Managing Emissions from Ammonia-Fueled Vessels

An overview of regulatory drivers, emission types, sources, scenarios, reduction technologies, and solutions

Mærsk Mc-Kinney Møller Center
for Zero Carbon Shipping

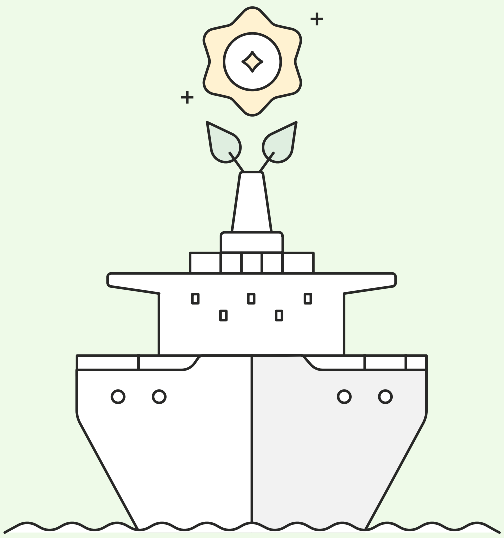
This paper is the third in the Onboard Vessel Solutions series:

Vessel Emission Reduction Technologies & Solutions

The paper series covers the impact and role of vessel greenhouse gas and air pollutant emission reduction in maturing alternative fuel pathways. Onboard impact is defined in terms of tank-to-wake global warming potential, with the role of onboard emission reduction either being for regulatory compliance or as an option to reduce emissions. Fuel pathway maturity is an assessment of solution readiness across the entire value chain.

Based on identified vessel emission risks, the paper series deep dives into specific emissions that need to be addressed to increase alternative fuel pathway maturity. The objective of these deep dives is to understand current or potential emission levels, set reduction targets, and identify and map applicable technologies and solutions. The emission reduction potential is then determined, and recommendations given to mature the selected fuel pathways. Finally, areas or concepts for further research and development are identified including recommended future project topics.

Papers are based on work completed as part of Center projects and working groups consisting of Center partners and external participants and contributors. Working groups provide a collaborative framework facilitated by the Center to jointly engage partners and external experts and companies on specific topics to deliver clear and impactful results.



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Abbreviations

Acronym	Definition
ASC	Ammonia slip catalyst
BOG	Boil-off gas
CCC	IMO's Sub-Committee on Carrage of Cargoes and Containers
Class	Classification society
CO_2	Carbon dioxide
CO_2eq	CO_2-equivalent
DF	Dual fuel
EGR	Exhaust gas recirculation
EU	European Union
GCU	Gas combustion unit
GE	Generator engine
GVU	Gas valve unit
GHG	Greenhouse gas
GWP	Global warming potential
HFO	Heavy fuel oil
ICE	Internal combustion engine
IGC Code	The International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk
IGF Code	The International Code of Safety for Ships using Gases or Other Low-Flashpoint Fuels
IMO	International Maritime Organization
LPG	Liquefied petroleum gas
LNG	Liquefied natural gas
LSFO	Low sulfur fuel oil
MDO	Marine diesel oil
ME	Main engine
MMMCZCS	Mærsk Mc-Kinney Møller Center for Zero Carbon Shipping
MSC	IMO Maritime Safety Committee
NH_3	Ammonia
N_2	Nitrogen
NO_x	Nitrogen oxides

Acronym	Definition
N_2O	Nitrous oxide
O_2	Oxygen
PRS	Plasma reduction system
PM	Particulate matter
PPM	Parts per million
SCR	Selective catalytic reduction
SOFC	Solid oxide fuel cell
SOLAS	International Convention for the Safety of Life at Sea
SO_x	Sulfur oxides
TTW	Tank-to-wake
VLSFO	Very low sulfur fuel oil
WTT	Well-to-tank
WTW	Well-to-wake

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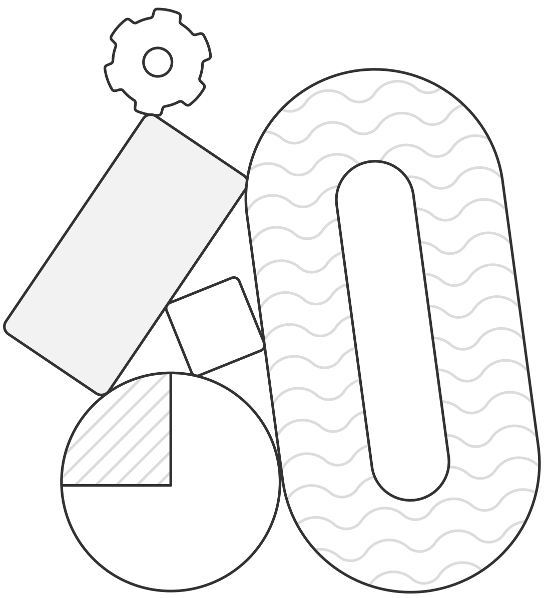


Executive Summary

The Mærsk Mc-Kinney Møller Center for Zero Carbon Shipping (MMMCZCS) has identified blue and electro-ammonia as potential low-emission alternative fuel pathways. The emissions profile for ammonia fuels is currently unknown, as ammonia engines are still under development. However, emissions from ammonia internal combustion engines (ICEs) may present safety, climate, and regulatory risks, necessitating onboard vessel emission management technologies and solutions.

While ammonia combustion presents emission risks that are not fully known today, a combination of emission management technologies are already available or under development. A dedicated MMMCZCS working group was established to study potential emission scenarios for ammonia ICEs and technologies that can reduce emissions to acceptable levels. The working group made the following conclusions:

– Ammonia combustion presents specific emissions risks related to safety, health, and climate:
  – Ammonia slip is highly toxic, presenting a safety risk for crew and passengers on board the vessel.
  – NO_X formed by incomplete ammonia combustion presents a health risk to local communities where vessels operate and must be managed to maintain regulatory compliance.
  – N_2O is a potent greenhouse gas (GHG) impacting the global climate (1 gram of N_2O is equivalent to 265 grams of CO_2).
  – Due to poor ammonia combustion characteristics, secondary or pilot fuel is required. If the pilot fuel is fossil based, it will result in CO_2 emissions.

– Onboard ammonia emission sources require a combination of emission management technologies: We defined three emissions scenarios based on potential emission profiles, and all scenarios required 3-4 different treatment technologies to achieve acceptable emissions levels. Emission management technologies are needed to treat ammonia boil-off gas (BOG) from fuel tanks, ammonia mixtures from purging and venting operations, and combustion emissions from the engine(s). While such combinations would enable significant emissions reduction, they would also increase the cost and complexity of vessel design compared with vessels operating on conventional fuels.

– Managing ammonia emissions is possible and management technology development timelines are expected to align with ammonia ICE development: Some emission management technologies are already commercially available for maritime use, including reliquefication and selective catalytic reduction (SCR). Others are based on existing maritime or shore-based concepts that need to be adapted for ammonia as a fuel, including engines, gas combustion units (GCU)/ boilers, catalysts, and water catchers/chemical absorbers.

– Industry-wide collaboration during engine and emission management technology development is needed to optimize ammonia-fueled vessel designs: All stakeholders, including engine manufacturers and emission management technology suppliers, must work together to develop ammonia-fueled vessel designs and optimize the use of materials, costs, and overall system efficacy. Without collaboration, specific parts of the vessel design will be developed in isolation, and interconnected systems and technologies could end up unnecessarily oversized, inefficient, or costly. Regulators should follow upcoming tests and technology development closely to ensure that practical, effective, and realistic targets and goals are set from the beginning.

– Acceptable ammonia emission levels are not yet clearly defined: Given the broad range of exposure limits in literature and the lack of knowledge on ammonia as a fuel for the maritime sector, there is a need to be conservative when defining guidelines as an additional safeguard. Thus, low limits are generally included in Classification Society (Class) guidelines, ahead of mandatory International Maritime Organization (IMO) instruments in response to the industry's interest in ammonia as a fuel. The operational ammonia limits defined in existing Class guidelines vary. Coordinated alignment on thresholds for adequate risk management is required to secure standardization and industry guidance.

Our analysis showed that, with industry-wide collaboration across ammonia engine development, emission management, and vessel design, emission risks will not be a showstopper for ammonia-based fuel pathways. However, well-to-tank (WTT) emissions from ammonia fuels still need to be better understood to assess the overall viability of ammonia-based alternative fuel pathways.

01 Introduction

A Mærsk Mc-Kinney Møller Center for Zero Carbon Shipping (MMMCZCS) assessment of vessel emissions from the main alternative fuel pathways[1] found that emissions of ammonia (NH_3) slip and nitrous oxide (N_2O) from ammonia internal combustion engines (ICEs) present both a safety risk and a potential increase in CO_2-equivalent (CO_2eq) emissions. N_2O is a potent greenhouse gas (GHG) that can be a byproduct of ammonia combustion, and ammonia slip is highly toxic. NO_x emissions must also be managed to maintain regulatory compliance using commercially available NO_x reduction technologies.

The impact of ammonia on human health and the environment is still being investigated[2] and has proven to be difficult to measure. As the science becomes clearer, learnings should be used in the development of regulations and ammonia-fueled ship designs.

The MMMCZCS assessment stated that the major challenges for ammonia are related to its currently unknown emission profile and the need to develop emission management technologies and solutions if the potential risks materialize. Knowledge of and experience with emissions from ammonia ICEs is limited as the engine technologies are still under development (see Figure 1).

Figure 1: Fuel Pathway Maturity Map (Source: MMMCZCS)

	Feedstock availability	Fuel production	Fuel storage, logistics & bunkering	Onboard energy storage & fuel conversion	Onboard safety & fuel management	Vessel emissions	Regulation & certification
e-ammonia	Mature	Solutions identified	Major challenges	Major challenges	Major challenges	Major challenges	Major challenges
Blue ammonia	Solutions identified	Solutions identified	Major challenges	Major challenges	Major challenges	Major challenges	Major challenges
e-methanol	Solutions identified	Solutions identified	Solutions identified	Mature	Mature	Mature	Solutions identified
Bio-methanol	Solutions identified	Solutions identified	Solutions identified	Mature	Mature	Mature	Solutions identified
e-methane	Solutions identified	Solutions identified	Mature	Mature	Mature	Solutions identified	Solutions identified
Bio-methane	Solutions identified	Solutions identified	Mature	Mature	Mature	Solutions identified	Solutions identified
e-diesel	Solutions identified	Solutions identified	Mature	Mature	Mature	Mature	Solutions identified
Bio-oils	Solutions identified	Major challenges	Solutions identified	Solutions identified	Mature	Solutions identified	Solutions identified

Mature
Solutions are available, none or marginal barriers identified

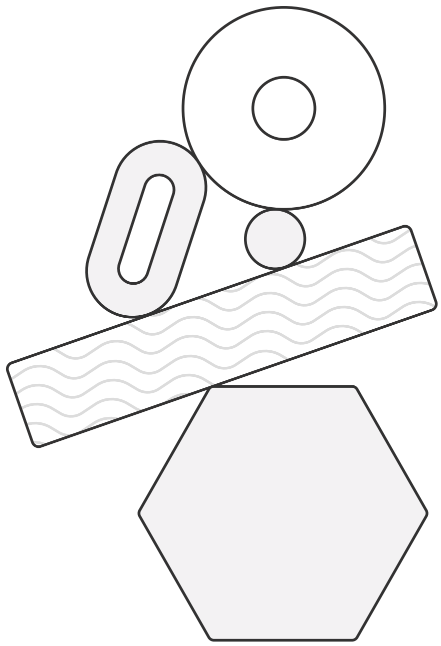
Solutions identified
Solutions exist, but some challenges on e.g., maturity and availability

Major challenges
Solutions are not developed or lack specification

1 Detailed in the first paper in the Vessel Emission Reduction Technologies & Solutions paper series titled "Determining the impact and role of onboard vessel emission reduction".
2 Zhu et al., 2015, "Sources and Impacts of Atmospheric NH_3: Current Understanding and Frontiers for Modeling, Measurements, and Remote Sensing in North America", Curr Pollution Rep (2015) 1:95–116.

The MMMCZCS established a dedicated working group to complete a deep dive into the emission risks from ammonia combustion and better understand the topic. This paper presents the results from the working group, including an overview of regulatory drivers, emission types, sources, scenarios and reduction technologies, and solutions. Due to limited publicly available information and references on ammonia-related emission management technologies, this paper leverages primary source data and expert knowledge from the working group members to provide today's best possible understanding.

