Emissions from engine operations with ammonia

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Introduction

The international shipping sector is undergoing a historic transformation to meet the IMO's target of achieving net-zero greenhouse gas emissions by or around 2050, compared to 2008 levels. In addition, the sector must comply with increasingly stringent regulations on sulfur, NO_x, and particulate emissions, while also ensuring fuel diversity and security of supply.

Ammonia has emerged as one of the most promising alternatives to conventional marine diesel and heavy fuel oil. Its appeal as a marine fuel stems from several important factors:

- **Flexible Production:** Ammonia can be produced from both fossil-based and sustainable sources. "Green ammonia" is synthesized using renewable electricity to generate hydrogen, which is then combined with nitrogen from the air via the Haber-Bosch process. This Power-to-X approach results in a fuel with minimal life-cycle greenhouse gas emissions.
- **Zero-Carbon Combustion:** When combusted, ammonia does not release carbon dioxide (CO_2), making it a truly carbon-free fuel at the point of use. However, although NO_x emissions are still present - as with conventional marine fuels - the use of ammonia also introduces the risk of ammonia slip (release of unburned ammonia) and the possible formation of nitrous oxide (N_2O, or laughing gas), a potent greenhouse gas. These emissions require careful management through advanced engine design and aftertreatment systems to minimize their environmental and climate impacts.
- **Established Infrastructure Potential:** Ammonia is already widely produced, transported, and stored globally, primarily as a fertilizer precursor. This existing infrastructure can, to some extent, be leveraged for bunkering and supply to ships. Major engine manufacturers are actively developing ammonia-fueled propulsion systems.

While the global ammonia industry is mature, the production of green ammonia -derived entirely from renewable energy - is still in its early development phase. Large-scale projects are underway, and capacity is expected to grow rapidly. Nonetheless, cost and availability of green ammonia remain key challenges for the maritime sector's climate ambitions.

It is important to note that ammonia has a high auto-ignition temperature and requires specialized combustion strategies or pilot fuels for reliable ignition in marine engines. Modern concepts often use a small amount of conventional fuel to initiate combustion and ensure stable engine operation.

A significant advantage of ammonia is its potential for zero-carbon propulsion. However, retrofitting existing ships for ammonia use entails substantial engineering

modifications—fuel supply systems, storage tanks, engine components, and safety systems must all be adapted or replaced to handle ammonia's specific properties. Additionally, ammonia's lower energy density compared to traditional marine fuels means larger tanks are needed to maintain range.

Ammonia presents notable challenges as a marine fuel: it is highly toxic, corrosive, and has a strong pungent odor. Enhanced safety measures must be implemented to manage risks of leaks and exposure. Material compatibility is a critical consideration to prevent equipment degradation or failure. Strict safety regulations and handling protocols are essential for the use of ammonia as a marine fuel.

Currently, ammonia is not associated with direct global warming potential (GWP) or ozone depletion potential. While it does participate in certain atmospheric processes, ammonia itself has a very short atmospheric lifetime. The main concerns related to its release are safety risks and its negative impact on local air quality.

Current state of ammonia engine technology

In November 2023, Wärtsilä announced the worlds first commercial ammonia engine, the Wärtsilä 25 Ammonia. The engine is a 4-stroke dual fuel (DF) engine developed from the existing LNG DF version, which uses diesel pilot injection to ignite a premixed charge of ammonia and air. The engine delivers up to 305 kW per cylinder, with 6-to-9-cylinder versions available.

Swiss engine manufacturer Win-GD was the first company to offer a 2-stroke engine dual fuel solution for ammonia. Currently the company offers three engine bore sizes for ammonia DF, covering a range of 5.1 to 31 MW. The engines employ a high-pressure direct injection principle (HPDI), as opposed to the low-pressure, premixed combustion principle used for the company's X-DF LNG fueled engines.

Everllence (formerly: MAN Energy Solutions) are still in the process of developing and testing their 2-stroke and 4-stroke engine concepts for ammonia. On December 3rd, 2024, MAN ES announced in a press release that they were scaling up their ammonia engine testing program from one to all four cylinders on their 2-stroke test engine. According to the press release, focus is now on tuning of the combustion process and emissions, as well as other parameters and systems that require the complete engine to operate with ammonia combustion. The 4-stroke development is driven by large collaboration projects such as AmmoniaMot 1 & 2.

The low speed 2-stroke ammonia engine combustion concepts offered by WIN-GD and MAN ES are based on high pressure direct injection of ammonia and fuel or diesel oil through separate fuel injectors. This principle enables a high energy share of ammonia in the combustion process as it makes it possible to operate with a stratified combustion,

in which conditions are favorable for complete combustion of ammonia. For 4-stroke medium-speed engines, the conditions are generally considered less suitable for direct injection of ammonia. As a result, a premixed dual-fuel combustion strategy with diesel pilot ignition may well be the preferred approach for future 4-stroke ammonia engines.

