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The Position of Ammonia in Decarbonising Maritime Industry: An Overview and Perspectives: Part II

Costs, safety and environmental performance and the future prospects for ammonia in shipping

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This is Part II of an overview of the state-of-the-art and emerging technologies for decarbonising shipping using ammonia as a fuel. Part I (1) covered general properties of ammonia, the current production technologies with an emphasis on green synthesis methods, onboard storage and ways to generate power from it. The safety and environmental aspects, as well as challenges for the adaptation of technology to maritime structure, and an insight for the level of costs during fuel switching are now discussed to provide perspectives and a roadmap for future development of the technology.

1. Cost Estimations

The capital investment needed to achieve the IMO target of reducing carbon emissions from shipping by at least 50% by 2050 would be approximately US$1–1.4 trillion from 2030 to 2050 if green ammonia is adopted as primary zero-carbon fuel, according to the analytical work conducted by University Maritime Advisory Services (UMAS) and Energy Transitions Commission (ETC) and published as a brief by the Global Maritime Forum, an industry group backed by shipping and port operators in January 2020 (2). If shipping were to fully decarbonise by 2050, this would require extra investments of approximately US$400 billion over 20 years, making the total investments needed between US$1.4–1.9 trillion. The report claims "Under different assumptions, hydrogen, synthetic methanol, or other fuels may displace ammonia's projected dominance, but the magnitude of investments needed will not significantly change for these other fuels."

While making the calculations, the authors broke down the investment into two main areas: (a) ship related investments, which include engines, onboard storage and ship-based energy efficiency technologies; and (b) land-based investments, which comprise capital costs for hydrogen production, ammonia synthesis and the land based storage and bunkering infrastructure. As shown in **Figure 1**, the biggest share of investment is needed in the land-based infrastructure and production facilities for low carbon fuels, which make up more than 85% of the total investment. Hydrogen production *via* water electrolysis takes up around half of the total land-based investments needed, while ammonia synthesis, storage and bunkering infrastructure fulfil the other half. Only 13% of the investments needed are related to the ships themselves, which include the machinery and onboard storage required for a ship to run on ammonia both in new build ships and, in some cases, for retrofits.

In addition to capital costs, the operational costs should also be considered while assessing the long-term economic feasibility and identifying the levelised cost of (green) ammonia (LCOA). It is outlined by

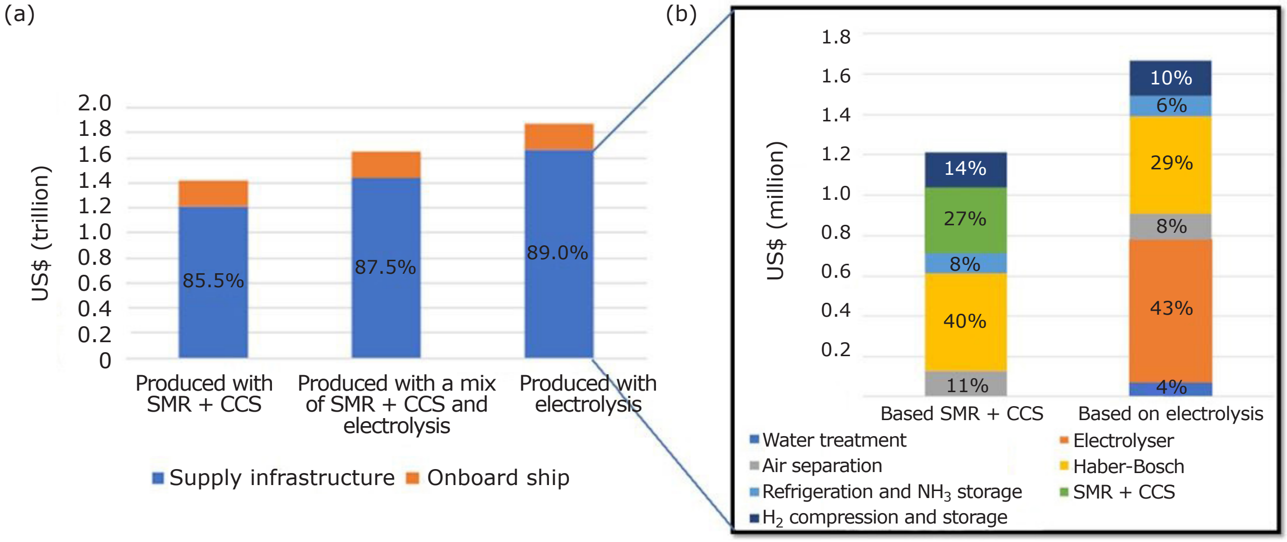


Fig. 1. (a) Aggregate investment for ammonia production *via* different routes; (b) capital cost breakdown for green ammonia production to decarbonise shipping by 2050. Redrawn using data in (3)