Onboard vessel emissions are directly related to the main onboard energy storage and conversion technologies. ICEs are predominantly used on vessels today and will continue to play a role in the future. The work outlined in this report studied the emissions from ammonia dual-fueled (DF) ICEs, which are currently under development, with the first commercially available engine expected during 2024. Other energy converters, such as fuel cells, are available or under development and could play a larger role in the future. The emissions from fuel cells and reformers are important to understand and are being covered in a separate MMMCZCS working group.



02 Ammonia fuel pathways

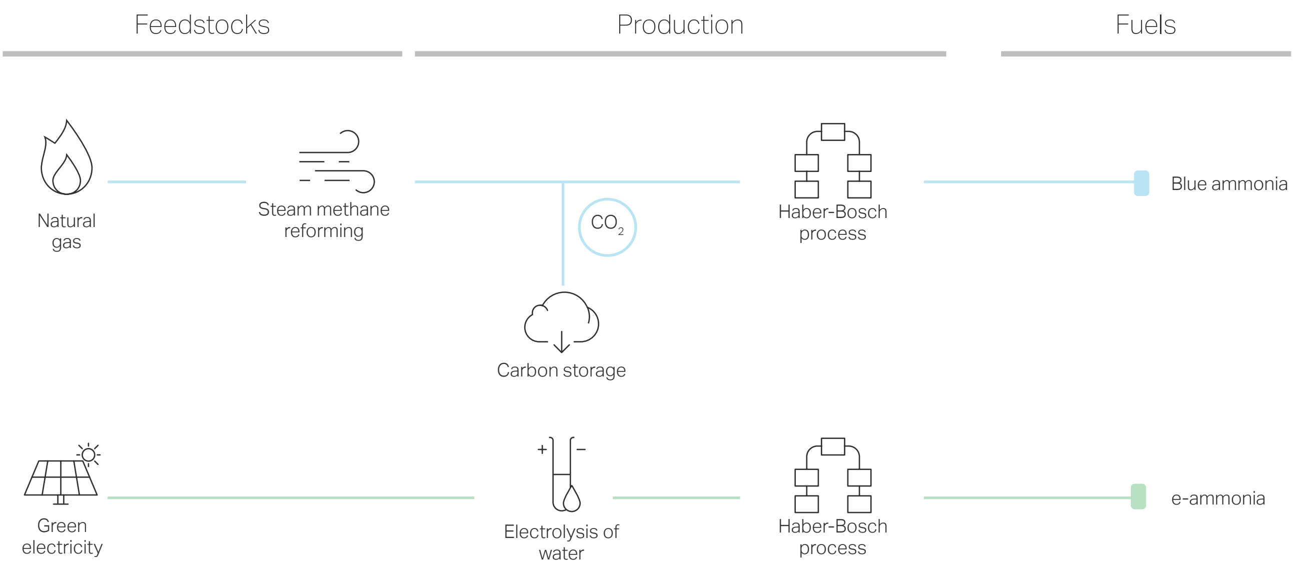
Two main low-emission ammonia pathways are blue ammonia and electro-ammonia (Figure 2). Ammonia is produced from hydrogen. For blue ammonia, hydrogen is generated using conventional methane reforming combined with carbon dioxide (CO_2) capture and storage. For electro-ammonia, hydrogen is generated using electrolysis of water powered by renewable sources. Gray ammonia, which is commonly produced today using conventional methane reforming without CO_2 capture and storage, is not considered an alternative fuel pathway because its price and emissions are higher than low sulfur fuel oil (LSFO).

Ammonia does not contain carbon and, therefore, its combustion does not emit any CO_2. However, due to poor combustion characteristics, secondary or pilot fuel is required (5-15% for two-stroke engines and up to 30% for four-stroke engines, based on suppliers' latest forecasts).

The resulting emissions profile of an ammonia DF ICE depends on the type and amount of pilot fuel used. However, using ammonia with a fossil-based pilot such as LSFO can still reduce tank-to-wake (TTW) CO_2 emissions by over 85% compared to using only LSFO Tier II levels (depending on pilot fuel amount). SO_x and particulate matter (PM) emissions can be reduced by 90-100% compared to heavy fuel oil (HFO) Tier II levels.

This paper focuses on the TTW emissions from ammonia DF ICEs and does not cover the WTT emissions associated with fuel production and transportation. For example, methane emissions occur throughout the natural gas supply chain, known generally as fugitive emissions in the upstream part. Managing these methane emissions should be addressed as part of blue ammonia production to minimize total well-to-wake (WTW) emissions for that pathway.

Figure 2: Ammonia fuel pathways

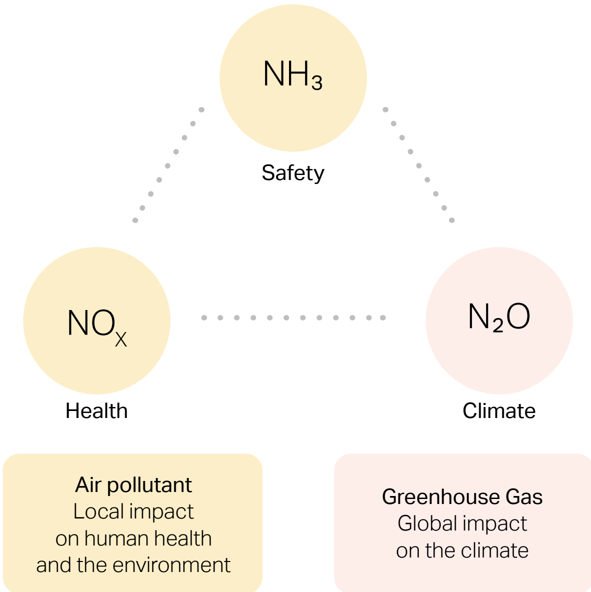


03 Ammonia combustion emission risks

Fundamental investigations on ammonia combustion have been performed since the 1950s to understand characteristics such as: flammability, ignition delay, flame propagation, and speciation. While the first three are important when optimizing the energy output from an engine, the speciation is central to the optimization of emissions. During the last decade, data from early experiments have served as validation targets for the chemical kinetics mechanisms and as references for further technical realizations. This has led to a considerable renewed interest in experimental work and modelling of ammonia combustion, since modern requirements to overall engine performance cannot be described with the existing data. As well as ammonia slip, NO_x formation and N_2O emissions are sought to be resolved, since previous work has mostly been concentrated on these species as trances in fossil fuel combustion and not as elements in the main fuel's combustion pathway. Thus, this species formation and potential emissions at relevant conditions are not clearly understood from, or mapped in, previous work. A comprehensive review on state of the art is available from Mashruk et al.[3]

Ammonia combustion presents three specific emissions risks that relate to safety, health, and climate: ammonia slip, NO_x, and N_2O. Ammonia slip is a safety risk for the crew on board the vessel, local communities, and the environment where ammonia-fueled vessels operate and have port calls. NO_x is a health risk to local communities where vessels operate, and N_2O is a GHG impacting the global climate. This multi-dimensional emission risk triangle (Figure 3) needs to be addressed as part of developing ammonia DF engines and after-treatment emission management technologies.

Figure 3: Ammonia combustion emission risk triangle



3.1 Ammonia slip

Ammonia slip is the escape of unburnt ammonia emitted via engine exhausts into the atmosphere during combustion. As ammonia is a toxic gas, acute exposure to humans, even at low levels, can lead to serious injury or death. A range of exposure limits and guidelines (in terms of parts per million (ppm) thresholds and exposure times) have been defined. These guidelines vary from 14 to 110 ppm with exposure time limits from 15 minutes to 24 hours.[4]

Given the broad range of exposure limits and lack of knowledge on ammonia as a fuel for the maritime sector, there is a need to be conservative when defining guidelines as an additional safeguard. Thus, low limits are generally included in Class guidelines, which are being developed ahead of mandatory IMO instruments in response to the industry's interest in ammonia as a fuel.

3 Mashruk et al., 2022, "Nitrogen oxide emissions in analyses in ammonia/hydrogen/air premixed swirling flames", Energy, Volume 260, 1 December 2022, 125183.
4 ABS "Sustainability Whitepaper: Ammonia as Marine Fuel", October 2022.

The operational ammonia limits defined within existing Class guidelines vary by Class (see Table 1). Some are specific to gas detection levels, others specify limits from the exhaust or vent mast, and one specifies limits associated with releases. Differences between Classes in terms of safe ammonia levels are expected, especially when dealing with a new type of fuel that is both toxic and corrosive, and for which the IMO has not yet developed a mandatory code. Such differences are part of the learning process by the industry. Nevertheless, ammonia limits in Class guidelines are expected to converge as experience increases.

While lower ammonia limits reduce the risk of potential exposure, achieving very low levels can also increase the size and cost of emission management technologies. As ammonia engine and emission management technologies are currently under development, it is difficult to align regulatory limits and technology performance. A common approach to setting standards is needed to avoid unnecessary uncertainty, and the risk of divergent design and development approaches. The IMO must drive that discussion with the support of industry stakeholders such as Class societies, engine makers, shipyards, and technology providers.

3.2Nitrous oxide (N_2O)

N_2O is a potential byproduct of both ammonia combustion and after-treatment technologies. It is also a combustion byproduct of conventional marine fuels like marine diesel oil (MDO) in Diesel-cycle engines with emission levels around 0.03 g/kWh.[5] The GWP potential of N_2O over a 100-year period is 265 (i.e., 1 gram of N_2O is equivalent to 265 grams of CO_2). Consequently, small quantities of N_2O may invalidate the case for ammonia as a low-emission fuel.

To better understand the potential impact of N_2O emissions on the total GHG emissions of a vessel, we calculated CO_2-eq GHG TTW emissions for different N_2O emission levels.[6] The first level (NH_3-1) studied assumed that N_2O emissions were double the levels of conventional fossil fuels (0.06 g/kWh), corresponding to 0.000158 gN_2O / gNH_3. Other levels studied (NH_3-2, NH_3-3) were based on the amount of N_2O slip necessary for the emissions (on a gCO_2eq/MJ basis) to be reduced by a quarter and by half relative to very low sulfur fuel oil (VLSFO). The final level studied (NH_3-4) is the amount of N_2O slip that would lead to GHG emissions equal to VLSFO. The levels studied are provided in Figure 4 as a percentage of gN_2O/gNH_3 and gN_2O/kWh.

Table 1: Ammonia limits (in ppm) from Class guidelines

Classification Society	ppm limits for release, alarm, and safety systems activation	Source
ABS	10 ppm as release/exhaust limit, gas alarms at 25 ppm and safety systems activated at 150 ppm	ABS, "Guide for Ammonia Fueled Vessels", September 2021
BV	30 ppm exposure limit, triggering shut down and other safety measures	Bureau Veritas, "AMMONIA-FUELED SHIPS TENATIVE RULES - NR671 - JULY 2022", 2022
Class NK	25 ppm as release/exhaust limit, same safety and alarm provisions as Korean Registry	ClassNK, "Guidelines for Ships Using Alternative Fuels (Edition 2.0) - Methy/Ethyl Alcohol/LPG/Ammonia, June 2022
DNV	30 ppm as release/exhaust limit, gas alarms at 150 ppm and safety systems activated at 350 ppm	DNV, RULES FOR CLASSIFICATION, Ships, "Part 6 Additional class notations, Chapter 2 Propulsion, power generation and auziliary systems", July 2022
Korean Register	Safety systems activated at 300 ppm. Alarm sounds at 25 ppm	Korean Register, "Guidelines for ships using Ammonia as fuels (2021.26)", 2021
Lloyd's Register	Prevent venting in normal and abnormal conditions. Safety systems activated at 220 ppm and alarm sounds at 25 ppm.	Lloyd's Register, Notice No. 1, Rules and Regulations for the Classification of ships using Gases or other Low-flashpoint Fuels, December 2022