The difficulties in achieving fast ignition and combustion of ammonia have resulted in an interest in using other fuels as ignition promoters, such as methane and hydrogen. These fuels ignite and burn very easily in the given conditions and provide the energy necessary to accelerate the combustion of ammonia even in lean combustion conditions. Hydrogen can be produced on demand by high temperature cracking of ammonia, while methane will need to be carried and stored in separate cryogenic tanks.

Ammonia engines operating with stoichiometric mixtures may however also be spark-ignited. When operating near stoichiometric conditions, ammonia can be ignited using high-power spark systems capable of delivering substantial amounts of energy to support consistent ignition. This enables the engine to operate without pilot fuel and hence large eliminate emissions related to diesel combustion, including CO2. If ammonia becomes a widespread fuel option, SI engine concepts may in time be the solution that can provide the highest emission reductions.

The dual fuel combustion process with methanol or ammonia is known to have a large impact on the formation of NO_x and PM (including black carbon) and in addition lead to formation of several new combustion products, which may require specific approaches to control and remove by subsequent aftertreatment of the exhaust gas.

Emissions from dual fuel engines

Emission products from pilot fuel combustion

Disregarding the main fuel (ammonia) in a dual-fuel combustion engine, the combustion of a hydrocarbon pilot fuel (containing hydrogen, carbon, and sulfur) with air (O_2 and N_2) results in the formation of several combustion products:

$$C_X H_Y S_Z + O_2 + N_2 \rightarrow CO_2 + H_2O + SO_2 + NO + NO_2 + CO + HC + PM$$

In this equation, excess O_2 and N_2 on the product side are omitted for simplicity.

CO_2 and H_2O are the ideal (complete) combustion products, along with surplus O_2 which is always present in diesel combustion.

SO_2, a regulated emission, is the dominating product from combustion of fuel sulfur.

NO_X, the sum of NO and NO_2, is a regulated emission for which conformity must be ensured by proper engine control and aftertreatment. It is formed when atmospheric and fuel bound nitrogen is oxidized at high temperatures.

CO, HC (or THC, for total hydrocarbons) and PM (particulate matter) are incomplete combustion products. CO and HC are normally present in concentrations in the range of 50-500 ppm and are not regulated for marine engines under IMO.

PM, also called soot, is a collecting term for the carbon particles which are formed by the combustion of fuel oil. Measured PM from engines also contain ash, lubrication oils and condensed species such as hydrocarbons and secondary particles.

This white paper does not discuss classical emissions such as hydrocarbons (HC), carbon monoxide (CO), and particulate matter (PM) from dual-fuel ammonia engines in detail. This is because the proportion of ammonia used in dual-fuel engines is relatively high. As a result, the levels of HC, CO, and PM are expected to be significantly lower than those from conventional marine diesel engines. Moreover, these emission components have already been extensively characterized in the literature for similar dual-fuel LNG engines and are not considered critical for compliance or environmental impact in the context of ammonia operation. Therefore, this paper focuses on the new challenges and emission species introduced specifically by ammonia combustion, such as ammonia slip and N_2O.

Emission products from ammonia combustion

Ammonia as fuel is very different from hydrocarbons. Looking at the chemical composition, hydrogen is bound to nitrogen rather than carbon. This effectively eliminates emissions of CO_2 and black carbon, while introducing other potentially problematic emissions:

$$NH_3 + O_2 + N_2 \rightarrow H_2O + NO + NO_2 + N_2O + NH3$$ + HCN? + secondar particles

In contrast, a range of new emission species may potentially be formed, as indicated in the reaction above simplified reaction mechanism. These will be discussed in this section and are based on existing experiences from various engine concepts.

NH3

Ammonia has relatively low reactivity and a high autoignition temperature, making efficient combustion more challenging than with conventional fuels. Complete oxidation of ammonia to nitrogen (N_2) and water (H_2O) is achieved only at sufficiently high combustion chamber temperatures. If the temperature is too low, oxidation is

incomplete, leading to significant emissions of unburned ammonia (NH_3), commonly referred to as ammonia slip.

To minimize NH_3 emissions, it is essential that ammonia is exposed to the hottest regions of the combustion process, where complete oxidation is most effective. This can be achieved in high-pressure direct injection (HPDI) engines, where ammonia is injected directly into the combustion chamber, allowing it to mix with the hot combustion products. This approach is the preferred concept for low-speed 2-stroke engines.

The HPDI principle has been successfully applied by WinGD in their new X-DF-A engine - a 2-stroke, low-speed engine developed for large ships. Full-load tests have shown that the engine can operate with ammonia as the main fuel, providing up to 95% of the total energy input, while only 5% of the energy comes from pilot diesel used to ensure reliable ignition. Emissions measurements demonstrated very low ammonia slip, with NH_3 emissions remaining below 10 ppm at full load. These low emissions are achieved without the need for exhaust aftertreatment, such as an Ammonia Slip Catalyst (ASC), highlighting the effectiveness of HPDI and optimized combustion control in minimizing unburned ammonia[1].

