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Safe use of ammonia as ICE fuel

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ABSTRACT

With more strict emission limit targets than before set to combat the climate change, companies have begun looking for alternative fuels. Green ammonia has been thought to be a suitable alternative, since like hydrogen, ammonia does not form carbon dioxide when it burns. Unlike hydrogen, ammonia is relatively easy and cost effective to transport and handle.

The purpose of the study was to determine whether ammonia could be safely used in internal combustion engines as fuel. The study was conducted as part of Wärtsilä's project R&D ammonia as an alternative fuel. The goals of the thesis were to identify what safety measures are needed when using ammonia and to identify what changes are needed for the fuel, engine and exhaust systems.

Due to the corrosive properties of ammonia all commonly used materials are not compatible with ammonia. Commonly used in fuel systems, FKM/FPM type sealant material also known for the brand name Viton is incompatible with ammonia. However, in the already existing sealant materials, a suitable alternative can be found. The FFKM/FFPM type elastomer is compatible with ammonia, as well as other conventional fuels. Stainless steel 304 and 316 were found to be well suited for use with ammonia.

Ammonia was accepted as safe fuel to use in engines. However, due to the toxicity of ammonia, various safety measures are required. Safety requirements recognized included; gas detection to detect potential leaks, control valves to minimize leakages, possibility to clean ammonia gas from ventilation air in scrubber, ammonia gas monitoring from the exhaust gases.

Using ammonia as a fuel requires safety training for staff. It is important that the staff is aware of the properties of ammonia, have a good knowledge of the system, know how to operate in the event of accident.

KEYWORDS: alternative fuels, renewable fuels, ammonia, green ammonia

VAASAN YLIOPISTO**Tekniikan ja innovaatiojohtamisen yksikkö**

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TIIVISTELMÄ

Ilmastonmuutoksen estämiseksi asetettujen yhä tiukempien päästöjen vähentämistavoitteiden vuoksi yritykset ovat alkaneet etsiä vaihtoehtoisia polttoaineita. Vihreä ammoniakki on arveltu sopivaksi vaihtoehdoksi, sillä vedyn tavoin ammoniakki ei muodosta hiilidioksidia palaessaan. Toisin kuin vety, ammoniakki on suhteellisen helppoa ja kustannustehokasta kuljettaa ja käsitellä.

Tutkimuksen tarkoituksena oli selvittää, voitaisiinko ammoniakkia käyttää turvallisesti polttoaineena polttomoottoreissa. Tutkimus tehtiin osana Wärtsilän tutkimus- ja kehitysprojektia Ammoniikki vaihtoehtoisena polttoaineena. Opinnäytetyön tavoitteena oli selvittää, mitä turvatoimia tarvitaan ammoniakkia käytettäessä, ja selvittää, mitä muutoksia tarvitaan polttoaine-, moottori ja pakokaasujärjestelmiin.

Ammoniakin syövyttävien ominaisuuksien vuoksi kaikki yleisesti käytetyt materiaalit eivät ole yhteensopivia ammoniakin kanssa. Polttoainejärjestelmissä yleisesti käytetty FKM/FPM-tyyppinen tiivistemateriaali tunnetaan myös tuotemerkillä Viton, mutta se ei ole yhteensopiva ammoniakin kanssa. Jo olemassa olevista tiivistemateriaaleista löytyy kuitenkin sopiva vaihtoehto. FFKM/FFPM-tyyppinen elastomeeri on yhteensopiva ammoniakin ja muiden tavanomaisten polttoaineiden kanssa. Ruostumattomien terästen 304 ja 316 todettiin soveltuvan hyvin käytettäväksi ammoniakin kanssa.

Ammoniikki hyväksyttiin turvallisesti moottoripolttoaineeksi. Ammoniakin myrkyllisyyden vuoksi tarvitaan kuitenkin erilaisia turvatoimenpiteitä. Turvallisuusvaatimuksiksi tunnistettiin: kaasuhälyttimet mahdollisten vuotojen havaitsemiseksi, säätöventtiilit vuotojen minimoimiseksi, mahdollisuus puhdistaa ammoniakki ilmanvaihtoilmasta ammoniakkipesurissa, ammoniakkipakokaasun seuranta pakokaasuista.

Ammoniakin käyttäminen polttoaineena vaatii henkilökunnan turvallisuuskoulutusta. On tärkeää, että henkilökunta on tietoinen ammoniakin ominaisuuksista, tuntee järjestelmän hyvin, osaa toimia onnettomuuden sattuessa.