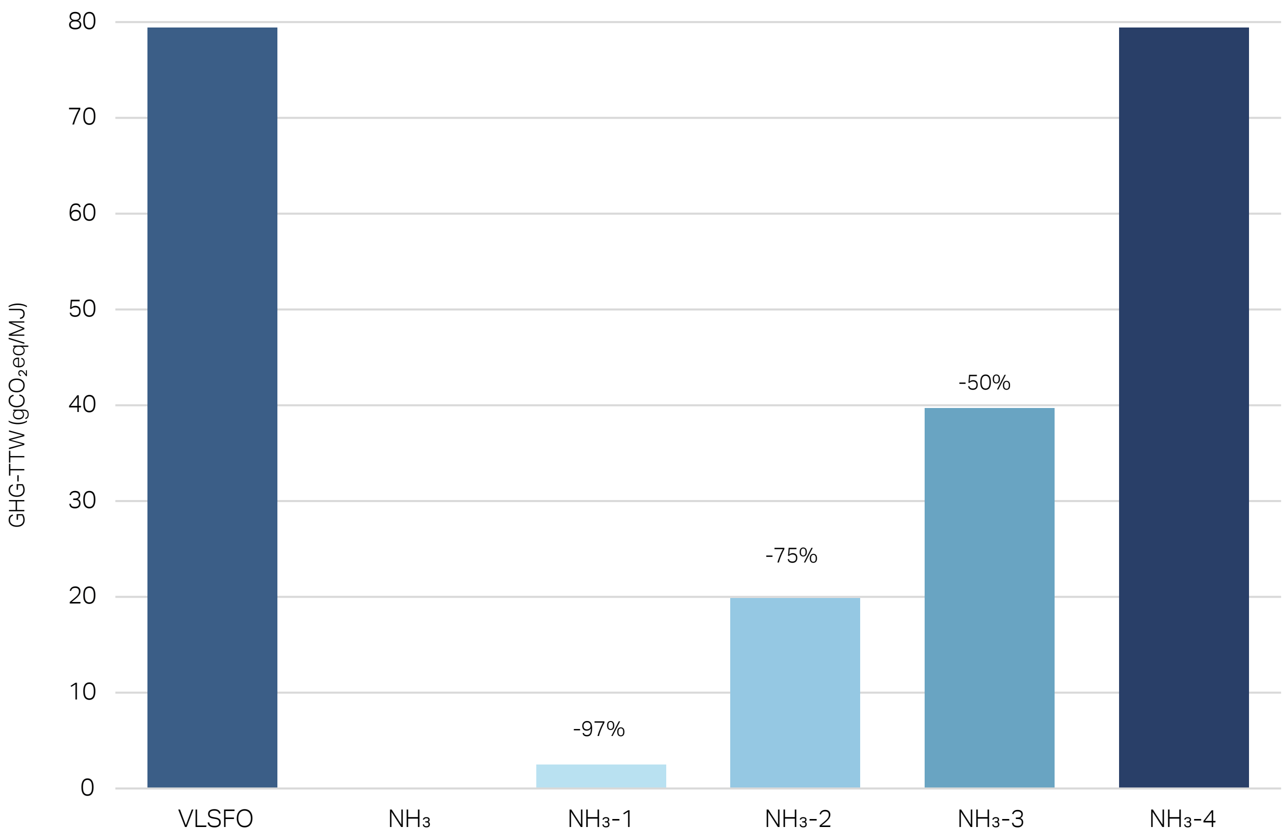
5 Fourth IMO GHG Study 2020.
6 Does not include pilot fuel emissions; assumes 51% engine thermal efficiency; FuelEU emission factors used.

The GHG emissions for the N_2O levels studied highlight the importance of minimizing N_2O emissions from ammonia DF engines. Even small amounts of N_2O can lead to high GHG emissions, which is a potential showstopper for using ammonia as a low-emission alternative fuel. Based on our best understanding today and N_2O emission level targets set in the working group, however, N_2O emission levels are expected to be at most around 0.06 g/kWh (NH_3-1). Higher N_2O emission levels (NH_3-2, NH_3-3, NH_3-4) are not likely or would not be accepted from an ammonia ICE design.

3.3 Nitrogen oxides (NO_X)

NO_X emissions remain a key design parameter for most alternative fuels to maintain regulatory compliance[7] while minimizing fuel consumption. Ammonia DF engines require after-treatment technology to be compliant with NO_X limits. Existing and known NO_X reduction technologies used with fossil fuels, including selective catalytic reduction (SCR) and exhaust gas recirculation (EGR), can also be used for ammonia DF engines. Instead of using urea as the SCR's reductant, it is possible to use ammonia directly onboard ammonia-fueled vessels.

Figure 4: Potential impact of N_2O on total GHG emissions



	% N_2O / NH_3 fuel	gN_2O / kWh
NH_3-1	0.01757%	0.06 g/kWh
NH_3-2	0.1336%	0.47 g/kWh
NH_3-3	0.2435%	0.95 g/kWh
NH_3-4	0.5572%	1.90 g/kWh

7 Regulation 13 of MARPOL Annex VI (limits for NOx emissions from diesel engines).

04 Regulatory drivers

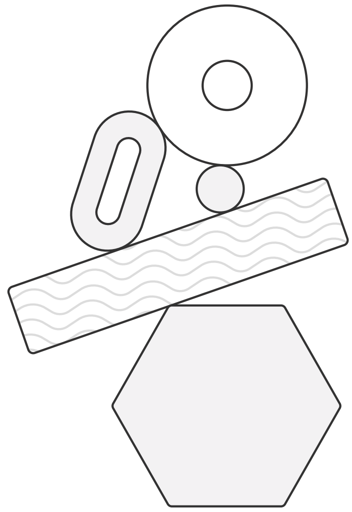
The main concern with ammonia as a fuel relates to its toxicity and associated safety issues. That said, ammonia is a known product for shipping, where 18-20 million tonnes are transported by gas carriers annually.[8] The International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk (IGC Code) regulates the transportation of ammonia as cargo. While IGC Code restricts the use of toxic products like ammonia as a fuel, there is a possibility to obtain flag state approval through a risk-based alternative design process demonstrating that alternative fuels have the same level of safety as liquefied natural gas (LNG). This approach was also used during the introduction of fuels like liquefied petroleum gas (LPG) and ethane.

The use of ammonia as a fuel is currently not included as prescriptive rules in the International Code of Safety for Ships using Gases or Other Low-Flashpoint Fuels (IGF Code). The IMO is developing guidelines and standards to allow ammonia to be used as a fuel. Like the IGC Code, an alternative design process can be used to gain approval for using ammonia as a fuel. Classification societies have also issued their own guidelines on the safety requirements associated with using ammonia as a fuel.

Ammonia was on the agenda of the 8th meeting of IMO's Sub-Committee on Carriage of Cargoes and Containers (CCC) which was held from 14-23 September 2022. It was agreed that the development of ammonia guidelines should follow the structure of the IGF Code. The committee recognized the unique risk profile of ammonia (vapor or liquid), toxicity, and corrosivity, which are important issues that the IGF Code does not address. The environmental effects of ammonia are also concerns that will be addressed in these guidelines.

The IMO must also revisit MARPOL Annex VI Regulation 18 and Chapter 16 of the IGC Code, which both prohibit the use of toxic or harmful fuels. Once these IMO guidelines are finalized, IMO Maritime Safety Committee (MSC) can consider the legal implications of this fuel type. These guidelines are expected to be completed in 2024.

Currently, N_2O emissions are not regulated by IMO, although work is underway via the establishment of lifecycle guidelines development reporting to MEPC 79. There are regional developments include N_2O in regulatory measures, such as in the European Union's (EU) FuelEU Maritime as part of the FitFor55[9] package. Regional measures propose covering not only CO_2 but other GHGs, including methane and N_2O, as part of a CO_2eq emission methodology on a WTW basis. For methane slip emissions from methane-based DF engines, FuelEU Maritime defines specific slip factors based on the engine type. However, there is no similar proposal for ammonia DF engines, as they are still under development and testing.



8 IRENA and AEA "Innovation Outlook: Renewable Ammonia" 2022.
9 https://www.consilium.europa.eu/en/policies/green-deal/fit-for-55-the-eu-plan-for-a-green-transition/

05 Ammonia emission sources

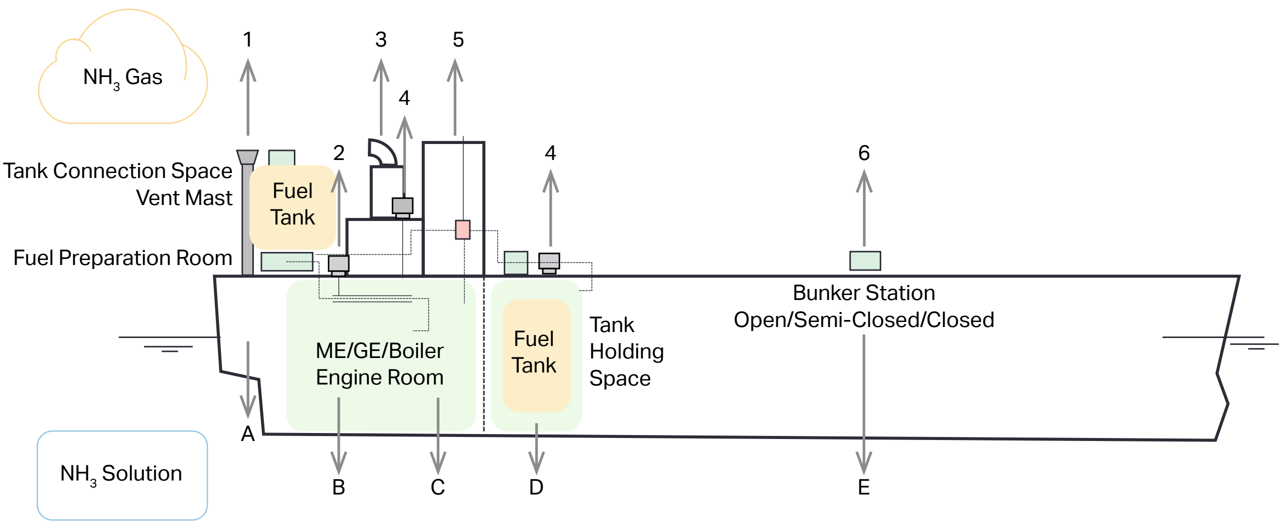
While ammonia slip is the predominant source of ammonia emissions on ammonia-fueled vessels, other potential sources of ammonia emissions are not directly related to the engine or combustion. Like vessels with methane-based DF engines, these non-engine-related emissions can be categorized into three main emission types: fugitive emissions, operational releases, and emergency releases. These ammonia sources need to be managed, even if at low levels, to limit emissions to acceptable safety levels.

Figure 5 provides an overview of expected ammonia emissions sources onboard vessels. Ammonia emissions can be both liquid and gas, depending on the source. Gaseous ammonia emissions are typically from consumers (i.e., energy converters), vent mast, bunker station, and ventilation of enclosed spaces or double-walled piping. Liquid ammonia emissions typically result from using safety systems like deck water spray, water curtains, spill tanks, and ammonia detox systems for consumers like engines.

All relevant ammonia emission sources and types must be identified to ensure that the potential hazards are mitigated properly during the vessel design stage. With multiple sources and types of ammonia emissions, multiple technologies and solutions must be used to ensure acceptable safety levels are achieved.

Figure 5: Onboard vessel ammonia emissions sources (for illustrative purposes; not based on a specific design)

No	Emission from	Source
1	Gas vent mast	Tank & line safety valve, catch & detox system
2	Ventilation of double wall pipe system	NH_3 fuel liquid and gas piping in engine room, piping from bunker station to engine room
3	NH_3 slip from various consumers	Main engine (ME), generator engine (GE), aux boiler, GCU, reliq. plant, compressor
4	Ventilation of enclosed space	Machinery/fuel handling system in that space or from surrounding space
5	Instrument	Gas detector, calorific meter, calibration gas
6	Bunker station	Hose connection/disconnection, quick coupler, emergency release system

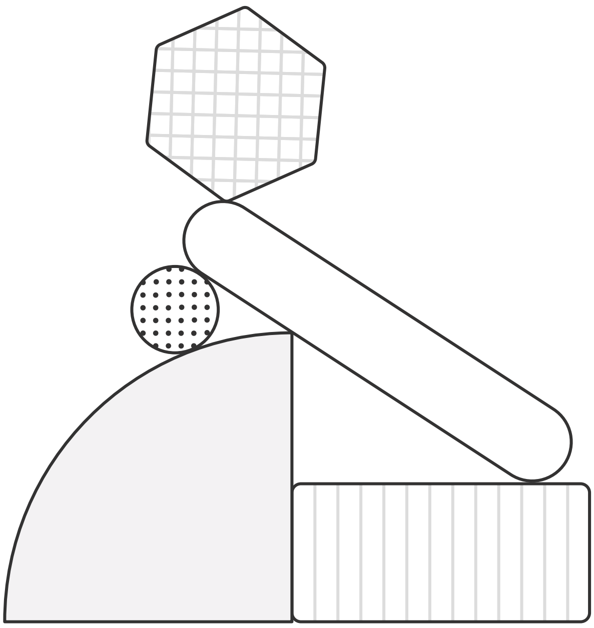


No	Discharge from	Source
A	Deck water spray system	Lekages from piping system and storage tank on exposed deck
B	NH_3 catcher and detox system	Main engine, generator engine, aux boiler, GCU, if equipped, compressor
C	Heat exchange fluid	Heat exhanger (tube/plate)
D	Enclosed space bilge system	Leakages from independent tank, piping, stub piece, valve, plug etc. If equipped, local water sprinkler for NH_3
E	Water curtain / spill tank system	Leakages from bunker hose, quick coupler, emergency release ystem

06 Setting emission reduction targets

Despite the currently uncertain emission profile of ammonia ICEs, it is still possible to set limits or targets for the main emissions identified as potential risks. As part of our working group analysis, we set emission targets for NH_3, N_2O, and NO_x (Table 2) by combining minimum safety and environmental requirements with realistic performance forecasts, based on ongoing technology development. While there may be some SO_x and PM emissions depending on the pilot fuel used, these levels should be well below conventional fuels.