In low-speed 2-stroke HPDI engines, ammonia passes through the hottest regions of the combustion chamber, reducing the risk of incomplete combustion. This also has a significant impact on other emissions resulting from incomplete ammonia combustion.

The use of direct injection of ammonia in medium- and high-speed engines presents additional challenges due to ammonia's low ignition properties and high heat of evaporation. These factors can increase the risk of misfires unless the ammonia substitution rate - that is, the proportion of energy supplied by ammonia relative to diesel - is kept low. Moreover, geometric factors, such as smaller combustion chambers and shorter injection intervals, can further complicate stable and reliable combustion. For these reasons, dual-fuel operation - where ammonia is premixed with the intake air - is often the preferred solution.

In engines utilizing a premixed combustion principle, ammonia is thoroughly mixed with the intake air - often supplied in the gaseous state, meaning it does not provide a cooling effect on the mixture. Nevertheless, an ignition source - such as a small amount of pilot diesel- is still required to initiate combustion, making it a dual-fuel system, unless spark ignition is used.

[1]WinGD (2024). Press release: WinGD delivers exceptional results in full-load X-DF-A ammonia engine test. Retrieved from wingd.com

Nadimi et al.[2] investigated ammonia slip emissions from a modified single-cylinder diesel engine with a displacement of approximately 0.4 liters (maximum power output 6.4 kW), operated in premixed dual-fuel mode with port-injected ammonia and diesel pilot injection. The engine was tested at full load (at 1200 rpm) with varying diesel-to-ammonia ratios and air–fuel ratios between 1.35 and 1.52. The results showed that unburned ammonia emissions increased significantly as more diesel was replaced with ammonia - reaching up to 14,800 ppm at the highest ammonia share (84.2% of the fuel energy).

Recent full-scale tests also offer valuable insights into ammonia slip from modern marine ammonia engines. The IHI 28ADF is a medium-speed, six-cylinder, four-stroke engine specifically developed for ammonia fueling, delivering 1,618 kW at 750 rpm. Using a premixed combustion concept - where gaseous ammonia is mixed with intake air and ignited by pilot fuel - the engine achieved an ammonia fuel share of over 90% at all loads when operating in E3 mode (a standardized test cycle for marine engines)[3]. Test results showed that engine-out (pre-catalyst) ammonia emissions could exceed 10,000 ppm. However, with an exhaust gas catalyst installed, ammonia emissions were consistently reduced to approximately zero across the entire load range.

When premixed ammonia is combusted, emissions of unburned ammonia are typically lowest near stoichiometric conditions. This has been observed in in-house engine experiments using a high-speed 9-liter engine with pilot injection. Similar observations are also reported by Jespersen et al. for spark ignited (SI) combustion.[4] However, in premixed combustion, ammonia emissions will typically still be on the order of a few thousand ppm or higher. These raw emissions can, however, be managed using aftertreatment systems.

The substantial ammonia emissions observed in premixed combustion can be attributed to several factors:

- **Low Reactivity and Slow Flame Speed:**
  Ammonia's low reactivity and slow flame speed make the combustion process more sensitive to lean mixtures, increasing the risk of incomplete combustion.
- **Lower Combustion Temperatures:**
  A higher air-fuel ratio reduces combustion temperature, which can hinder the complete oxidation of ammonia.

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[2] Nadimi, E., Przybyła, G., Lewandowski, M. T., & Adamczyk, W. (2023). Effects of ammonia on combustion, emissions, and performance of the ammonia/diesel dual-fuel compression ignition engine. Journal of the Energy Institute, 107, 101158. https://doi.org/10.1016/j.joei.2022.101158

[3] Masuda, Y., Mashima, Y., Kazama, S., Naruse, H., Aiba, K., & Hirose, T. (2025). *Development of an ammonia-fueled engine (28ADF) for future marine industries*. 31st CIMAC World Congress 2025, Paper No. 214.

[4] Jespersen, M. C., Rasmussen, T. Ø. H., & Ivarsson, A. (2024). Widening the operation limits of a SI engine running on neat ammonia. Fuel, 358, 130159. https://doi.org/10.1016/j.fuel.2023.130159

- **Incomplete Flame Propagation:**
  Due to lower temperature and reactivity, the flame cannot efficiently propagate throughout the entire cylinder. This is especially true in small cavities, crevice volumes, and along cylinder and piston walls, where thicker quenching layers can form.

Ammonia present in these colder regions often escapes unburned with the exhaust gases because there is insufficient time and temperature for full oxidation during the piston's expansion stroke.

