D2.7 SAFE WORKING ENVIRONMENT IN LABORATORIES DEALING WITH AMMONIA

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Executive Summary

This report is describing safe working environment laboratories working with ammonia.

Due to the high toxicity level of ammonia, safety is one of the main concerns to address. Since ammonia use as fuel in ICE's is currently in testing phase early learning from the ammonia engine laboratories can provide essential knowledge on usage of ammonia as fuel and how to operate it safely. Ammonia engine laboratory testing teams contributed to this report providing knowledge on how they have operated the ammonia engine and the fuel system during testing.

The report also provides background knowledge on properties of ammonia and on the health hazard of ammonia.

Version and contribution control

Version	Date	Modified by	Modification description
V1.0	30.11.2022	Laura Sariola	First version
V1.1	22.12.2022	Laura Sariola	Final version

Glossary

Term	**Explanation**
STP conditions	standard temperature and pressure; 25°C, and 1 atm
Pasquill-Gifford stability classes	A method to for classifying atmospheric conditions

Acronyms and abbreviations

Acronym or abbreviation	**Description**
CO_2	Carbon dioxide, a greenhouse gas
ICE	Internal combustion engine
DF	Dual Fuel engine, able to run on both gaseous and liquid fuel
GHG	Green House Gas, such as carbon dioxide and methane
NO_x	Nitrogen Oxides, in this context not including N_2O

N_2O	Nitrous oxide, commonly known as laughing gas
PM	Particulate Matter
NH_4^+	Ionized ammonia
NH_3	Ammonia
H_2O	Water molecule
OH^-	Hydroxide, a diatomic anion
PRV	Pressure relief valveF
PPE	Personnel protective equipment
PAPR	Powered Air-Purifying Respirator
ppm	Parts per million

1 Introduction

Cross all industries decarbonization has become one of the most challenging goals that our generation must solve. Carbon dioxide (CO_2) emissions are greenhouse gases (GHG) that contribute to global warming. The shipping industry is responsible for global CO_2 emissions of 2.9% (European commission 2022). But emissions produced by the shipping industry are thought to only increase if action to reduce emissions is not taken. To reduce CO_2 emissions, new technologies have begun to be developed that would allow the use of alternative fuels. Ammonia is one of the most promising options because it does not contain carbon and therefore no CO_2 is emitted in the combustion reaction of ammonia. Although currently ammonia is produced worldwide 235 million tons experience of using ammonia as fuel in internal combustion engines (ICE) is still limited.

Wärtsilä Finland began testing ammonia as fuel in 2021 laboratory conditions. A fuel system was developed for this testing as well as safety systems to make it safe to use ammonia as fuel. The test team and other experts involved in developing ammonia testing have gathered early-stage knowledge over the past few years of how ammonia can be used as fuel in ICE safely. Due to ammonia's properties, using it as fuel requires safety systems and training. Although ammonia is a globally used chemical as fertilizer and in cooling systems its use as fuel is in research stages.

2 Properties of ammonia

Anhydrous ammonia is naturally occurring compound consist of a nitrogen atom and three hydrogen atoms. Ammonia is a widely used chemical and is already transported by sea as a cargo. At atmospheric pressure, ammonia is a colourless gas with an easily recognizable strong odour at relatively low concentrations. At a higher pressure, ammonia is in liquid form.