The ability to achieve the individual emission targets for NH_3, N_2O, and NO_x are not mutually exclusive, as measures to reduce one could lead to an increase in another. Their emission levels will be heavily influenced by the degree of optimization in the overall combustion process. In addition, due to ammonia's poor combustion properties, the amount of pilot fuel needed for the different engine types is still unknown and will influence the emission levels. The most suitable types of emission management technologies will strongly depend on the respective levels of each specific emission.



Values shown in Table 2 are indicative. It is important to note that different thresholds could be defined for different operational conditions. For example, thresholds applicable to normal operating conditions should be stricter than emergencies or extraordinary situations where higher emissions might be acceptable for shorter periods. Further, threshold values are still being discussed within the industry and should be validated once full-scale test results are available. Table 2 provides a good starting point for these discussions, as these values appear realistic, safe, and achievable based on current knowledge and available emission management technologies.

Table 2: Working group emission target levels

Emission	Target Level
NH_3	10-30 ppm
N_2O	0.06 g/kWh
NO_x	Tier III (≈2 g/kWH)
SO_x	N/A
PM	N/A

07 Emission management technologies

While exact emission levels generated from ammonia combustion are still largely unknown, we expect existing technologies to be adapted for use with ammonia, to ensure safe operations on board. Similarly to what can be obtained with adequate methane slip management for methane-based DF engines, ammonia emissions management will require a holistic approach. This will result in a combination of engine optimization/tuning and emission management technologies. This section describes the main technologies that are best positioned to manage emissions from all sources on ammonia-fueled vessels.

Based on the chemical composition of ammonia combustion and associated safety, health and climate risks, it is not realistic to expect that one single emission management technology will be able to address each emission risk sufficiently. As a result, we can expect multiple emission management technologies on future ammonia-fueled vessels. Although some of these systems are already available (but commonly used in other applications), some are still under development, in parallel with engines, to optimize size, material use, and efficacy. Considering the potential emission scenarios for ammonia DF engines, it is possible to define what technologies are applicable and have the highest potential to mitigate each specific emission risk.

The relative capacity, size, and complexity of these emission management technologies and their interdependency with other components must be validated based on actual emission measurements that will become available once full-scale engine tests are successful.

In the meantime, preparing and ensuring that the most likely and hazardous outcomes are accounted for within the vessel design and development process is valuable. Ship designers and technology providers should collaborate early to optimize capacity and system efficiency. In the current uncertainty, collaboration is the best approach to avoiding inefficiency or unaffordable final designs.

In this work, we have divided the emission sources into three main groups depending on their origin and indicated which emission management technologies apply to each group. The groups are:

1. Fuel tanks: Pure ammonia emissions from fuel tanks (i.e., boil-off gas (BOG)), which are pure ammonia emissions
    - When using a fully pressurized (18 bar) ammonia fuel tank, no BOG management system is required as this pressure will keep ammonia in a liquid state at all times. BOG must be managed when using semi-, fully refrigerated, or membrane tanks.

2. Fuel systems: Pure ammonia emissions from fuel systems during operational conditions such as purging, venting, or gas-freeing, which may be emitted in two scenarios:
    - Fuel changeover: it is reasonable to expect that there will be restrictions to the use of ammonia as fuel within specific areas or ports, and, in that case, ships will need to changeover to compliant fuels without negatively affecting their operational safety
    - Planned Maintenance: need for drydocking will require ammonia fuel system and tanks to be gas freed
    - Emergency: in case of an incident (system failure, breakdown, hazardous event), it may be necessary to shut down the ammonia fuel supply to the engines [10]

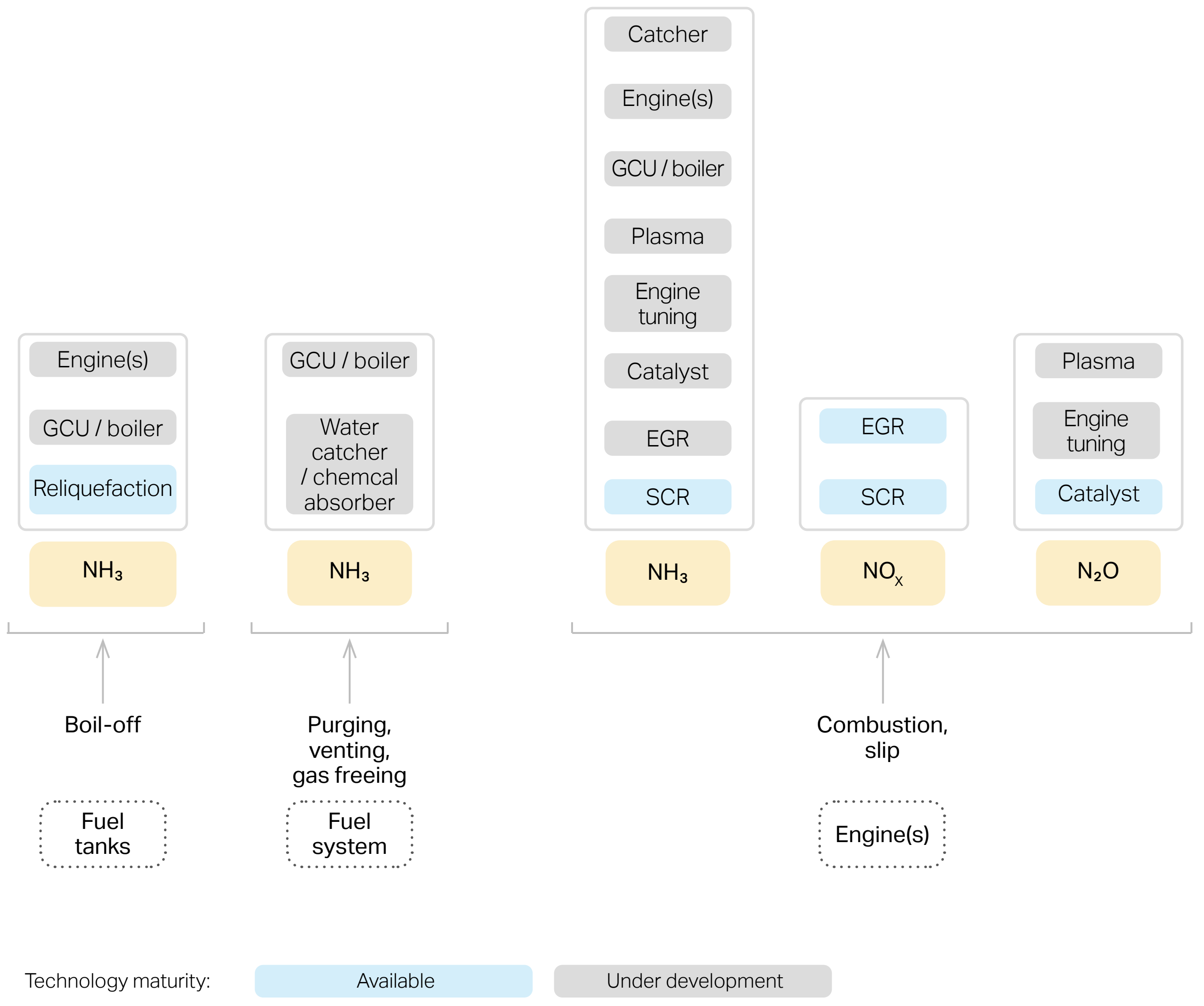
3. Engine(s): Ammonia slip, N_2O, and NO_X emissions from the combustion of ammonia within onboard engines that may require reduction using separate technologies

10 Leaks due to damaged piping to be assessed in a separate MMMCZCS project.

Ammonia emissions must be managed from all three sources, while N_2O and NO_x emissions are only relevant in the engine exhaust. We identified which technologies can be used to reduce the emissions for each group, resulting in the emission management technology map shown in Figure 6.

The following sections provide a general description of each technology identified in Figure 6, its development status, and emission reduction potential. As most of these technologies are currently under development, information is limited, and quantitative emission reduction potentials are not provided.

Figure 6: Ammonia-fueled vessel emission management technologies



7.1 Gas combustion unit/boiler

A gas combustion unit (GCU) is used primarily to regulate cargo or fuel tank pressure by removing the surplus BOG that cannot be utilized in the engines or boilers, safely combusting the vapor. A boiler can also manage BOG (the same function as a GCU) by generating steam or heating thermal oil or water. In the basic operational mode of a boiler, ammonia as fuel will be supplied in a gaseous state at the admission to the boiler's gas valve unit (GVU). In addition to BOG management and steam generation, a boiler can also manage ammonia during other operations, including gassing up/gas freeing, purge handling. Figure 7 provides a simplified schematic of the systems on board an ammonia DF vessel and the potential roles of the GVU plus boiler.

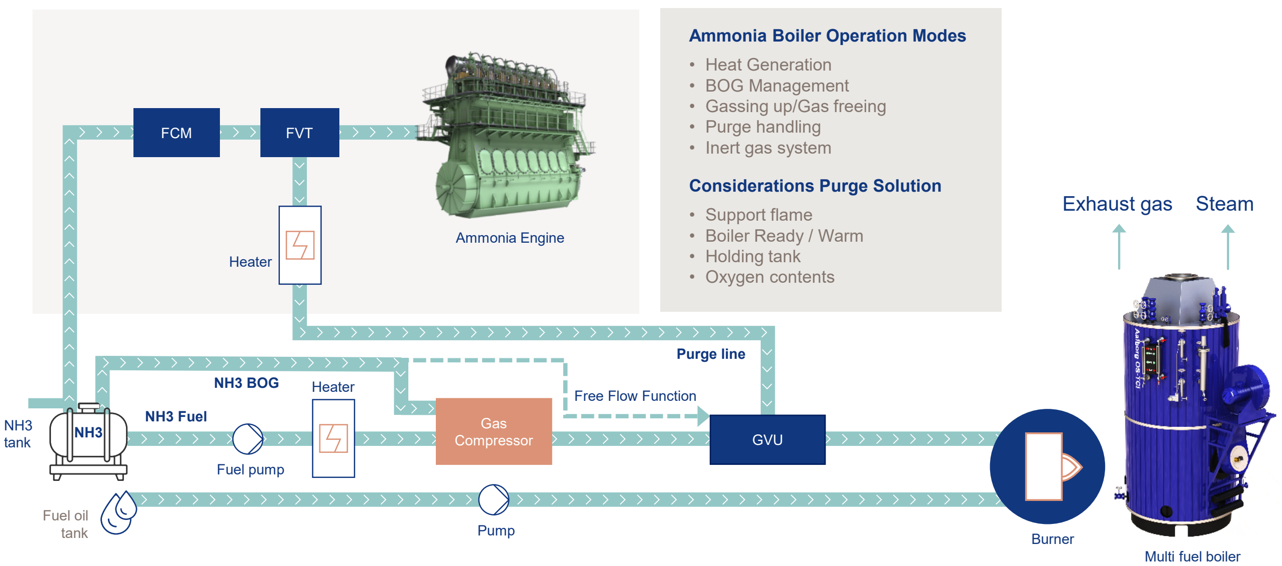
Fuel tanks

Typically, there are two ways of managing BOG using a boiler. One way is to compress the BOG, and the other is to let it flow without compression to the burner (free flow). When the boiler consumes BOG, additional requirements are applicable. For liquefied natural gas (LNG), provisions in IMO Resolution MSC.391(95) (IGF code) specify the following:

– The capacity of the oxidation system is sufficient to consume the required quantity of vapors (with no consumption from propulsion or other services).
– Availability of the system and its supporting auxiliary services shall be such that in case of a single failure, the fuel tank pressure and temperature can be maintained by another service/system
– Standby heat exchangers or 25% extra capacity on heat exchangers to maintain pressure and temperature in fuel tanks

Currently, requirements for ammonia BOG are not available in the IGF code. However, similar requirements to LNG are expected to be implemented.