N2O

N_2O, commonly known as nitrous oxide or laughing gas, is a highly potent greenhouse gas with a Global Warming Potential (GWP) of 273 (according to IPCC AR6) over both 20-year and 100-year timescales. Its estimated atmospheric lifetime is 114 years. This means that, per tonne emitted, N_2O causes 273 times more global warming than CO_2. Since the molecular weights of CO_2 and N_2O are nearly identical, the GWP is also comparable on a volumetric basis.

A concentration of 100 ppm (0.01% vol) N_2O is equivalent to a CO_2 concentration of 2.73% in terms of global warming potential. Therefore, even low concentrations of N_2O can significantly impact the CO_2-equivalent emissions from ammonia dual-fuel engines, reducing one of the main advantages of ammonia as a zero-carbon fuel.

During the combustion of ammonia in an engine, local incomplete oxidation can lead to the formation of N_2O as an intermediate product. Generally, N_2O is produced during ammonia combustion at temperatures between approximately 600 °C and 1,000 °C. At lower temperatures, reaction rates are too slow to generate significant amounts of N_2O. At higher temperatures, especially near flame temperatures, N_2O is rapidly decomposed to N_2 and O_2. Consequently, N_2O formation mainly occurs at moderate temperatures, where oxidation of ammonia to N_2O is significant, but subsequent conversion to N_2 has not yet been completed.

Even in engines with premixed combustion—where ammonia and air are thoroughly mixed before ignition—local regions can exist, such as near the cylinder walls (cold zones) or in crevices and gaps, where the temperature is too low for complete conversion of ammonia to N_2. In these areas, ammonia may undergo only partial oxidation, leading to the formation of N_2O.

Experimental data from a high-speed 9-liter engine in our laboratory - where one of five cylinders operated on premixed ammonia with diesel pilot injection - show that N_2O emissions are lowest near stoichiometric conditions, with measured levels around 25 ppm. At higher excess air ratios (e.g., above 2), N_2O emissions can easily exceed 100

ppm. Similar trends have also been observed by Jespersen et al. for SI combustion[5]. Full-scale testing of the IHI 28ADF ammonia-fueled engine showed that engine-out N_2O emissions were measured at approximately 20 ppm across a broad load range[6].

Engines operating on a more diesel-like principle with diffusion combustion, such as 2-stroke low-speed HPDI engines, are generally less susceptible to N_2O formation. In these engines, combustion is concentrated around a hot flame within the combustion chamber, and this mode is less influenced by cold cylinder walls. As a result, the formation of local cold zones - where incomplete oxidation and hence N2O formation could otherwise occur - is limited.

For large low speed marine engines with direct injection, the engine manufacturer Everllence has stated that N_2O emissions can typically be expected to be below 5 ppm. Similarly, WinGD reports that N_2O emissions can in some cases be as low as 3 ppm[7].

N_2O is relatively difficult to oxidize in the exhaust gas, even in the presence of a catalyst. Effective catalytic decomposition of N_2O generally requires temperatures around 500°C, which are often not reached in the exhaust system under typical engine operating conditions, such as after the turbocharger. Based on these observations, this issue is particularly relevant for engines with premixed combustion, where the need for effective N_2O aftertreatment may be greater.

NOx

In ammonia engines, a potential issue is the formation of NO. The primary mechanism for NO formation is the oxidation of fuel-bound nitrogen, which is more easily oxidized than the molecular nitrogen present in the combustion air. However, high concentrations of NO in the exhaust can be effectively reduced using most commercial SCR catalyst technologies, ensuring compliance with current IMO NOx regulations.

NO_x ($NO + NO_2$) is also produced during ammonia combustion, particularly under certain operating conditions. In premixed combustion, fuel-bound NO_x tends to dominate total NO_x emissions at excess air ratios above approximately 1.3, where emission levels can be relatively high - often exceeding 4,000 ppm. Notably, experiments have shown that NO_x emissions decrease sharply near stoichiometric conditions, frequently dropping below 1,000 ppm at stoichiometry. Given the relatively high ammonia emissions

[5] Jespersen, M. C., Rasmussen, T. Ø. H., & Ivarsson, A. (2024). Widening the operation limits of a SI engine running on neat ammonia. Fuel, 358, 130159. https://doi.org/10.1016/j.fuel.2023.130159
[6] Masuda, Y., Mashima, Y., Kazama, S., Naruse, H., Aiba, K., & Hirose, T. (2025). *Development of an ammonia-fueled engine (28ADF) for future marine industries*. 31st CIMAC World Congress 2025, Paper No. 214.
[7] https://ammoniaenergy.org/articles/emission-performance-of-ammonia-fueled-two-stroke-marine-engines/

associated with premixed combustion, NO_x may be effectively reduced using SCR technology.

For engines using direct injection of ammonia, such as low-speed 2-stroke dual-fuel engines, thermal NO_x is the primary source of emissions. In these engines, NO_x emissions are significantly lower than those observed with conventional diesel operation[8]. According to WinGD, ammonia operation results in nitrogen oxide emissions at least 40% lower than with diesel fuel. Everllence similarly reports that NO_x emissions in ammonia mode are approximately 40% lower than in fuel oil mode, with recent full-scale engine tests at their Research Centre in Copenhagen showing reductions of at least 50%. Consequently, the $DeNO_x$ (SCR) system required to achieve IMO Tier III limits for ammonia-fueled engines may actually be smaller than for engines operating on diesel or fuel oil.