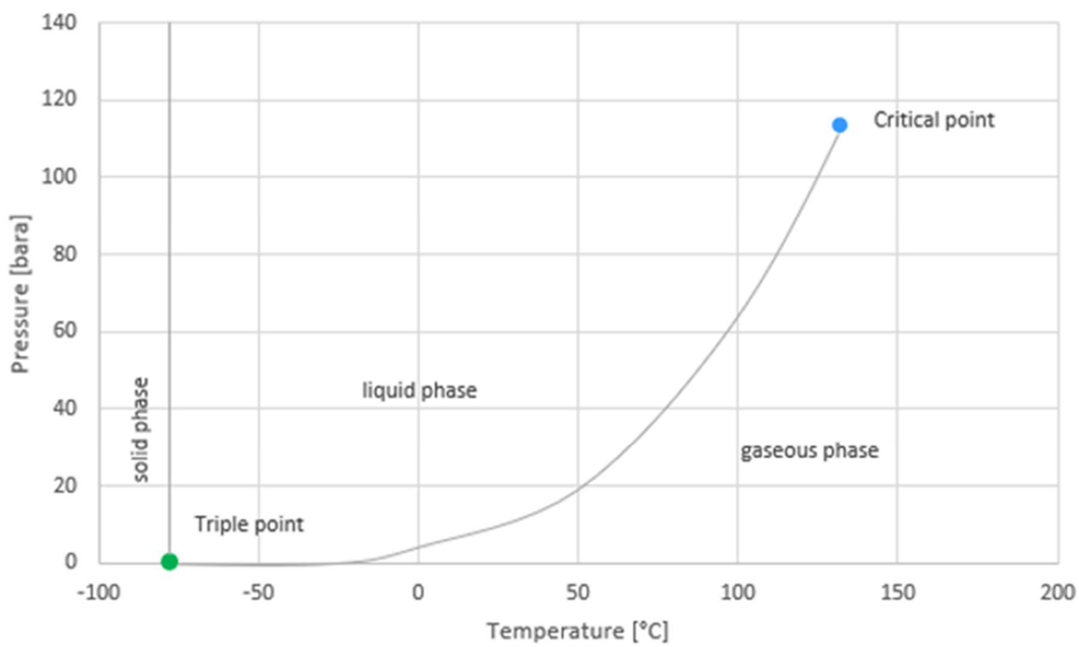

Figure 1. Phase diagram of ammonia

2.1 Physical and chemical properties

Although in atmospheric pressure ammonia is a gas that is lighter than air, in high relative humidity ammonia can become heavier than air. This occurs since ammonia is hydrophilic compound and it will react with the water droplets in the air. When ammonia dissolves in water it is partly ionized. The reaction exists in equilibrium with NH_4^+ (aq), NH_3 (aq) and NH_3(g)

$$NH_3 + H_2O \rightleftharpoons NH_4{}^+ + OH^- \qquad (1)$$

The amount of NH_3(aq) (dissolved ammonia) increases with the temperature of water and pH. With the average seawater pH of 8 equilibrium of NH3(aq) and NH4+(aq) is at the range of 0,8% at 0 °C to 7,4% at 30 °C. Dissolved ammonia nh3(aq) is toxic to marine life when ionized NH4+ ammonium ion does not have toxic properties. (Franklin & Edward, 2019, as cited in European Maritime Safety Agency 2022)

The key properties of ammonia are listed in the following table 1.

Table 1. Key properties of ammonia (IIAR 2008)

Chemical formula	NH_3
Physical state in room temperature	Gas
Colour	None
Molar mass	17,034 g/mol
Density STP conditions	0,769 kg/m^3
Density −33,4 °C	681,9 kg/m^3
Energy density	18,6 MJ/kg
Boiling point	−33,4 °C
Melting point	−77,7 °C
Vapor pressure	882 kPa, 20 °C
Solubility in water	529 g/l 25 °C 898 g/l 0 °C
Odour threshold	5-50 ppm
Specific Gravity, Gas @ 0° C., 1 atm. (Air = 1):	0,597
Flammability range in air	15 – 28 vol %
Minimum autoignition temperature	651 °C

Ammonia has a good soluability in water. The hydrophilic properties of anhydrous ammonia cause ammonia gas to diffuse readily in the air. The liquid ammonia is also highly soluble in water. The reaction between water and ammonia is exothermic, meaning that it releases heat. Comparably to other compunds the water solubility is depended on temperature. Ammonia gas solubility in water degreases when the temperature increases (see table 1).

The flammability range of ammonia is relatively narrow at 15 – 28 % in air (see table 1). This combined with the high minimum autoignition temperature at 651 °C means that the fire and explosion risk is lower than some other hydrocarbon fuels and gases.

