it requires a higher life-cycle cost than the other solutions investigated. As reported by Jeerh et al. [70], some challenges remain to be overcome for a successful application of ammonia fuel cells, including material selection, NO_X emissions, limited power densities and long-term stability.

Fuel-cell-powered vessels are gaining increasing interest, thanks to the possibility of operating them on hydrogen, ammonia and methanol [35]. Installing a fuel cell requires a complete overhaul of the engine systems, which is economically significant. In addition, compared to other alternative sources of shipping fuel, FC volumetric energy density is much lower [69], and currently they can be used only on short- and medium-range vessels; however, advances in this technology could lead to efficiency improvements, making FCs a viable option for large-scale deployment in the shipping industry. Currently, there is no existing infrastructure for FCs in shipping; thus, significant investment is needed to become competitive with other alternative fuels.

4.3. Ammonia Used in Other Energy Technologies

While ammonia energy applications are mostly focused on engines and fuel cells, there are also studies related to its use in gas turbines, although it remains an immature field compared to the previously mentioned applications [19]. Although ammonia provides some potentially interesting advantages in terms of performance, the important emissions of NO_X remain an important limitation [71]. Ammonia has also been co-fired in coal power plants in some trials in Japan, as a solution to decarbonize power generation without affecting the conversion efficiency [19].

Ammonia can also be applied as a working fluid in thermodynamic cycles for power generation and for refrigeration applications. Ammonia, mixed with water, is at the basis of the operation of the Kalina cycle [72], which has been proposed as a more efficient alternative compared to the Rankine cycle, especially in low-temperature applications such as power generation from geothermal sources. Ammonia is also considered as a good refrigerant, especially thanks to its very low global warming potential when compared to other fluids that are currently used in the industry. However, the uses of ammonia as a working fluid will clearly lead to a much lower annual demand when compared with its use as a fuel.

4.4. Cracking Process of Ammonia

If ammonia needs to be converted back to hydrogen, it is important to account for the energy costs associated with the cracking process, which can generally be assimilated to the reverse reaction of its synthesis ($2NH_3 \rightarrow N_2 + 3H_2$). The endothermic cracking reaction, in order to have conversion levels higher than 99%, requires process temperatures higher than 400 °C. Although there are emerging processes still being tested, currently the only process pursued is thermal reforming, which requires 52 GJ/t_{H_2} with a conversion rate of 98.5 % [73].

The relatively low maturity of this technology is currently one of the most crucial bottlenecks for the use of ammonia as a hydrogen energy carrier, requiring the development of efficient catalysts, hydrogen purification equipment and reactor technology [74].

5. Open Issues

In addition to the technological and economic aspects that have been discussed for the different steps of the ammonia supply chain, encompassing its production, transport and final uses, some additional points need to be highlighted. These aspects may not directly affect the economic domain, but they need to be addressed for an effective use of ammonia as a hydrogen transport and storage solution.

5.1. Health and Safety Issues

Ammonia is colorless and characterized by a pungent and distinctive odor, perceptible by humans at low concentrations in the air (20 ppm) [19]. However, thanks to this feature, even small leaks can be easily detected by sensors in concentrations below the harmful limit. When ammonia is released accidentally into the atmosphere, although its dissipation is rapid, it may take enough time to generate a dangerous concentration in the site for human health and aquatic life. Even in low concentrations, inhalation or contact with ammonia can cause cough and irritation, and high levels can be even fatal (2000 and 3000 ppm within half an hour of exposure [19]). Workers must be informed about the risks of exposure to ammonia.

Given the relatively narrow explosion limit (16–25% in air), the risk of explosions generated by ammonia is lower than that of other traditional fuels [75]. These safety and health issues must also be addressed in the case of ammonia-fuelled vessels; as stated in [64], additional efforts are needed compared to the HFO baseline, requiring necessarily safer designs for implementation.

Due to its toxicity, appropriate safety precautions must be implemented. On the other hand, it is worth to mention that the level of maturity of the process for ammonia production, handling and supply has been optimized for over a century. Finally, community engagement plans are required in order to achieve public acceptance, thus allowing the widespread use of ammonia in global energy systems [74].

5.2. Environmental Impacts

Ammonia emissions leakages in the different stages of the supply chain may lead to a wide range of direct and indirect environmental impacts, as already partially discussed in the previous sections. In addition to the direct negative effects of NH_3 emissions on air quality, ammonia can also be a precursor of particulate matter, worsening PM_{10} and $PM_{2.5}$ concentrations, especially in large urban areas [76].

The combustion of ammonia could also lead to the formation of nitrogen oxides, that can have an important impact on air quality, and also N_2O, which is a strong GHG [77]. For this reason, it is important to use proper abatement measures to limit the formation of these chemicals in some specific applications.

The use of ammonia-based fertilizers is also impacting the global nitrogen cycle, representing an important share of total human impacts on the nitrogen cycle. Around 80% of annual ammonia production is used for agricultural fertilizers, but only 17% of that nitrogen is consumed by humans in crops or derived products [78]. The remainder leaches into the soil, air and water, leading to several environmental impacts, including soil and water acidification, eutrophication of water systems and toxicity issues for living species.