Secondary Particle Formation from Ammonia Combustion

Particle formation from ammonia combustion in engines differs significantly from that seen with conventional, hydrocarbon-based fuels. Ammonia contains no carbon, so soot (black carbon) is essentially not formed during combustion, and emissions of primary particles are thus very low. However, secondary particles - particularly in the form of ultrafine aerosols - can form as a result of chemical reactions occurring after combustion.

When ammonia slip occurs in the exhaust gas, the ammonia can react with acids formed from other pollutants such as NO_x (nitrogen oxides) and possibly SO_x (sulfur oxides), either within the exhaust system or in the surrounding atmosphere. NO_x can be converted to nitric acid (HNO_3), and SO_x can be oxidized to sulfuric acid (H_2SO_4). When ammonia (NH_3) encounters these acids, it forms salts such as ammonium nitrate (NH_4NO_3) and ammonium sulfate ($(NH_4)_2SO_4$). These compounds condense to form fine and ultrafine particles, also known as secondary inorganic aerosols (SIA).

The quantity and type of particles generated depends on the exhaust conditions, especially temperature, humidity, and the concentrations of ammonia, NO_x, and SO_x. If the engine is also equipped with SCR (Selective Catalytic Reduction) aftertreatment, interactions between excess ammonia and NO_x can further increase the formation of secondary particles. However, installation of an efficient ammonia slip catalyst (ASC) in the exhaust system can significantly reduce or even virtually eliminate the formation of these secondary salt aerosols, as excess ammonia is removed before it can react with the acids.

[8] https://ammoniaenergy.org/articles/emission-performance-of-ammonia-fueled-two-stroke-marine-engines/

HCN – hydrogen cyanide

Hydrogen cyanide (HCN) is an intermediate combustion product that can form when ammonia is burned together with hydrocarbons such as diesel or fuel oil. HCN is acutely toxic to humans and represents a potential health risk. This risk is heightened if the exhaust is not properly diluted, for example, in situations where crew members or passengers are directly exposed to the exhaust plume.

During the simultaneous combustion of ammonia and a secondary fuel, hydrogen- and carbon-containing intermediates produced during the process can react with nitrogen compounds, potentially leading to the formation of HCN. This typically occurs under oxygen-deficient conditions, at elevated combustion temperatures, and when high concentrations of both ammonia and carbonaceous compounds are present.

Model studies have shown that adding ammonia to a diesel-like fuel (such as n-heptane) can increase the formation of HCN during combustion[9]. HCN is primarily produced in high-temperature regions (above approximately 1400 K) and under fuel-rich conditions (equivalence ratio ≥ 2), where both carbon- and nitrogen-containing radicals are present.

However, HCN is not particularly stable at the high temperatures inside the engine and will often react further. If the combustion is incomplete and the temperature drops rapidly, HCN may remain sufficiently stable to be present in the exhaust gas.

There does not appear to be published material on direct measurements of HCN emissions from dual-fuel engines operating on ammonia. HCN is generally expected to occur only in very small amounts (lower ppm level), as it is rapidly consumed at the high temperatures typical of combustion engines and because modern engines generally ensure good oxygen availability. However, under highly incomplete combustion conditions, measurable concentrations of HCN may occur in the exhaust.

HCN can however be reduced effectively with aftertreatment systems such as oxidation catalysts and SCR under normal operating conditions. Ammonia fueled engines will generally be equipped with an SCR for NOx reduction to comply with IMO Tier II and III, which the risk of exposure to HCN is very low.

[9] Pedersen, K. A.; Lewandowski, M. T.; Schulze-Netzer, C.; Pasternak, M.; Løvås, T.
Ammonia in Dual-Fueled Internal Combustion Engines: Impact on NOx, N_2O, and Soot Formation.
Energy Fuels 2023, 37, 17585–17604. https://doi.org/10.1021/acs.energyfuels.3c02549

Measuring Emissions from Ammonia Combustion

This section reviews various measurement principles for detecting emissions from ammonia combustion, including ammonia, nitrous oxide, and HCN. Although these emissions are not unknown, they are not yet widely monitored within the maritime industry, as they have not been considered significant in relation to conventional fuels.

N_2O (NDIR, FTIR, and GC-ECD)

Several methods are available for measuring N_2O in exhaust gas, with the most commonly used being NDIR, FTIR, and GC-ECD. NDIR (Non-Dispersive Infrared Spectroscopy) operates by passing infrared light through a measurement cell with a continuous flow of sample gas. N_2O absorbs light at specific infrared wavelengths, and this absorption is detected and converted into a concentration reading. The main advantages of NDIR are its ability to provide continuous, real-time measurements and its robust, user-friendly operation. However, NDIR can be influenced by interference from other gases such as water vapor or carbon dioxide, and it is typically limited to measuring one or a few gases at a time.

