

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

Technological advantages and the momentum towards ammonia-propelled shipping

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Shipping, which accounts for 2.6% of global carbon dioxide emissions, is urged to find clean energy solutions to decarbonise the industry and achieve the International Maritime Organization (IMO)'s greenhouse gas (GHG) emission targets by 2050. It is generally believed that hydrogen will play a vital role in enabling the use of renewable energy sources. However, issues related with hydrogen storage and distribution currently obstruct its implementation. Alternatively, an energy-carrier such as ammonia with its carbon neutral chemical formula, high energy density and established production, transportation and storage infrastructure could provide a practical short-term next generation power solution for maritime industry. This paper presents an overview of the state-of-the-art and emerging technologies for decarbonising shipping using ammonia as a fuel, covering general properties of ammonia, the current production technologies with an emphasis on green synthesis methods, onboard storage and ways to generate power from it.

1. Introduction

Climate change is the most pressing environmental challenge of our time. Transport, particularly shipping, has a huge carbon footprint with around 1 billion tonnes of CO₂ equivalent every year (1). If no further action is taken, then estimates from the IMO (2) and European Parliament (3) suggest that the CO₂ emissions from international shipping could grow between 50–250% by 2050, accounting for 17% of global emissions. In 2018, IMO's Marine Environment Protection Committee (MEPC) announced an initial strategy on the reduction of GHG emissions from ships, setting out a vision to reduce GHG emissions from international shipping and eventually suspend them as soon as possible in this century. According to their level of ambition, the total annual GHG emissions (combination of CO₂, methane, nitrous oxide and fluorinated gases (4)) from international shipping need to be reduced by at least 50% before 2050 compared to 2008 (5). In addition, under the revised International Convention for the Prevention of Pollution from Ships (MARPOL) Annex VI, the global sulfur limit is lowered from 3.50% to 0.50% as effective from 1st January 2020 (6). Following IMO's regulations, many initiatives, including some in the United Nations (UN), European Union (EU) and various national governments, are making critical infrastructure and energy integration decisions to decarbonise the energy and transport sectors until 2050 (7–9). It is certain that renewable energies are key players in the global energy transformation to mitigate

climate change. However, the intermittent nature of renewables hinders their integration into the electricity distribution grid. A general consensus is that the (excess) electrical energy generated by renewable sources should be stored for later use on demand to alleviate the impacts of intermittent production. Storage requirements of the electric grid vary widely depending on specific applications (10). Most storage technologies fall into five generalised categories, which are mechanical, electrical, thermal, electrochemical and chemical energy storage (Figure 1). Among them, chemical energy storage, which relies on storing energy in the chemical bonds of molecules, provides storage of high energy density over a long period of time and easy transportation from generation to demand sites.

It is believed that the chemical energy storage in the form of hydrogen will play a vital role in enabling the use of renewable energy sources (for example solar, wind, waves) to reduce CO₂ emissions from various industries in the near future. Particularly, the progressive decrease in the cost of electrolyzers and the increase in carbon taxation may justify large-scale hydrogen production from water *via* electrolysis, powered by renewable electricity in centralised installations. This stored energy can then be released again by using the gas as a fuel in a combustion engine or a

fuel cell, which are relatively mature technologies for hydrogen application. Hydrogen not only provides a carbon-free energy solution but also offers flexibility as most technologies that use fossil fuels such as natural gas can be adapted to use hydrogen and still provide the same level of service (12, 13). The benefits of using renewable hydrogen are already being recognised commercially for niche applications, including water transport. For instance, in February 2020, Enviu, The Netherlands, announced that passengers in Rotterdam will board a water taxi powered by hydrogen fuel cell in 2021 (14). The hydrogen-water taxi is being developed by the SWIM consortium (consisting of Enviu, Watertaxi Rotterdam and the (maritime) innovation companies Flying Fish and ZEPP solutions) that was initiated as part of Enviu’s zero-emission shipping programme Towards Hydrogen-based Renewables Used for Ship Transportation (THRUST). When the project comes to life, it is going to be the world’s first demonstration for a commercial boat on this scale running entirely on a zero-emission fuel. To overcome the infrastructure barrier, parallel to this project, Enviu is also working on a green hydrogen tank station. However, powering long distance shipping with hydrogen is not practical because at scale it must be compressed to around 350 to 700 times atmospheric pressure or cryogenically cooled to -253°C which is an energy intensive and

