Ammonia as a marine fuel

an introduction

Version 1.0

sgmf
the society for gas as a marine fuel

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Disclaimer

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The Society for Gas as a Marine Fuel (SGMF)

The Society for Gas as a Marine Fuel (SGMF) is a membership-based non-governmental organisation (NGO) established in 2013 to promote the safe and sustainable use of gas as a marine fuel. The Society has full consultative status at the IMO and is the recognised representative body for the gas-fuelled shipping industry.

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About this publication

As its name suggests, Ammonia as a marine fuel – an introduction sets out the key facts about ammonia (NH_3):

- what it is
- how it is used
- its safety and environmental profile
- the technical considerations of NH_3-fuelled ships
- systems designs
- bunkering facilities and processes, and
- how personnel involved in handling NH_3 should be trained

Although out of necessity it is a high-level document, the aim of this publication is to provide key information that will assist the eventual ammonia-fuelled ship industry to develop.

Ammonia as a marine fuel

Marine fuels and emissions in context

Currently, the world's commercial fleet mainly uses fossil fuels. The choice of fuel has been based on availability, energy density, and economic considerations.

Today, however, the maritime transport industry is under mounting pressure to improve its environmental performance and reduce its emissions from fuel consumption. Sulphur oxides (SO_x), nitrogen oxides (NO_x) and particulate matter (PM) harm both the atmosphere and human health while carbon dioxide (CO_2) and other greenhouse gases (GHGs) contribute to climate change.

Since 2005, the International Maritime Organization (IMO), the United Nations body that controls and regulates many aspects of the global shipping industry, has addressed fuel combustion emissions to the atmosphere through the International Convention for the Prevention of Pollution from Ships (MARPOL), Annex VI. This is done under the auspices of its Marine Environmental Protection Committee (MEPC).

As part of this effort, the IMO has set targets to reduce SO_x, NO_x, and GHG emissions.

Local air pollutants

- SO_x emissions are fuel related. The latest stage of the sulphur emission rules (the 'global sulphur cap') was successfully implemented in 2020 and reduced the global fuel sulphur limit to 0.5%. More stringent emissions controls of 0.1% sulphur limits apply in designated Emission Control Areas (ECAs). Fuels exceeding the limits may only be used in combination with an approved exhaust gas cleaning system (EGCS). Ammonia does not contain any sulphur, so SO_x emissions will be eliminated.
- NO_x emissions are mainly engine technology related but will also depend on the nitrogen content of the fuel. These emissions are regulated under the NO_x Technical Code for marine engines. Engine manufacturers have made improvements to their engine designs to reduce NO_x emissions. Ammonia contains nitrogen and has combustion characteristics that would suggest higher NO_x levels compared with other alternative fuels.

- PM emissions are both fuel and engine technology related and though not individually addressed, PM emissions are improved by regulations on SO_x. The lack of carbon and sulphur in ammonia should eliminate soot and particle emissions from exhaust gases. Ammonia itself, however, is a precursor to PM2.5 (particulates that are two and a half microns or less in width).

Focus on climate change

The industry's attention has increasingly focussed on CO_2 and other GHGs including methane (CH_4), nitrous oxide (N_2O), and black carbon (soot, a subset of PM).

Shipping currently emits 3% of all greenhouse gases worldwide, the equivalent of the contribution of the 5th largest producer country Japan or of Germany (6th) and France (19th) combined. About 80% of these maritime emissions come from deep sea shipping.

The IMO's objective is to reduce the industry's total annual GHG emissions by at least 50% by 2050 compared to 2008. But the target cannot be met without the introduction of alternative zero-carbon fuels and carbon-neutral fuels produced from sustainable sources.

CO_2 emissions are proportional to both the quantity and type of fuel used. Technical and operational measures to reduce carbon intensity of ships have been adopted by the IMO. The most recent is the Carbon Intensity Indicator (CII) which came into force in January 2023.

Emissions may be reduced in two ways:

- first, by improving the vessel's fuel efficiency and thus reducing its fuel consumption; and
- second, by introducing low- and zero-emission fuels. All emissions across a fuel's whole lifecycle must be considered for any reductions to be worthwhile.

The IMO is under pressure to set even more challenging reduction targets than those mentioned above. A review of the 2018 Initial IMO Strategy on the reduction of GHG emissions from ships is planned for 2023.

The maritime fuel landscape

Shipowners can today choose from three types of conventional oil fuels: heavy sulphur fuel oil (HSFO), very low sulphur fuel oil (VLSFO) and marine gas oil (MGO).

Shipowners can also opt for lower-carbon options such as liquefied natural gas (LNG), or to use biofuel blends in their engines to reduce GHG emissions. In addition, ethane and liquefied petroleum gas (LPG) are available, but in practice are only used on ethane and LPG carriers.

A variety of alternative fuels including 'oil-like' blended biofuels such as hydrogenated vegetable oils (HVO) and fatty acid methyl esters (FAME), are also being considered, along with sustainably produced methane, methanol, ammonia, and hydrogen.

Blends of biomethane and fossil LNG have been used on IGF vessels (vessels to which the International Code of Safety for Ships Using Gases or Other Low-flashpoint Fuels (IGF Code) applies), and methanol has been successfully introduced on methanol carriers and (so far) one ferry. January 2022 saw the delivery of the first ammonia-fuel ready container vessel and hydrogen has been used on various small boats since 2000.

The use of combustion enhancing agents (fuel additives), aftertreatment equipment, and onboard carbon capture and storage (CCS) are also being investigated with a view to further reducing ship SO_x, NO_x, PM and GHG emissions.

It is important to consider and evaluate all alternatives as there will likely be a fuel mix in the future, and every option has its pros and cons. Stakeholders must compare each fuel like-for-like and account for multiple factors including vessel type, fuel characteristics, safety, regulation, environmental footprint, technological maturity, availability, and cost.

Introduction

Like LNG, ammonia is a liquefied gaseous fuel. It is a carbon-free molecule so emits no CO_2 during combustion, and the absence of carbon and sulphur compounds in ammonia should prevent the formation of soot and SO_x. It has therefore been proposed as a cleaner fuel for industry including its use in power generation and in shipping, provided NO_x and N_2O emissions from fuel combustion are removed. Ammonia-powered engines are currently being designed, developed, and tested by manufacturers.

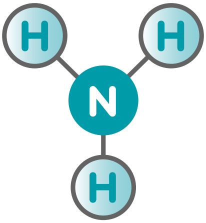
The widespread adoption of ammonia as a shipping fuel will depend on overcoming various regulatory, production and technical challenges, with its toxicity, availability, and upstream environmental performance being the main concerns.

The hazards surrounding ammonia's toxicity are well understood, and the industry's cumulative experience and knowledge will help establish safety and handling regulations for its bunkering and use as a fuel aboard vessels. IMO started the regulatory process for ammonia in 2022, and interim guidance would therefore be expected in 2023-2024.

Ammonia as it is currently produced (from fossil feedstocks without CCS) will not provide a GHG reduction benefit to shipping. But like other alternative fuels, ammonia can help achieve decarbonisation targets so long as its sustainable variants, such as ammonia made from renewable electricity, become commercially available and are utilised.

What is ammonia?

Ammonia (NH_3) is a chemical compound containing only nitrogen and hydrogen. Each nitrogen atom is bonded to three other hydrogen atoms making ammonia an effective hydrogen carrier: 10.7kg of hydrogen by mass would be found in 100 litres of liquid ammonia.



Ammonia is common in nature and an important source of nitrogen for plants and animals. For humans, it contributes significantly to efficient agricultural production as a precursor for nitrogen based fertiliser for 45% of the world's food crops. Ammonia is also widely used as an industrial refrigerant, in cleaning agents, and as a precursor in pharmaceutical products.

Fertliser (Source: Yara International ASA)

Ammonia cleaning product (Source: SGMF)

Ammonia is a harmful chemical – toxic to life including humans at low concentrations (its threshold limit value (TLV), i.e. the level a worker can be exposed to per shift without experiencing adverse effects over their working lifetime, is 25–50ppm), and due to its alkaline properties is highly corrosive, especially in the presence of moisture, to copper, zinc and tin.