FTIR (Fourier Transform Infrared Spectroscopy) is based on a similar principle but measures the entire absorption spectrum in the infrared range for the sample gas. This makes it possible to analyze multiple gases simultaneously with high selectivity and sensitivity. FTIR is suitable for both advanced process monitoring and research, but the instruments are more expensive and complex than NDIR, requiring ongoing calibration and maintenance.

Gas chromatography with electron capture detection (GC-ECD) is a well-established and widely used method for measuring N_2O in exhaust gas, offering both high sensitivity and good accuracy. According to Zafonte et al.[10], the measurement is carried out by collecting sample gas in bags - such as Tedlar® bags - typically after dilution with background air. Before analysis, the samples may undergo pretreatment to remove impurities and interfering substances such as water vapor, hydrocarbons, and oxygen by filtration and, if necessary, chemical scrubbing. The pretreated sample is then analyzed using a gas chromatographic system equipped with an electron-capture detector, where N_2O is separated from other components and measured with high sensitivity. The result is corrected for the background level of N_2O to determine the actual emission. The method is calibrated using standard gases of known concentrations, and the instrument's

[10] Zafonte, L., Rieger, P.L., Fuentes, M., & Ling, R. (2010). *A Precise Gas Chromatographic Method Using ECD Detection for the Measurement of Nitrous Oxide in Vehicle Exhaust*. California Air Resources Board. Presented at 2010 EPA/AWMA Symposium on Air Quality Measurement Methods and Technology, Los Angeles, California.

response is often evaluated using a non-linear calibration curve to ensure accurate quantification across the entire measurement range. This method has a very low detection limit and provides high precision, making it well suited for reference or verification purposes

In summary, NDIR and FTIR are the preferred technologies for real-time measurement of N_2O in vehicle exhaust, while GC-ECD is mainly used for laboratory analysis and as a reference method where particularly high requirements for sensitivity and accuracy apply.

NH3 (TDLAS)

As described by Li et al. [11], ammonia slip in exhaust gas can be measured using Tunable Diode Laser Absorption Spectroscopy (TDLAS). In this method, a sample of exhaust gas is introduced into a heated gas cell of known length. A tunable diode laser—typically a mid-infrared quantum cascade laser—is adjusted to a specific absorption band for NH_3 (for example, around 1103.45 cm^{-1}). The laser light passes through the gas cell, and a sensitive photodetector measures the transmitted light. By comparing the laser intensity before and after passing through the cell, the amount of NH_3 present is determined. The concentration is calculated using the Beer-Lambert law, and the system is calibrated with standard gases. Wavelengths in the mid-infrared region are chosen to minimize interference from other gases and to target strong absorption features of ammonia.

In practice, TDLAS instruments for NH_3 typically achieve detection limits in the ppm range and can provide measurement precision better than 5% under well-controlled conditions. This makes TDLAS suitable for both research and industrial monitoring of ammonia emissions in combustion exhaust.

NH_3 (CLD)

The ammonia content in air or flue gas can be measured very precisely using advanced chemiluminescence equipment. This method is widely used in environmental and process monitoring, particularly for determining NOx (the sum of NO and NO_2), but it can also be used for the indirect measurement of ammonia.

The method works by first passing the sample through a heated converter, where both ammonia (NH_3) and nitrogen oxides (NO_2) are converted to nitric oxide (NO). When the sample is then mixed with ozone, a faint flash of light – chemiluminescence - is produced,

[11] Li, J., Guo, S., Wang, Z., et al. (2025). Measurement of NH_3 emission in CH_4/NH_3 combustion exhaust gas with the mid-infrared laser absorption. *Infrared Physics & Technology*, 147, 105802. https://doi.org/10.1016/j.infrared.2025.105802

which is detected with high sensitivity by the instrument. The intensity of the light is used to calculate the NO concentration in the sample.

With this approach, it is possible to measure not only ammonia but also NOx. The instrument first performs a measurement, recording only NOx (NO + NO_2). Afterwards, a second measurement is made in which both NOx and ammonia are converted to NO, and the total amount - i.e., NO + NO_2 + NH_3 - is measured. This combined value is referred to as Nt (total nitrogen), since all three components are converted to NO and subsequently detected by the chemiluminescence signal. To determine the ammonia concentration, the difference between the two measurements - Nt and NOx - is calculated, corresponding to the ammonia content in the sample.

The equipment is typically designed to measure very low concentrations and can detect ammonia down to parts per billion (ppb). Depending on the type of instrument used and its intended concentration range, dilution may be necessary. Some instruments are built to handle very high concentrations directly, while others—such as high-sensitivity environmental monitors—require dilution to measure accurately and to avoid overloading.