AVAINSANAT: vaihtoehtoiset polttoaineet, uusiutuvat polttoaineet, ammoniakki, vihreä ammoniakki

Preface

This thesis was written as a part of ammonia as an alternative fuel project at Wärtsilä.

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Abbreviations

AFC	Alkaline fuel cells
C ₃ H ₈	Propane
CLP	Classification, Labelling, and Packaging of chemical substances and mixtures
CO	Carbon monoxide
CO ₂	Carbon dioxide
DF	Dual fuel engine
DN VGL	Classification society
FEP	Fluorinated ethylene propylene
FFKM	Perfluoroelastomer
FFPM	Perfluoro rubber
FPM	Fluorocarbon Rubber
GD	Gas-diesel engine
GHG	Greenhouse gas
H ₂	Hydrogen
HAZID	Hazard Identification study
ICE	Internal combustion engine
IGC code	Construction and Equipment of Ships Carrying Liquefied Gases in Bulk
IMO	International maritime organization
LFO	Light fuel oil
LG	Liquefied gas
LNG	Liquefied natural gas
LPG	Liquefied petroleum gas
LVH	Lower heating value
MGO	Marine gasoil
N ₂	Nitrogen
N ₂ O	Nitrous oxide, also laughing gas
NFPA	National (US) fire protection association
NH ₃	Ammonia

NO	Nitric oxide
NO _x	Nitrogen oxides
P2A	Power to ammonia
PEMFC	Proton-exchange membrane fuel cells
PFA	Perfluoroalkoxy alkane
PM	Particulate matter
PPE	Personal protective equipment
PTFA	Polytetrafluoroethylene
SCC	Stress corrosion cracking
SCR	Selective catalytic reduction
SG	Spark-ignition engine
SMR	Steam methane reforming
SOFC	Solid oxide fuel cell
SO _x	Sulfur oxides
SSAS	Solid-state ammonia synthesis
STP	Standard Temperature and Pressure
UN	United Nations
USGS	United States Geological Survey

1 Introduction

In December European commission (2019) published a new European growth strategy called the European Green Deal. The aim is to solve climate and environmental issues that pose the most significant challenge for this generation. The European Green Deal target is producing zero net emissions of greenhouse gases (GHG) in 2050. The European Green Deal strategy sets more stringent conditions as far as net emissions are considered compared with the Paris agreement. The increased concern of global warming forces policymakers to compile stricter rules. Paris Agreement (2015), drafted by the United Nations (UN), fights against climate change by limiting the increase in the global average temperature below 2 °C compared with pre-industrial levels. To achieve this, GHG's global peaking should be reached at the earliest possible date, and zero net emissions of GHG's should be achieved in the second half of this century.

Carbon dioxide (CO₂) released from fossil fuel combustion is a greenhouse gas that impacts global warming. Achieving goals to reduce future climate warming caused by greenhouse gases will only be feasible by cutting significantly CO₂ emissions (Montzka et al., 2011). To respond to the tightened emission policies, engine manufacturers have developed engines that can run on lower-emission fuels. Liquefied natural gas (LNG) combustion emits almost no sulfur oxide (SO_x), and the particle matter (PM) emissions are low; also, compared with heavy fuel oils, nitrogen oxide (NO_x) emissions are low. Since LNG is still a fossil fuel, although cleaner than some other fossil fuels, significant amounts of CO₂ are still produced by the combustion. A significant reduction in CO₂ emissions requires that the carbon in the fuel must be reduced or eliminated. (Wärtsilä, 2017)

Zamfirescu & Dincer (2018) explain that, although hydrogen is recognized good clean non-fossil fuel, its large-scale introduction is challenging due to the difficult handling and high cost. Ammonia is considered a feasible option since, like hydrogen, ammonia emits zero CO₂ when combusted. The handling and storing of ammonia are considerably more accessible than hydrogen since it can be stored similar conditions as propane, at room temperature at a moderate pressure of 8 bar. Ash & Scarbrough (2019) points out that,

ammonia is also relatively energy-dense in a liquid form, and utilizing ammonia does not require complex onboard processing in internal combustion engines (ICE).

Green ammonia is ammonia produced entirely using renewable energy, such as wind and solar. When utilized as fuel, no GHG in its product lifetime is produced. International Maritime Organization (IMO) has also set goals to decarbonize international shipping at a minimum of 50 % by 2050 when 2008 is considered a baseline. Developing new renewable carbon-free fuels, such as green ammonia, is essential for reducing GHG emissions. These fuels enable the shipping industry and ship owners to reduce CO₂ emissions and reduce fossil fuel usage. (Ash & Scarbrough, 2019; IMO, 2018).