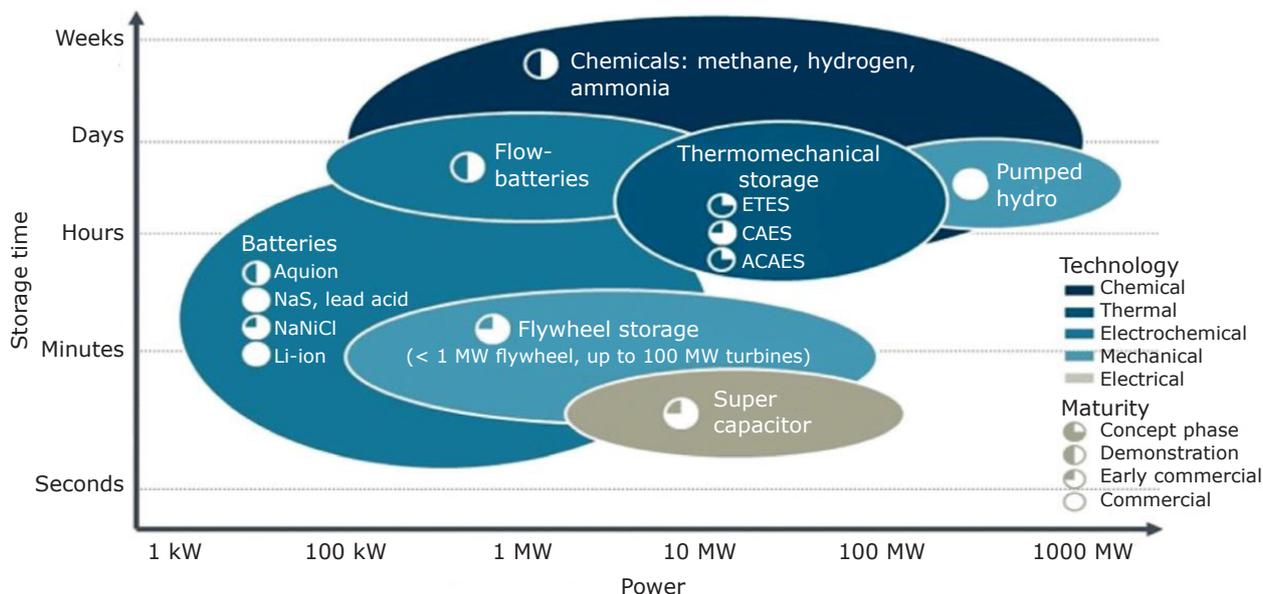


Fig. 1. Energy storage technologies based on power density and discharge time. ETES = electrothermal energy storage, CAES = compressed air energy storage, ACAES = adiabatic compressed air energy storage (11) Copyright Siemens AG

expensive process. In addition, liquid hydrogen requires eight times more storage space than heavy fuel oil (HFO) while this is even 30 times more for compressed hydrogen (15, 16). As an alternative, a hydrogen-carrier such as ammonia with higher volumetric energy density and carbon neutral chemical formula has recently been under investigation as a potential fuel for transport (17–24). The countries with the world's top container ports such as Australia, the UK, Japan and Saudi Arabia have recently announced their national zero-emission fuel switch strategies, in which ammonia plays an important part together with hydrogen, and invested millions of US dollars for their large scale demonstrations (25–29). The steps of major energy players towards alternative zero-carbon emission fuels will certainly have impacts not only in these countries but also beyond.

1.1 Momentum in Maritime Industry Towards Ammonia-Propelled Shipping

Following the directions, policies and roadmaps of IMO and national regulatory authorities, a number of ventures are already underway to test viability of ammonia in the shipping sector. The engine manufacturers, MAN Energy Solutions (MAN ES, Germany) and Wärtsilä, Finland, are currently developing two-stroke and four-stroke engines, respectively, designed to operate on ammonia and anticipate that the first ammonia engine could be in operation in 2024 (30, 31). Both companies reported that they had successfully conducted a preliminary study into ammonia combustibility, which revealed that slow flame velocity, slower heat release and combustion characteristics of ammonia were no obstacle to combustion in these engines (32). Based on their research on combustion in smaller engines and turbines, the challenges related to ammonia combustion are determined to be the high nitrogen oxides (NO_x) generation, low flammability and low radiation intensity. Further full-scale engine tests will continue to overcome these challenges in 2021. These tests will serve as the platform for the ammonia engine development at Copenhagen Research Centre of MAN ES and the Sustainable Energy Catapult Centre's testing facilities of Wärtsilä at Stord, Norway. Following that, Lloyd's Register (LR, UK) has granted Approval in Principle to Dalian Shipbuilding Industry Company (DSIC, China) and MAN ES for an ammonia-fuelled 23,000 twenty-foot equivalent unit (TEU) ultra-large container ship (ULCS)

concept design, the first ammonia as fuel design of its kind in China (33). MS Color Fantasy, the world's largest roll on/roll off (RORO) cruise liner, has also plans to pilot ammonia as a marine fuel (34). In addition, like Enviu's THRUST programme from The Netherlands, another non-profit organisation, the Mærsk Mc-Kinney Møller Center for Zero Carbon Shipping, was launched in Denmark on 25th June 2020 (35). The organisation aims to bring the best minds from science, engineering and business in order to implement new energy systems and technologies for shipping. Although it is not clear yet how the decarbonisation of shipping will be achieved, given the tremendous drive around ammonia as a potential zero-carbon emission fuel, more ammonia-related shipping projects are expected to be announced in the near future.

Besides the efforts of individual companies on developing and expanding their ammonia powered technologies, recently there has been a tremendous increase in the announcement of consortium projects aiming to demonstrate ammonia-fuelled vessels operating at sea. The ShipFC consortium could secure €10 million fund from the EU's research and innovation programme Horizon 2020 under its Fuel Cells and Hydrogen Joint Undertaking (FCH JU) to deliver the world's first high-power fuel cell to be powered by green ammonia (36). The ShipFC project is being run by a consortium of 14 European companies and institutions, coordinated by the Norwegian cluster organisation NCE Maritime CleanTech. The project aims to demonstrate an offshore vessel, Viking Energy, which is owned and operated by Eidesvik AS, Norway, and on contract to energy major Equinor, Norway, powered only with a large 2 MW ammonia fuel cell to sail up to 3000 h annually. One of the main objectives is to ensure that a large fuel cell can deliver total electric power to shipboard systems safely and effectively. This is the first time an ammonia-powered fuel cell, scaled up from 100 kW to 2 MW, will be installed on a vessel. The design, development and construction of ammonia-fuelled solid oxide fuel cell (SOFC) will be undertaken by Prototech, Norway. Testing will be executed at the Sustainable Energy Norwegian Catapult Centre and the ship-side ammonia system will be supplied by Wärtsilä. It is envisaged that the ammonia fuel cell system will be installed in Viking Energy, UK, in late 2023. The ultimate goal is to demonstrate that long-distance, emission-free voyages on big ships are possible.

Another European based consortium in the Nordic region was announced in May 2020 (37). The

Global Maritime Forum has launched The Nordic Green Ammonia Powered Ships (NoGAPS), a major consortium that aims to prove the feasibility of a large ammonia-powered deep-sea vessel by 2025. Funded by Nordic Innovation, partners of the project include Danish Ship Finance, shipowner J. Lauritzen, engine maker MAN ES, Ørsted energy group and consultancy group Fürstenberg Maritime Advisory, all from Denmark, along with Oslo-based bank DNB, the class society DNV GL, chemical group Yara International and the Helsinki-listed Wärtsilä.