NH3 (FTIR)

Measurement of ammonia using FTIR (Fourier Transform Infrared Spectroscopy) is based on the principle that the ammonia molecule absorbs infrared light at characteristic wavenumbers. When a gas sample is passed through the FTIR instrument's measurement cell, the absorbance is recorded as a function of wavenumber, with NH_3 exhibiting distinct absorption bands, particularly around 930–970 cm^{-1} and 1600–1700 cm^{-1}. To ensure accurate measurements, a spectral range is selected where interference from other gases is limited. If necessary, the sample can be dried to prevent water vapor from interfering with the analysis, as water also has IR-active bands.

The measurement itself involves passing the gas sample through a measurement cell of suitable optical path length, after which the FTIR instrument records an infrared spectrum. The absorption bands attributed to NH_3 are identified and compared with reference spectra. The concentration of ammonia is determined using the Beer-Lambert law, where the absorbance at the selected wavenumbers is proportional to the concentration and the path length of the cell.

This method is selective and sensitive, and allows for the simultaneous measurement of multiple gases if desired. Furthermore, FTIR requires only minimal sample preparation and provides rapid analytical results. However, it is important to be aware of potential interferences from other IR-active gases, especially water vapor and certain organic

compounds, and to ensure that the instrument is regularly calibrated with standard gases to guarantee accurate quantification of NH_3.

HCN (GC, PTR-MS and FTIR)

There are several methods available for measuring HCN, each with its own advantage. One of the most used laboratory techniques is gas chromatography (GC). In this method, a gas sample is passed through a column where different components are separated. HCN is then detected using a selective detector, such as a nitrogen-phosphorus detector (NPD) or a mass spectrometer (MS), both of which are highly sensitive to cyanide compounds. It is important to note that GC is primarily used for off-line analyses, as samples require collection and pre-treatment; however, the method offers high precision and sensitivity.

Another method is Proton Transfer Reaction Mass Spectrometry (PTR-MS). In this technique, the gas sample is mixed with a special reagent so that certain compounds - such as HCN - accept an extra proton and become charged. These charged molecules can then be identified and measured in a mass spectrometer. PTR-MS is particularly suitable for real-time (on-line) measurement, as it enables rapid and direct analysis of low concentrations of HCN in complex gas mixtures. It also allows for the simultaneous measurement of several volatile compounds. However, the technology often requires regular calibration to ensure accurate distinction between compounds in complex exhaust gas matrices.

A third method is Fourier Transform Infrared (FTIR) spectroscopy, where infrared light is passed through the gas sample, and the resulting absorption patterns are analyzed to identify and quantify HCN. FTIR can be used both in the laboratory and in the field, and allows for continuous (on-line) measurement of HCN and other gases. However, it is important to pay particular attention to proper calibration and potential interferences from, for example, water vapor or other exhaust gas constituents in order to achieve sufficient sensitivity and accuracy for HCN.

Human Exposure Risks from Unburned Ammonia

Incomplete combustion of ammonia in marine engines can result in the release of unburned ammonia and byproducts such as nitrogen oxides (NO_x), nitrous oxide (N_2O), and - under certain conditions - hydrogen cyanide (HCN). The concentrations of these substances may exceed established safe exposure limits for humans. This raises important concerns regarding occupational and health risks for crew members and others potentially exposed to exhaust from ammonia-fueled vessels. Therefore,

understanding the formation mechanisms, emission levels, and potential health effects of both especially unburned ammonia and HCN is essential to ensuring safe working environments and informing future regulatory developments.

Information on TWA limits (8-hour exposure limits) for chemical substances in Denmark is published in the guidelines from the Danish Working Environment Authority, available on their website. For an overview of applicable limits at the EU level, the European Agency for Safety and Health at Work (EU-OSHA) provides harmonized European exposure limits. Relevant TWA and STEL values for ammonia and hydrogen cyanide are summarized in Table 1.

STEL (Short-Term Exposure Limit, 15 minutes) defines the maximum allowable concentration of a chemical substance for short-term exposure without health risk. STEL protects against adverse effects from brief, high exposures.

Details about STEL and TWA limits for ammonia and HCN can be found in the Danish Working Environment Authority's guidelines and in documentation from the European Agency for Safety and Health at Work (EU-OSHA).

Table 1. TWA and STEL exposure limits for methanol and formaldehyde according to the Danish Working Environment Authority[12]

Species		**TWA (8-hour)**		**STEL (15-minute)**	
		mg/m³	ppm	mg/m³	ppm
Ammonia	NH3	14	20	36	50
Hydrogen Cyanide	HCN	1	0.9	5	4.5

Emissions reductions

Recent development and testing of ammonia-fueled engines, such as the Wärtsilä 25 medium-speed, four-stroke marine engine, have provided valuable insights into emissions reduction possibilities associated with ammonia combustion[13]. The Wärtsilä 25, available in configurations with 6 to 9 cylinders and a power output up to 3.4 MW, utilizes pilot-ignited, dual-fuel technology with premixed combustion - where ammonia typically accounts for approximately 95% of the total energy supplied across a broad load range.