On the other hand, an effective use of fertilizers increases the crop yield, reducing the need for additional land for agriculture, which in turns can limit deforestation and land degradation [26]. However, research suggests that human activities had already significantly altered the natural nitrogen and phosphorus cycles through artificial fertilizers and other activities [79].

5.3. Competition between E-Fuels and Fertilizers Markets

The main current application of ammonia is its use as feedstock in the fertilizers sector. Global ammonia demand increased steadily from 1990 to 2019, together with the world population growth. Ammonia has a traditional role in fertiliser production, in addition to urea, ammonium nitrate and ammonium phosphate. Between nitrogen-based fertilizers, it has the highest mass content of nitrogen, which is 82%.

In the IEA's Stated Policies Scenario, which represents the future baseline scenario, global ammonia production is estimated to increase by 40% in 2050, driven by population and economic growth [26]. The increase in demand could be partially mitigated by a more efficient use of fertilizers. The current efficiency of nitrogen fertilizers is very low, as it is estimated that up to 80% is lost into the environment when considering the entire supply chain [80]. The estimated effect of policies and strategies to support a more efficient nitrogen use allows for a decrease in traditional ammonia uses of 5% by 2030 and 10% by 2050, compared to the Stated Policies Scenario.

If ammonia is intended to fully replace conventional fuel in maritime transportation, ammonia production should rise by 319% to meet the current demand [81]. Therefore, the global demand for ammonia covering several sectors can cause scalability issues. The limited availability for energy purposes must be taken into account.

5.4. Comparison with Other Hydrogen Storage Solutions

The success of ammonia in supporting the development of hydrogen pathways will also depend on its advantages compared to other hydrogen storage solutions. As already discussed in this analysis, key indicators include operating temperature and pressures, as well as the gravimetric and volumetric energy density that can be achieved. A summary of the main indicators for the different hydrogen storage options is reported in Table 3. The values confirm that ammonia has among the highest volumetric hydrogen content, and can be stored at ambient temperature and moderate pressure levels.

Table 3. Comparison of different hydrogen storage solutions. Sources: [17,82]. Metal hydrides include TiFe, $TiMn_2$ and $LaNi_5$; complex hydrides include $LiBH_4$ and $NaAlH_4$.

	Temperature	**Pressure**	**Gravimetric H_2 Content**	**Volumetric H_2 Content**
	K	MPa	wt%	kWh/dm^3
Compressed hydrogen	*ambient*	35	100%	0.8
Compressed hydrogen	*ambient*	70	100%	1.3
Liquefied hydrogen	−253	*ambient*	100%	2.2
Ammonia	*ambient*	1	18%	4.0
Methanol	*ambient*	*ambient*	13%	3.3
Metal hydrides	252–285	0.2–0.8	2%	4–4.1
Complex hydrides	473–573	n.a.	8–19%	3.2–4.1

Metal hydrides and complex hydrides include different chemicals, and, thus, the indicators are provided as ranges (values in the table refer to TiFe, $TiMn_2$ and $LaNi_5$ for metal hydrides, and $LiBH_4$ and $NaAlH_4$ for complex hydrides. For additional details see [17]). The emergence of a specific technology for hydrogen storage will most likely depend on its actual operating cost, which is caused by different factors. Operating conditions and energy density are important factors, but others include the availability and cost of infrastructure, the conversion efficiency and conditions to and from hydrogen, and other technical and regulatory aspects.

5.5. Ammonia as an Alternative Maritime Fuel

Currently, the most common fuels for shipping are heavy fuel oil (HFO), marine diesel oil (MDO) and liquefied natural gas (LNG), although HFO use is the most economical for long-range shipping. Recently, very-low sulphur fuel oil has been introduced, to limit SO_X emissions, especially nearby coastlines. Given the stringent regulations established by the International Maritime Organisation to reduce the ship-related NO_X and SO_X, and the reduction of 50% of CO_2 emissions by 2050, the introduction of alternative maritime fuels derived from abundant renewable resources has been proposed. As a result, hydrogen, ammonia, biodiesel, DME, ethanol and methanol are receiving increasing attention to tackle shipping's contribution to global climate change [83]. Recently, projects and research works have been advocating the uptake of ammonia as an alternative maritime fuel [35,84]. According to [85], ammonia-powered vessels are clearly the preferable fuel option for large, deep-sea and long-distance vessels, mainly in internal combustion engines, in comparison with hydrogen.

However, the use of ammonia in shipping vessels is not yet commercially available since the replacement of the traditional ship fossil fuels, such as the residual fuels and distillate fuels, requires careful considerations regarding energy density, flammability, storage and production cost. The use of ammonia requires 4.1 times as much space as fossil fuels and safety and environmental risk measures, due to toxicity. Moreover, the need to limit the NO_X emissions has been widely investigated by means of selective catalytic reduction (SCR), which is already applied to marine engines in order to comply with IMO Tier III requirements in designated NO_X Emission Control Areas [84].