Physical properties

At ambient temperatures, ammonia is a colourless gas with a strong irritating odour. The gas can be readily liquefied at moderate pressure and ambient temperature (e.g., about 7.5 bar(g) at 20°C), or when cooled down to approximately -33°C at atmospheric pressure.

Anhydrous ammonia (ammonia gas) has a high solubility in water which increases with decreasing temperature: 1 volume of water will dissolve approximately 500 or more volumes of ammonia gas. Ammonia's solubility in seawater may vary depending on temperature, pH, and salt concentration.
Ammonia dissolves in water to make ammonium hydroxide (NH3OH), also known as aqueous ammonia or ammonia solution, which is a 'base' in nature (i.e., an alkali, not an acid) and toxic to aquatic life and humans. This process releases significant amounts of heat (exothermic).

Ammonia's energy density is 22.5 MJ/kg and if heated sufficiently it can combust to release energy. It is less flammable than other fuels but, once ignited, will burn readily in air within concentrations between 15% and 27%.

Liquefied ammonia has a low volumetric energy density:

- $NH_{3(liquid)}$: 12.7 megajoules per litre (MJ/Litre) on a lower heating value (LHV) basis

compared with other fuels, for example:

- MGO: 36.6 MJ/Litre on an LHV basis
- LNG: 20.8 MJ/Litre on an LHV basis
- Methanol: 15.8 MJ/Litre on an LHV basis

Its energy density on a volumetric basis is about half that of LNG and a third that of conventional oil fuels. This means for the same journey distance, the volume of ammonia fuel required will be at least three times the amount of MGO, and almost double that of LNG.

Only liquid and compressed hydrogen have lower volumetric energy density than ammonia.

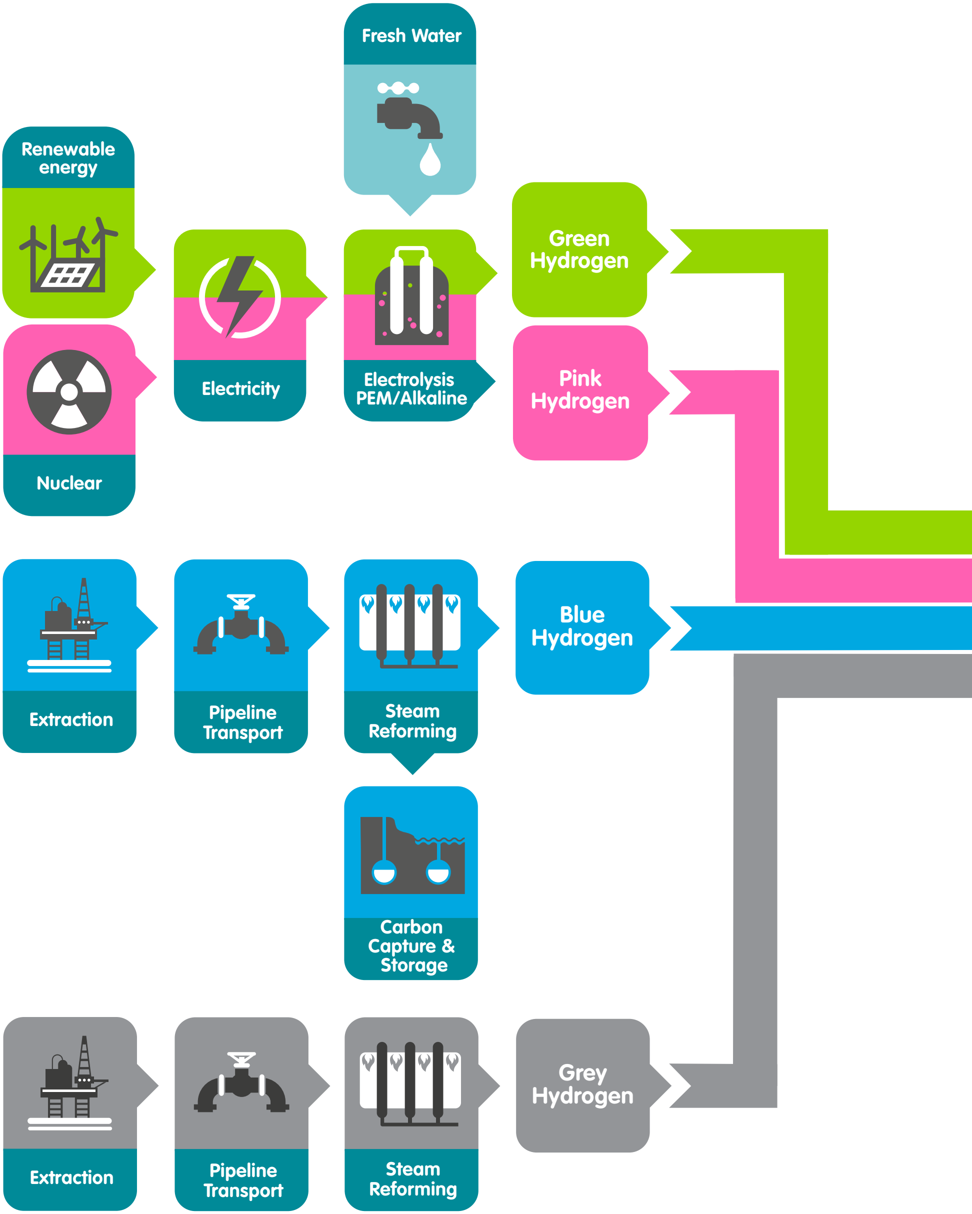
- $L_{(liquid)}H_2$: 8.5 MJ/Litre on an LHV basis
- $C_{(ompressed)}H_2$: 4.7 MJ/Litre at 690 bar and 25°C on an LHV basis

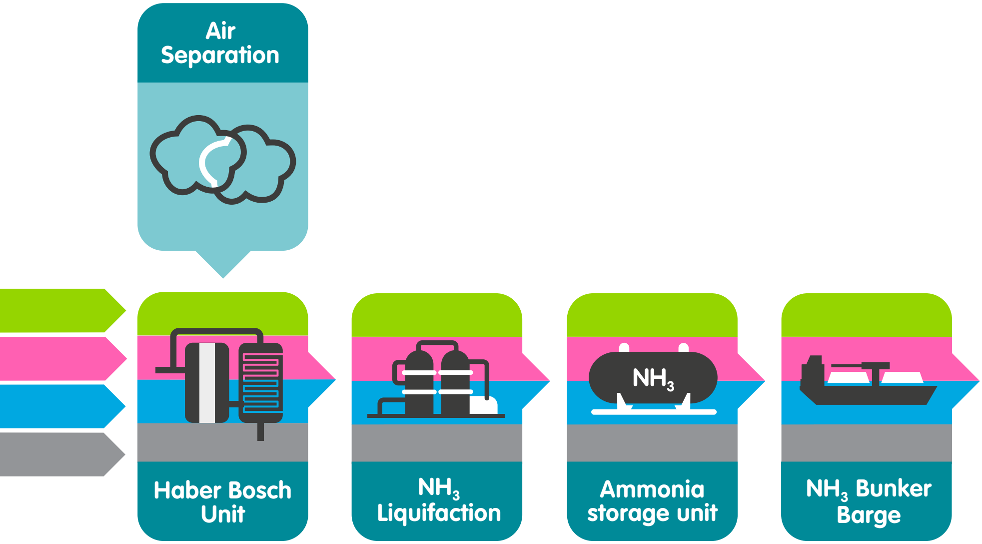
Ammonia is produced by heating nitrogen and hydrogen to ~500°C at pressures ranging between 200-400 bar over an iron catalyst. This is known as the Haber-Bosch process ($N_2 + 3H_2 \rightleftharpoons 2NH_3$).