1.1 Objective

Although ammonia has been utilized on an industrial scale from the beginning of the 20th century, utilizing ammonia as fuel in marine ICE's is an inexperienced ground. Therefore, the purpose of this study was to discuss safety risks concerning ammonia as fuel. How can ammonia be used safely in ICE? In this study, the safety requirements of the fuel system, the engine system, and the exhaust gas system were investigated. The aim was to identify possible material issues in the testing facilities of the Wärtsilä engine laboratory and evaluate safety measures. All of these mentioned requirements were considered for using ammonia in gas form and liquid form. The following study questions should be answered in this study:

- Can ammonia be used safely in internal combustion engines?
- How and what safety precautions should be taken?
- What changes need to be made to the fuel system, engine system, and exhaust system?

1.2 Structure

The study is structured as follows. In the second chapter, the general properties of ammonia are discussed. The third chapter looks into how ammonia is produced by conventional methods and how green ammonia can be produced. Additionally, in chapter three, a price comparison between different production ways is made, and ammonia usage is discussed. The utilization of ammonia as fuel is discussed in chapter four. Chapter five focuses on general safety precautions, regulations related to ammonia, and ammonia risks to humans and the environment. Chapter six focuses on how the fuel system for ammonia fuel is constructed and its special requirement. The description of the existing test cell configuration in the Vaskiluoto engine testing laboratory is given in chapter seven. In chapter eight, the risks concerning using ammonia as internal combustion engine fuel are studied. The safety requirements for ammonia usage in the engine are identified in chapter eight. In chapter nine, a recommendation of test cell configuration is given, suitable for a testing engine that uses ammonia as fuel. Chapter ten discusses this study's results, explaining and evaluating the findings. Chapter 11 gives answers to the questions asked in this chapter and discusses what actions and further research should follow. The final chapter summarizes this research.

2 Ammonia properties

In this chapter, the properties of ammonia are discussed. Ammonia formation in nature is briefly examined; the physical and chemical properties of ammonia are studied. Furthermore, the combustion properties of ammonia are investigated.

In nature, almost all ammonia occurs in the form of ammonium salts. Ammonia is formed in nature, mostly by decomposing organic materials containing a source of nitrogen or volcanic processes. Ammonia also occurs naturally in the form of nitrate and nitrite. Ammonia nitrate and nitrite are formed from nitrogen and water vapor as a result of atmospheric electrical discharges. Ammonia salts formed naturally and in industrial processes provides nitrogen source for plants. (Appl, 2011a)

2.1 Physical properties of ammonia

In normal atmospheric pressure, ammonia is a colourless gas with recognisable pungent odour. Ammonia gas is lighter than air in normal atmospheric conditions. When one litre of liquid ammonia is vaporised in atmospheric pressure, approximately 750 litres of ammonia gas are formed (Työterveyslaitos, 2019a). Ammonia is in liquid form at normal atmospheric pressure at a temperature of $-33,3\text{ }^{\circ}\text{C}$. At the temperature of 20-25 degrees of Celsius, the ammonia remains liquid if the pressure is raised to about 10 bar (see Figure 1).

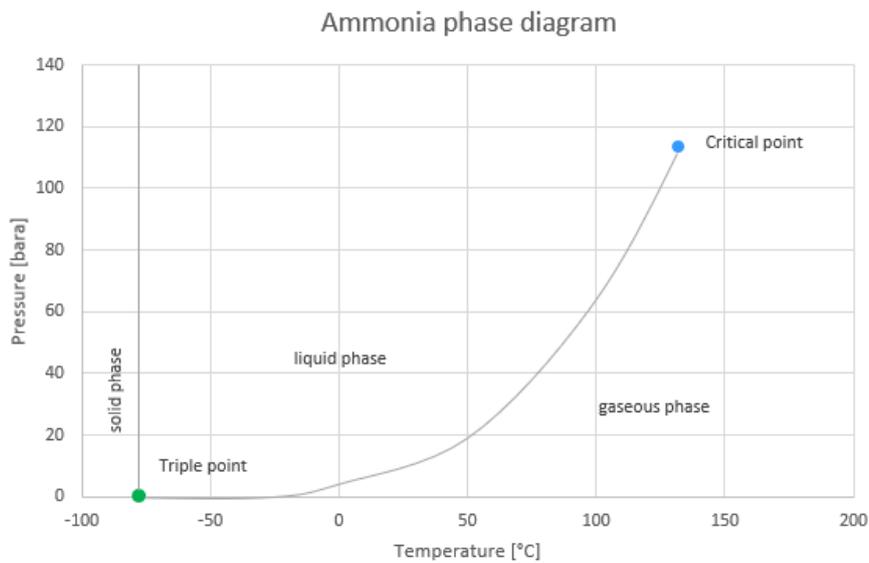


Figure 1. Phase diagram of ammonia.