Together with green ammonia, renewable methanol is the most promising fuel for decarbonising the shipping sector [35], although methanol, if combusted, generates CO_2 emissions. Nevertheless, since methanol is liquid at room temperature, it can benefit from the simplicity of storage, due to non-pressurised steel tanks that can be easily installed on old ships [86], and requiring only 2.3 times as much space compared to fossil fuels [62]. In addition, it is characterized by low acute toxicity [87]. Methanol requires the least amount of biomass and hydrogen in the production process in their fuel categories [88]; for instance, only around 130 kg hydrogen is required as feedstock per tonne of methanol against 180 kg of hydrogen required for ammonia production. More specifically, Korberg et al. [88] concluded that, for all of the types of ships and voyage lengths investigated in their analysis, methanol exhibits the lowest total cost, including production, storage and propulsion costs. Also, Bilgili et at. [62] provided a systematic review on the acceptance of alternative maritime fuels, highlighting advantages and disadvantages of several candidates, among which were also hydrogen, ammonia and methanol.

Finally, in [89], methanol appears more competitive in the short-term, while ammonia is likely to be more appealing in the long-term. Currently, methanol can easily enter the market because engines fueled with methanol are already present and ordered by shipping companies. However, green methanol production is highly dependent on the availability of carbon dioxide and, at a certain point, it would require the use of direct air capture. If effective solutions will be implemented to overcome safety and NO_X emissions issues, ammonia utilization could be a more efficient option for the future.

A recent report by DNV [90] evaluated different scenarios for maritime fuel uses by 2050, comparing the ambitions set in the current IMO GHG Strategy (with a 50% reduction of total GHG emissions in 2050) with a zero-carbon shipping by 2050. A total of 24 scenarios have been analyzed, and the distribution of the different fuel shares is reported in Figure 3. Carbon-neutral ammonia (i.e., either green or blue) is expected to play a limited role in the case of a 50% GHG emissions reduction, while for a full decarbonization of shipping its importance increases, reaching up to around 60% of the fuel share in some scenarios. Methanol has a mostly marginal role in the majority of scenarios, while carbon-neutral marine gas oil (MGO) and carbon-neutral LNG (both from synthetic or biogenic routes) are seen as a promising solution to decarbonise shipping.

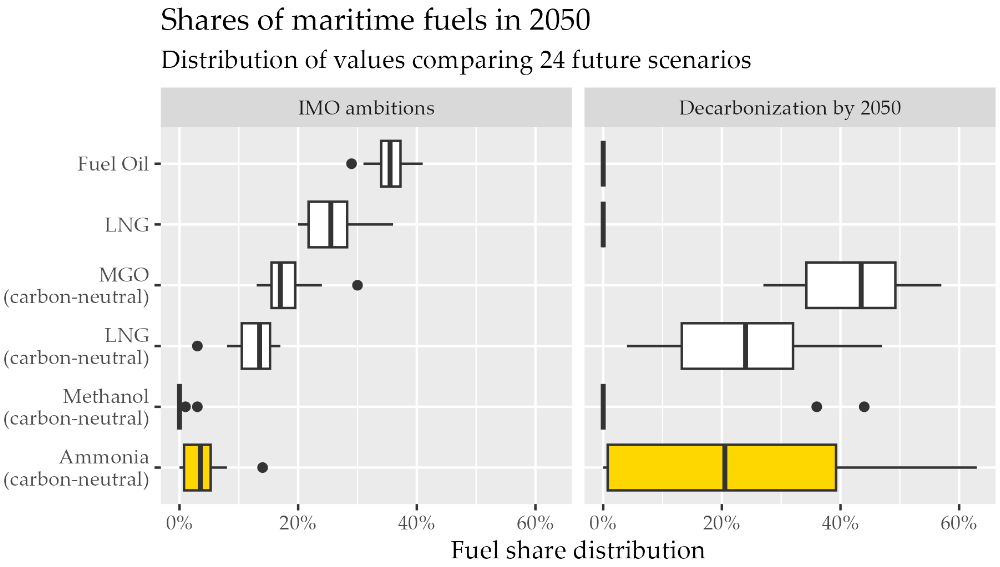

Figure 3. Distribution of fuel shares in 2050 across different scenarios (elaboration of data from [90]). Ammonia is represented in gold. LNG = liquefied natural gas, MGO = marine gas oil.

6. Conclusions

Given the widely accepted issues related to hydrogen distribution and transportation systems, and their technological immaturity, ammonia may represent an effective hydrogen carrier. Ammonia is being increasingly considered as a potential option for decarbonized energy systems, being a carbon-free energy carrier that could represent a solution to store hydrogen at mild conditions. Moreover, a notable advantage is represented by the possibility of exploiting an already well-established infrastructure used for decades in the fertilizers sector.

This review paper has investigated the main opportunities and barriers to the development of ammonia as a large-scale hydrogen storage solution, especially for shipping low-carbon hydrogen over long distances. Technical, economic and environmental aspects have been discussed, also comparing ammonia to other possible alternatives.

Critical issues remain to be addressed for a successful deployment of ammonia, including aspects related to efficiency of the supply chain, energy density, safety and toxicity, environmental impacts and technical maturity in final applications. Specifically, greater advantages are expected in the applications that can directly use ammonia, without the need for further conversion back to hydrogen, due to the low energy efficiency of the conversion process. Furthermore, similarly to hydrogen, the current lack of rules and guidelines regarding the use of ammonia as a fuel is seen as an important barrier.