Nitrogen is obtained by separating it from air (as air contains 78% nitrogen by volume), while hydrogen can be sourced from many different feedstocks and production routes with varying environmental emissions. These production routes are colour coded for ease of identification (see ammonia production illustration above).

Introduction

How ammonia is made and where it comes from





Production pathways of ammonia

Illustrative only. Arrow widths are not proportional to supply.

Introduction

Brunsbüttel ammonia plant and storage facility (Source: Yara Clean Ammonia)

Roughly 40% of global hydrogen production is used in the Haber-Bosch process for producing ammonia.

Just over 70% of ammonia production uses grey hydrogen generated from steam methane reforming (SMR) of natural gas (and oil) and is referred to as ‘grey ammonia’. Most of the remainder is produced using hydrogen from coal feedstocks (‘black’/‘brown’ ammonia). Conventional ammonia production is emission intensive. Its direct emissions amount to approximately 450 Mt (million tonnes) CO_2 per annum, the equivalent of the total energy system emissions from South Africa.

The main constituent of natural gas is methane. The SMR process heats methane with steam to produce syngas, a mixture of carbon monoxide (CO) and hydrogen. A further reaction between carbon monoxide and excess water, known as the water-gas shift, produces carbon dioxide and more hydrogen.

Steam methane reforming hydrogen production site in Port-Jérôme
(Source: Air Liquide)

The main CO_2 emissions from SMR come from:

1. the process in which the natural gas is converted into carbon dioxide and hydrogen. These emissions can be separated and used for other purposes (e.g. to make urea).
2. the combustion of a fuel, often natural gas, to achieve the high temperature and pressure required for reforming. These emissions are more difficult to separate, due to low concentrations in the flue gas, and are often released into the atmosphere.

'Blue ammonia' is ammonia made from hydrogen produced through either SMR of natural gas or coal gasification but utilising CCS to reduce emissions.

Hydrogen can also be produced using electrolysis – a process which uses electricity to split pure water into hydrogen and oxygen. This electrochemical process is carbon free and releases no carbon dioxide ($2H_2O + \textit{electricity} \rightarrow 2H_2 + O_2$).

Introduction

Green hydrogen is produced via electrolysis powered by 100% renewable electricity (wind, solar, geothermal, hydro, etc). If grid electricity is used, it is called yellow hydrogen, or if the electricity is derived from nuclear power, pink hydrogen. Less than 1% of current global hydrogen production is produced using electrolysis and the power for that electrolysis is predominantly non-renewable.

To produce truly green ammonia, the hydrogen must be green hydrogen and the energy required for air separation and the Haber-Bosch process must also be from renewable sources.

HyLYZER - electrolyser system (Source: Air Liquide)

Ammonia industry overview

Ammonia has been produced safely in bulk for over 100 years and has been shipped in bulk for over 60 years. It is now one of the most produced inorganic chemicals worldwide and there is established infrastructure for its storage and global transportation. Today, about 80% of the ammonia produced is used in agriculture as fertiliser, and the remainder is used for industrial applications.

Approximately 185 MT of ammonia was produced in 2021, with 44 MT being merchant capacity (i.e., ammonia that can be exported as such from a production site, instead of being consumed on-site to produce fertilisers and industrial chemicals). Of this merchant capacity, 44% was globally traded via ships, barges, pipelines, railways, and road tankers. Terminals and storage facilities for the safe handling and storage of ammonia exists in over 100 ports worldwide.

The largest ammonia producer is China (29% of global production in 2019) followed by Russia, the US, the Middle East, the European Union, and India (8-10% each). In 2020, Russia was the largest exporter at 4.22 MT or 23% of global exports, this volume decreased to about 3.5 MT in 2022. Trinidad & Tobago rank second at 4 MT. The other major exporters include Saudi Arabia, Indonesia, and Canada. In terms of imports, the largest demand can be found in India (14%), US, Morocco (10%) and South Korea (7%) (2020 data).

The availability of low cost renewable energy will be a major determinant of where green hydrogen, and hence green ammonia, will be produced. It is likely, therefore, that new production and bunkering infrastructure will be built in places with abundant renewable energy resources such as Australia, Europe, parts of south America, Africa, and the Middle East. Norway has historically produced green ammonia on a small scale since 1927 in hydro-powered production facilities, but production stopped in 1993 as the price was no longer competitive with grey ammonia.

Introduction

Refrigerated ammonia storage tank (Tank 3201 - left) with 10,000 cmb capacity at Vopak's Banyan Terminal on Jurong Island, Singapore (Source: Vopak)

Ammonia truck (Source: Yara Clean Ammonia)

How ammonia is transported at sea as a cargo

Since ammonia liquefies at approximately -33°C at atmospheric pressure, it may be easily transported in bulk on vessels that are designed to carry liquefied gases, either fully refrigerated or in pressurised storage conditions. Most ammonia is shipped in the fully refrigerated state in mid-sized vessels (approximately 20,000-50,000m^3) but larger vessels may also be used. However, a significant number of vessels also trade ammonia at ambient temperature in pressurised tanks.

Ammonia has a higher density than the other hydrocarbon gases that may be carried (680 kg/m^3 compared to propane and butane 583-600 kg/m^3) so tank structures have to be designed accordingly. Most vessels that carry ammonia are equipped with tanks constructed of steel alloys suitable for the cargo temperature and have equipment and fittings adapted to provide the necessary corrosion protection.

Containerised pressure vessels may also be used for carriage of ammonia in quantities limited by the International Organization for Standardization (ISO) tank containers, if they meet the International Maritime Dangerous Goods (IMDG) Code criteria.

A fully refrigerated LPG / ammonia carrier vessel - The 'Gaz Millennium'
(Source: Capt. Jad Ghamraoui, Naftomar)

Ammonia demand and availability

Demand for ammonia in existing markets is expected to grow as the global population rises. New applications, including ammonia as a marine fuel, for power generation, and as a hydrogen carrier, are expected to further increase global demand. Shipping has historically used low value fuel grades that few other industries want, but in future will have to compete with these other fuel sectors.

Ammonia production will need to be significantly scaled to meet future demand and will require substantial onshore capital investment (most investment into ammonia as a marine fuel will be land-based rather than related to vessels).

In 2022, 680 large-scale hydrogen project proposals were proposed, equivalent to USD240 billion in direct investment through 2030. Up until now, approximately 10% of those proposals have reached their final investment decision to proceed to construction.

In the *Innovation Outlook on Renewable Ammonia (2022)* produced by the International Renewable Energy Agency (IRENA) and Ammonia Energy Association (AEA), it is estimated that by 2050 the global demand for ammonia will be 688 Mt per year – 197 Mt of which is expected to be consumed by the shipping industry. This compares to the current annual production of about 185 Mt of ammonia worldwide.

As previously described, only sustainable versions of ammonia (green or blue) will be effective in improving maritime environmental performance.

So far, blue ammonia projects amounting to 16 Mt/yr capacity have been announced, though their level of certainty remains unclear. Green ammonia projects with start-up dates within the next decade amount to approximately 34 Mt/yr capacity. Additional green ammonia projects in the pipeline could increase this capacity to almost 100 Mt/yr beyond 2030.

Alternative fuels will initially cost more than conventional fuels. Renewable energy costs, especially for wind and solar, have fallen as it has become more widely available, but the rate of renewable expansion is not yet where it needs to be to keep up with growing demand. Electrolyser technologies on the other hand are still undergoing rapid development and are yet to be deployed on a large scale, at which point costs will reduce because of economies of scale, improvements in electrolyser efficiencies, and government policies and subsidies. In the longer term, green fuel costs have the potential to reduce considerably and be competitive with, or have economic benefits compared to, conventional production methods.

Ammonia regulation

Although common in nature, ammonia is both caustic and hazardous. Onshore, it is classified as an extremely hazardous substance in the USA and is subject to strict reporting requirements by facilities which produce, store, or use it in significant quantities.

The EU has a different approach whereby anhydrous ammonia is included in the major accident (Seveso III) directive at volumes greater than 50 tonnes (the same limit as many other liquefied gases such as LNG and LPG).