Figure 7: Ammonia boiler and operational modes (Source: Alfa Laval)



FCM = Fuel conditioning module, FVT = Fuel valve train, GVU = Gas valve unit.

Fuel system

The gassing up/gas freeing operational mode is related to tank emptying and filling (e.g., before and after drydocking), where the boiler will combust a mixture of ammonia and inert gas from the tank. The main flame will be from liquid fuel. The size of the boiler and burner capacity will be dependent on the gas flow.

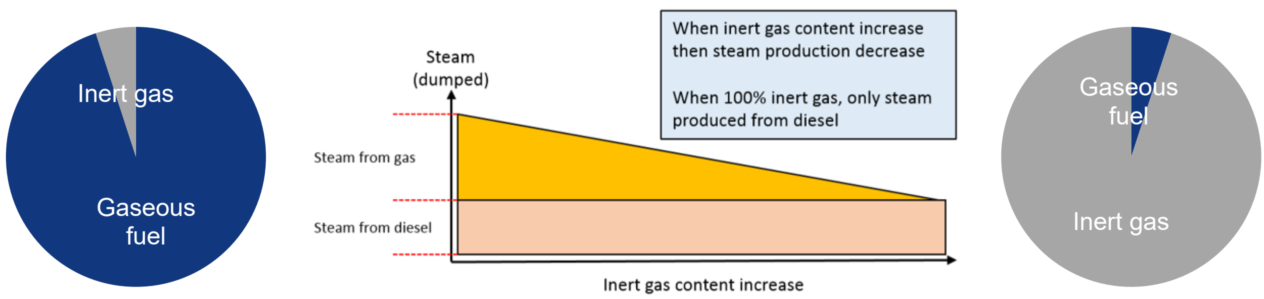
Like the gassing up/gas freeing operational mode, in purge gas handling, the boiler will combust a mixture of ammonia and inert gas with the main flame firing liquid fuel. The gas mixture will likely have low ammonia content. An ammonia boiler can also potentially generate the inert gas needed for the various operational modes on board. Inert gas volumes generated will depend on actual emissions measured during combustion of ammonia.

According to the International Convention for the Safety of Life as Sea (SOLAS) as amended and the IGF code, an inert gas system shall be capable of delivering not more than 5% oxygen content by volume. Flue gas from an auxiliary boiler may generate inert gas on board for this requirement.

Flue gas is extracted from the boiler by fans, after which it is drawn through a scrubber, where the gas is cooled and washed before being delivered to the cargo tanks.

For LNG carriers, it is typically specified that the inert gas system shall deliver less than 1% oxygen, requiring a dedicated inert gas generator system to be installed on board. For ammonia, under the IGC code, Annex 6 to IMO Resolution MSC.379(93), it is further advised to keep the dissolved oxygen content below 2.5 ppm w/w (indicative reference value; the actual requirement might not be as strict) to minimize the risk of ammonia stress corrosion cracking, which can be achieved by reducing the average oxygen content in the tanks prior to the introduction of liquid ammonia to less than the values given as a function of the carriage temperature. Ammonia carriers, therefore, may require having a dedicated inert gas generator system to meet this requirement. The feasibility of using an ammonia boiler as an inert gas system will be largely dependent on the flue gas composition, which must still be verified through system development and testing.

Figure 8: Steam output in gassing up/gas freeing operation (Source: Alfa Laval)



7.2 Reliquefication

Reliquefication plants can be considered an option to address both BOG management from the fuel tanks and ammonia from the fuel system.

Fuel tanks

Reliquefication plants for ammonia BOG management are already available from the LPG/ammonia business and consist of ammonia vapor compressors, combined with a seawater-cooled condenser unit and pressure relief via a Joules Thomson valve, designed to lower temperature and return condensate ammonia to the tank. These systems are affordable and available as ammonia is used as a refrigerant in many large cooling systems in other industries. The size of the reliquefication plant depends on the tank storage conditions. Semi-refrigerated tanks require smaller plants, while fully refrigerated or membrane tanks require larger plants.

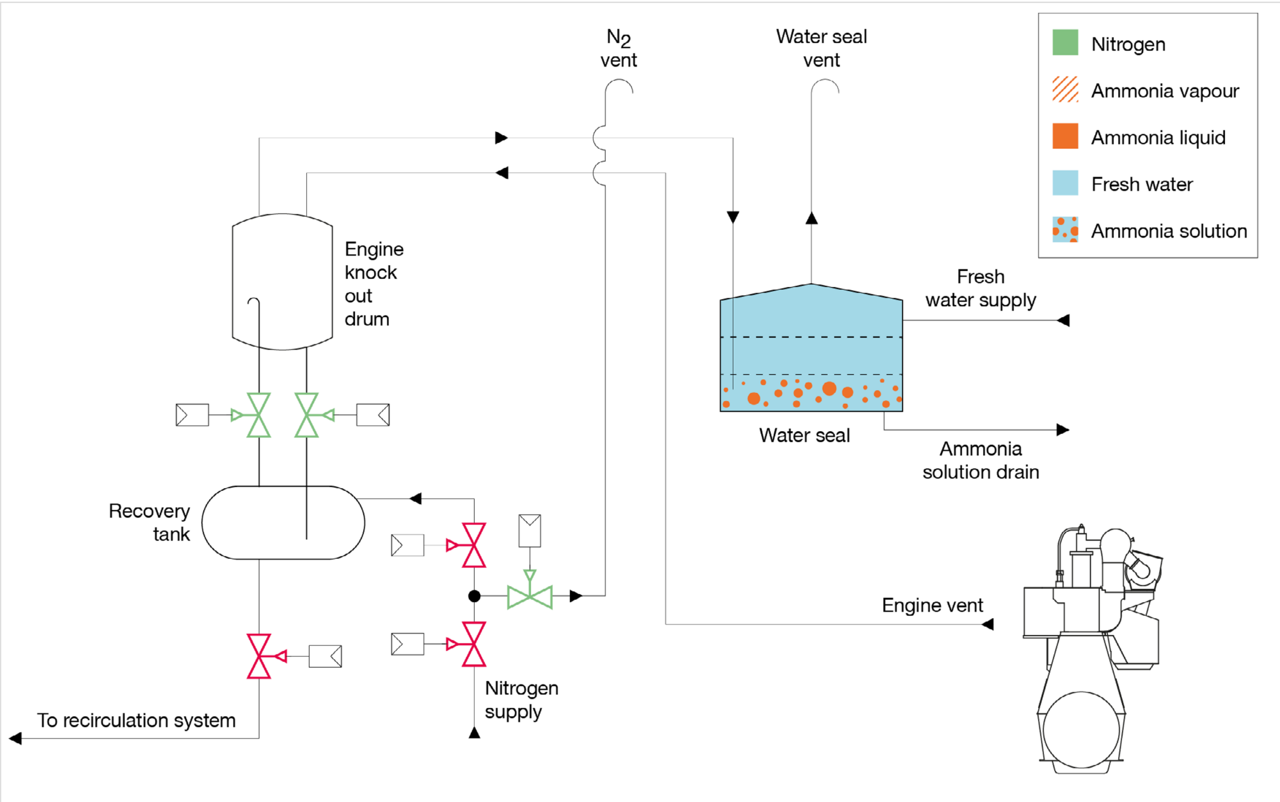
7.3 Water catcher/chemical absorber

Ammonia water catchers (also known as chemical absorbers) can treat ammonia emissions from fuel systems. Typically, emissions from purging and venting operations do not need to be treated onboard. For example, LNG-fueled vessels usually release the gases from this operation into the atmosphere. However, due to ammonia safety concerns, onboard treatment of the ammonia or ammonia mixtures is needed. Water catchers can treat ammonia releases resulting from purging and venting operations, emergency operations, and shutdowns. They use new technology based on existing concepts to reduce other emission types like SO_x.

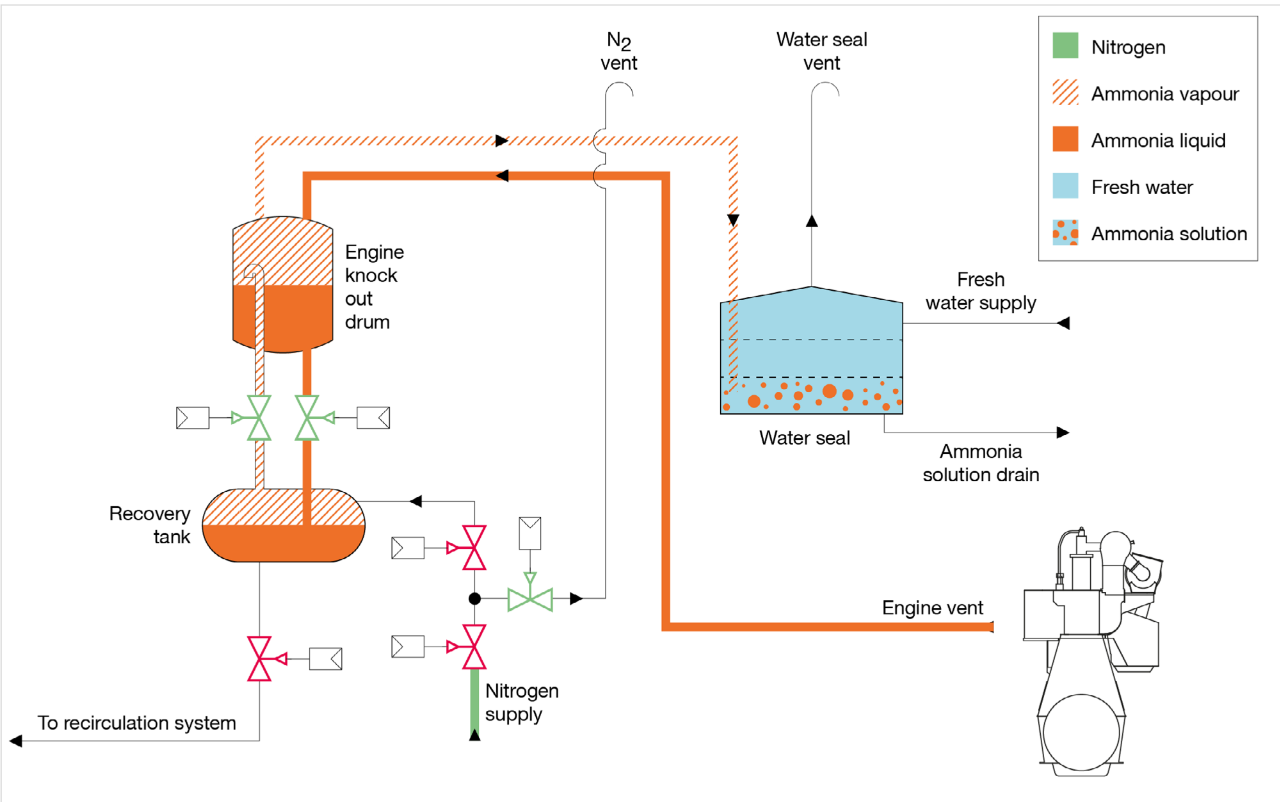
Water catchers could be designed in different ways. One design consists of knockout tanks, a recovery tank, and a water seal. NH_3 is vented to the knockout tank before all lines are purged with nitrogen (N_2). The liquid NH_3 collected within the knockout tank is pushed by nitrogen towards a recovery tank, while the vapors are mixed with fresh water within a water seal. Fluids in the recovery tank are sent back towards the recirculation system, while NH_3 vapors are collected within the water seal until the NH_3 content is sufficient to be combusted within the engine(s).