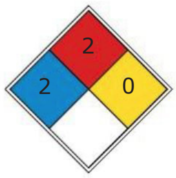
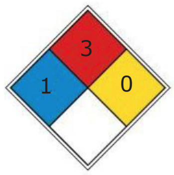
Cédric Philibert at the IEA that "ammonia production in large-scale plants based on electrolysis of water can compete with ammonia production based on natural gas, in areas with world-best combined solar and wind resources." Lately, this statement has been confirmed by Nayak-Luke *et al.* who found that with the current technology, islanded green ammonia can only be produced at US$473 per tonne at the most favourable geographic locations, but by 2030 this will decrease to a highly competitive US$310 per tonne (4). They have identified five key variables that have a significant impact on the estimated LCOA for islanded production which are levelised cost of electricity, electrolyser capital expenditure, minimum Haber-Bosch process load, maximum rate of Haber-Bosch process load ramping and renewable energy supply mix (5, 6). In practice, a combination of improvements on these key variables in a convenient geographical location (i.e., with favourable supply profiles) has the potential to make this carbon-free process economically viable for the first time and replace conventional ammonia production. Nevertheless, these calculated values are even now cheaper than the current anhydrous ammonia price, which is in the range of US$500–600 per tonne in the US (7) but still more expensive than LNG and MGO (8). Therefore, a key component of the commercial adoption of green ammonia as an energy vector in the future will probably be the level of incentives provided or regulation enforcing its use. The most likely incentive could come in the form of CO_2 taxation and credits. Based on the calculations of Argus Media, UK, the CO_2 pricing in Europe needs to be at least doubled to level the playing field for green *vs.* brown ammonia (9). Furthermore, the results reveal that significant utility grid backup is required for an all-electric ammonia plant built with present-day technologies. The total levelised cost of ammonia is driven in large part by the cost of producing hydrogen *via* intermittent renewable sources and operation of Haber-Bosch process. In order to reduce the costs, research is required to develop new, cost-effective yet highly efficient catalysts for electrolysers and ammonia production by either thermal or electrochemical methods.

2. Safety and Environmental Aspects

Safety and environmental hazards for selected marine fuels are presented in **Table I**. As seen from the table, all fuels pose hazards in some way. Compared to the alternatives, ammonia is less flammable, thus presents a lower fire risk. The risks from cryogenic burns are also lower than for liquid hydrogen or LNG as ammonia can be liquefied easily by increasing pressure to ~10 bar at room temperature or by cooling to –33°C at atmospheric pressure, due to strong hydrogen bonding between molecules.

The main risks of ammonia arise from its toxic and corrosive nature. Ammonia is a gas at atmospheric pressure and room temperature, which is lighter than air. It has a strong odour, which can be detected at concentrations as low as 5 ppm; therefore, its smell provides an adequate early warning for a leakage. The US National Institute of Occupational Safety and Health (NIOSH) recommendations state that the maximum permissible time-weighted average (TWA) exposure of anhydrous ammonia for

Table I Safety Data Information of Selected Marine Fuels (10–15)