Bulk transportation of ammonia by sea is covered by the International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk (IGC Code) with specific requirements incorporated because of ammonia's toxicity, including special requirements for materials, tank gauging systems and personal protective equipment (PPE). For example, the IGC Code forbids direct contact between ammonia and mercury and copper-bearing alloys because of the risk of chemical reaction as well as corrosion, and requires that all liquefied gas cargo must be forward of the ship's accommodation. Currently the use of ammonia as fuel for gas carriers is prohibited under the IGC Code.

The IGF Code does not yet include ammonia, but work started in 2022 at IMO to develop the necessary provisions.

The Standards of Training, Certification & Watchkeeping for Seafarers (STCW) Code will need to be developed alongside IGF to provide additional rules for training.

Classification society rules exist for the use of ammonia as a refrigerant on board (e.g., on fishing ships). These define requirements for maximum leakage limits at parts per million (ppm) levels within certain areas. There is also extensive onshore geography-specific regulation which addresses these and many other issues which could be used to accelerate regulatory development.

Environmental

All fuels available today, except biofuels, are either fossil fuels or produced from fossil sources and contribute to global warming and the degradation of local air quality. To reach GHG emission reduction targets and comply with NO_x, SO_x and PM regulation requirements, the use of these fuels will need to incorporate CCS, and/or onboard aftertreatment of exhaust gas. Otherwise, they need to be replaced by alternatives with lower lifetime emissions.

Fuel Life Cycle Assessments (LCAs) are a fundamental tool for comparing the GHG emissions and overall environmental performance of fuel types and their production pathways. It is vital for shipping to adopt well-to-wake LCA methodologies when considering future fuels.

The most promising alternatives for most current fuels may be produced from bio sources and/or from sustainable electricity feedstocks ('e-fuels'). Blue production pathways for hydrogen-based fuels may also provide low life cycle emissions. Other alternatives include nuclear power, batteries, and wind propulsion.

The range of e-fuels includes green hydrogen (e-hydrogen) and any of its derivatives. These are zero- or low-carbon fuels with low emissions production pathways. In general, the production of e-fuels is energy inefficient and requires high levels of renewable energy availability. Candidate e-fuels are, for example, liquefied synthetic methane (LSM), e-methanol and e-ammonia (green ammonia).

Life Cycle GHG emissions Analysis

A life cycle GHG emission analysis determines a fuel's GHG emissions across its entire lifetime (well-to-wake) by calculating both upstream (well-to-tank) and on board (tank-to-wake) emissions (see Life Cycle Emissions Analysis illustration). GHG emissions are then expressed on a CO_2 equivalence basis to allow easy comparisons between different fuel types.

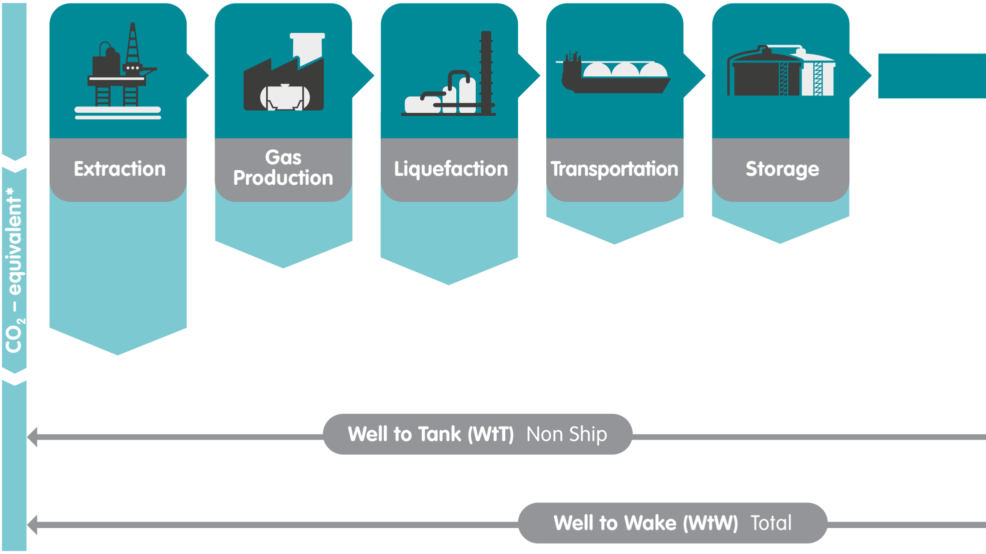
A full scope life cycle assessment will also assess other environmental criteria such as impacts on air, soil, and water pollution but also indicators on resource consumption and use.

Comparing fuels on a tank-to-wake only basis will yield different and often misleading results in contrast to a life cycle analysis of the same fuels on a well-to-wake basis. Even if the fuel itself is carbon-free, it is likely that GHG emissions will occur at some point in its supply chain.

Calculating the environmental performance of a fuel is complicated. Well-to-wake GHG emissions will depend on the type of feedstock and processes used in its production as well as on the emissions released during its distribution, storage, transformation/refining, and bunkering. Tank-to-wake emissions will mainly depend on the characteristics of the fuel and engine type. Currently there are no industry standards for conducting LCAs on marine fuels, though the IMO is in the process of developing maritime LCA guidelines. This process should be completed in 2023.

Life cycle analysis of GHG emissions may, in future, be used for determining carbon taxes, carbon levies or similar market-based measures once these have been introduced.

Environmental



Life Cycle Emissions Analysis - key stages for a liquefied gaseous marine fuel

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*The size of the GHG emissions (CO_2 equivalent) emitted at each of the stages in the delivery chain is for illustrative purposes only and will vary in scale on a project-by-project basis.

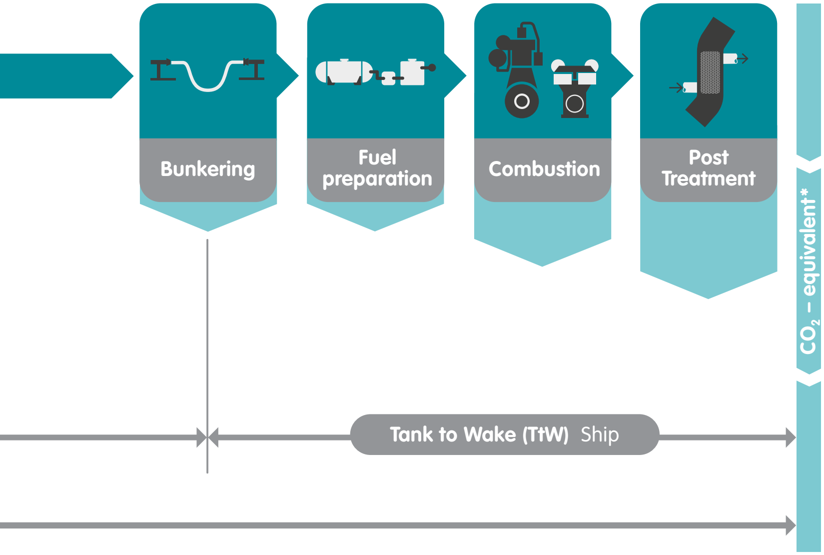
Ammonia's environmental performance

Life cycle GHG emissions analysis of ammonia

Well-to-tank

Grey ammonia production is responsible for approximately 1% of global CO_2 emissions. Several studies have been published on the well-to-tank performance of ammonia. The results vary considerably, but they all indicate that grey ammonia has higher well-to-tank GHG emissions than oil-based marine fuels and LNG.

Commercial production of blue and green ammonia has not started yet, so LCAs of these variants are based on assumptions and estimations whose accuracy cannot yet be confirmed. It is however understood that e-ammonia has a significantly reduced GHG production footprint than grey ammonia and fossil fuels since it utilises non-fossil feedstocks and renewable energy in its synthesis.



In the case of e-fuels, scientists are now warning of the indirect effects of hydrogen leakage from infrastructure on climate change and global warming. Hydrogen reacts with hydroxyl radicals (OH^-) in the upper atmosphere. The reduced concentration of OH^- lengthens the lifetime of methane (a strong GHG) and interferes with the formation of ozone.