2.2 Properties of liquid ammonia and gaseous ammonia

Liquid ammonia is colourless as its gaseous form. However, in very high concentration ammonia gas can appear as white cloud. This same phenomenon occurs when liquefied ammonia starts to boil in atmospheric conditions. The formed very cold ammonia vapour appears as a white cloud and is heavier than air. When these formed gases warm up it becomes colourless and lighter than air. Accordance to the law of partial pressure the boiling liquid ammonia, when spilled or released in atmospheric conditions will produce pool of boiling liquid that is significantly colder than the boiling temperature of ammonia at −33,4 °C. In the occurrence of liquid ammonia spillage, the of density of ammonia is lower than water in standard conditions meaning that the liquid ammonia will form a layer top of the water. (IIAR 2008)

3 Hazards of ammonia

The toxicity is the main hazard of ammonia as fuel. With other more conventional fuel flammability and risk of explosion is the main hazard. However, with training and proper precautions, ammonia does not generate greater hazard than other liquified gas fuels.

3.1 Effects on humans

Ammonia is classified as highly toxic chemical. Ammonia gas can cause acute toxicity on estimation at 700 ppm. In 0,07 % acute toxicity level is well below the lower explosion limit (15 %) of ammonia. It is extremely water soluble and, therefore it is easily absorbed through mucous membranes. When ammonia is dissolved in body fluids, its alkalinity causes local irritation. A cold burn may occur when skin or eyes are exposed to liquid ammonia. Liquid ammonia is extremely corrosive and causes extreme cooling. High concentrations of ammonia can cause chemical burns to skin. Ammonia does not build up in the body and does not cause long-term symptoms. Ammonia has not been found to cause cancer and is not classified as carcinogenic agent. (Meulenbelt, J. 2012)

5 ppm	Odour threshold
20-50 ppm	Mild discomfort (irritation in eyes and nose) Depends on if the individual is accustomed to smelling ammonia.
100-200 ppm	General discomfort. Irritation in eyes and nose. Tearing of the eyes. Irritation in throat and chest.
300-700 ppm	Upper respiratory tract irritation. Tearing of the eyes and severe irritation. Urge to cough. Short exposure <30 min causes no serious damage, although symptoms may persist up to 24 hours.
800-1700 ppm	Incapacitation from tearing of the eyes and coughing. Damage to eyes and respiratory tract may occur if not treated immediately. Long exposure can be fatal.
2000-5000 ppm	Fatal exposure
10 000 ppm	Immediately fatal

Figure 2. Effects of ammonia on humans

At only 5 ppm some individuals can detect the odour of ammonia. The odour threshold of ammonia varies from human to human, but most can detect ammonia at a concentration of 20-50 ppm. This provides beneficial early warning system. Concentration of 300 ppm can cause moderate symptoms. Tearing of eyes and severe irritation can cause difficulty to escape. Ammonia concentrations of 220 ppm and 300 ppm are usually defined as dangerous level of ammonia.

3.2 Effects on environment

Although ammonia is not a GHG, however it is classified as environmental pollutant. This is because, when ammonia is released into environment it can act as excess source of nitrogen. Ammonia releases in air can have a negative effect on air quality through formation of PM particles. (Krupa, S. V. 2003)

Ammonia and excess nitrogen that is formed affect negatively on soil condition and eutrophication of inland and coastal waters.

Ammonia is very toxic to aquatic life, and it can cause long lasting effects. The acute toxicity levels vary species to species. The toxicity limit of some species has been reported to be some tens of grams per liter and other species the acute toxicity levels can be more than 500 g/l. (Batley & Simpson, 2009, as cited in European Maritime Safety Agency 2022)

4 Ammonia as fuel laboratory engine testing

Due to the toxicity of ammonia safety aspects need a careful consideration to ensure safety of the personnel during engine testing. To ensure safety, many safety devices were added to the system to deal with potential ammonia leaks. These systems were added so that even in the event of a leak, ammonia posed no danger to the personnel. In addition to this, extensive hazop study was carried out to ensure safety even in case of failure. As one further study, dispersion modelling was carried out to simulate potential leakage situations. Using dispersion modelling, it was possible to assess what effects would be in the worst possible leakage situation.