Fuel	Physical hazards	Health hazards	Environmental hazards	NFPA[a]
MGO	H226 – Flammable liquid and vapour	H304 – may be fatal if swallowed and enters airways H315 – causes skin irritation H332 – harmful if inhaled H351 – suspected of causing cancer H373 – may cause damage to organs through prolonged or repeated exposure	H411 – toxic to aquatic life with long lasting effects	
HFO	Not classified	H304 – may be fatal if swallowed and enters airways H332 – harmful if inhaled H350 – may cause cancer H361 – suspected of damaging fertility or the unborn child H373 – may cause damage to organs through prolonged or repeated exposure	H410 – very toxic to aquatic life with long lasting effects	
LNG	H224 – extremely flammable liquid and vapour Category 1 H281 – contains refrigerated gas; may cause cryogenic burns or injury	Not classified	Not classified	
Liquid ammonia	H221 – flammable gas Category 2 H280 – gases under pressure: liquefied gas	H331 – acute toxicity (inhalation: gas) Category 3 H314 – skin corrosion/ irritation Category 1B H318 – serious eye damage/ eye irritation, Category 1	H400 – hazardous to the aquatic environment – Acute Hazard Category 1	
Liquid hydrogen	H220 – extremely flammable gas H281 – contains refrigerated gas; may cause cryogenic burns or injury OSHA-H01 – may displace oxygen and cause rapid suffocation CGA-HG04 – may form explosive mixtures with air CGA-HG08 – burns with invisible flame	Not classified	Not classified	
Methanol	H225 – flammable liquids Category 2	H301 – acute toxicity, oral Category 3 H331 – acute toxicity, inhalation Category 3 H311 – acute toxicity, dermal Category 3 H370 – specific target organ toxicity – single exposure Category 1, eyes	Not classified	

[a]NFPA: National Fire Protection Association is the US-based standard. Each of health (blue), flammability (red) and reactivity (yellow) is rated on a scale from zero (minimal hazard) to four (severe hazard). White colour represents a special notice

an 8 h workday of 40 h week is 25 ppm. The short-term exposure limit (STEL) or the concentration at which exposure of longer than 15 min is potentially dangerous is 35 ppm. The concentration at which the gas is immediately harmful to life or health (IDLH) is 500 ppm (16).

In addition, when anhydrous ammonia, either in gas or liquid phase, comes in contact with the human body, three types of injuries may result (17):

- Dehydration: anhydrous ammonia is hydrophilic, meaning that it has a strong affinity for water. Hence any contact with human body will lead to water extraction from body tissue
- Caustic burning: when ammonia combines with water from body tissue it forms ammonium hydroxide (Equation (i)) that can chemically burn tissue
- Freezing: as liquid ammonia vaporises it removes heat away from body tissue causing frostbite in an instant.

Therefore, the existing safety principles and systems used throughout the global ammonia industry would need to be deployed on ships and the crew onboard need to be equipped with suitable chemically resistant protective clothing and breathing apparatus.

Ammonia is also labelled as very toxic to aquatic life with long lasting effect. When liquid ammonia is spilled directly into water, most of it will dissolve into the water forming a balance of mostly ammonium hydroxide and a little ammonia depending on the pH and temperature of the water (Equation (i)) (18):

$$NH_3(g) + nH_2O(l) \rightleftharpoons NH_3{\cdot}nH_2O(aq) \rightleftharpoons NH_4^+ + OH^- + (n{-}1)H_2O(l) \quad (i)$$

The remaining ammonia will evaporate resulting in a gas cloud with unpleasant smell. The dissolved ammonia is a serious threat to aquatic organisms killing most in close proximity as lethal concentrations can easily be exceeded. Long lasting effects of ammonia spillage are related to the time that the aquatic life requires to restore its original state through the nitrogen cycle (**Figure 2**). In this cycle, dissolved ammonia species are converted to nitrite (NO_2^-) and nitrate (NO_3^-) by *Nitrosomonas* and *Nitrobacter* bacteria, respectively, which is then used by plants. As this process consumes part of the available oxygen in water, the oxygen for other organisms, especially for the ones that are higher up the food chain such as fish, becomes limited, thus threatening their lives.