Ammonia molecule consists of one nitrogen atom and three hydrogen atoms. Ammonia molecule construction is a pyramid shape (Figure 2)—nitrogen on the top and the hydrogen atoms below, forming the triangle-shaped bottom. The ammonia molecule has a relatively high dipole moment 1.5 D caused by the chemical bond polarization and the unsymmetrical structure of the molecule. Ammonia and water act similarly in various reactions. This is because the ammonia molecule has a similar shape to the water molecule, and the chemical bond angle between atoms of the molecules is close to each other. (Appl, 2011a).

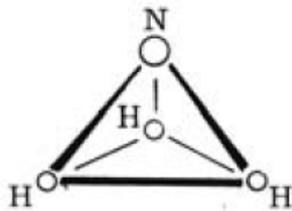


Figure 2. Illustration of an ammonia molecule (Appl, 2011a).

According to Appl (2011a), ammonia is a highly soluble chemical in many substances. This is because the dielectric constant of ammonia in a liquid state is approximately 15

or higher than for most liquefied gases. Ammonia is highly water-soluble. Inorganic salts (nitrates, nitrites, iodides, cyanides, and acetates) are highly soluble in liquid form ammonia.

2.2 Chemical properties of ammonia

Ammonia is a chemical thought to be relatively stable as a compound, but dangerous reactions are possible with chemically inappropriate substances or materials. Ammonia may react violently, producing heat with acids and oxidizers. For example, gold, silver, and mercury and their compounds can form an explosive reaction with ammonia. Ammonia is a base, and ammonia dissolved in water reacts alkaline. (Ijar, 2008; Työterveyslaitos, 2019a).

Oxygen or air oxidizes ammonia to NO, NO₂, N₂O, or nitrogen and water determined by the reaction conditions (Figure 3) (Appl, 2011a). The autoignition temperature of ammonia is significantly higher than that of conventional fuels such as heavy fuel oil. The proportion of NO_x in exhaust gases without exhaust gas after-treatment is higher if the cylinder's combustion temperature rises high. Nitrogen oxides are created in the combustion state at high temperatures as air nitrogen reacts with oxygen. In addition to the nitrogen contained in the air, as ammonia burns, NO_x are also created when the nitrogen contained in ammonia reacts with oxygen. It can be seen from figure 3 that nitrous oxide may be formed when ammonia burns. When nitrous oxide is realised into the atmosphere, the impact on global warming is 300 times that of the same mass of CO₂. Also, the nitrous oxide molecules persist in the atmosphere for an average of 120 years before being destroyed by chemical reactions. (Wärtsilä, 2020a; Wärtsilä, 2020b)

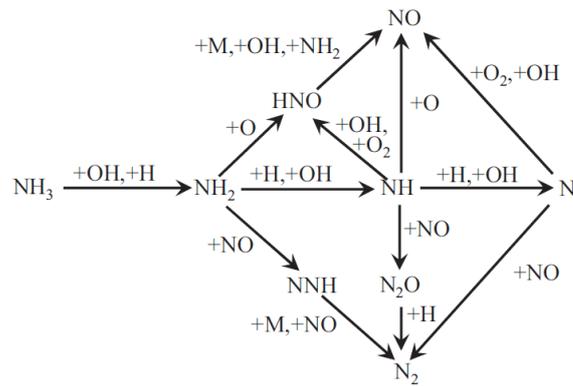


Figure 3. Ammonia oxidation pathways. (Miller et al., 1983)

In the presence of water or any moisture, ammonia precipitates the more noble metals, such as copper, zinc, and cadmium (Appl, 2011a). For this reason, these metals or alloys are not recommended to use with ammonia pipelines and systems where ammonia is present. Therefore, in ammonia pipelines, valves, and systems, metals such as steel, ductile iron, and aluminium are used.

2.3 Combustion

The complete combustion reaction of ammonia is



The minimum autoignition temperature of ammonia is 650 °C. The ignition temperature of ammonia is significantly higher compared with other typical hydrocarbon fuels, such as propane (C_3H_8), the minimum autoignition temperature of which is 450 °C (Kobayashi et al., 2019). The flammability range of ammonia-air mixture (16 – 27 vol % NH_3) is also narrow (Appl, 2011a). High ignition temperature combined with a narrow range suggests that ammonia has low flammability. The maximum laminar burning velocity of an ammonia-air flame is also considerably lower than hydrocarbon fuels. Ammonia-air mixture combustion is related to high fuel NO_x emission. However, as shown in formula (1), NO_x

is not an end product of ammonia combustion. The heat of ammonia combustion is approximately 40% of the other hydrocarbon fuels shown in the Table 1. (Kobayashi et al., 2019).