For these reasons, it is important that future research focuses on solutions to improve energy efficiency and minimize environmental impacts of the different steps of the ammonia pathway, and not only limit the analysis on its benefits as a carbon-free energy carrier. Furthermore, technological solutions and best practices to reduce the risk of leakage would further decrease the potential damage to human health.

Finally, it is worth noting that ammonia currently has a well-established market, especially for fertilizers, which is also expected to grow in the future. Thus, a possible use of ammonia for energy purposes would need to compete with (or complement) other uses, especially when considering the availability of supply facilities and transport infrastructure.

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Abbreviations

The following abbreviations are used in this manuscript:

ATR	auto-thermal reforming
BAT	best available technology
CCS	carbon capture and storage
CI	compression ignition
EGR	exhaust gas recirculation
ESS	energy storage system
EU	European Union
FC	fuel cell
GHG	greenhouse gas
HFO	heavy fuel oil
HHV	high heating value
IEA	International Energy Agency
IMO	International Maritime Organization
LCOA	levelized cost of ammonia
LHV	low heating value
LNG	liquefied natural gas
LOHC	liquid organic hydrogen carrier
MDO	maritime diesel oil
MGO	marine gas oil
PEM	proton exchange membrane
RES	renewable energy source
RFNBO	renewable fuel of non-biological origin
SCR	selective catalytic reduction
SI	spark ignition
SMR	steam methane reforming
SOFC	solid oxide fuel cell
UK	United Kingdom

References

1. IPCC AR6 WGI. Climate Change 2021 the Physical Science Basis. 2021. Available online: https://www.ipcc.ch/report/ar6/wg1/ (accessed on 23 June 2023).
2. European Union. Clean energy for all Europeans package. 2019. Available online: https://energy.ec.europa.eu/topics/energy-strategy/clean-energy-all-europeans-package_en (accessed on 23 June 2023).
3. EU. REPowerEU: A Plan to Rapidly Reduce Dependence on Russian Fossil Fuels and Fast Forward the Green Transition. 2022. Available online: https://ec.europa.eu/commission/presscorner/detail/en/IP_22_3131 (accessed on 23 June 2023).
4. Council of the European Union. Council and Parliament Reach Provisional Deal on Renewable Energy Directive. 2023. Available online: https://www.consilium.europa.eu/en/press/press-releases/2023/03/30/council-and-parliament-reach-provisional-deal-on-renewable-energy-directive/ (accessed on 10 July 2023).
5. Mucci, S.; Mitsos, A.; Bongartz, D. Power-to-X processes based on PEM water electrolyzers: A review of process integration and flexible operation. *Comput. Chem. Eng.* **2023**, *175*, 108260. [CrossRef]
6. Wang, A.; Jens, J.; Mavins, D.; Moultak, M.; Schimmel, M.; van der Leun, K.; Peters, D.; Buseman, M. European Hydrogen Backbone: Analysing Future Demand, Supply, and Transport of Hydrogen. 2021. Available online: https://hydrogen-central.com/2021-european-hydrogen-backbone-demand-supply-transport-hydrogen/ (accessed on 23 June 2023).