When ammonia is combusted, it releases NOx species. NOx in the atmosphere contribute to photochemical smog, the formation of acid rain precursors, the destruction of ozone in the stratosphere and to global warming (19, 20). Despite the detrimental effect of NOx, control methods for reducing NOx emissions are already widely in place in land-based industrial installations and in the transport sector. One of the most common techniques is selective catalytic reduction (SCR) or deNOx technology. In this process, a reductant gas (ammonia or hydrogen) is added to the NOx-containing exhaust gas which is then passed over a catalyst that converts the NOx (NO and NO_2) to naturally occurring nitrogen and water (21, 22). The maritime sector has also had more than two decades of experience with SCR. More than a thousand SCR systems have been installed on marine vessels in the past decade (23). Despite the fact that SCR is a well-known process and the safe transportation and use of ammonia is well-established, it is clear that new applications will require careful risk

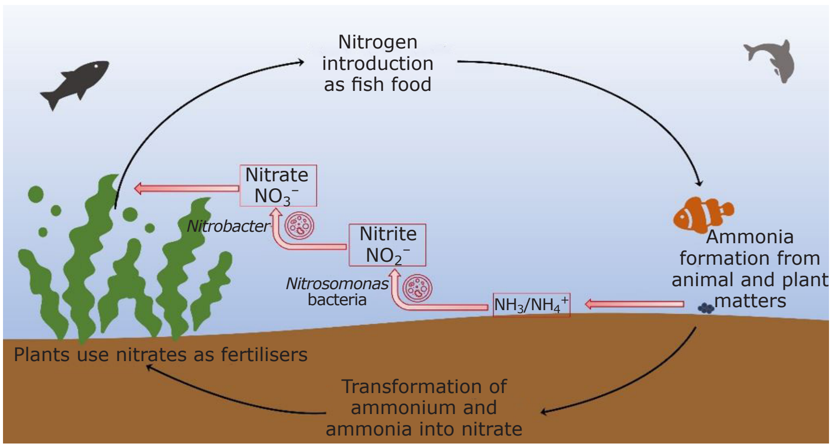


Fig. 2. Illustration of nitrogen cycle in water

assessment and additional control measures. If ammonia is going to be used as a new marine fuel, then the existing safety principles and systems used throughout the global ammonia industry would need to be adapted and deployed on ships to ensure that the risks of ammonia leakage and NOx formation are negligible. It has been reported that an average car needs only approximately 30 ml of ammonia per 100 km to neutralise any NOx emissions using SCR technology (24). If the vehicles run with ammonia as a fuel, this amount is unimportant with respect to the fuel tank volume. Similar calculations should also be performed for maritime sector in order to decide on the most feasible deNOx technology. The preliminary risk assessment forms using ammonia and hydrogen as marine fuels onboard and hazard mitigation strategies were reported by de Vries (25) which need to be improved and tested before implementation. It is also essential that the global use of ammonia at large-scale is well-thought out from a wider perspective in the roadmap. The effect of anthropogenic activities on the overall nitrogen cycle is generally overlooked in the literature. It has only been recently that MacFarlane and coworkers (26) provided a detailed discussion on cycling of nitrogen compounds and their environmental effects. As they stated, our understanding of the mechanisms of the global nitrogen cycle is not yet complete. Hence, further investment to basic scientific research is required to comprehend the environmental impacts of increased quantities of fixed nitrogen before implementing ammonia technology for transport. Finally, besides toxicity, the corrosive nature of ammonia also needs to be taken into account while selecting materials for storage and operation. Ammonia forms complexes with copper, brass and zinc alloys (27). Ammonia corrosion on these metals is even more drastic when there is some moisture. As previously discussed, ammonia is an alkaline reducing agent and it reacts with acids, halogens and oxidising agents.

3. Roadmap for the Adoption of Ammonia as a Marine Fuel

The roadmap for the adoption of green ammonia as a marine fuel involves alterations of two systems in parallel, which are the ammonia manufacturing process and shipping propulsion structure. This ammonia-based economy will emerge through multiple generations of technology development and scale-up in the next 30 years.

Haldor Topsøe, a Danish catalysis company, presented a roadmap to all-electric ammonia plants (28) at the 2018 AIChE Annual meeting. According to its vision and strategy, ammonia production will be decarbonised in the 2030s by electrifying the production of hydrogen and nitrogen feedstock. The company is currently working on development of solid oxide electrochemical cell (SOEC) powered by renewable sources to produce nitrogen and hydrogen syngas using water and air which will then be used as a feedstock for Haber-Bosch process. In 2025, its aim is to demonstrate the production of ammonia *via* SOEC and Haber-Bosch processes at a scale of 500–1000 kg ammonia per day. After that, it intends to commercialise the technology starting from 2030. Until SOEC technology is mature enough to substitute the current brown ammonia production method, the company is suggesting to use a hybrid system (conventional and electrified Haber-Bosch) to decrease the amount of CO_2 emission whilst supplying the demand.