Figure 9: Water catcher/chemical absorber concept (Source: MAN ES)

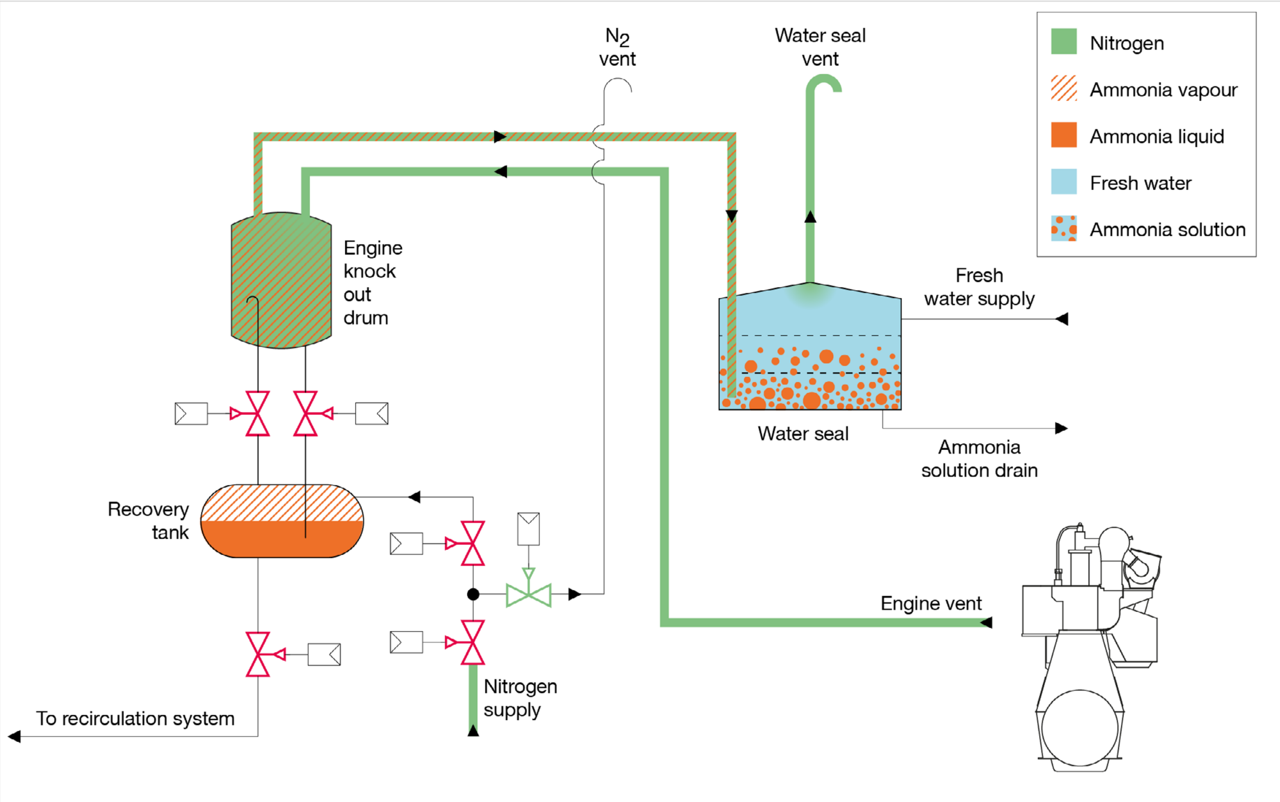
ME-LGIA engine operating on NH_3



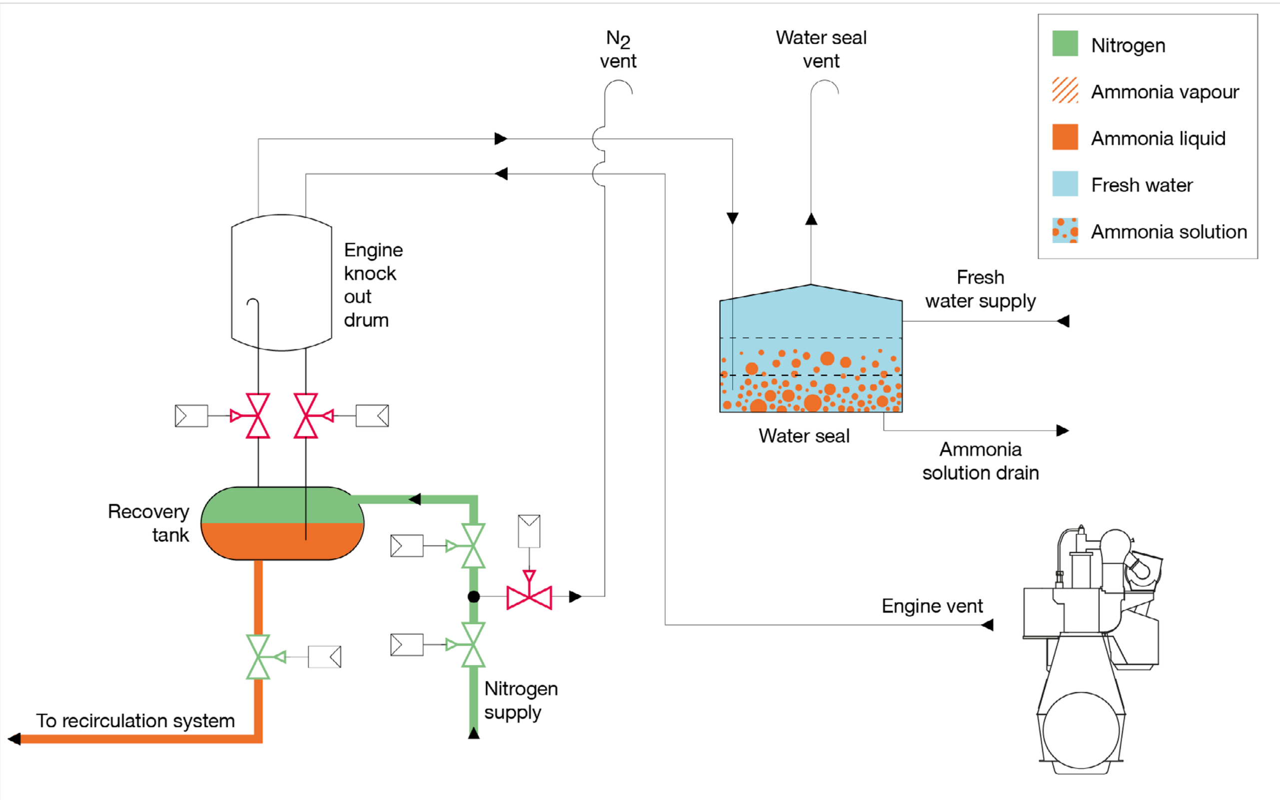
NH_3 Shutdown liquid freeing



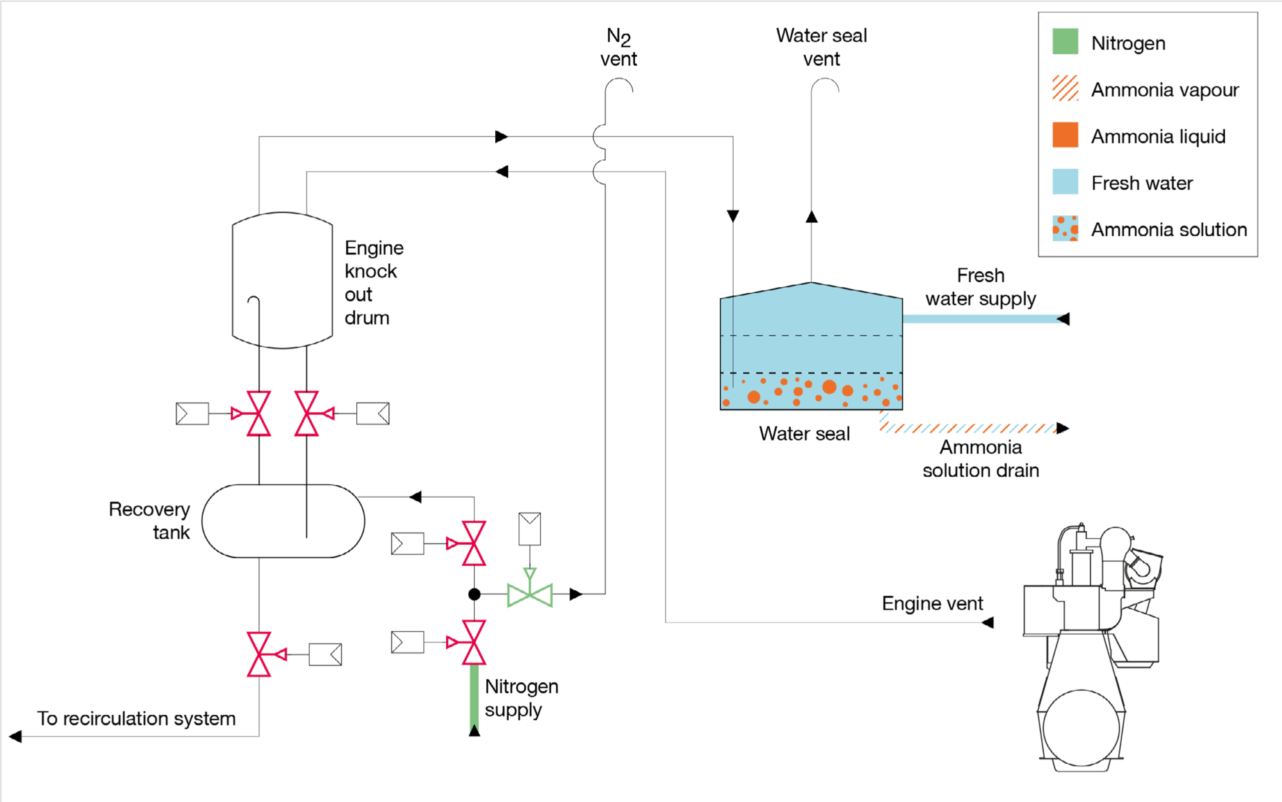
Nitrogen purging



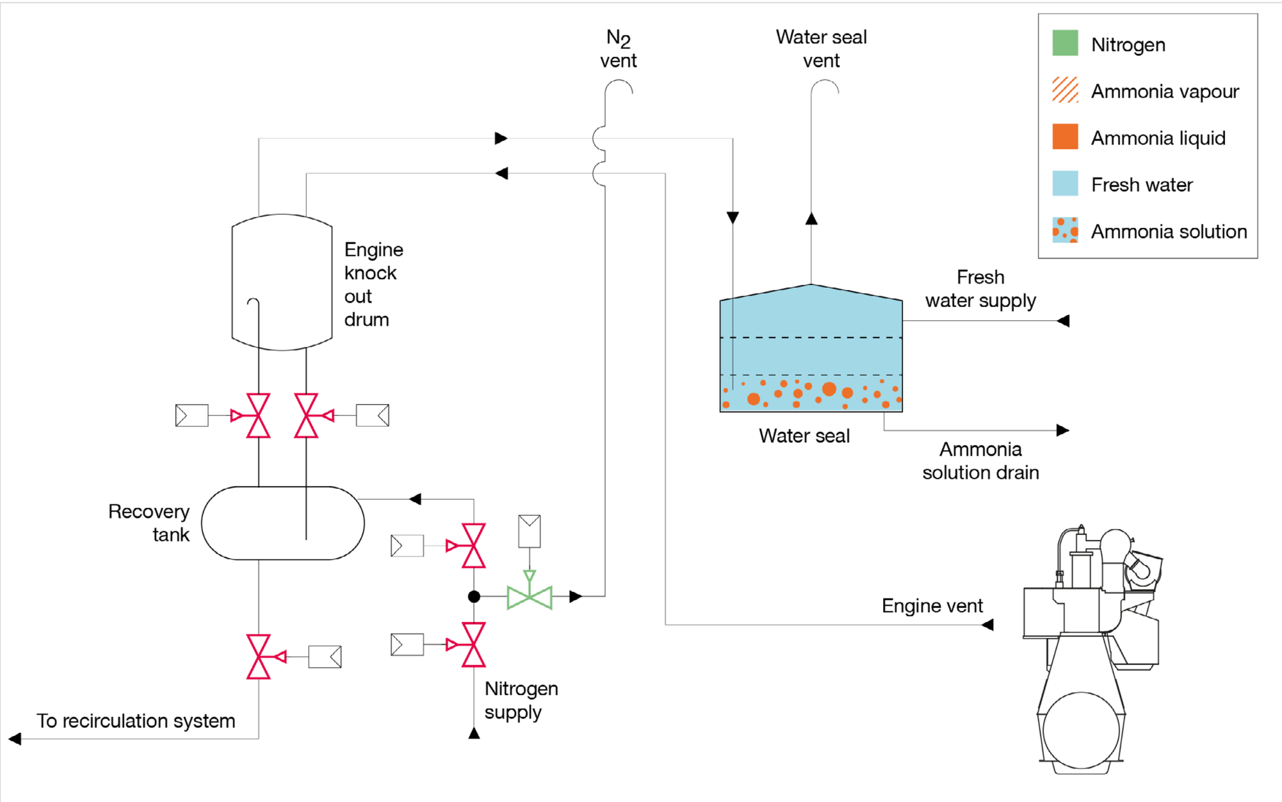
NH_3 recovery



Water seal reconditioning



Stopped



7.4 Engine design and optimization

Engine design and optimization is the starting point for managing emissions from ammonia DF engines, including ammonia slip, N_2O, and NO_X. Engine designers are currently targeting a scenario where acceptable ammonia slip and N_2O emission levels are achieved without the need for after-treatment technology. NO_X regulatory compliance would then be achieved with after-treatment, similarly to other fuels.