4.1 Hazop study and dispersion analysis

A hazop study was carried out in the final stages of re-designing the laboratory systems to enable ammonia engine testing. Hazop study is systematic examination of the system to identify and assess possible problems that could cause risk to personnel or equipment. The hazop study was carried out in multiple sessions in early 2021. The hazop study was divided into two sections. The first section dealt with the part of the system that is used when the ammonia engine is running on liquid ammonia and diesel blend. The latter section dealt with those system components and functions that are active when the ammonia engine is running on ammonia gas and natural gas blend. Hazop study was guided by third party experts.

The Hazop study did not consider the monetary implications for possible damage to the components of the system. Possible leakage of the ammonia was evaluated to be the most significant risk. It was found that more automation is needed for the ammonia engine system to prevent leakage event caused by improper operation of the system or equipment. Also, improper actions of the engine operators could be the cause for hazardous situation that can be prevented by added automation functions. During the hazop study it was perceived that a dispersion analysis would be needed to be carried out to simulate possible leakage situations.

A dispersion analysis is an evaluation of the outcome of an incident and the effects on the surroundings and the people. The dispersion study assessed potential leakage situations that had been identified in hazop study. The event of the ammonia container would be damaged to the extent that the entire contents would release was not considered, since this event was seen highly unlikely. The ammonia container is equipped with pressure relief valve (PRV). Opening pressure of the PRV is set to 22 bar, when the opening pressure of the burst disk of the container is at 24,2 bar. In the event of the ammonia container pressure rising too high the PRV opens to lower the pressure in the container. When the pressure is reduced lower than 22 bar the PRV closes. This prevents a large leakage caused by too high pressure. The PRV outlet is located at 6 meters high from ground to reduce the exposure risk for ammonia. The rate of outflow of ammonia is evaluated to be about 7 kg/s. The blowing lasts about 7-8 seconds. (Sweco, 2021)

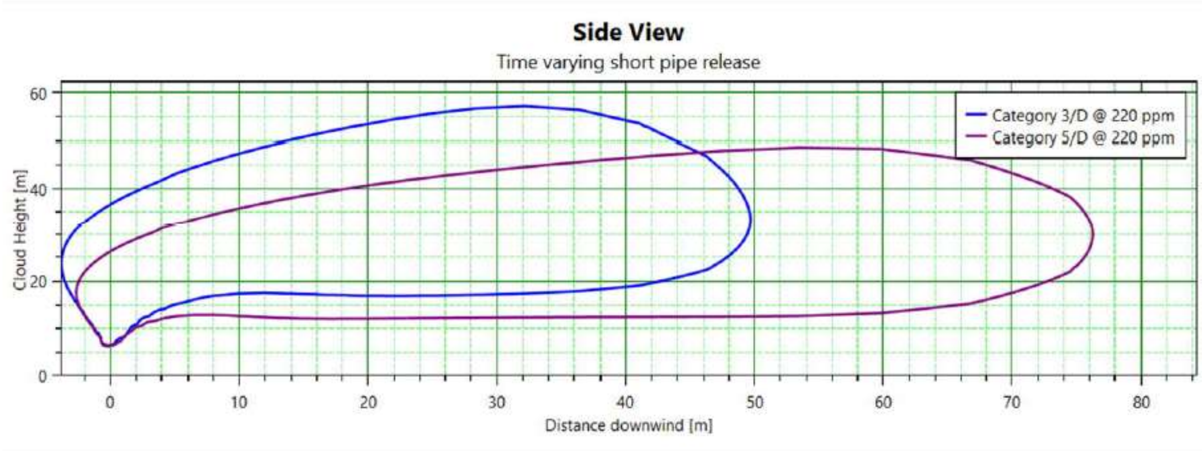

Figure 3. Side view ammonia cloud PRV open. (Sweco, 2021)

In figure 3 is modelled the ammonia cloud at the hight of the PRV at 6 meters from ground. The ammonia concentration inside the cloud is higher than 220 ppm. The categories presented in the figure 3 are descriptions of wind conditions and overall weather conditions. Category 3/D means 3 m/s windspeed and Pasquill-Gifford D class, which stands for neutral weather conditions. Category 5/D is describing neutral weather conditions with 5 m/s windspeed.