Ammonia is not a GHG, but it plays a role in the formation of particulate matter (PM2.5) when it reacts with other air pollutants in the atmosphere. PM2.5 causes respiratory health problems and adversely effects the climate.

Upstream emissions of ammonia and hydrogen will enter the atmosphere from fugitive leaks in the supply chain. The magnitude and overall effects of hydrogen and ammonia leaks from equipment, storage tanks, and pipework remain uncertain.

Tank-to-wake

Ships using ammonia as a marine fuel should have almost zero CO_2 tank-to-wake emissions regardless of the ammonia production process because the molecule contains no carbon atoms. However, due to its low flammability compared to other fuels, ammonia requires a higher fraction of pilot fuel to initiate combustion. Initially, this pilot may be a fossil-based fuel, like diesel or MGO, but hydrogen or biofuel may be used in future. If pilot fuels are fossil based, the CO_2 reduction benefit will be reduced.

Theoretically, ammonia burns to produce only nitrogen and water ($4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$). In reality, like all other fuels, the high temperature of combustion also generates by-products of nitrogen in the air, NO_x and N_2O.

- NO_x is a toxic air pollutant and a precursor to smog.
- N_2O is a potent GHG with a global warming potential (GWP) 273 times that of CO_2 over 100 years.

Impacts of key GHGs are shown in Table 1.

Table 1: Global warming potential (GWP) of key GHGs and ammonia

Name	Formula	20-year GWP	100-year GWP
Carbon dioxide	CO_2	1	1
Methane	CH_4	81.2	27.9
Nitrous oxide	N_2O	273	273
Hydrogen	H_2	33	11
Ammonia	NH_3	0	0

Note: Global warming potential taken from IPCC AR6 and for hydrogen from Warwick et al "Atmospheric implications of increased Hydrogen Use", 2022 report for the UK Government

Ammonia marine engines are currently being developed and have not yet reached commercial maturity, so emissions data is limited to early test bed results which are unlikely to represent later commercial practice.

Ammonia slip, NO_x, and N_2O emissions will be technology dependent and subject to variation according to engine type. The combustion by-products of both NO_x and N_2O will need to be removed by post combustion treatment.

Typically, this will require engines to be fitted with selective catalytic reduction (SCR) equipment. Some vessels, particularly LNG Floating Storage and Regasification Units (FSRU), already have SCR in operation. This technology also converts ammonia fuel slip into nitrogen and water.

Well-to-wake

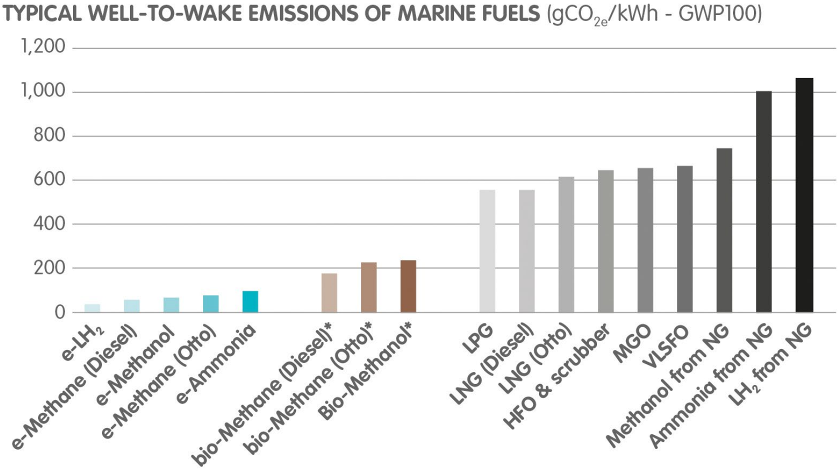
Available information today shows that operating an ammonia-fuelled engine on grey ammonia will result in higher overall well-to-wake GHG emissions than burning conventional fossil fuels. In addition, emissions from grey ammonia could be up to 66% worse than those from LNG across its lifetime.

For an example, see Figure 1 below; Bureau Veritas, in their recent white paper 'Alternative Fuels Outlook for Shipping' (2022), provide an overview of different alternative fuels and their WtW emissions.

From an environmental perspective, therefore, it does not make sense to burn grey ammonia (or grey methanol or grey hydrogen). The exception perhaps is for its very limited use in pilot projects and demonstrations to test the technical feasibility of later, cleaner ammonia.

E-ammonia on the other hand produces lower well-to-wake emissions than conventional fuels, LNG and advanced biofuels, and is a promising fuel for maritime.

Environmental



***Advanced biofuels** Source: Bureau Veritas

Figure 1: Typical Well-to-Wake emissions of marine fuels (gCO2e / kWh – GWP 100) (Source: Bureau Veritas)

In 2021, SGMF commissioned Sphera to carry out the *2nd Life Cycle GHG Emissions Study on the Use of LNG as a Marine Fuel.* SGMF has commissioned Sphera to carry out a further study, the *1st Life Cycle GHG Emission Study on the Use of* ***NH_3*** *as a Marine Fuel, in 2023.*

Safety

The fact that ammonia is toxic to humans introduces a new hazard compared to all other alternative fuels except methanol, so existing safety management philosophies must be adjusted. The main focus remains on preventing the ammonia fuel from escaping from pipes or equipment. This can be achieved by methods very similar to those already in use in today's fleet. Effective procedures will have to be developed to deal with any ammonia leakage. These include, for example:

- safety design and engineering for minimising the probability of leakage
- ensuring safe evacuation routes
- detection and mitigation measures
- safety/emergency procedures for minimising the impact of any leakage

Ammonia is also toxic to aquatic life and because of its high solubility in water can damage the marine ecology if large quantities are spilled.

One important benefit of ammonia physical properties is its very low smell threshold. Ammonia can be smelled at concentrations far below hazardous levels. This warning effect in the early phase of a leak incident is, most of the time, an effective barrier to prevent further exposure.

Is ammonia safe?

Over the last 100 years' experience of ammonia, operators have developed safety protocols to ensure its safe handling and use including:

- adopting inherently safe design solutions
- developing dedicated safety procedures
- training programs to ensure that staff handling ammonia are competent

Throughout the worldwide use of the product and its variety of uses, the level of safety has proved to be high. Many food processing plants with large ammonia refrigerant inventories operate close to, or actually in, residential areas, under strict regulation. Similarly, ammonia is the refrigerant of choice for ice skating rinks enjoyed directly by the public.

Safety

Learning from experience

Most loss of containment accidents involving ammonia occur during the operation and maintenance of refrigerant systems or during ammonia bulk transport, especially by road tanker where external impact and potential public exposure likelihoods are significantly higher. An aggravating factor is the pressurised liquid state in which ammonia is handled in these instances. At sea, on the other hand, a significant proportion of the trade involves refrigerated ammonia carried at ambient pressure. The sector has a good track safety record, with very few incidents recorded.

The long experience of ammonia in industry and its high degree of technical maturity makes it very unlikely that an unknown degradation mechanism remains unidentified today. Leaks or equipment failure are therefore normally the result of either error in the design/construction processes, wrong or poor maintenance programme/practices or a departure from safe operating envelopes. High consequence accidents with ammonia therefore remain rare and the lessons learned from them demonstrate that they could all have been prevented by adequate safety management systems.

Risk management

A hierarchy of hazard controls (Figure 2) is used by the industry to minimise or eliminate exposure to hazards, and can be defined to show the effectiveness of risk management and risk assessment measures.