Engine(s)

Two-stroke ammonia engine concepts are typically based on LPG engines used on LPG carriers. This design gives full flexibility to control fuel injection pressure, timing, and amount as the injection is an electronically controlled combined fuel booster and injector. Moreover, exhaust valves will enable users to control compression pressure, which will help reduce ammonia slip further.

Additionally, engine tuning provides various options to reduce ammonia slip to minimal levels, including:

- High-pressure injection.
- Variable exhaust valve timing for increasing compression pressure to compensate for cold ammonia transfer.
- Variable cooling of the combustion chamber.
- 100% variable pilot oil dosage system to ignite the ammonia.
- Variable turbocharger efficiency and turbocharger bypass to regulate scavenging airflow.

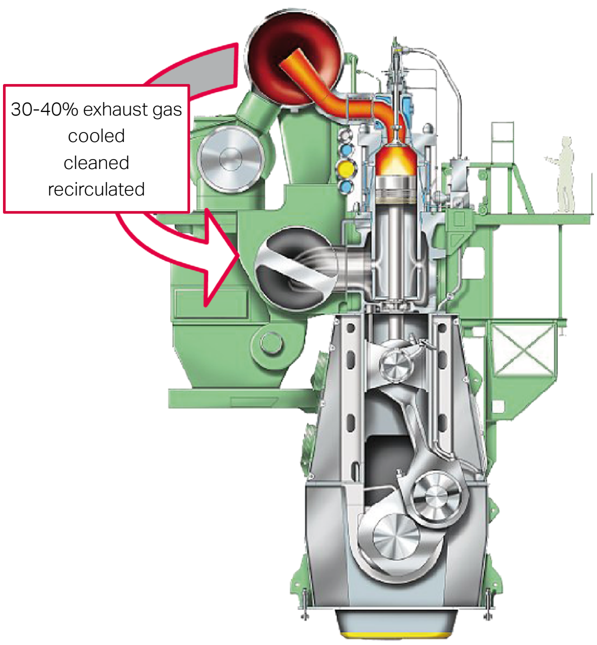
Fuel tanks

In addition to the baseline engine design and optimization, a four-stroke engine (e.g. auxiliary) can be used to manage BOG from the ammonia fuel tanks. When using semi-, fully refrigerated, or membrane tanks, BOG can be handled by supplying the low-pressure gas to four-stroke ammonia DF main or auxiliary engines using the Otto cycle principle.

7.5 Exhaust gas recirculation

EGR recirculates a portion of the exhaust gas back into the engine. An EGR can treat emissions from two-stroke engines, including ammonia slip and NO_X. The EGR system draws around 30 to 40% of the engine's exhaust gas into the EGR receiver, passing it through a pre-spray to lower its temperature before passing it through a cooler spray (Figure 10). After passing through a water-mist catcher, the gas goes through a blower to increase pressure back up to the scavenging air pressure before being fed back into the compressor and the engine. This process improves the overall combustion stability by improving the gas-to-air mixture inside the chamber and thus reducing combustion instabilities that lead to ammonia slip. An EGR is also designed to reduce NO_X emissions to be compliant with Tier III limits.

Figure 10: Exhaust gas recirculation concept (Source: MAN ES)



7.6 Catalysts

Ammonia slip, N_2O, and NO_x emissions from engines can be reduced using catalytic emission treatment technologies that are well-known and commercially available. SCR systems are common in shipping and primarily reduce NO_x emissions using NH_3 or urea as a reducing agent. While most vessels today use urea as a reducing agent, ammonia is preferred for ammonia-fueled vessels, as there will already be ammonia slip in an engine's exhaust. For two-stroke engines, a high-pressure SCR integrated into the engine design can more efficiently reduce the potential increased NO_x emission levels relative to conventional fossil fuels, due to higher temperature before the turbocharger.

Ammonia slip exceeding the need for the SCR reactions can be removed by an ammonia slip catalyst (ASC). ASC technology is known from automotive applications, but can potentially form NO_x and/or N_2O when eliminating ammonia. Potential NO_x and N_2O emissions as a byproduct of the ASC can be controlled by choosing the proper catalyst and process conditions.

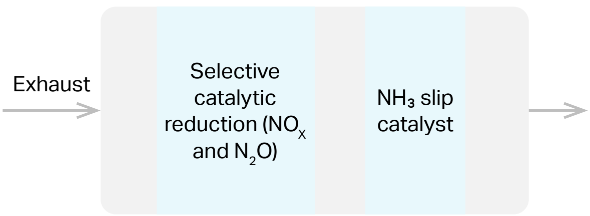
Catalytic N_2O emission reduction is known and used commercially, but a wide range of different catalysts are used. N_2O catalysts are used in a range of temperatures and gas conditions and with or without reducing agents.

Catalytic solutions also exist where NO_x and N_2O emission reduction is simultaneous by using NH_3 as a reducing agent. These can offer a simple and compact solution where an NH_3 dosing system ensures adequate ammonia for NO_x and N_2O reduction if ammonia slip levels within the exhaust are insufficient. If ammonia slip levels exceed the amounts needed as a reducing agent, an ASC can be included downstream. Figure 11 provides a simple schematic of how a combined SCR and ASC would look. Such a catalytic system will convert NO_x, N_2O, and NH_3 emissions into N_2 and water, which can be emitted safely.

Emissions are dynamic and vary depending on engine load and operational conditions. There could be scenarios where ammonia slip in the engine exhaust is sometimes enough for proper catalytic efficiency and, in other cases, not enough.

Among the challenges for catalytic N_2O removal in marine applications are potentially low exhaust temperatures at certain operating conditions, along with sulfur and other potential contaminants from the pilot fuel and the lubrication oil affecting the catalytic performance.

Figure 11: Combined SCR and ammonia slip catalyst (Source: Topsoe)



7.7 Plasma reduction system

Plasma reduction systems (PRS) are currently being developed for methane slip emission reduction and could also potentially be used to reduce ammonia slip. PRS systems consist of a catalyst and an absorbent-free after-treatment technology aimed at producing a non-thermal plasma containing a high density of electrons with high energy. The non-thermal plasma is obtained by means of dielectric barrier discharge which is generated by applying a high voltage between an arrangement of electrodes separated by a dielectric material layer. The processing of the exhaust gas by means of plasma results in the conversion of pollutants in harmless molecules via a chain of complex chemical-kinetic reactions.

PRS are still in the early stages of development, and it is too early to estimate power consumption and reduction rates. Current development plans aim to finalize the technology in 2024. Depending on their performance during development, PRS are expected to be installed on the low-pressure side of a turbocharger, either before or after the economizer.

08 Emission scenarios and technology combinations

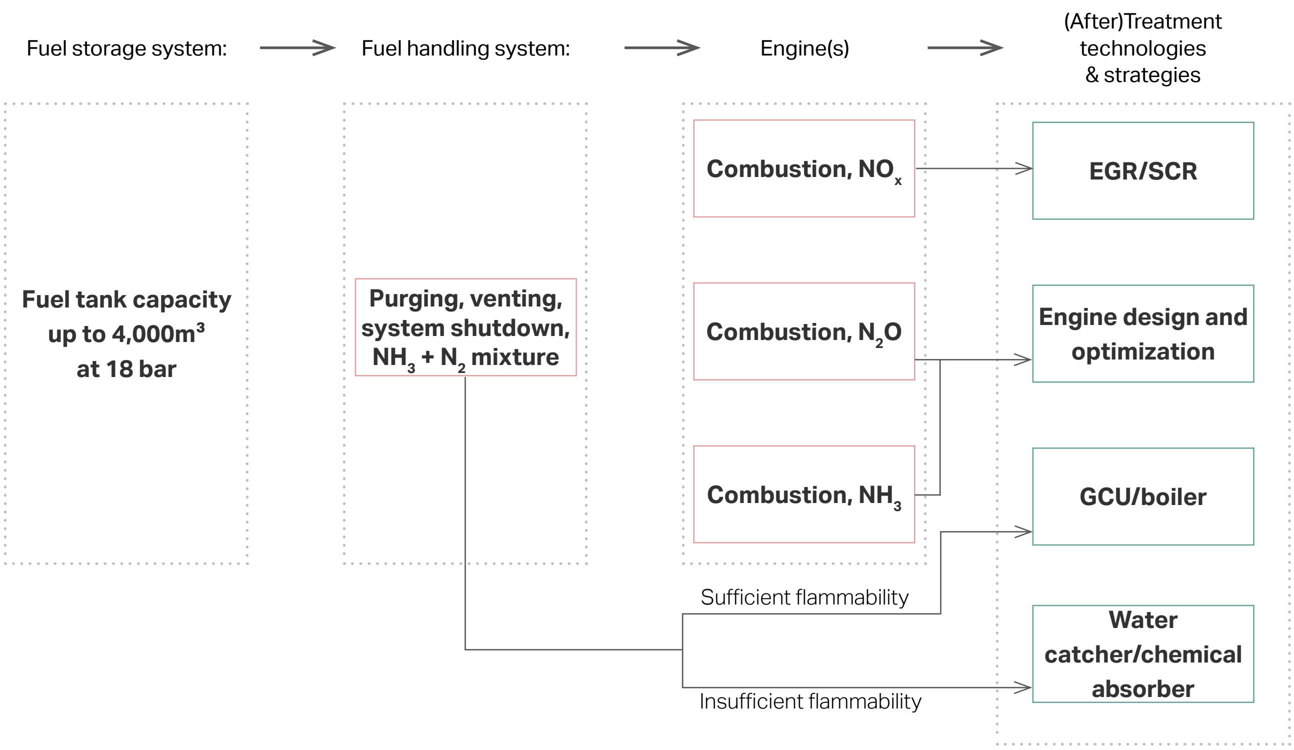
As knowledge of and experience with emissions from ammonia ICEs is limited, various emission scenarios are currently being considered. We defined three main emission scenarios based on insights from ongoing ammonia DF engine development and testing, expert knowledge, and experience. Depending on the specific emission levels associated with the emission profile in each scenario, it is possible to define certain combinations of emission management technologies that would be needed on board. The following sections provide the details of each scenario and the associated emission management technologies needed. These assumptions must be validated once more test results become available.

8.1 Scenario 0

Scenario 0 is the base case and most simple setup predicted by engine technology suppliers based on ongoing development. The scenario consists of a fully pressurized fuel tank with no BOG, one emission management technology for the fuel handling system (a GCU/boiler or water catcher/chemical absorber) based on NH_3 levels, and one after-treatment technology for NO_x emissions. This scenario assumes that ammonia slip and N_2O emissions are successfully managed through engine design and optimization. Figure 12 provides an overview of Scenario 0 conditions and emission management technology options.

A fully pressurized fuel tank (at 18 bar) is typically used for tank volumes up to 4,000 m^3, which can be used on smaller vessels or when multiple tanks are placed on deck, in particular on tankers and bulk carriers. As they are fully pressurized, management of ammonia BOG is not needed.