In Japan, an industry consortium is collaborating in a project to develop ships designed to use ammonia as fuel and go beyond onboard ship technology to include "owning and operating the ships, supplying ammonia fuel and developing ammonia supply facilities." The participants of the consortium are Nippon Kaiji Kyokai (ClassNK), Imabari Shipbuilding, Mitsui E&S Machinery, MAN ES, Itochu Corporation and Itochu Enex (38). In addition, on 6th August 2020, NYK Line, Japan Marine United Corporation and ClassNK signed a joint research and development (R&D) agreement for the commercialisation of an ammonia-fuelled ammonia gas carrier (AFAGC) that would use ammonia as the main fuel, in addition to an ammonia floating storage and regasification barge (A-FSRB) for offshore bunkering and stable supply of ammonia fuel (39).

It is likely that more ammonia propelled shipping demonstration projects will be announced in the following years. The winners of the contest will dominate their positions in the value chains to deploy zero-carbon vessels and bunkering infrastructure across the sector.

1.2 Why Ammonia?

Recently ammonia has taken considerable attention and pointed as one of the most promising alternative chemical energy and hydrogen-carriers in many technical reports (19, 40), white papers (23, 41) and research articles (18, 22), due to the following reasons:

- Ammonia has an existing infrastructure for production, storage and global transport. With over 200 million tonnes production per year (42), it is one of the largest chemical industries in the world
- It can be stored as a liquid at relatively low temperature and pressure (cooling to -33°C at atmospheric pressure or compressing to 10 bar at room temperature)
- It has high energy density (**Table I**) which enables sufficient capacity for long ship voyages without refuelling for weeks (46)
- With minor modifications, ammonia can be adopted to be used in internal combustion engines (ICEs) and gas turbines (GTs) in the short term. It has also a strong potential to be used directly in fuel cells in the future
- Ammonia has higher ignition temperature and narrower flammability range; therefore, fire risk is lower compared to hydrogen
- It does not contain carbon or sulfur in its chemical formula, thus does not contribute to CO_2 and sulfur oxides (SOx) emissions during utilisation (**Table I**).

To meet IMO's targets and ultimately decarbonise the maritime sector, vessels powered by zero

Table I List of Selected Marine Fuels and their Characteristics (20, 43–44)

Fuel ^a	Energy density, LHV ^b , MJ kg^{-1}	Volumetric energy density, GJ m^{-3}	Storage pressure, bar	Storage temperature, $^{\circ}\text{C}$	CO_2 emission $\times 10^3$, kg per trip ^c	SOx emission $\times 10^3$, kg per trip ^c
MGO	42.7	36.6	1	rt ^d	277	0.18
HFO	40.4	38.3	1	rt ^d	286	2.12
LNG	50	23.4	1.0	-162	220	0.09
Compressed hydrogen	120.0	7.5	700	20	0	0
Liquid hydrogen	120.0	8.5	1	-253	0	0
Liquid ammonia	18.6	12.7	1 or 10	-34 or 20	0	0
Methanol	19.9	15.8	1	20	254	0.09

^aMGO: marine gas oil; HFO: heavy fuel oil; LNG: liquified natural gas

^bLHV: lower heating value

^c CO_2 and SOx emissions were calculated using "THRUST Impact Model" of Enviu (45). The values are based on a single trip from Piraeus to Rotterdam (5893 km) of a container ship with a size 1000 TEU and engine power of 4609 kW

^drt: room temperature

GHG emitting fuels need to be implemented to the international shipping fleet in the early 2020s. Ammonia offers several potential advantages over hydrogen and the conventional marine fuels such as HFO, MGO and LNG. However, several factors such as sustainable production routes, power generation, cost of transition and safety and environmental aspects still need to be considered thoroughly before the implementation and deployment of an ammonia-powered fleet. The following sections of the paper will cover these aspects. It is also noted that there are many valuable studies that have assessed the potential of ammonia as an alternative fuel for transport (17–23). This paper adds to this body of literature by providing collective, up-to-date knowledge, introducing state-of-the-art and emerging technologies as well as identifying the critical research gaps necessary for practical application of these technologies. The paper follows an approach to show the picture from a wide-ranging perspective that is of interest particularly for industry without overwhelming with technical details. Instead, the key and recent studies have

been identified, summarised and cited in the paper for interested readers to explore further.

2. Production of Ammonia

Ammonia is currently produced *via* the Haber-Bosch process that involves reaction of hydrogen and nitrogen molecules on a catalyst surface at a temperature range of 450–600°C and a pressure of 100–250 bar. Nitrogen is supplied by air separation unit and hydrogen is obtained from steam methane reforming (SMR) or, to a lesser extent, coal gasification. This process (so-called ‘brown ammonia’) is energy intensive, consuming 1% of the world’s total energy production, and environmentally unfriendly, accounting for 1.8% of global GHG emissions, as hydrogen is supplied from fossil fuels. From a product lifecycle point of view, brown ammonia would not offer much environmental benefit if used as a shipping fuel.