A more comprehensive roadmap to the ammonia economy has lately been published by Doug MacFarlane and coworkers (26). In this roadmap, the authors envisage renewable ammonia being produced in the future at a scale that is significant in terms of global fossil fuel use. The paper diagrams an evolution of ammonia synthesis through three overlapping generations of technology development and scale-up (**Figure 3**). Generation 1 (Gen1) involves the integration of sequestration or offsets to current-day Haber-Bosch ammonia production in order to bring the net carbon impact of the ammonia production to zero (blue ammonia). Generation 2 (Gen2) remains the Haber-Bosch process with existing and new plants, but hydrogen is derived from renewable sources (green ammonia). As the Haber-Bosch process is a well-established technology, the authors anticipate that ammonia production will remain dominated by it over the next two decades. Generation 3 (Gen3) rules out the need for the Haber-Bosch process by direct electrochemical conversion of nitrogen in water to ammonia. This renewable-powered entirely electrochemical ammonia production technology is expected to enter the market at scale as soon as it achieves commercial readiness index (CRI) 1 and start significantly contributing to global ammonia production thereafter, as plant size and capacity increases. The timeline of Gen3 to enter and dominate the market is highly dependent on progress in catalyst development. While several thousand catalysts were screened in the development of thermal ammonia synthesis,

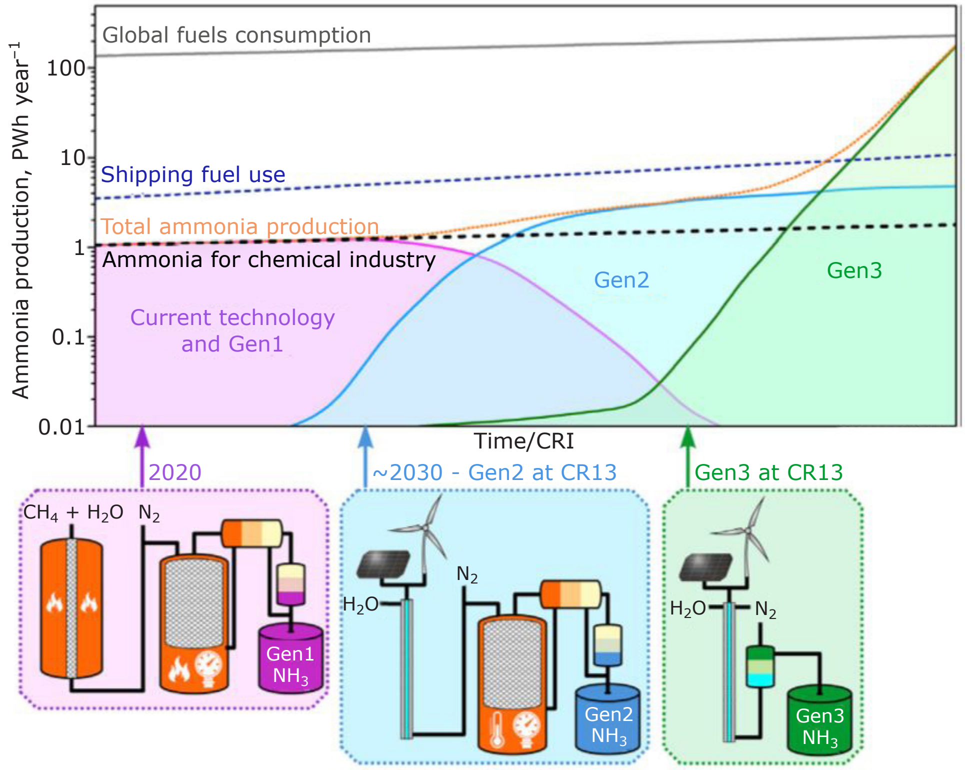


Fig. 3. Ammonia economy roadmap revealing current and projected contributions of the brown, blue (Gen1), green (Gen2) and electrochemical (Gen3) ammonia production technologies in terms of production volume in petawatt hours (PWh) *vs.* time at a scale of commercial readiness index (CRI). 1 PWh = 10^{12} kWh = ~193 million tonnes of ammonia based on LHV of 5.18 kWh kg^{-1}. Data from (26). Copyright 2020. Reprinted with permission from Elsevier

relatively few catalysts have been tested systematically for electrochemical activity. At present, the electrochemical ammonia production rates remain over an order of magnitude away from US DoE targets as mentioned in Section 2.2, Part I (1). Therefore, continuous development of routes to new materials, more control experiments and extended stability studies are necessary before the implementation of Gen3.