Figure 12: Ammonia emission Scenario 0 (base case)



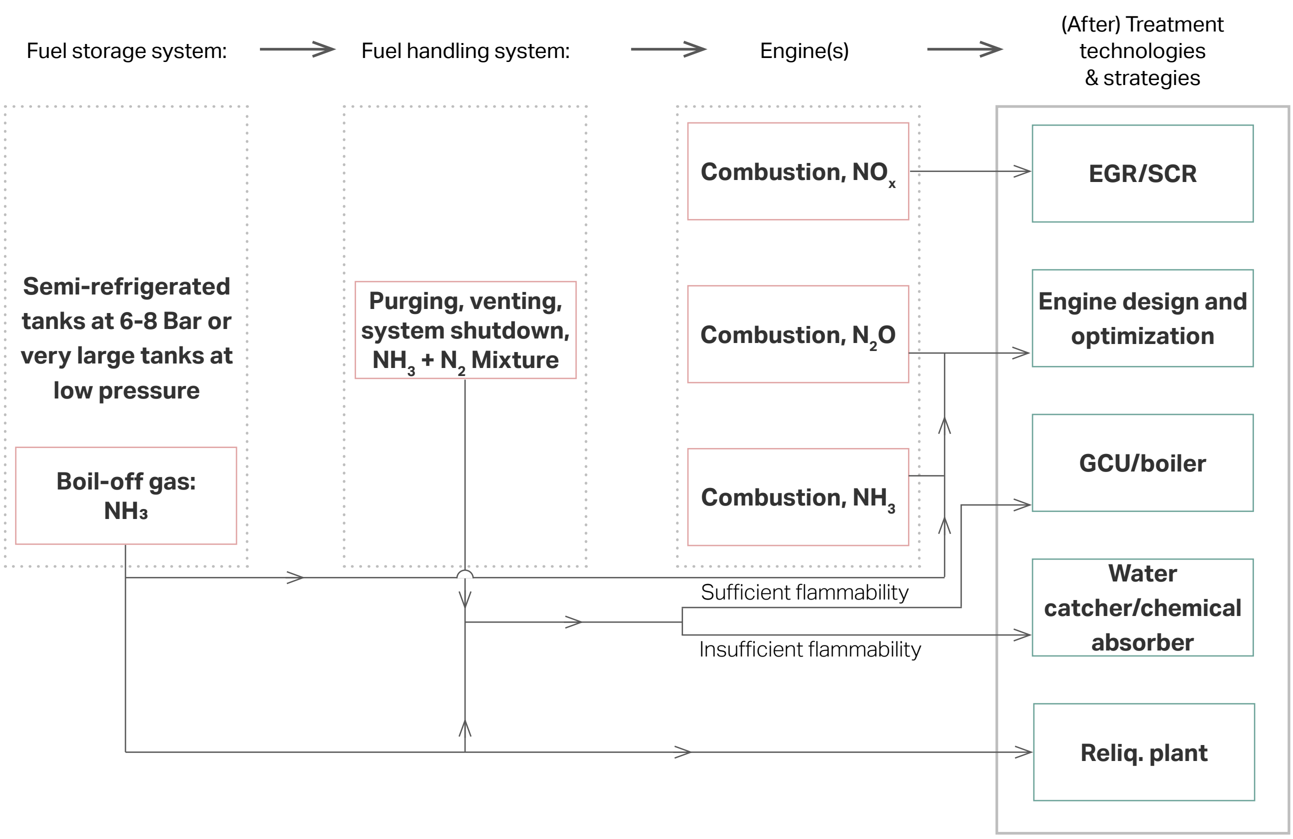
Purging and venting operations, including system shutdowns and fuel changeovers, will create a mixture of typically N_2 and NH_3 that needs to be treated. Depending on the flammability of the mixture, the proper emission management technology can be selected. In this case, an arrangement similar to existing LNG vessels with a GCU or boiler can be expected. If the mixture is insufficient for combustion, a water catcher/chemical absorber system would be needed.

It is also assumed that NO_x emissions can be treated using an EGR for two-stroke engines and an SCR for four-stroke engines, based on input from engine manufacturers.

8.2 Scenario 1

Scenario 1 is more complex than scenario 0, mainly due to the introduction of NH_3 BOG management. The scenario consists of a semi-refrigerated fuel tank (at 6-8 bar) or a fully refrigerated fuel tank (at ambient pressure), one emission management technology for the fuel handling system (a GCU/boiler or water catcher/chemical absorber) based on NH_3 levels, and one after-treatment technology for NO_x emissions. BOG can be managed in different ways, either using one of the existing emission management technologies or a reliquefication plant. This scenario also assumes that ammonia slip and N_2O emissions are successfully managed through engine design and optimization. Figure 13 provides an overview of scenario 1 conditions and emission management technology options. Cylindrical or bi-lobe Type-C semi-refrigerated fuel

Figure 13: Ammonia emission scenario 1



tanks can be used typically for tank volumes up to 7,000 m^3, which can be used as deck tanks on vessels like tankers and bulk carriers. Fully refrigerated prismatic Type-A/B or membrane tanks can store larger volumes (up to 20,000 m^3) and can be used for larger vessels and container vessels where the tanks are placed inside the hull. Both semi- and fully refrigerated fuel tanks have lower tank pressures than fully pressurized ones and require BOG management.

If possible, BOG should be effectively utilized on board for a value-added activity. BOG can be managed by consuming it in low-pressure four-stroke engines, which are typically used as auxiliary gensets (like LNG-fueled vessels such as LNG carriers). Another option is to have a reliquefication plant that will liquefy the BOG and send it back to the fuel tank (like LPG vessels). The BOG can also be used in a boiler if there is onboard heat demand. The final option is to use a GCU, which results in a non-value-added activity as the gas is not utilized better. The best BOG management technology selection will depend on the specific vessel being considered, including type, size, onboard requirements, and machinery configuration optimization.

Purging and venting operations, including system shutdowns and fuel changeovers, are handled similarly to scenario 0. With the introduction of BOG in scenario 1, the BOG can potentially be treated using the same system used for purging and venting operations, including a GCU/boiler or water catcher/chemical absorber (or even an engine). Depending on the purity of the gas mixture, a reliquefication plant used for BOG management could also be considered as an emission management technology for purging and venting operations.

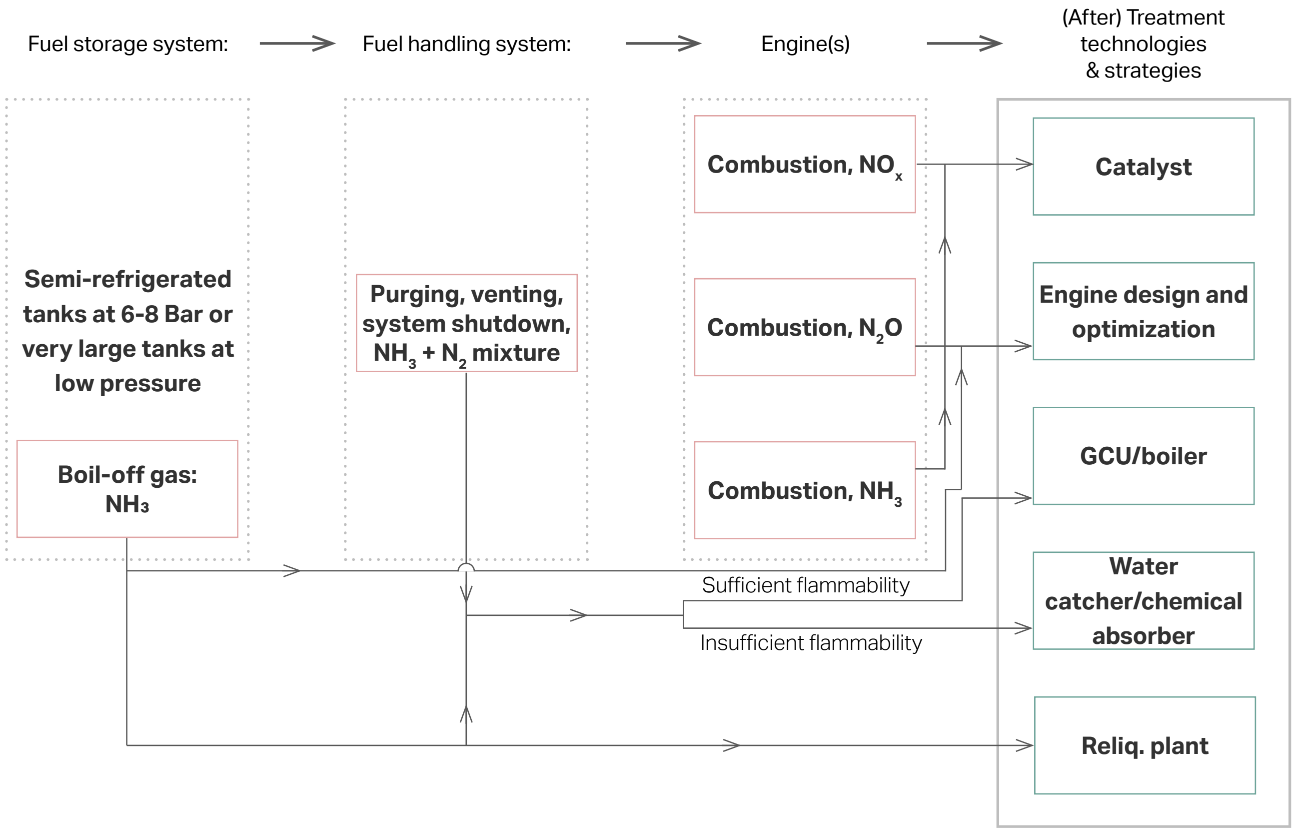
Like scenario 0, engine technology providers expect that engine design and optimization adjustments will be sufficient to ensure that ammonia slip is within acceptable limits, and that N_2O emission levels are not higher than for conventional fuels. It is also assumed that NO_X emissions can be treated using an EGR for two-stroke engines and an SCR for four-stroke engines. If additional NH_3 is needed as a reducing agent in the SCR, the use of BOG can also be considered.

8.3 Scenario 2

Scenario 2 is the most complex according to input from ongoing engine development teams. The main difference from scenarios 1 and 2 is the addition of an after-treatment technology to manage engine exhaust emissions. It is possible that NH_3 slip and/or N_2O emission levels are above acceptable limits and need to be treated. While maintaining the additional complexity of BOG management, scenario 2 considers what is required to treat excessive NH_3 slip and N_2O emissions. Figure 14 provides an overview of scenario 2 conditions and emission management technology options.

Scenario 2 addresses the BOG management and purging and venting operations as with scenario 1, where a combination or selection of a GCU/boiler, water catcher/chemical absorber, and/or a reliquefication plant is needed. If N_2O emission levels are too high, an after-treatment technology like a catalyst would be required. N_2O emissions can also be treated as part of an SCR in combination with NO_X emissions if properly dimensioned. If NH_3 slip levels are higher than needed as a reducing agent in an SCR for NO_X/N_2O emission reduction, it is possible to have a combined catalyst designed to reduce NH_3 slip to acceptable levels after the SCR (as presented in Section 7.6).

Figure 14: Ammonia emission scenario 2



09 Conclusions

With a currently unknown emission profile from ammonia DF ICEs, it can seem as if all that can be done is wait for more clarity. However, we believe now is the time for key stakeholders to come together and develop the needed emission management solutions that will mitigate the identified emission risks. As initial guidance and a basis for further discussion, we have provided ammonia-related emission thresholds including target levels for ammonia of 10-30 ppm and for N_2O of 0.06 g/kWh.

While ammonia combustion presents emission risks that are not fully known today, emission management technologies that can sufficiently mitigate the potential risks are available or under development. For the three emissions scenarios studied in this project, at least 3-4 different treatment technologies are needed to achieve acceptable emissions levels. These treatment technologies are being developed and supplied by different technology providers in parallel with engine manufacturers.

All stakeholders, including engine manufacturers and emission management technology suppliers, must work together to develop ammonia-fueled vessel designs and optimize the use of materials, costs, and overall system efficacy. Without collaboration, specific parts of the vessel design will be developed in isolation, and interconnected systems and technologies could end up unnecessarily oversized, inefficient, or costly. There is a critical need for standardization and alignment on safety levels and fast-tracking prescriptive guidance. Regulators should follow upcoming tests and technology development closely to ensure that practical, effective, and realistic targets and goals are set from the beginning.

With industry-wide collaboration during engine and emission management technology development and ammonia-fueled vessel design, ammonia emission risks should not be a showstopper for the ammonia-based fuel pathways. Increased focus has been placed on the emission risks of ammonia as a marine fuel during the design and development on ammonia DF ICEs, which can give confidence that safety and emissions expectations are being properly set from the beginning. This proactive approach is also informed by the learnings from the introduction of LNG as a marine fuel where methane slip was not fully understood and addressed upfront.

Due to ongoing development of ammonia DF engines and associated emission management technologies, the information and scenarios presented in this paper should be considered as a foundation of collaborative knowledge and collective intelligence for the development of sustainable and safe ammonia-fueled technology systems and ship designs.

10 Related projects and future development areas

To properly assess the viability of ammonia-based alternative fuel pathways like blue and electro-ammonia, WTT emissions also need to be better understood. For blue ammonia, the ability to reduce upstream fugitive emissions needs to be fully understood. Upstream fugitive emissions are not covered in this paper but are currently being studied at the MMMCZCS to enable a complete viability assessment of the blue ammonia pathway.

In addition to assessing onboard emissions from ammonia-fueled vessels, the MMMCZCS is actively engaged in other areas related to enabling ammonia-based fuel pathways, as this pathway is currently the least mature. This includes working to understand the blue ammonia value chain, including upstream fugitive emissions, carbon capture, storage and utilization, and regulatory barriers to implementation. Ongoing vessel-related projects are focused on ammonia safety, newbuild preparation and conversion from fuel oil and LNG to ammonia, the environmental impacts of ammonia leakages, ammonia bunkering, development of ammonia-fueled solid oxide fuel cells (SOFC), and dedicated ammonia-fueled vessel design projects, including initial design development of an ammonia-fueled gas carrier and container vessel.

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