The dispersion analysis also assessed smaller leaks into the ammonia container spillage pool that could be caused by leakage within the flange connections or hose detachment. As a precaution, the container is equipped with a spillage pool, which in leakage situations spilled ammonia is collected. Water cannons have also been placed in the surroundings of the container, with which evaporated ammonia gas can be controlled.

In the event of power outage, the ammonia inside of the process tank will leak through the ammonia scrubber and is let out through the ammonia scrubber air outlet. It was evaluated that maximum of 43 kilograms of ammonia can be leaked in this situation. It was found that this amount of ammonia is dispersed very quickly. The ammonia scrubber air outlet is located high on the roof.

From the results of the dispersion analysis, it was concluded that in the case of leakage, the gas clouds, NH_3 concentrations can become dangerously high. However, it should also be noted that the scenarios in question have examined the accident incidents according to the worst case possible. The ammonia gas clouds caused by leakage can be controlled with the water cannons and prevent any toxic levels of ammonia gas spreading.

4.2 Ammonia engine laboratory

The ammonia engine laboratory was modified from existing engine laboratory. The liquid anhydrous ammonia container is positioned in the tank area. Water mist cannons were added to the vicinity of the container. Water mist cannons form a fine-grained water mist curtain near the container in case of emergency. Water mist on the curtain can control the possible spread of ammonia gas leakage. There is also a water cannon in proximity of the container for the purpose of cooling the container in case of a fire. However, it should be noted that in case of liquid leakage, injecting water into liquid ammonia is not recommended, as this will accelerate the vaporization of liquid ammonia and thus increase the amount of toxic ammonia gas in the air.

Figure 4. Ammonia container

In Figure 4 is the ammonia container and spillage pool under the ammonia container and liquid ammonia connections. Ammonia can be pumped from the tank area as a liquid fuel into the engine through high-pressure pump, or alternatively vaporized and transferred as gaseous ammonia to the engine. The system includes about twenty ammonia sensors to detect possible leaks. If a leak is detected in the test cell ammonia washer can be started by the operator. The ammonia washer is connected the test cell ventilation outlet. It contains water nozzles that create water curtain. In ammonia washer the contaminated test cell air is directed through water curtain to reduce the ammonia concentration in the air coming out of the ventilation outlet. A flare is also utilized in the ammonia engine testing that was already present. With the flare fuel pipes containing ammonia can be safely flushed if needed. Also, when running the engine on liquid ammonia in diesel mode the lean leakage that naturally occurs can be collected and the ammonia in lean leak origin can be handled with the flare. The flare operates on a separate diesel flame and must be kept on at all times while running the engine on ammonia fuel. Ammonia scrubber system was installed as a backup system for the flare to ensure safety while testing the ammonia engine. The wastewater from the ammonia scrubber is collected into separate tank.

As one of the safety measures, real time CCTV cameras are installed in the test cell. Surveillance cameras have also been added to the roof of the laboratory where the flare is located. The tank area is also captured by CCTV. One surveillance camera can observe wind direction from a wind indicator.

4.3 Safe operating

Since ammonia is entirely new fuel for marine – and power plant engines safety has been one of the main focuses alongside of understanding how ammonia can be used as fuel in ICE's. Because ammonia is brand new as fuel and still in the testing stage the laboratory personnel testing ammonia engines have no previous experience with ammonia as a fuel. And with this size of engine ammonia fuel usage, there were no previous experiences. Because of this, and the toxic properties of ammonia, laboratory tests have adopted the philosophy already at the system design phase, "better to be too-careful". This chapter presents some aspects of safe behaviours reported by the ammonia test team.

As a safety precaution while running the engine on ammonia at least two operators need to be present at all times. The access into ammonia test cell is strictly limited. Entering test cell while running the engine on ammonia must be avoided. However, when necessary, entering the test cell permission must be obtained from the operator running the engine and in addition ammonia specific personal protective equipment (PPE) must be used.