For the decarbonisation of ammonia production, three possible methods (**Figure 2**) are currently

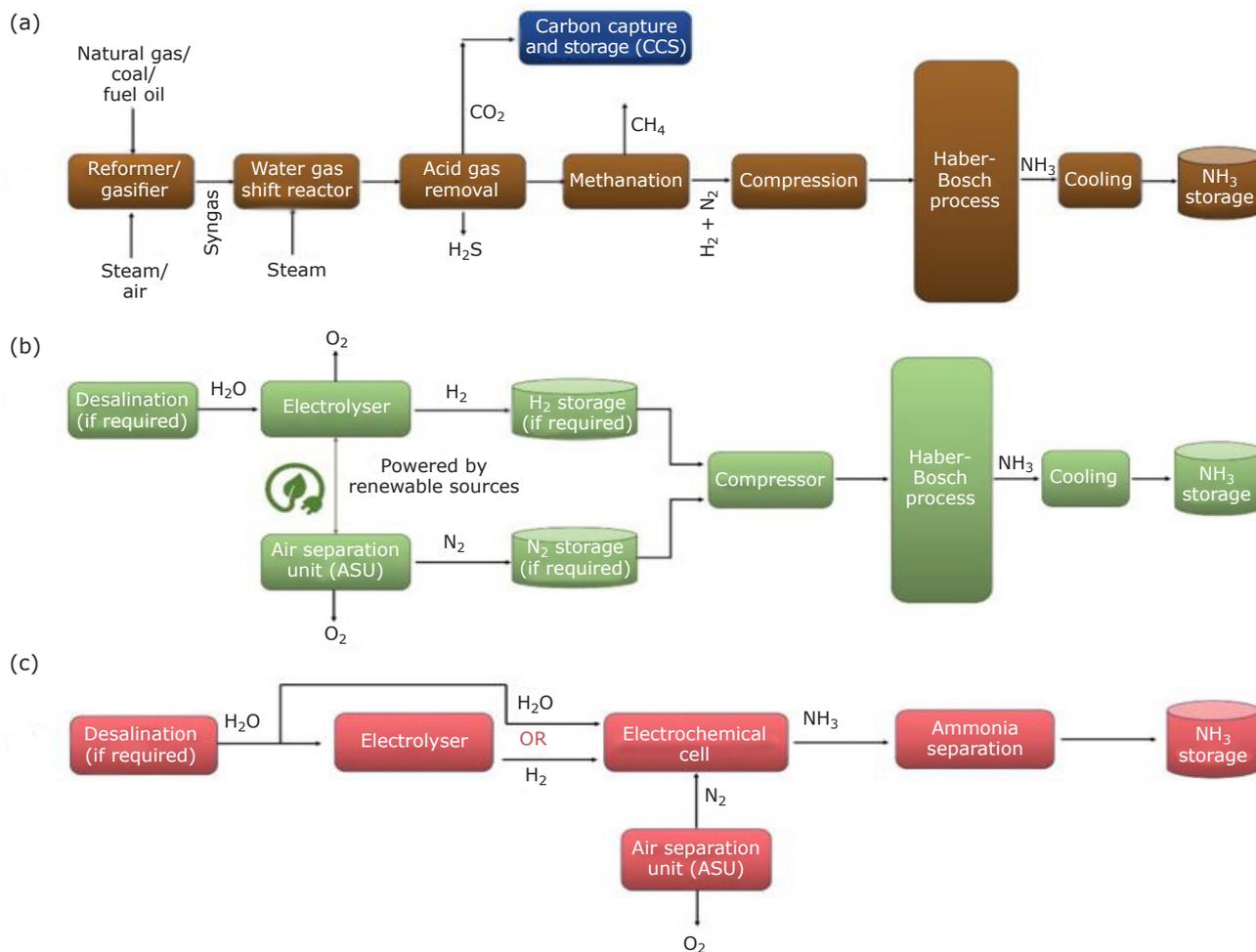


Fig. 2. (a) Brown (without CCS) and blue (with CCS) ammonia production flowchart; (b) green ammonia production flowchart; (c) electrochemical ammonia production flowchart

being considered: (a) conventional Haber-Bosch production with carbon capture and sequestration (CCS) – so called ‘blue ammonia’; (b) a modified Haber-Bosch process in which hydrogen is supplied by water electrolysis using renewable energies (wind, solar, tidal wave) – ‘green ammonia’; and (c) direct production of ammonia from water and air in an electrochemical cell – ‘electrochemical ammonia’.

Designing new ammonia plants with integrated CCS or retrofitting CCS to conventional plants does have notable potential and will probably be an intermediate solution in the short term. However, integrating CCS into the existing structure will not only increase the energy consumption, which is already very high, but will also lead to further challenges to find a place to securely store the captured CO₂. The techno-economic study carried out by Santos and coworkers for the International Energy Agency (IEA) Greenhouse Gas R&D Programme (47, 48) demonstrates that the integration of a CO₂ capture plant to an SMR plant could reduce the CO₂ emission between 53% to 90% whereas the natural gas consumption would increase by 0.46 MJ Nm⁻³ to 1.41 MJ Nm⁻³ hydrogen and the amount of surplus electricity exported to the grid by the SMR plant would be reduced. These changes lead to an increase in the operating cost of hydrogen production by 18% to 33% compared to the SMR without CCS; thus the levelised cost of hydrogen production could increase by €0.021–€0.051 Nm⁻³ hydrogen depending on capture rate and technology selected. Therefore, the use of hydrogen gas generated from water electrolysis using renewable energies in the Haber-Bosch process for ammonia production would be the most convenient route in the medium term because the process does not contribute to CO₂ emission, electrolyzers are already commercially available with a scale ranging from kilowatt to megawatt and the cost of electricity from renewable sources is declining, making the overall process economically viable. The use of biomass as a feedstock to provide synthesis gas (syngas) for ammonia production *via* Haber-Bosch process might also be regarded as a green process because the CO₂ emitted by a biomass-based plant is biogenic which means that the CO₂ released during biomass gasification and digestion processes is later consumed by biomass-plants as they grow, thus, no extra CO₂ is added to the atmosphere (49). Techno-environmental analyses of ammonia production using biomass as feedstock (50, 51) show that the cost of ammonia produced from biomass feedstock can be competitive with brown ammonia and lead to

global warming potential reductions of 54–68%, when compared to conventional ammonia plants. However, scalability of biofuels remains as a challenge. Land used to produce biomass feedstock has similar environmental characteristics to that of agriculture, thus putting biofuels in competition with other land uses and leading to implications for food security, sustainable rural economies and the protection of nature and ecosystems (52). Nevertheless, biomass-derived ammonia production might effectively meet the ammonia requirements for small territories or isolated applications.