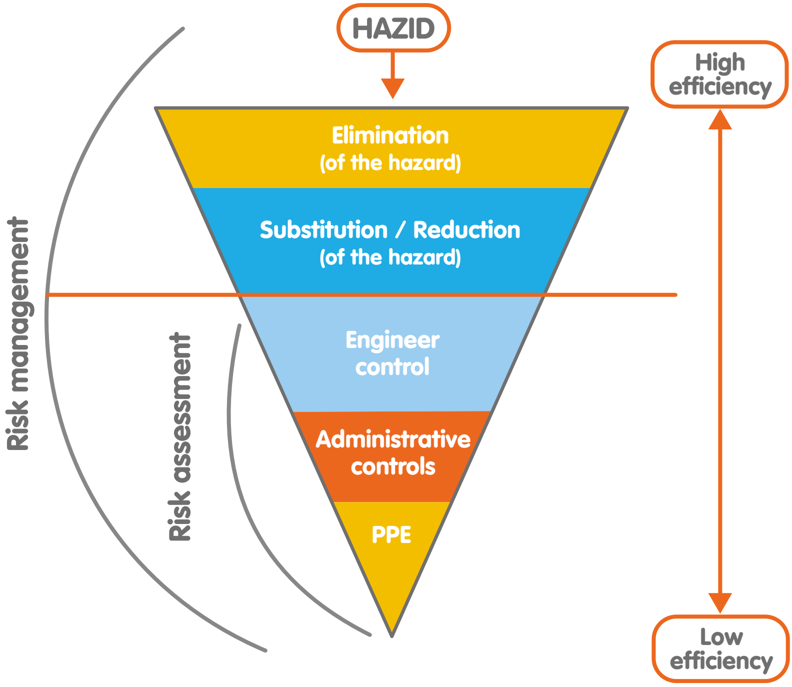


Figure 2: Hierarchy of hazard controls (Source: Yara)

The identification and use of effective controls, such as those shown below, should result in safer ammonia fuel handling:

Hazard isolation: Ammonia storage and associated equipment should, as far as possible, be kept away from potential external impacts. For example, tank location requirements in the IGF Code for LNG (and expected for ammonia) reduce the likelihood of a significant leak that affects individuals outside of the ship and/or the port. Secondary confinement such as a pipe-in-pipe/double wall systems and separation by specific safety zones are very efficient in mitigating many potential consequences of leaks.

Hazard reduction: Risk can be reduced by altering storage conditions to change the consequence and/or likelihood of a loss of containment. Liquid ammonia stored and handled in its fully refrigerated form is inherently safer than pressurised ammonia, as the initial flash occurring on the liquid phase release is significantly decreased, reducing the initial size and dispersion of the toxic cloud during a loss of containment event. However, pressurised ammonia has the advantage that its more robust systems required for the elevated pressure are less prone to damage, and generally less equipment is required reducing potential leak sources.

Engineering controls: Integrating safety features as early as possible in the design stages is the most effective approach to managing safety, where a good balance between cost and safety level can be achieved. The long experience gained from ammonia handling means that a wide variety of safety solutions are available to select from.

The following non-exhaustive list provides examples:

1. Linked ship-shore shutdown systems are considered essential so that fuel transfer can be stopped quickly in the event of problems developing.
2. Construction material selection to prevent well-known degradation mechanisms capable of initiating material failures (for example, stress corrosion cracking (SCC), corrosion under insulation (CUI) and other issues mentioned in the IGC Code).
3. Auxiliary equipment/systems to handle **expected** process releases, such as pressure and temperature relief valves (PSVs/PRVs, TRVs) and the inerting/purging associated with maintenance and start-up/shutdown operations. Proper design should integrate these expected process releases so that no ammonia emission occurs during normal operations or maintenance.
4. Auxiliary equipment/systems to handle **unexpected** process loss of containment (leaks and spills). A specific focus must be applied to early leak detection and automatic isolation to limit the released quantity. Other features such as drip trays and water mist systems, etc. can effectively impact the gas cloud size and dispersion, significantly reducing the area exposed to hazardous concentration levels.
5. As the vast majority of accidents are caused by human error, human factors must be taken into account in the design phases, and barriers such as automated sequences and interlocks or permissives must be considered.

6. Organisational measures such as a comprehensive set of procedures must be drawn up to cover normal, abnormal and emergency conditions. In port, emergency response plans will need to be developed jointly with terminals and bunker suppliers. Training and competency in conjunction with proper PPE selection according to potential exposure type is essential to ensure the safety of immediate users/responders.

It is important to note that, as with all risk management strategies, safety culture maturity is driven by high class safety leadership. Commitment from management is paramount to ensure that all the above protection layers are available and operate efficiently.

Accidental leakage handling

The toxic nature of ammonia makes its leak handling philosophy very different from all the alternative fuels. When a flammable leak of those fuels occurs, the concerns are about the likelihood of a fire or explosion which can be mitigated by ignition control, about preventing the accumulation of flammable substances through design, and about removing the flammable substances through depressurisation or dilution. Any ignited release can be mitigated by fire protection and this is where it differs from ammonia. During an ammonia leak, because of its toxicity, the dilution effect can increase the gas cloud dispersion and its harmful effect may be extended.

In addition to automated emergency and process shutdown systems, specific approaches and tools have been developed in the fertiliser industry onshore, and on ammonia carriers, to prepare and train first responders in controlling ammonia leaks and so reduce gas dispersion. These approaches and tools could be transferred to ammonia as a marine fuel.

The safe use of ammonia as marine fuel requires the following considerations for its use in confined spaces, such as in engine/fuel preparation rooms:

- locations of vents and exhausts
- ammonia detectors and ventilation of confined spaces
- emergency shutdown for the ammonia fuel system
- air locks to prevent escape of potential ammonia leaks

- water fog system for suppression of ammonia releases
- emergency escape breathing apparatus
- additional PPE, eyewash and safety showers
- toxic emergency response, training and competency

Fire and explosion prevention

Although ammonia is classed as a non-flammable material in maritime regulation (IGC Code), this is only correct in open air scenarios. Compared with methane, ammonia has a significantly lower, but definite, fire and explosion risk. Nevertheless, ammonia explosions have occurred, but only in confined spaces, when high leak rates cause a minimum of 16% in air to be reached.

In the open air, the vapour phase of an atmospheric boiling liquid pool is almost impossible to ignite. To reach ignition, heat must be provided to the boiling liquid in order to artificially force the vaporisation rate and reach the lower flammable limit (LFL). If heat input is removed, the combustion stops by itself.

In addition to the relatively narrow flammability window, both the ignition temperature and minimum energy ignition are high. Data indicates that the ignition energy is about 1,000 times higher than for methane and approximately 10,000 times higher than for hydrogen. This means that the likelihood of an ammonia gas cloud ignition is low.

Finally, even if the gas cloud ignition does occur, ammonia burns very slowly. This leads to a phenomenon called a flash fire where the cloud burns back, relatively slowly in the case of ammonia, to the leak source, rather than causing an explosion. The damage that could be expected to be caused by the generated pressure wave is therefore limited. Like LNG, ammonia will only explode if a flash fire occurs in a confined space.

Toxicity, causticity and cold exposure

Human exposure limits to ammonia (Table 2) are defined by legislation and can vary slightly from country to country. They are typically a function of concentrations and exposure time.

Table 2: Typical examples of human exposure limits to ammonia

Vapour concentration (ppm)	General effect	Exposure period
25	Smell detectable by most people	Maximum 8 hours working period
100	Discomfort but no adverse effect for average worker	Deliberate exposure for long period not permitted
400	Immediate nose and throat irritation	No serious effect after 30 min to 1 hour
700	Immediate eye irritation	No serious effect after 30 min to 1 hour
1,700	Convulsive coughing, severe eye, nose, and throat irritation	Could be fatal after 30 min
2,000 to 5,000	Convulsive coughing, severe eye, nose, and throat irritation	Could be fatal after 15 min
5,000 to 10,000	Respiratory spasm and rapid asphyxia	Fatal within minutes
160,000	Lower flammable/explosive limit (LFL/LEL)	

There is a significant gap between the first concentration level, where ammonia can be detected by most people by smell, and the hazardous level. Injuries triggered by ammonia toxic hazards therefore only happen during large and sudden losses of containment. The exposure period is then the critical factor in injury severity. Escape or sheltering in place philosophies are critical to the emergency response planning.