To reduce the amount of ammonia remaining in the pipelines and in engine, the engine is run in diesel mode for at least 15 minutes to flush the ammonia before stopping. DF engine's pipes up to gas ramp are flushed with nitrogen to make sure that the ammonia is flushed away. After running on ammonia, the engine and fuel system should be flushed efficiently if there is a need to open the engine or fuel system components. Despite thorough flushing, small amounts of ammonia may remain in the system and cause odour, therefore PPE should continue to be used while working with the engine.

4.4 Maintenance

It is important to note that when conducting maintenance, a work permit must be obtained. In addition, the person performing the maintenance work must ensure that the part on which the maintenance work is done is empty. Before starting the maintenance work the location of the nearest emergency shower must be checked. When performing maintenance work, double block and bleed valve is used to upstream and downstream the serviceable point. The laboratory test team has as often in practice emptied the entire pipeline, as it is possible in laboratory conditions. Even if the fuel pipe is purged and flushed with nitrogen, it is still possible that it contains small amounts of ammonia as a liquid or a gas. It is therefore important to use PPE as well as a hand-held ammonia sensor. Maintenance work is always carried out by two individuals, and never alone. To safely dispose of ammonia trapped in pipes, a hose has also been used to suck air out of the pipe and blow it to a safe location in the roof of the laboratory. This ensures that the ammonia gas does not spread into the breathing air of the worker performing maintenance work.

5 Personal protection and safe behaviour

When working with or around ammonia it is very important to be trained on proper handling procedures. Training on ammonia properties, safety, health hazards, first aid, how to act in case of emergency and how it can be detected is vital to ensure safe operating.

5.1 Personal protective equipment

The required PPE is determined according to the working conditions. Laboratory conditions safety equipment level was defined to protect from minor ammonia gas leakage. In ammonia engine testing, protective equipment is intended to protect against low ammonia concentrations below 300 ppm, as well as ammonia gas leakage for short periods. In the event of a major leak, the test team's protective equipment is not sufficient. In the preparedness plan, in the event of a large leak, the staff will gather to the assembly point and the fire department will handle the leak management with appropriate protective equipment.

PPE must be available for each of the ammonia engine testing team.

Ammonia specific PPE set consist of:

I. Powered Air-Purifying Respirator (PAPR) with ammonia cartridge with full face coverage.

II. Gas tight protective suit, boots and gloves suitable material for protection against ammonia.

III. Hand-held ammonia detector.

To facilitate the work and improve safety, the test team has walkie-talkies with which the operator in the operating room can communicate with a member of the test team performing the work. The type of protective gear described above is not suitable to enter ammonia gas filled space.

To obtain permit to enter and work in the gas-filled space, a higher level of protection PPE set consisting of:

I. independent positive pressure air-breathing apparatus including an air bottle. The air-breathing apparatus must have full face coverage.

II. Protective gas tight clothing without any skin exposed; including gas tight protective suit, boots and gloves.

III. Explosion-proof light.

would be required. (ABS 2021)

5.2 Training

To ensure safe operation using ammonia as fuel in ICE’s it is vital that the testing team have adequate level of training. Other personnel working near the testing site must have basic safety training concerning of ammonia.

The training is consisting of training how to operate the system under normal operation and unnormal conditions and how to act in case of an emergency. Additionally, it very important to have a comprehensive ammonia safety training consisting of ammonia properties (ammonia gas and liquid), health hazard, safety systems (such as detectors, voice and colour signals) and first aid.

Many accidents are caused by human error. By organizing ammonia safety training for personnel operating the systems the accidents caused by ignorance of ammonia toxicity can be minimized. Trainings on how the systems work are crucial. Such training can prevent accidents caused by improper use of the system.

6 Conclusions

Despite the high toxicity of ammonia, it can be used safely as fuel in ICE's. During the one of the very first tests using ammonia as fuel in engines of this size safely, has been one of the main focuses. Learning how ammonia can be used safely has been equally interesting as learning how it can be combusted. The laboratory setting has enabled to test safety systems as well.

In the upcoming ammonia engine testing in Wärtsilä Norway, the ammonia engine is tested at engine laboratory that system differs some from the engine laboratory Wärtsilä Finland that is described in this report. This will help deepen the knowledge on how ammonia engine is operated safely.

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