Another conspicuous alternative pathway for ammonia production is electrochemical synthesis where nitrogen is reduced electrocatalytically in the presence of water or hydrogen. It has been foreseen that ammonia production *via* electrochemical routes can save more than 20% of energy consumption as compared to the conventional Haber-Bosch method because water can be directly fed into the anode chamber of the reactor as a hydrogen source without the requirement of initial water electrolysis, and electrochemical reaction can be operated at low temperatures and atmospheric pressure. However, none of the electrochemical ammonia synthesis routes has achieved the level of technological maturity required for commercial deployment yet, although a high rate ($2.4 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$ at a maximum current efficiency of 4.2%) has recently been achieved when ammonia was synthesised in molten salt medium using the electrochemical approach (53).

2.1 Catalysts for Green and Direct Electrochemical Synthesis of Ammonia

As described above, green ammonia production incorporates two catalytic processes: (a) hydrogen production from water electrolysis; and (b) ammonia synthesis from hydrogen and nitrogen *via* Haber-Bosch reaction. The high cost of commercial electrolyzers arises from the usage of expensive noble metals such as platinum and palladium on a carbon support as catalysts in the electrochemical cells. The catalyst itself has taken up a considerable portion of the total system and capital cost, especially if there is degradation or corrosion on the carbon support. Hence, one crucial aspect of the development in hydrogen evolution reaction (HER) technology is to replace the catalysts with earth-abundant alternatives to produce hydrogen in a more economical way. Mo *et al.* (54) has recently reported that inexpensive silver catalysts,

particularly the cubic form of silver nanoparticles, can clearly exhibit superior HER activity over platinum at the same metal content by altering the rate-determining step in a proton exchange membrane (PEM) electrolyser when practically more negative potential is applied. High activity was attributed to the weaker Ag–H bond at the surface than Pt–H which is more favourable for H recombination to form H₂. This study is significant to rectify the misconception that platinum is always at the 'optimal volcano' position among all monometals in HER, which has led to an inaccurate description of the surface electrocatalysis under real PEM conditions at high workload. Beside this scientific achievement with a monometallic catalyst, start-up company Hymeth, Denmark, announced in 2019 that it would commence the production of Hyaeon™ which is a low temperature and high pressure electrolyser, at a commercial scale after completing tests. The company uses an inexpensive trimetallic nickel-copper-iron core-shell electrocatalyst, possessing high electrochemical activity for both oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) (55). Another method of hydrogen evolution is photocatalytic water splitting. This process benefits from direct usage of solar renewable energy without the requirement for the installation of an extra electricity generator such as photovoltaic panels or wind turbines to supply power to electrolysers. Although various studies have been reported in the past decade (56), no practical application has been implemented yet mainly due to low catalytic activities, a narrow range of light absorption and poor quantum efficiencies (QE) (the measure of the effectiveness of a light absorbing material to convert incident photons into electrons) as a result of fast recombination of charge carriers. In 2019, Tsang and coworkers (57) reported a nitrogen-doped titania nanocatalyst on MgO(111) photocatalyst that has a hydrogen evolution rate of over 11,000 μmol g⁻¹ h⁻¹ in the absence of any sacrificial reagents at 270°C. An exceptional range of QE from 81.8% at 437 nm to 3.2% at 1000 nm was also stated. High activity was attributed to formation of oxygen vacancies upon introducing nitrogen into the titania structure and prolongation of exciton lifetime over the polar MgO(111) surface. The technology readiness level (TRL) of this invention is currently at TRL3–4 but it has a strong potential in the future to harness solar energy (light and heat) for hydrogen production in large scale.

Another energy intensive and costly process in ammonia production is the Haber-Bosch process

where hydrogen and nitrogen react at 15–25 MPa and 400–450°C using an iron-based catalyst (either magnetite or wurtzite). Low equilibrium single-pass conversion (~15%) necessitates the recycle of unreacted gases, leading to higher energy consumption (58). Compared with commercial iron catalysts, ruthenium-based catalysts offer advantages in Haber-Bosch reaction because they are relatively active at low pressure. Ruthenium with a higher electron density in *d*-orbitals, in assistance with strong electron donor dopants such as alkali metals, can donate electrons into the anti-bonding orbital of adsorbed nitrogen, facilitating its dissociation, and thus, can work under lower pressure. However, ruthenium-based catalysts have found limited uses in conventional Haber-Bosch processes because they are relatively more expensive and are easily poisoned by carbon deposition from methane in syngas (59). The electrified Haber-Bosch system, where hydrogen is derived from water, does not contain methane, so the carbon poisoning effect can be well avoided. However it is also known that another surface poisoning of ruthenium sites by competitive strong hydrogen dissociative adsorption limits the overall reaction rate. Lately some workers have demonstrated that changing the surface polarity by either decorating terrace sites of ruthenium nanoparticles with Li⁺ (60) or using an electrostatically polar MgO(111) in place of nonpolar MgO as the support (61), can significantly alleviate the hydrogen poisoning and facilitate an unprecedented ammonia production rate. Another outstanding study reported by Hattori *et al.* (62) has demonstrated the ability of ruthenium catalysts to produce ammonia from nitrogen and hydrogen at a temperature as low as 50°C. The researchers used a stable electron-donating heterogeneous catalyst, cubic CaFH, a solid solution of calcium fluoride and calcium hydride formed at low temperatures to achieve high performance with an extremely small activation energy of 20 kJ mol⁻¹ at 50°C, which is less than half that for conventional catalysts.