A case specific policy analysis reported by the Organisation for Economic Co-operation and Development (OECD) (29) anticipates that it would be feasible to scale-up low-carbon ammonia production and deploy ammonia fuel technology swiftly enough to reduce the carbon emission from maritime shipping by up to 80% by 2035. In the OECD's 80% carbon factor reduction scenario (**Figure 4(a)**), hydrogen and ammonia will fuel around 70% of the mix of ships. This, along with the increase in the uptake of biofuels (22%) and LNG (5%), could diminish the use of oil-based fossil fuels significantly to around 3% by 2035. Another scenario analysis performed by UMAS (3) suggests that ammonia is likely to represent the least-cost pathway for international shipping and play a leading role in replacement of fossil fuels with a rapid growth after 2040 and between 75–99% market share by 2050 (**Figure 4(b)**).

The roadmap for the adoption of ammonia as a marine fuel was limited to the fuel mixing trajectories to reduce carbon emissions without specifying a specific timeline for the development of propulsion engine systems that are adapted to run with ammonia until the report of Environmental Defence Fund, USA, published in 2019 (30). The report focuses on ammonia in combustion engines and fuel cells. A possible roadmap for development and adoption of these technologies is depicted in **Figure 5**. The authors anticipate that the use of green ammonia in ship propulsion systems will most likely begin in the 2020s with modified ICE given that the shipping industry is dominated by the use of these engine types. MAN ES (31) and Alfa Laval, Sweden, (32) have already started developing a dual-fuel combustion engine to run with liquefied petroleum gas (LPG) and ammonia. Starting from 2020, further development is required in the use of green ammonia in fuel cells to pave their way for deployment in the 2030s. With the current state of technology readiness, the initial fuel cells are expected to be the PEM type that might give way to SOFCs over time.

4. Conclusions and Perspectives

Following the direction of IMO towards the reduction of harmful gas emissions by 2050, the maritime sector is getting ready for an energy switch. Many reports (33–36) can be found in the literature that discuss the alternative fuels in a comparative

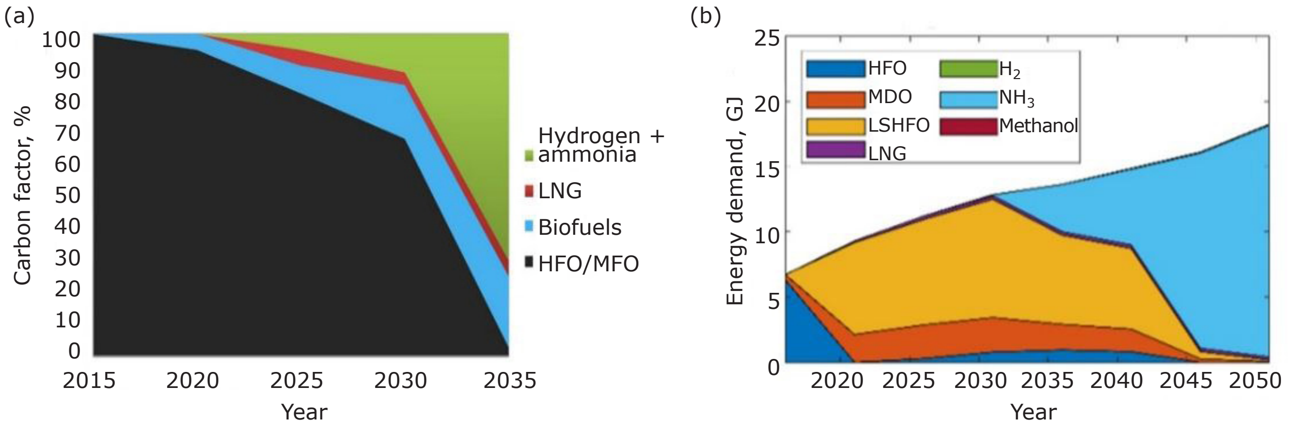


Fig. 4. (a) Fuel mix evolution between 2015–2035 for 80% carbon factor reduction (29); (b) 2050 scenario for the market share of fuels (3)