7. Hydrogens. Available online: https://energy.ec.europa.eu/topics/energy-systems-integration/hydrogen_en (accessed on 23 June 2023).
8. Atchison, J. Hydrogen Europe: The Role of Clean Ammonia. 2023. Available online: https://www.ammoniaenergy.org/articles/hydrogen-europe-the-role-of-clean-ammonia/ (accessed on 20 June 2023).
9. International Energy Agency. *The Future of Hydrogen*; International Energy Agency: Paris, France, 2019. [CrossRef]
10. Bermudez, J.M.; Evangelopoulou, S.; Pavan, F. Hydrogen Report. 2021. Available online: https://www.iea.org/reports/hydrogen (accessed on 20 June 2023).
11. European Commission. A Hydrogen Strategy for a Climate-Neutral Europe. 2020. Available online: https://knowledge4policy.ec.europa.eu/publication/communication-com2020301-hydrogen-strategy-climate-neutral-europe_en (accessed on 10 July 2023).
12. Noussan, M.; Raimondi, P.P.; Scita, R.; Hafner, M. The Role of Green and Blue Hydrogen in the Energy Transition—A Technological and Geopolitical Perspective. *Sustainability* **2021**, *13*, 298. [CrossRef]
13. Liponi, A.; Pasini, G.; Baccioli, A.; Ferrari, L. Hydrogen from renewables: Is it always green? The Italian scenario. *Energy Convers. Manag.* **2023**, *276*, 116525. [CrossRef]
14. Ramanan, A. Five Reasons to Be Concerned about Green Hydrogen. 2021. Available online: https://www.cleanegroup.org/wp-content/uploads/Five-Reasons-to-be-Concerned-About-Green-Hydrogen.pdf (accessed on 30 June 2023).
15. Amin, M.; Butt, A.S.; Ahmad, J.; Lee, C.; Azam, S.U.; Mannan, H.A.; Naveed, A.B.; Farooqi, Z.U.R.; Chung, E.; Iqbal, A. Issues and challenges in hydrogen separation technologies. *Energy Rep.* **2023**, *9*, 894–911. [CrossRef]
16. Hydrogen Production, Distribution, Storage and Power Conversion in a Hydrogen Economy—A Technology Review. *Chem. Eng. J. Adv.* **2021**, *8*, 100172. [CrossRef]
17. Klopčič, N.; Grimmer, I.; Winkler, F.; Sartory, M.; Trattner, A. A review on metal hydride materials for hydrogen storage. *J. Energy Storage* **2023**, *72*, 108456. [CrossRef]
18. International Energy Agency. Global Hydrogen Review 2022. Available online: https://www.iea.org/reports/global-hydrogen-review-2022 (accessed on 23 June 2023).
19. Valera-Medina, A.; Xiao, H.; Owen-Jones, M.; David, W.; Bowen, P. Ammonia for power. *Prog. Energy Combust. Sci.* **2018**, *69*, 63–102. [CrossRef]
20. Lhuillier, C.; Brequigny, P.; Contino, F.; Mounaïm-Rousselle, C. Combustion Characteristics of Ammonia in a Modern Spark-Ignition Engine. In Proceedings of the Conference on Sustainable Mobility, Catania, Italy, 4–7 October 2022. Available online : https://saemobilus.sae.org/content/2019-24-0237/ (accessed on 15 June 2023).
21. Marbán, G.; Valdés-Solís, T. Towards the hydrogen economy? *Int. J. Hydrogen Energy* **2007**, *32*, 1625–1637. [CrossRef]
22. Reuß, M.; Grube, T.; Robinius, M.; Preuster, P.; Wasserscheid, P.; Stolten, D. Seasonal storage and alternative carriers: A flexible hydrogen supply chain model. *Appl. Energy* **2017**, *200*, 290–302. [CrossRef]
23. Aslam, R.; Müller, K.; Müller, M.; Koch, M.; Wasserscheid, P.; Arlt, W. Measurement of Hydrogen Solubility in Potential Liquid Organic Hydrogen Carriers. *J. Chem. Eng. Data* **2016**, *61*, 643–649. [CrossRef]
24. Dias, V.; Pochet, M.; Contino, F.; Jeanmart, H. Energy and Economic Costs of Chemical Storage. *Front. Mech. Eng.* **2020**, *6*, 21. [CrossRef]
25. Forsythe, R.C.; Cox, C.P.; Wilsey, M.K.; Müller, A.M. Pulsed Laser in Liquids Made Nanomaterials for Catalysis. *Chem. Rev.* **2021**, *121*, 7568–7637.
26. International Energy Agency. Ammonia Technology Roadmap. 2021. Available online: https://www.iea.org/reports/ammonia-technology-roadmap (accessed on 6 June 2023).
27. Khaselev, O.; Bansal, A.; Turner, J. High-efficiency integrated multijunction photovoltaic/electrolysis systems for hydrogen production. *Int. J. Hydrogen Energy* **2001**, *26*, 127–132.
28. Shiva Kumar, S.; Lim, H. An overview of water electrolysis technologies for green hydrogen production. *Energy Rep.* **2022**, *8*, 13793–13813. [CrossRef]
29. Anwar, S.; Khan, F.; Zhang, Y.; Djire, A. Recent development in electrocatalysts for hydrogen production through water electrolysis. *Int. J. Hydrogen Energy* **2021**, *46*, 32284–32317. [CrossRef]
30. Feng, D.; Liu, X.Y.; Ye, R.; Huang, W.; Tong, Y. Carbon-encapsulated Co2P/P-modified NiMoO4 hierarchical heterojunction as superior pH-universal electrocatalyst for hydrogen production. *J. Colloid Interface Sci.* **2023**, *634*, 693–702. [CrossRef] [PubMed]
31. Energy and environmental assessment of hydrogen from biomass sources: Challenges and perspectives. *Biomass Bioenergy* **2022**, *165*, 106556. [CrossRef]
32. IEA. Net Zero by 2050: A Roadmap for the Global Energy Sector. 2021. Available online: https://iea.blob.core.windows.net/assets/063ae08a-7114-4b58-a34e-39db2112d0a2/NetZeroby2050-ARoadmapfortheGlobalEnergySector.pdf (accessed on 30 June 2023).
33. Cesaro, Z.; Ives, M.; Nayak-Luke, R.; Mason, M.; Bañares-Alcántara, R. Ammonia to power: Forecasting the levelized cost of electricity from green ammonia in large-scale power plants. *Appl. Energy* **2021**, *282*, 116009. [CrossRef]
34. Bouaboula, H.; Ouikhalfan, M.; Saadoune, I.; Chaouki, J.; Zaabout, A.; Belmabkhout, Y. Addressing sustainable energy intermittence for green ammonia production. *Energy Rep.* **2023**, *9*, 4507–4517. [CrossRef]
35. IRENA. A Pathway to Decarbonise the Shipping Sector by 2050. 2021. Available online: https://www.irena.org/publications/2021/Oct/A-Pathway-to-Decarbonise-the-Shipping-Sector-by-2050 (accessed on 30 June 2023).