If the future green ammonia production *via* Haber-Bosch process is carried out in decentralised, islanded locations in small scale, then hydrogen manufactured from an electrolyser at lower pressure and temperature would require coupling with an efficient catalyst to achieve high ammonia production rate. In this manner, ruthenium stands out from the other alternatives and high cost may actually not be a disadvantage. In fact, developing countries, particularly ones located in Africa may use this opportunity to attract investment as they

Table II Momentum in Green Ammonia Projects (67–73)

Participants	Location	Capacity, tonnes per year	Renewable source	Year	Purpose
University of Minnesota	Morris, Minnesota, USA	25	Wind	2014	Supply of local fertiliser demand
FREA, JGC Corporation	Koriyama, Japan	7	Wind, solar	2018	Low temperature/low pressure H-B catalyst optimisation, demonstration of ammonia combustion in gas turbines
Siemens	Harwell, UK	10	Wind	2018	Power-to-ammonia-to-power demonstration unit
Iberdrola, Fertiberia	Puertollano, Spain	4000	Solar	2021	Becoming a European reference for sustainable solutions for agriculture
Yara	Porsgrunn, Norway	5000 (estimate)	Hydroelectric grid	2022	The first small step towards carbon free fertiliser production by installing 5 MW electrolyser corresponding to 1% of the hydrogen production in Porsgrunn
Haldor Topsøe	Foulum, Denmark	300	Wind	2025	Demonstration of direct ammonia production from water and air using solid oxide electrolyser without air separation unit
Air Products, ACWA Power, Thyssenkrupp, Haldor Topsøe, NEOM	Saudi Arabia	1.2×10^6	Wind, solar	2025	Production of green ammonia at oil and gas scale and distribute the green ammonia globally and crack it back to 'carbon-free hydrogen' at the point of use, supplying hydrogen refuelling stations
OCP	Jorf Lasfar	700	Solar	TBD	Fertiliser production and supply of power to marine vessels
Enaex	Antofagasta, Chile	20,000 and 350,000	Solar	TBD	Feasibility study (pilot plant scale at 64 MWp solar and 47 MW electrolyser, full scale at 1030 MWp solar and 778 MW electrolyser)
Proton Ventures, Siemens, Yara	Goeree-Overflakkee, The Netherlands	20,000	Wind, tidal	TBD	Part of regional green hydrogen economy roadmap
Siemens Gamesa, Energifonden Skive	Skive, Denmark	TBD	Wind	TBD	Ammonia production as a way to store surplus electricity from wind turbines
Ballance Agri-Nutrients, Hiringa Energy	Kapuni, New Zealand	5000 (estimate)	Wind	TBD	The \$50 million showcase project as a catalyst for the development of a sustainable green hydrogen market
Queensland Nitrates, Incitec Pivot, Wesfarmers JV, Neoen, Worley	Moura, Australia	20,000	Solar	TBD	Determining the technical and economic feasibility of producing renewable ammonia at a commercial scale
Dyno Nobel	Moranbah, Australia	60,000	Solar	TBD	Feasibility study to decarbonise their own nitrogen-based commodity production facility
Yara	Pilbara, Australia	25,000	Solar	TBD	Feasibility study for carbon-free fertiliser production
H2U, Thyssenkrupp	Port Lincoln, Australia	20,000	Wind, solar	TBD	Business case demonstration for renewable energy exports (Hydrogen Hubs)

Today, commercial manufacturing of green ammonia is not available anywhere. But, with renewed interest and global drive, it is highly likely that by 2030, there will be a body of demonstration plants that can show the viability of producing ammonia from renewable energy at scale.

3. Onboard Storage and Power Generation from Ammonia

3.1 Onboard Space Requirement

With an energy density of 12.7 GJ m^{-3} , ammonia would require a larger volume of space onboard in order to deliver the same power as conventional marine fuels. For instance, if a HFO fuel tank has a volume of 1000 m^3 , an ammonia fuel tank would require 2.75 times more space than that of HFO to provide the same power (30). This might make ammonia appear unfeasible; however, the space requirement for ammonia remains significantly smaller compared to other carbon-free options as the tank volume would be 4117 m^3 for liquid hydrogen at -253°C ; $14,000 \text{ m}^3$ for a Tesla Model 3 battery (Tesla, USA) and $120,896 \text{ m}^3$ for the battery pack of Corvus Energy, Norway, the marine battery market leader (30). Even carbon-based methanol does not offer significant advantage, needing a tank volume of 2333 m^3 . Therefore, the space requirement for ammonia-propelled shipping is not found to be unrealistic or inapplicable (24).

3.2 Propulsion Systems

Two kinds of propulsion systems (direct combustion and fuel cells) that could use ammonia as a marine fuel stand out regarding the current and emerging technologies. **Figure 4** illustrates the simplified configuration of these propulsion systems.

3.2.1 Direct Combustion

Direct usage of ammonia in combustion engines dates to 1942 when Belgium's public bus system ground to a halt by a wartime shortage of diesel (78). As a result, the engine systems of the buses were adapted to run with an alternative fuel: liquid ammonia with a small amount of coal gas to help combustion. Although the lifetime of ammonia-powered buses was short, it demonstrated that ammonia could be used as a transport fuel.

Ammonia can be combusted in ICEs or in GTs, both of which are well established as prime movers in naval vessels. However, burning

ammonia effectively within these engines is rather challenging because ammonia has poor ignition that requires high temperature or a secondary fuel to initiate the combustion process, low burning velocity (0.015 m s^{-1}) and narrow flammability limit (12–25% air), causing unstable combustion conditions at very low and high engine speeds and ammonia slip.