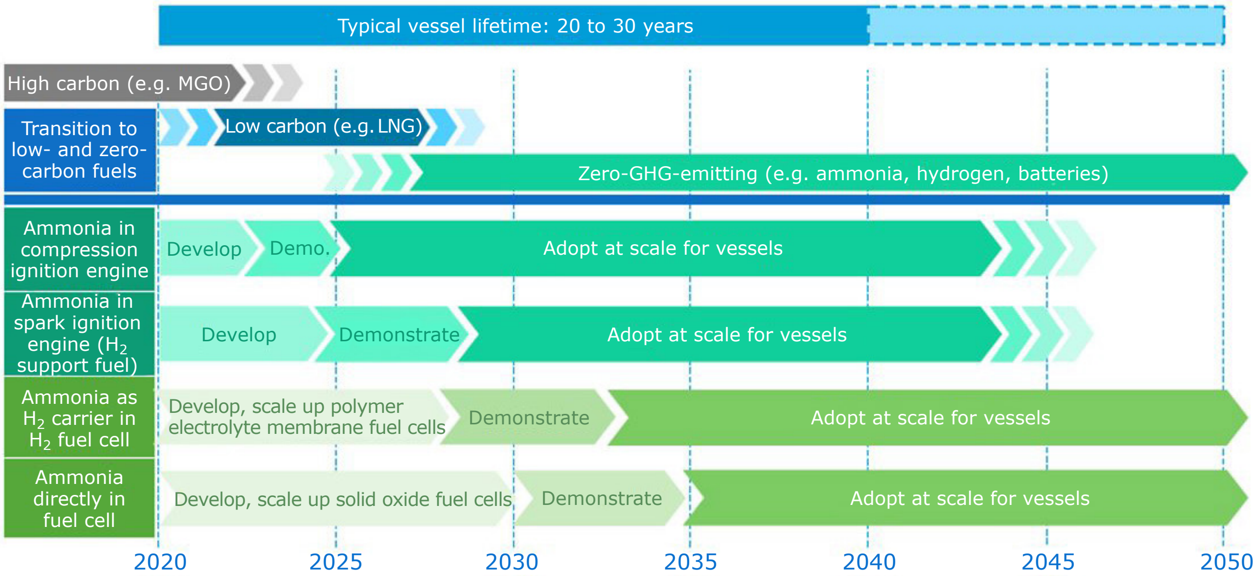


Fig. 5. Technology roadmap for ammonia propulsion technologies. Copyright 2021 Environmental Defense Fund. Used by permission (30)

manner to reduce GHG emissions from shipping. Of these alternative fuels, ammonia is prominent due to its carbon neutral chemical formula, high energy density, established production, transportation and storage infrastructure and competitive cost as discussed through this review. However, to satisfy the energy demand of the maritime industry, the production capacity of ammonia needs to be expanded substantially (i.e. 2.5 times larger production (~500 million tonnes per year)) to decarbonise the international fleet (30)) and production routes have to be green in order to reduce emissions of CO_2. This means that together with other sectors, shipping will add additional stress to renewable electricity production, around the order of magnitude of the current power sector, which itself is yet to fully decarbonise. One possibility for maritime is to build their own infrastructure for the production of green ammonia on existing ports and on offshore marine farms. Lately, the main ports of Morocco have been identified as potential locations to produce and store green ammonia (30). For instance, Jorf Lasfar Port has an existing ammonia storage infrastructure with a total capacity of 100,000 tonnes due to the ammonium phosphate fertiliser production complex of the state-owned OCP group. Upon integration of 300 MW solar panels near the port, it is envisaged that 700 tonnes of ammonia per day, which is equivalent to the daily fuel consumption of about four post-Panamax size vessels, can be produced and stored. In the case study, the daily amount of renewable electricity to produce green ammonia for fuelling all container and dry bulk vessels passing through Morocco's ports is calculated as 280 GWh which is only 0.6% of the renewable (wind and solar) energy capacity of Morocco. Taking this case study as a basis, more research on technoeconomic analysis for green ammonia production needs to be performed in different ports, considering not only onshore but also offshore options and the use of a combination of two or more intermittent renewable energy sources (solar, wind, wave or tidal) to provide a virtually continuous supply and thereby improve the efficiency and cost-effectiveness of the whole process.