36. Hine, L. Ammonia Swings into Frame as a Potential Future Marine Fuel. 2019. Available online: https://www.tradewindsnews.com/gas/ammonia-swings-into-frame-as-a-potential-future-marine-fuel/2-1-523024 (accessed on 6 June 2023).
37. Reuters. Explainer: Why a Clean Energy Transition Is so Important to G7 Chair Japan. 2023. Available online: https://www.reuters.com/business/environment/why-clean-energy-transition-is-so-important-g7-chair-japan-2023-04-12/ (accessed on 6 June 2023).
38. Reuters. Japanese Gov't Awards $1.62 bln to Japan-Australia Hydrogen Energy Supply JV. 2023. Available online: https://www.reuters.com/business/energy/japanese-govt-awards-162-bln-japan-australia-hydrogen-energy-supply-jv-2023-03-07/ (accessed on 6 June 2023).
39. Reuters. Japan Receives First Low-Carbon Ammonia Cargo from Saudi Arabia. 2023. Available online: https://www.reuters.com/business/sustainable-business/japan-receives-first-low-carbon-ammonia-cargo-saudi-arabia-2023-04-21/ (accessed on 6 June 2023).
40. Zawya Projects. Saudi Arabia Ships World's First Accredited Low-Carbon Blue Ammonia to South Korea. 2022. Available online: https://www.zawya.com/en/projects/industry/saudi-arabia-ships-worlds-first-accredited-low-carbon-blue-ammonia-to-south-korea-bj3dz936 (accessed on 6 June 2023).
41. Hayek, S. First Low-Carbon Ammonia Shipment from the UAE to Germany. 2022. Available online: https://www.hydrogen-worldexpo.com/industry_news/first-low-carbon-ammonia-shipment-from-the-uae-to-germany/ (accessed on 6 June 2023).
42. TÜV Rheinland. Certified Product: Production of Blue Ammonia, ID 0000083801. 2022. Available online: https://www.certipedia.com/quality_marks/0000083801?locale=en&certificate_number=C01-2022-07-21256370 (accessed on 6 June 2023).
43. TÜV Rheinland. Certified Product: Production of Blue Ammonia, ID 0000083803. 2022. Available online: https://www.certipedia.com/quality_marks/0000083803?locale=en&certificate_number=C02-2022-07-21256370 (accessed on 6 June 2023).
44. Giddey, S.; Badwal, S.P.S.; Munnings, C.; Dolan, M. Ammonia as a Renewable Energy Transportation Media. *ACS Sustain. Chem. Eng.* **2017**, *5*, 10231–10239. [CrossRef]
45. Gerlitz, L.; Mildenstrey, E.; Prause, G. Ammonia as Clean Shipping Fuel for the Baltic Sea Region. *Transp. Telecommun. J.* **2022**, *23*, 102–112. [CrossRef]
46. Al-Breiki, M.; Bicer, Y. Technical assessment of liquefied natural gas, ammonia and methanol for overseas energy transport based on energy and exergy analyses. *Int. J. Hydrogen Energy* **2020**, *45*, 34927–34937.
47. IRENA. Hydrogen: A Renewable Energy Perspective. 2019. Available online: https://www.irena.org/publications/2019/Sep/Hydrogen-A-renewable-energy-perspective (accessed on 10 July 2023).
48. Cihlar, J.; Villar Lejarreta, A.; Wang, A.; Melgar, F.; Jens, J.; Rio, P. *Hydrogen Generation in Europe: Overview of Costs and Key Benefits*; European Commission and Directorate-General for Energy Publications Office: Brussel, Belgium, 2020. [CrossRef]
49. BNEF. Hydrogen Economy Outlook. 2020. Available online: https://data.bloomberglp.com/professional/sites/24/BNEF-Hydrogen-Economy-Outlook-Key-Messages-30-Mar-2020.pdf (accessed on 10 July 2023).
50. Papadias, D.; Ahluwalia, R.K.; Connelly, E.; Devlin, P. Total Cost of Ownership (TCO) Analysis for Hydrogen Fuel Cells in Maritime Applications—Preliminary Results. 2019. Available online: https://www.energy.gov/sites/prod/files/2019/10/f68/fcto-h2-at-ports-workshop-2019-viii5-ahluwalia.pdf (accessed on 10 July 2023).
51. The Royal Society. *Ammonia: Zero-Carbon Fertiliser, Fuel and Energy Store*; The Royal Society: London, UK, 2020.
52. Reuters. Russian Forces Repeatedly Shell Ammonia Pipeline in Ukraine's Kharkiv Region, Governor Says. 2023. Available online: https://www.reuters.com/world/europe/russian-forces-repeatedly-shell-ammonia-pipeline-ukraines-kharkiv-region-2023-06-06/ (accessed on 5 July 2023).
53. Egerer, J.; Grimm, V.; Niazmand, K.; Runge, P. The economics of global green ammonia trade—"Shipping Australian wind and sunshine to Germany". *Appl. Energy* **2023**, *334*, 120662. [CrossRef]
54. Rodríguez, C.G.; Lamas, M.I.; Rodríguez, J.d.D.; Abbas, A. Possibilities of Ammonia as Both Fuel and NOx Reductant in Marine Engines: A Numerical Study. *J. Mar. Sci. Eng.* **2022**, *10*, 43. [CrossRef]
55. Gross, C.W.; Kong, S.C. Performance characteristics of a compression-ignition engine using direct-injection ammonia–DME mixtures. *Fuel* **2013**, *103*, 1069–1079. [CrossRef]
56. Mørch, C.; Bjerre, A.; Gøttrup, M.; Sorenson, S.; Schramm, J. Ammonia/hydrogen mixtures in an SI-engine: Engine performance and analysis of a proposed fuel system. *Fuel* **2011**, *90*, 854–864. [CrossRef]
57. Hansson, J.; Brynolf, S.; Fridell, E.; Lehtveer, M. The Potential Role of Ammonia as Marine Fuel—Based on Energy Systems Modeling and Multi-Criteria Decision Analysis. *Sustainability* **2020**, *12*, 3265. [CrossRef]
58. Lan, R.; Tao, S. Ammonia as a suitable fuel for fuel cells. *Front Energy Res* **2014**, *2*, 35. [CrossRef]
59. Kim, K.; Roh, G.; Kim, W.; Chun, K. A Preliminary Study on an Alternative Ship Propulsion System Fueled by Ammonia: Environmental and Economic Assessments. *J. Mar. Sci. Eng.* **2020**, *8*, 183. [CrossRef]
60. Julia, H.; Erik, F.; Selma, B. *Ammonia as Fuel for Shipping—A Synthesis of Knowledge*; Lighthouse: Bandar Lampung, Indonesia, 2020; 20p. Available online: https://fudinfo.trafikverket.se/fudinfoexternwebb/Publikationer/Publikationer_004101_004200/Publikation_004185/FS2_2019_The%20potential%20of%20ammonia%20as%20fuel%20for%20shipping.pdf (accessed on 5 July 2023).
61. Schönborn, A. Aqueous solution of ammonia as marine fuel. *Proc. Inst. Mech. Eng. Part M J. Eng. Marit. Environ.* **2021**, *235*, 142–151. [CrossRef]
62. Bilgili, L. A systematic review on the acceptance of alternative marine fuels. *Renew. Sustain. Energy Rev.* **2023**, *182*, 113367. [CrossRef]