[12] TWA and STEL exposure limits for methanol and formaldehyde according to the Danish Working Environment Authority

[13] Krook, T., Engsbo, R., Torrkulla, J., & Hattar, C. (2025). *Ammonia-powered future: introducing Wärtsilä 25*. 31st CIMAC World Congress 2025, Paper No. 528.

Effective emissions control is achieved by combining optimized engine management with advanced aftertreatment systems. Ammonia slip and NO_x emissions are controlled using a selective catalytic reduction (SCR) system, where unreacted ammonia can react with NO_x and be removed. Any excess ammonia that remains after SCR treatment can be further reduced using dedicated oxidation catalysts, ensuring that overall emissions are kept very low.

Nitrous oxide (N_2O) emissions are also effectively managed. Due to optimized engine control and the relatively high temperature of the engine exhaust, aftertreatment systems are able to achieve more than a 50% reduction in N_2O emissions under suitable operating conditions. This high efficiency is a key factor in minimizing the climate impact of ammonia-fueled engines.

Similar results have been documented in full-scale tests with the IHI 28ADF ammonia engine[14], where N_2O emissions were substantially reduced across a wide range of load conditions by using appropriate catalyst-based aftertreatment. These findings demonstrate that, with suitable catalysts in place, N_2O emissions from ammonia-fueled engine operation can consistently remain at very low levels.

In contrast to conventional diesel engines, ammonia engines emit almost no soot or carbonaceous particles. However, significant quantities of fine salt aerosols may form under certain conditions. These can largely be mitigated with effective slip catalysts, which is particularly important for protecting air quality and health around vessels and port areas.

Hydrogen cyanide (HCN), another potential emission from ammonia combustion, can also be efficiently reduced using aftertreatment systems such as oxidation catalysts and SCR under typical operating conditions. Since ammonia-fueled marine engines will generally be equipped with SCR systems to meet IMO Tier II and Tier III requirements for NO_x reduction, the risk of HCN exposure is considered low.

For large, slow-speed engines employing direct injection of ammonia, studies have shown that engine-out emissions of both ammonia and N_2O are already very low. This reduces the critical need for extensive exhaust aftertreatment compared to premixed or high-speed engines. Nevertheless, to comply with IMO Tier III standards when operating on ammonia, some form of $DeNO_x$ system is still likely required, although, thanks to the inherently low NO_x emissions during ammonia operation, the aftertreatment system can often be less extensive than that used for traditional diesel engines.

[14] Masuda, Y., Mashima, Y., Kazama, S., Naruse, H., Aiba, K., & Hirose, T. (2025). *Development of an ammonia-fueled engine (28ADF) for future marine industries*. 31st CIMAC World Congress 2025, Paper No. 214.

Conclusion

The transition to ammonia as a marine fuel represents a significant step towards achieving the shipping industry's climate targets, primarily due to ammonia's elimination of CO_2 emissions at the point of use. Unlike conventional hydrocarbon fuels, ammonia combustion does not produce soot or black carbon, and can therefore significantly reduce particulate emissions from shipping. However, the use of ammonia introduces new challenges related to emissions of unburned ammonia (ammonia slip), nitrous oxide (N_2O), NO_x, secondary aerosols, and under certain conditions, hydrogen cyanide (HCN).

Recent technological advances have demonstrated that these emissions can be managed effectively in both medium-speed, four-stroke and low-speed, two-stroke ammonia engines. The combination of modern engine concepts with optimized combustion control and state-of-the-art aftertreatment

Measurement methods for ammonia engine emissions - such as NH_3, N_2O, and HCN - are generally well established and form a solid basis for reliable monitoring and control. However, many of these methods are primarily developed for laboratory use and controlled environments. In the maritime sector, onboard measurement presents specific challenges due to variable operating conditions, vibrations, humidity, and the need for robust instruments that can deliver accurate and fast results under demanding circumstances.

Moreover, emissions from ammonia engines differ significantly from those typically encountered in conventional diesel operation, both in their chemical nature and in the concentrations involved. Therefore, further development and adaptation of measurement technologies is likely required to ensure their suitability for routine onboard monitoring, long-term durability, and straightforward operation by vessel crews rather than laboratory staff.

Advancing these measurement techniques for maritime application will thus be crucial—not only to enable effective emission control and verification, but also to support documentation, classification, and compliance with increasingly stringent environmental regulations.

With continued innovation and systematic application of advanced aftertreatment, ammonia-fueled engines have the potential to deliver very low emissions of regulated and climate-relevant pollutants. Ammonia thus remains a strong candidate for deep decarbonization of international shipping - provided that remaining issues around toxicity, fuel handling, and the availability of green ammonia are also addressed in parallel.