Today, the price of green ammonia is significantly higher than for brown ammonia and for conventional marine fuels such as HFO, MGO and LNG. However, looking towards the future where fossil fuels must be substituted, the price of ammonia is expected to be in the same range in comparison with other renewable alternatives such as biofuels and hydrogen. The high cost of green ammonia derives from the capital cost of electrolysers, which take up almost half of the total land-based investments. To bring these expenses down, the usage of expensive noble metal based catalysts should be reduced or ideally be replaced with earth-abundant alternatives.

The adoption of ammonia as a marine fuel in the short term is envisaged to be driven by ICE under current market and regulatory conditions. The preliminary small-scale test results reported by MAN ES and Wärtsilä demonstrate that the technology is ready to start working on a full-scale pilot with relatively few additional design modifications. Although ammonia combustion in ICEs does not contribute to carbon emission, thus can be regarded as a clean solution compared to fossil fuels, it is not 100% harmful emission free and requires NOx elimination. Therefore, ICEs should predominantly be seen as an important intermediate step to introduce ammonia as a new fuel in the maritime industry before pursuing towards truly 100% zero emission shipping by using fuel cells. In the medium to long term, ICEs are expected to leave their places to SOFCs as technology develops and price levels drop.

It should also be noted that there is no single solution and transition to zero emission will be through a combination of several technologies including new fuel sources and vessel efficiency improvements such as renewable assisted propulsion, hydrodynamics, paints and hull coatings, velocity optimisation, engine and ship design. Balcombe *et al.* (37) assessed GHG emission reductions *via* the use of alternative fuels (LNG, methanol, biofuels, hydrogen, nuclear and electricity) by incorporating various energy efficiency measures and they concluded that the decarbonisation requirements of the maritime industry could be met *via* a combination of several technological and operational pathways. Such a combined assessment is currently missing for green ammonia. It is recommended that future research activities focus on collective impact of changing fuels and implementing efficiency measures. In addition, an integrated system engineering is required to assess several factors such as space for onboard energy storage, energy requirement for a round trip, geography, infrastructure, costs and safety to decide on the ultimate energy transition pathways based on individual shipping operation conditions.

Overall, our analyses indicate that an effective fuel switching in maritime industry can only be achieved through engagement and synchronisation of three sectors, which are science and technology, industry and business, governance and policy. For a constructive transition, we need a round table that can link the key players from these industries and enable them work in a collaborative manner by involving in consortium projects. The global maritime energy shift council members may consist of, but not limited to, representatives from shipping companies, port managers, (renewable) energy firms and associations, politicians, policy makers, financial sectors and investors. Last but not least, the involvement of scientists should also not be forgotten. The efficiency and cost-competitiveness of the whole power-to-ammonia-to-power cycle explicitly depend on the development of new state-of-the-art materials and establishing an integrated system engineering. Scientists need support for carrying on fundamental research but also for increasing the commercial readiness of the discoveries. Various solid-state materials and techniques, that offer cost, efficiency and performance benefits, have already been reported in the literature and more will continue to come in the near future. However, there is a gap between transfer of knowledge to application. To increase the TRL value of these technologies within a compressed time frame and for large-scale implementation of carbon-free energy, scientific entrepreneurship should be encouraged and supported more.

Lastly, among the transportation sector, the shipping industry has long been criticised for being too conservative and too passive to change. In an interview with ShippingWatch, Henrik O. Madsen, the former CEO of major classification company DNV GL, stated "The attitude in the industry is mainly that any new regulation introduced is basically negative. I could hope that, going forward, they will change from seeing every new regulation as a risk to instead also thinking of a regulation as an opportunity" (38). To make this come true, local and international authorities need to join their forces and lead the round table meetings to bring innovative ideas collectively that can disrupt the conservativeness and fragmented nature of the maritime sector and help them change for a better future and business opportunities.

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