63. Dimitriou, P.; Javaid, R. A review of ammonia as a compression ignition engine fuel. *Int. J. Hydrogen Energy* **2020**, *45*, 7098–7118. [CrossRef]
64. Together in Safety. Future Fuels Risk Assessment—Together in Safety. 2022. Available online: https://togetherinsafety.info/wp-content/uploads/2022/06/Future-Fuels-Report.pdf (accessed on 30 June 2023).
65. Reiter, A.J.; Kong, S.C. Diesel Engine Operation Using Ammonia as a Carbon-Free Fuel. In Proceedings of the 2010 Internal Combustion Engine Division Fall Technical Conference, San Antonio, TX, USA, 12–15 September 2010.
66. Reiter, A.J.; Kong, S.C. Combustion and emissions characteristics of compression-ignition engine using dual ammonia-diesel fuel. *Fuel* **2011**, *90*, 87–97. [CrossRef]
67. Gill, S.; Chatha, G.; Tsolakis, A.; Golunski, S.; York, A. Assessing the effects of partially decarbonising a diesel engine by co-fuelling with dissociated ammonia. *Int. J. Hydrogen Energy* **2012**, *37*, 6074–6083.
68. Zero Carbon Shipping. Managing Emissions from Ammonia-Fueled Vessels. 2023. Available online: https://www.zerocarbonshipping.com/publications/managing-emissions-from-ammonia-fueled-vessels/ (accessed on 30 June 2023).
69. EMSA. Study on the Use of Fuel Cells in Shipping. 2017. Available online: https://www.emsa.europa.eu/publications/item/2921-emsa-study-on-the-use-of-fuel-cells-in-shipping.html (accessed on 30 June 2023).
70. Jeerh, G.; Zhang, M.; Tao, S. Recent progress in ammonia fuel cells and their potential applications. *J. Mater. Chem. A* **2021**, *9*, 727–752. [CrossRef]
71. Karabeyoglu, A.; Evans, B.; Stevens, J.; Cantwell, B.; Micheletti, D. Development of Ammonia Based Fuels for Environmentally Friendly Power Generation. In Proceedings of the 10th International Energy Conversion Engineering Conference, Atlanta, GA, USA, 30 July–1 August 2012. Available online: http://xxx.lanl.gov/abs/https://arc.aiaa.org/doi/pdf/10.2514/6.2012-4055 (accessed on 25 June 2023).
72. Fallah, M.; Mahmoudi, S.M.S.; Yari, M.; Akbarpour Ghiasi, R. Advanced exergy analysis of the Kalina cycle applied for low temperature enhanced geothermal system. *Energy Convers. Manag.* **2016**, *108*, 190–201. [CrossRef]
73. European Commission; Ortiz Cebolla, R.; Dolci, F.; Weidner, E. *Assessment of Hydrogen Delivery Options: Feasibility of Transport of Green Hydrogen within EUROPE*; Ufficio delle Pubblicazioni dell'Unione Europea: Brussels, Belgium, 2022. [CrossRef]
74. Morlanés, N.; Katikaneni, S.P.; Paglieri, S.N.; Harale, A.; Solami, B.; Sarathy, S.M.; Gascon, J. A technological roadmap to the ammonia energy economy: Current state and missing technologies. *Chem. Eng. J.* **2021**, *408*, 127310. [CrossRef]
75. Wan, Z.; Tao, Y.; Shao, J.; Zhang, Y.; You, H. Ammonia as an effective hydrogen carrier and a clean fuel for solid oxide fuel cells. *Energy Convers. Manag.* **2021**, *228*, 113729. [CrossRef]
76. Shim, C.; Han, J.; Henze, D.K.; Shephard, M.W.; Zhu, L.; Moon, N.; Kharol, S.K.; Dammers, E.; Cady-Pereira, K. Impact of NH3 Emissions on Particulate Matter Pollution in South Korea: A Case Study of the Seoul Metropolitan Area. *Atmosphere* **2022**, *13*, 1227. [CrossRef]