In all ammonia exposure cases, whether vapour or liquid, it is extremely important to provide first aid by flushing with water, then, depending on the respiratory exposure period, to give oxygen to the victim.

Note that the concentration needed for a flammable cloud is 16 to 100 times larger than potentially fatal doses based on toxicity. The discomfort of working in areas with low amounts of ammonia, particularly in warm, humid areas, will strongly encourage individuals to leave the area before toxic effects become serious.

Experience also shows that long lasting or permanent injuries such as scarring are likely to occur if an individual in very close proximity to a leak source is exposed to either a liquid or aerosol spray. These result from third-degree burns caused by both the alkaline (caustic) properties of ammonia combined with the low temperatures associated with some types of leaks – where temperatures as low as -70°C are possible.

Safety distance and exclusion zone

For ammonia fuel handling, a succession of different safety envelopes will need to be defined – in a similar way to those adopted for LNG bunkering.

For an ammonia bunkering process, a highly restricted area or 'safety zone', must be defined in the close vicinity of any potential leak sources (mainly the manifold and tank connection area). In this zone only specially trained and equipped (for example, with specific PPE (see below)) operators can be accepted. Simultaneous operations (SIMOPs) including passing traffic are prohibited or under strict control.

Immediately outside this restricted area, a second safety envelope must be defined. Inside this layer, specific means to escape and/or shelter in place must be provided. Individuals entering/working in this envelope must receive dedicated training about emergency response plans and may be required to wear/have access to PPE. This envelope would be defined by port authorities either deterministically or through risk assessment which might include consequence modelling, computational fluid dynamics (CFD) assessments or other suitable techniques.

Finally, an outer zone, the 'assessment zone', will need to be defined to prepare and inform the public of the possibility of ammonia releases and the appropriate behaviour in case of exposure. Ammonia's distinctive smell will alert the public of a leak and may, if not supported by advice on what to do, cause panic, resulting in greater personal exposure and/or additional incidents, for example road accidents, as people attempt to escape a perceived hazard. Some ports may find it challenging to meet these separation distance guidelines and may need to look at bunkering at anchorages.

Personal protective equipment (PPE)

The level of PPE required depends on the expected exposure time to ammonia vapour and liquid that the role requires. Three levels are suggested:

1. Emergency responders who need to access contaminated areas to make the system safe, for example by closing valves which requires a long time, will need a gas-tight suit. This should cover the whole body, be impermeable to ammonia and provide some protection in cold environments. Self-contained breathing apparatus (SCBA) is also likely to be required.
2. For operators dealing with ammonia, for example connecting the bunkering system, a lighter chemical suit should be sufficient to guard against ammonia leaks and splashes. A full face mask with ammonia removal cartridge is likely to be sufficient for an operator to escape quickly, within seconds, to a safe area.
3. Other staff may need to carry cartridge type gas masks to allow them to escape to a place of safety/gas protection room should an ammonia leak occur.

Left: Persons wearing full chemical suits with external air supply whilst connecting an ammonia loading arm (Source: Yara International ASA)

Below Ammonia operators wearing full-face gas masks (Source: Industrial Refrigeration Technical College (IRTC))

Technical

What does an ammonia-fuelled ship look like?

Ship design

Gas carriers have been carrying anhydrous ammonia in bulk under the auspices of the IGC Code for many years. The challenges that ammonia presents are well known and can either be engineered out or suitable mitigations provided.

The current IGF Code (for LNG) will provide many of the main technical headings that ammonia-fuelled vessels will need to address. However, there are significant differences at a more detailed level, notably:

- Ammonia is more chemically aggressive but the metallurgy for ammonia systems is well understood and recorded in the IGC Code. Corrosion can be avoided by the use of appropriate steels, post weld heat treatment, and by using small quantities of water (minimum 0.2%) as a corrosion inhibitor. The presence of oxygen (hard to detect in liquid ammonia) is the main corrosion vector.
- Liquid ammonia may be carried under pressure at ambient temperatures or under refrigerated conditions. Liquefied ammonia is cold, not cryogenic.
- Ammonia carriers have pipelines which may not be fully welded but incorporate bolted flanges. However, contraction/expansion issues for bolted flanges are much less significant, as cryogenic temperatures are not a factor. However, it is essential to use the correct gaskets to prevent leakage.
- Different electrical protection systems are required (Ex or ATEX) and these are covered by International Electrotechnical Commission (IEC) guidance.
- The ventilation requirements of confined ship spaces also need attention to prevent exhaust gases containing ammonia from going untreated to atmosphere affecting the public/crew, or to safe refuges within the ship affecting the crew. The use of air locks is also recommended to isolate possible leak sources.

Fuel storage

Ammonia storage tank technology used on ammonia gas tankers is appropriate for use as fuel tanks on ammonia-fuelled vessels. For fully refrigerated ammonia at approximately atmospheric pressure, a variety of tanks are available (Types A, B and integral-membrane, as defined in the IGC Code) which need to be designed for -33°C temperatures. Pressurised systems use Type C tanks that can operate at pressures up to 17 bar(g) for worldwide service or at atmospheric pressure (i.e. with the ammonia at about -33°C) if the tank metal is suitable.

Ammonia fuel tank location will need careful consideration to avoid any leaks that could affect the accommodation. Classification and the design process should limit the need for people to be regularly present in areas where ammonia is stored, processed, piped and consumed. The design must also address the risk of ammonia leakage entering accommodation spaces.

Tanks must not contain oxygen prior to the introduction of liquid ammonia. Tanks can be gassed up using nitrogen (onshore practice) or hot, gaseous ammonia (on ammonia carriers).

Ship fuel systems

If a fully refrigerated storage system is selected, the ammonia-fuelled ship will need to manage its boil-off gas (BOG) by means of a reliquefaction system or through combustion in its engines, boilers and generators. The issue is reduced for pressurised storage in a Type C tank but may still occur.

Power generation and propulsion for ships

Using ammonia as a fuel in the marine industry will require the design and development of ammonia-specific engines and associated systems as currently no mature technology exists that can use ammonia as a marine fuel. Historically ammonia has been used as a motor transport fuel at much smaller scale.

Several internal combustion engine options are currently being developed and evaluated at test bed scale to produce a commercially available option.

Technical

As a marine fuel, ammonia is expected to be usable in Diesel and Otto cycle 2-stroke and 4-stroke engines. Because ammonia burns so poorly, ignition needs to be started by a pilot fuel. Ultimately this might be hydrogen, but at the present stage of development a marine oil, most likely MGO, will be used.

Fuel cells

About 17.5% of ammonia's mass is hydrogen, so if ammonia can be dissociated into hydrogen and nitrogen, the fuel would be ideal for fuel cells.

One type of fuel cell, the alkaline fuel cell, can use ammonia directly but its development is significantly behind some other fuel cell technologies.

Ammonia bunkering

Many of the issues with ammonia are expected to be similar to those for LNG bunkering. Human factor challenges are likely to dominate, so in general a similar set of procedures to LNG bunkering would be envisaged. However, there are important differences, as described below.

Bunkering hoses will be specifically designed for ammonia service. They are likely to be of lighter construction than those used for LNG because of the reduced change in temperature making them easier to handle. Some form of emergency release system would be required. Flanged connections are common (as for oil bunkering). A dry disconnect connect coupler (DD-CC) could be used.

Nitrogen is normally used for purging in onshore facilities. Nitrogen is used both to avoid flammability, and to prevent the introduction of oxygen into the ammonia system (to reduce as much corrosion as possible, particularly SCC). When nitrogen is used, it must be disposed of responsibly as it may contain ammonia vapour. Small volumes of nitrogen remaining in fully refrigerated ammonia systems can interfere with the operation of the reliquefaction plant. On ammonia tankers ammonia gas is normally used for purging. Nitrogen is only used if human access is required.

Onshore, ammonia hoses are drained by gravity into the storage tank or road tanker. This represents good practice. Transferring these types of procedures to maritime, as LNG has previously proven, is not straightforward. Movement of the hose caused by ship movement, icing and stresses imposed on connecting systems may all prevent such a drainage system. The hose can then be gas freed using nitrogen.