To date, many studies have been conducted to assess the performance and emissions of ammonia propelled combustion engines. Two useful reviews published by Kobayashi *et al.* (79) and Valera-Medina *et al.* (18) provide comprehensive information about fundamental aspects of ammonia combustion, the details of the chemistry of NO_x production, processes for reducing NO_x and validation of several ammonia oxidation kinetics models. Results show that ammonia as a sole fuel in a compressed ignition ICE (CI-ICE) is not possible due to the high compression ratios needed for ignition and combustion. Therefore, co-feeding of ammonia with only 5% of a pilot fuel with higher cetane number (hydrogen, diesel, methanol, dimethyl ether) would be enough to facilitate its combustion. On the other hand, combustion of ammonia as the only fuel might be possible in spark ignition ICEs (SI-ICEs) (80). In fact, Toyota, Japan, filed a patent (81) where it claimed that several plasma jet igniters arranged inside the combustion chamber or plural spark plugs that ignite the ammonia at several points can enable ammonia combustion. Most of the work in the literature examines the combustion stability and emissions from gaseous ammonia blended with carbon-based fuels or hydrogen in ICEs. It is recognised that there is generally only a narrow equivalence dual-fuel ratio where high stability, low emissions and high temperature can be achieved, leaving a vast field of research, modelling and testing on how to improve these parameters to obtain wider operational ranges and adapt the technology to large marine engines.

3.2.2 Fuel Cell Systems

An alternative to generating power from ammonia in a combustion engine is to use fuel cells, which may provide advantages in terms of high thermal efficiencies, less noise and lower emissions of air pollutants. Basically, ammonia can either be used directly in fuel cells or be used as a hydrogen carrier where first, a cracker is used to decompose ammonia into hydrogen and nitrogen and after, hydrogen is fed into a fuel cell to generate electricity. Among

several of the chemical hydrides (82) suggested for hydrogen storage, such as methanol, formic acid and liquid organic hydrogen carriers, liquid ammonia steps forth with its high gravimetric (17.7 wt%) and volumetric (123 kg m⁻³) hydrogen density, exceeding the 2015 US DoE targets for hydrogen storage (9.0 wt% hydrogen content, 81 kg m⁻³ volumetric capacity). It also benefits from the absence of carbon oxides (COx) emissions associated with hydrogen as a fuel in fuel cells.

Ammonia can be directly used in alkaline fuel cells (AFCs) and SOFCs, whereas PEM fuel cells (PEMFCs) require high purity hydrogen (>99.5%) as the catalyst is poisoned in the presence of small amount of ammonia (22, 83). The fuel cells

identified as the most promising for the maritime sector are PEM and SOFCs (23). For use in PEMFCs, either highly active yet cost-effective ammonia cracking catalyst operating at low temperature regime is required to achieve high purity hydrogen *via* complete ammonia conversion in a single gas stream pass or gas purifier equipment needs to be installed which would involve additional costs together with mass, space and energy demand onboard. Compared to PEM, SOFC is much more promising for maritime application as ammonia can be used directly instead of separating hydrogen from it first. However, further research is required to optimise the operation conditions, increase the system lifetime and scale-up.