77. Boero, A.J.; Kardux, K.; Kovaleva, M.; Salas, D.A.; Mooijer, J.; Mashruk, S.; Townsend, M.; Rouwenhorst, K.; Valera-Medina, A.; Ramirez, A.D. Environmental Life Cycle Assessment of Ammonia-Based Electricity. *Energies* **2021**, *14*, 6721. [CrossRef]
78. Leach, A.M.; Galloway, J.N.; Bleeker, A.; Erisman, J.W.; Kohn, R.; Kitzes, J. A nitrogen footprint model to help consumers understand their role in nitrogen losses to the environment. *Environ. Dev.* **2012**, *1*, 40–66. [CrossRef]
79. Steffen, W.; Richardson, K.; Rockström, J.; Cornell, S.E.; Fetzer, I.; Bennett, E.M.; Biggs, R.; Carpenter, S.R.; de Vries, W.; de Wit, C.A.; et al. Planetary boundaries: Guiding human development on a changing planet. *Science* **2015**, *347*, 1259855. [CrossRef] [PubMed]
80. Sutton, M.; Bleeker, A.; Howard, C.; Bekunda, M.; Grizzetti, B.; de Vries, W.; van Grinsven, H.; Abrol, Y.; Adhya, T.; Billen, G.; et al. *Our Nutrient World: The Challenge to Produce More Food and Energy with Less Pollution*; NERC/Centre for Ecology & Hydrology: Edinburgh, UK, 2013.
81. McKinlay, C.J.; Turnock, S.R.; Hudson, D.A. Route to zero emission shipping: Hydrogen, ammonia or methanol? *Int. J. Hydrogen Energy* **2021**, *46*, 28282–28297. [CrossRef]
82. Aziz, M.; Wijayanta, A.T.; Nandiyanto, A.B.D. Ammonia as Effective Hydrogen Storage: A Review on Production, Storage and Utilization. *Energies* **2020**, *13*, 3062. [CrossRef]
83. Prussi, M.; Scarlat, N.; Acciaro, M.; Kosmas, V. Potential and limiting factors in the use of alternative fuels in the European maritime sector. *J. Clean. Prod.* **2021**, *291*, 125849. [CrossRef]
84. Department for Transport. Clean Maritime Plan. 2019. Available online: https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/815664/clean-maritime-plan.pdf (accessed on 30 June 2023).
85. Global Maritime Fuel. Mapping of Zero Emission Pilots and Demonstration Projects. 2022. Available online: https://www.globalmaritimeforum.org/content/2022/03/Mapping-of-zero-emission-pilots-and-demonstration-projects_third-edition.pdf (accessed on 30 June 2023).
86. Gray, N.; McDonagh, S.; O'Shea, R.; Smyth, B.; Murphy, J.D. Decarbonising ships, planes and trucks: An analysis of suitable low-carbon fuels for the maritime, aviation and haulage sectors. *Adv. Appl. Energy* **2021**, *1*, 100008. [CrossRef]
87. SEA-LNG. Comparison of Alternative Marine Fuels. 2019. Available online: https://sea-lng.org/wp-content/uploads/2020/04/Alternative-Marine-Fuels-Study_final_report_25.09.19.pdf (accessed on 6 June 2023).
88. Korberg, A.; Brynolf, S.; Grahn, M.; Skov, I. Techno-economic assessment of advanced fuels and propulsion systems in future fossil-free ships. *Renew. Sustain. Energy Rev.* **2021**, *142*, 110861. [CrossRef]

89. Böck, H. Here's What You Need to Know: Ammonia and Methanol 101 Pros and Cons. 2023. Available online: https://fathom.world/ammonia-methanol-101/ (accessed on 6 June 2023).
90. DNV. Maritime Forecast to 2050—Energy Transition Outlook 2022. 2022. Available online: https://www.dnv.com/maritime/publications/maritime-forecast-2022/ (accessed on 31 July 2023).