On ammonia tankers 'hot' ammonia gas (taken from the outlet of a compressor) is used to vaporise the liquid ammonia and the hose is not gas freed. The loss of ammonia vapour at atmospheric pressure, although minimal, may be sufficient for ports to be concerned about the **nuisance** level of the odour released and its perception by terminals and the public. This practice also contravenes the current requirements in the IGF Code (for LNG).

For **pressure testing** prior to transfer on bulk ammonia carriers (to which the IGC Code applies), 'hot' gas from the compressors is used because the piping systems are kept under ammonia vapour atmosphere. This hot gas is circulated via crossover pipework and recirculated to the cargo system (storage tank).

The IGF Code has taken a different approach for LNG, requiring nitrogen purging of lines. If this approach is continued for ammonia, the onshore ammonia industry practice of using compressed nitrogen for pressure testing prior to gassing up will be required.

Leak detection systems and mitigation philosophies must be considered early during the design process. When assessing a ship's safety requirements, a layered strategy should be considered to design the most comprehensive gas detection system. Ammonia sensor technology has substantially improved compared to just 20-30 years ago. Ammonia levels can be reliably detected down to 1ppm with some technologies. Ammonia emission measurement should rely on detectors and not the human nose which may desensitise over time. There is no single perfect solution, and different technologies are used for different applications such as piping, point leaks or entire rooms/spaces. So understanding the monitoring environment and the specific benefits and limitations of the sensors selected is paramount for optimal plant safety.

The high solubility of ammonia means that traditional techniques used to check for hydrocarbon gas leaks – for example, soapy water – will not work as an ammonia leak detection system even for small leaks. Portable gas detectors should be used where possible.

Bunkering rates will be determined by the vessel's ability to manage BOG. A fully refrigerated transfer would produce less BOG as flashing into the tank will normally be lower. The use of pressurised Type C tanks would reduce the impact of flashing. Additional equipment may be required for these scenarios. A vapour return system is normally required for the management of emergency conditions and may or may not be used in normal operations.

Returning some vent pipes to the fuel tank if the vent volume is small compared to the fuel tank volume, for example TRVs, may be possible. This, however, is currently prohibited by the LNG version of the IGF Code. The fuel tanks themselves are protected by PRVs for emergency venting directly to the vent mast.

Technology maturity

Because ammonia use has been common onshore for several decades and as it has also been transported in bulk at sea for many years, most handling technologies exist, but some may need to be adapted for more specific use in marine fuel systems.

The greatest technical uncertainty surrounds the combustion of ammonia in propulsion systems (which could result in emissions of NO_x, N_2O and possible ammonia slip). Ammonia has not been used in this application at this scale before, so the technology is having to be developed, based on experience with other fuels. Specific issues have been identified but these look solvable. Emissions from the nitric acid production process faced similar issues 15 years ago in terms of NO_x/N_2O emissions, and these were solved with dedicated technologies which should be adaptable to ammonia engine exhaust gas treatment.

Training and Competence

The level of seafarer training for ammonia handling is a major area for consideration. Experience with LNG bunkering suggests that it is the competence of the crew on the gas-fuelled vessel that is crucial to the success of the industry.

Although the physical behaviours of ammonia are similar to liquefied gases, ammonia is very different to LNG. The main concerns about LNG are its flammability and its cryogenic nature. In contrast, ammonia is relatively warm and hard to ignite but is toxic. Different training will be required and will need to be developed. Existing courses for ammonia carriers might be suitably adapted.

An extensive human factors framework needs to be developed. Most of this is available from existing bulk ammonia practice and procedures. Some ‘LNG-like’ bunkering behaviours may also be appropriate. There should not be a reliance on PPE but on the use of good safety practices, such as inherent safe design options taken during project development. A comprehensive process safety management (PSM) system should be considered and embedded in the ship’s safety management system (SMS) to support the continuous development of a mature safety culture. This will require training and competence development for all the parties involved (crews, managerial staff, ports/regulators and terminal personnel). SIMOPs are one area of concern as these are not common practice on ammonia carriers.

For LNG/LPG, training providers follow the IGF Code and STCW competence tables, and a similar approach will need to be developed for ammonia.

Summary

Ammonia is a marine fuel candidate for the following reasons:

- the molecule contains no carbon and can be produced with low GHG emissions
- it may be usable in an internal combustion engine
- it is a widely distributed chemical that can be carried in bulk at non-cryogenic temperatures

Its weaknesses are:

- its toxicity (though its hazards are well known and understood)
- its potentially higher NO_X and N_2O combustion emissions compared to other marine fuels
- its availability (from low emission production methods) compared to fossil marine fuels

Though the molecule contains no carbon, it is necessary to address and eliminate GHG emissions across ammonia's whole lifecycle if it is to play a significant role in decarbonising the shipping industry. LCAs are the best tools the maritime sector has for analysing and comparing environmental performance, but they require high quality emissions data of which there is currently little for ammonia as fuel. Nevertheless, available data shows that only green and blue production pathways will produce ammonia with a GHG reduction benefit. Commercial production of these variants, however, has not yet begun and will require significant investment into R&D and supply chain infrastructure.

Current regulation does not permit the use of ammonia as a marine fuel due to its toxicity. The IMO is currently evaluating how the IGF Code needs to change to allow ammonia as fuel, a process expected to complete in 2023/2024.

The toxic properties of ammonia require that appropriate design, operational and maintenance processes and procedures are adopted. This will involve changes to design practices and equipment which will not be consistent with the current IGF Code. It will also require enhancements to safety management, working practices and training needs.

The long experience gathered in the shipping and fertiliser industries where large volumes of ammonia are produced, stored, transferred, and transported, combined with its extensive usage as a refrigerant in more complex and confined installations, should be taken into account and guide ship and bunkering terminal designers in developing solutions that are suitable for ammonia's use as a marine fuel.

Port procedures will need development to define necessary rules and safety distances for bunkering. Any simultaneous operation of ships for cargo and bunkering requires thought and may require additional risk mitigation.

The speed of transition will be important to allow design and training activities to keep up and provide assurance that leaks/releases affecting the ship's crews, jetty staff, the public, the environment, and other stakeholders can be minimised.

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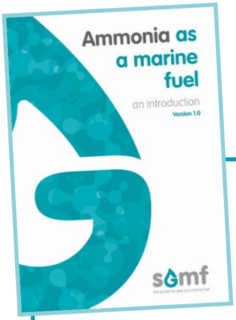

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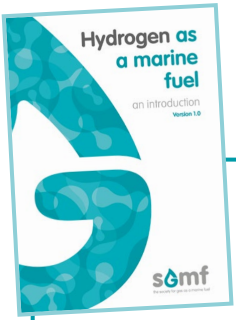

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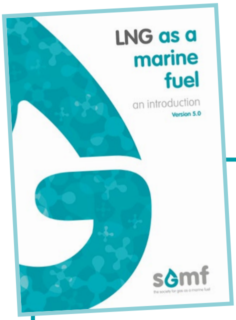

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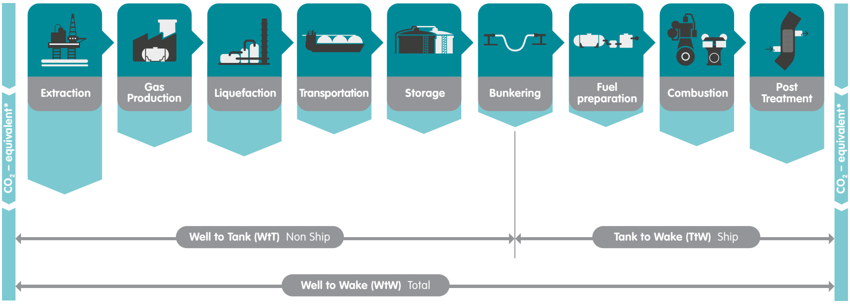

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