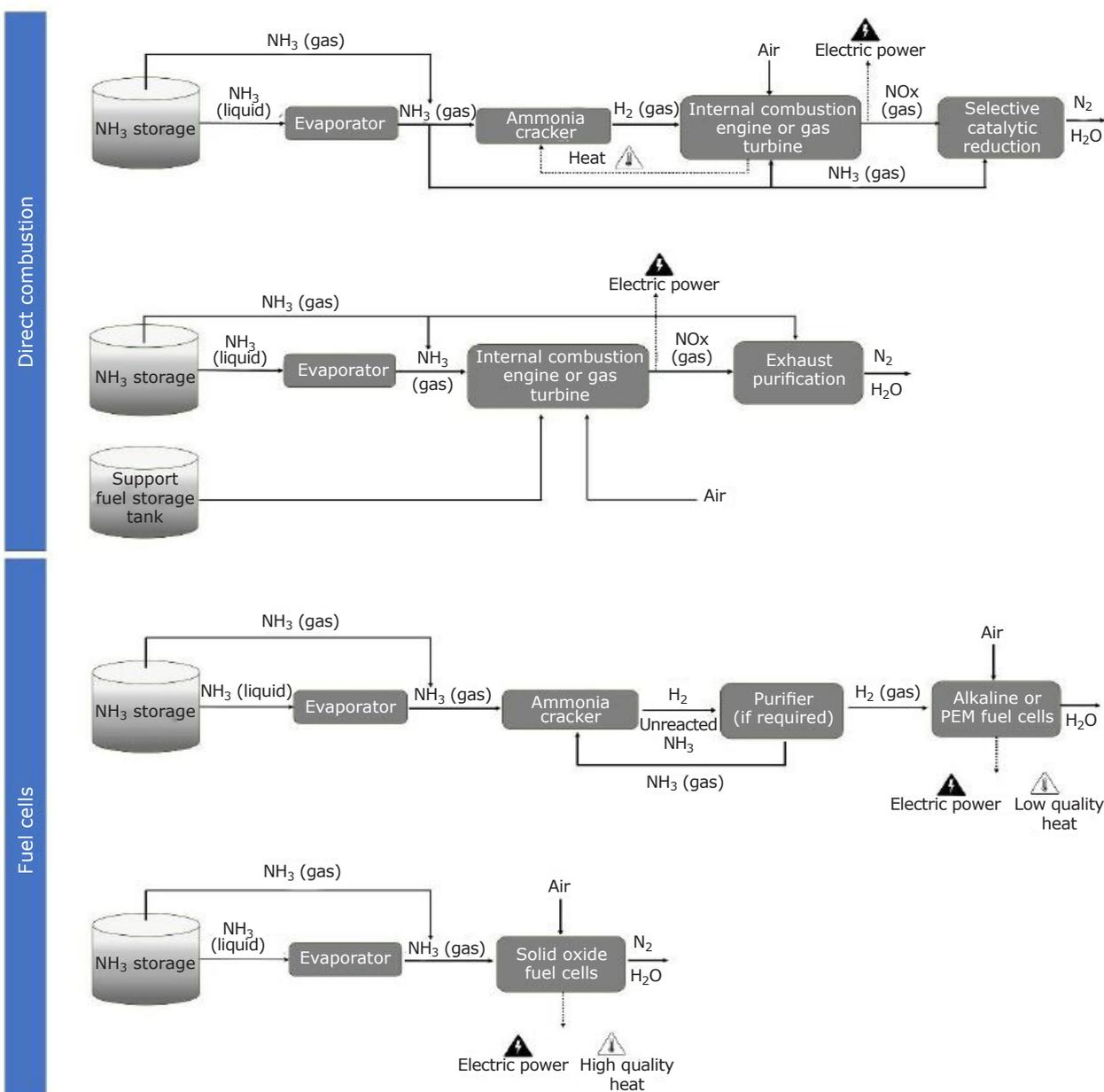


Fig. 4. Possible propulsion systems process diagrams using ammonia as a marine fuel

3.2.3 Catalytic Processes Involved in Ammonia to Power

For the onboard usage of ammonia, two propulsion systems are considered as stated in previous sections. Because of the low flammability of ammonia, generally a second fuel with higher cetane number needs to be fed into the combustion engine to start ignition and combust ammonia. One of the fuel options to assist the combustion might be hydrogen due to its high flammability and environmental friendliness. As ammonia is a hydrogen carrier, extra storage space for hydrogen may not be necessary. Instead, ammonia can be cracked to its forming molecules, nitrogen and hydrogen, catalytically onboard. Ammonia decomposition is not new, and has long been used in industry. The process is endothermic; however, the equilibrium conversion shows diminishing returns for temperatures above 400°C. Inexpensive catalysts such as nickel or iron might be suitable to crack ammonia onboard at low temperatures (using the heat generated from the combustion engine) as only 5% hydrogen in the gas stream would be enough to combust ammonia effectively. However, for PEMFC applications, high purity hydrogen (>99.5%) is required since a large quantity of ammonia leads to catalyst poisoning in fuel cells. Although nickel catalysts can achieve this conversion, more than 900°C is required. The reviews reported by us (59) and by others (84, 85) present a comprehensive list of ammonia decomposition catalysts and the activity values under their optimum working conditions. Among all these reported materials, ruthenium catalysts appear to be the most promising candidates due to their high ammonia conversion rates at lower temperatures. Considering the high costs and scarcity of noble metals, a low cost but highly active catalyst working at temperatures aligned with those of the PEMFCs, in the range of 150–200°C, is needed for the practical conversion of ammonia under industrial conditions. For instance, a core-shell catalyst preparation approach might be followed to decrease the amount of any expensive metal component and replace it at the core with a cheaper metal in the working catalysts. With this method, the stability of catalysts against metal sintering may also be improved. The alkali amide (–NH₂) (86) and imide (–NH) materials (87, 88) are also emerging as promising inexpensive catalysts for ammonia decomposition at mild conditions. The UK's Department for Business, Energy and Industrial Strategy (BEIS) recently published

a Phase One feasibility study for its Ammonia to Green Hydrogen Project (89). In the report, lithium imide catalyst is highlighted as a low-cost and high performance state-of-the-art catalyst. Phase Two of this project will be related to further development of the cracker to raise the TRL of a lithium imide based ammonia cracker catalyst from TRL4 to TRL6/7 by demonstrating and validating the feasibility of the technology developed. Compared to PEMFCs, SOFCs offer direct usage of ammonia without the requirement of precracking and gas purification processes. With an operation temperature in the 700–1000°C range, ammonia cracking can be thermally integrated within the fuel cell stack. The key challenges with ammonia SOFCs in the literature were thought to be the durability of the anode/electrolyte interface and a risk for NO_x emission (83). However, research conducted at the University of Perugia, Italy, with the support of Enviu indicated that the degradation rate of a SOFC operating at 750°C during 100 h of testing with ammonia is equivalent to one operating under the same conditions with hydrogen (90). Moreover, analysis shows that there was no nitrification of the anode, which practically means no NO_x formation. This study showed that at operative temperature there is no risk of anode degradation when applying ammonia. In addition, the off-gas analysis showed no presence of ammonia, indicating that a complete decomposition of ammonia occurred inside the cell. With these tests a system efficiency of 57.5% at a power density of 0.39 W cm⁻² has been achieved. SOFCs are now becoming an important field of R&D. The translation of these scientific findings to technology will pave the way to their commercialisation and deployment in the near future.

3.3 Technology Status of Ammonia Powered Ship Propulsion Systems

So far, none of these propulsion technologies for ammonia has yet been commercialised and deployed for shipping but a design study for such a vessel was recently published by de Vries (43). The author reviewed all options covering ICE, PEMFC, AFC and SOFC for marine applications. It has been concluded that the SOFC scores best in efficiency but lacks power density, load response capability and is still too expensive. The ICE is second in efficiency and thus more efficient than the PEMFC and the AFC (in case these are operated close to maximum power). Additionally, the ICE is less expensive, more robust with acceptable

power density and load response. Based on these comparisons, the ICE has been identified as the best option for maritime applications at the current technology status but SOFCs are considered to have a lot of potential in the future.

As mentioned in Section 1.1, MAN ES and Wärtsilä are working on the development of the ammonia-fuelled engine for shipping. The overall message from MAN ES is that the liquid gas injection (LGI) engine family that works with dual-fuel is a good candidate for the conversion to ammonia and the ships running with LNG can be retrofitted for ammonia operation as the tanks used for storage of LNG with the same requirements can also be used for ammonia (30, 91). However, when designing the storage and propulsion systems, the chemical properties of ammonia should be taken into consideration. Due to the corrosive nature of ammonia, copper, brass and zinc alloys need to be avoided as discussed in Part II (92).

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