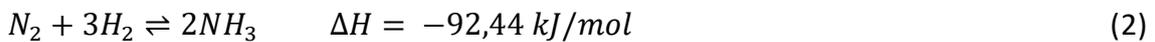
Table 1. Properties of ammonia and propane, methane and hydrogen (Modified from Kobayashi et al. 2019).

Fuel	Ammonia	Propane	Methane	Hydrogen
Chemical Formula	NH ₃	C ₃ H ₈	CH ₄	H ₂
The boiling temperature at 1 atm (°C)	-33,4	-42,1	-161	-253
Minimum auto-ignition temperature (°C)	650	450	630	520
Lower heating value, LHV (MJ/kg)	18,6	46,4	50	120
Explosive limits air mixture (at 20 °C, 101.3 kPa)	15–28	2,1–9,5	5–15	4–75

3 Ammonia production and usage

3.1 Production

Based on Appl (2011b), the ammonia production process can be divided into three stages: synthesis gas production, compression, and synthesis with purge gas management. The aim of the synthesis gas production is to produce a pure gas mixture of nitrogen and hydrogen. The gas mixture should contain a stoichiometric ratio of 1:3 nitrogen and hydrogen. The ammonia synthesis relies on the reaction between hydrogen and nitrogen.



that occurs under specific conditions over a catalyst.

Ammonia is among the most produced synthetic chemicals. USGS Mineral Commodity Summary, Nitrogen (2020) estimated that nitrogen content of worldwide produced ammonia 2019 was around 150 million tons. Nitrogen is 82.2 % of ammonia weight, so approximately 180 million tons of ammonia was produced in the year 2019. According to Appl (2011b), over 90 % of ammonia consumed globally is manufactured via the Haber-Bosch process.

The Haber-Bosch process is a catalytic process where pure iron is usually used as a catalyst. Nowadays, various other types of catalysts may also be used e.g., ruthenium (is used with graphite support and alkali metal promotion, such as rubidium or cesium) and magnetite containing some percentage of cobalt. The process has not changed much after it was invented German scientists Fritz Haber and Carl Bosch in the early 1900s. In the ammonia synthesis, hydrogen and nitrogen gases react over iron catalysts. Today, the reaction temperature is adjusted to 400–500 °C when the reaction temperature was around 600 °C in the original process. The pressure is kept above 100 bar. Unreacted gases are recycled in the process in order to enhance the process efficiency while maintaining high pressure. At high pressure, the reaction rate is faster even though one cycle

efficiency would be higher at lower pressure. Ammonia gas formed in the process is separated under high pressure. The pure hydrogen-nitrogen mixture production technology has encountered substantial changes after the Haber-Bosch process was first invented, but the technical ammonia process has stayed almost unchanged. The only changes to the process are the preparation of synthesis gas and purification technology. (Appl, 2011b).

Conventional ammonia production utilizing fossil fuels and green ammonia production utilizing renewable energy such as wind or solar differ mainly on the synthesis of gas production; in the cases green ammonia production plant utilizes Haber-Bosch process. Also, in green ammonia production that includes the Haber-Bosch process, the entire process is powered by renewable energy. (Appl, 2011b).

3.1.1 Conventional ammonia production

According to Appl (2011b) fossil fuels are used to separate hydrogen and nitrogen from air and water through chemical reactions. Most often, fuels such as natural gas, LPG (liquefied petroleum gas), naphtha, and coal (in China) are used. Wang et al. (2018) points out that, although ammonia's combustion does not produce CO₂ emissions, the conventional production of ammonia is causing CO₂ emissions around 400 Mt yearly released into the atmosphere.

In the first phase of the conventional ammonia production process, sulfur is removed from the fossil fuel through hydrodesulfurization. Any sulfur compounds present could poison the catalysts used in the process (Appl, 2011b). A catalytic steam reforming process forms hydrogen, carbon monoxide, and carbon dioxide from fossil fuel. The reforming process is repeated with the secondary reforming, in which air is added to the process. In secondary reforming, the formed gas is a mixture of hydrogen, nitrogen, carbon monoxide (CO), and CO₂. The gas mixture is purified through a three-phased process that removes CO and CO₂ from the gas mixture. The purified gas mixture is compressed and processed through the Haber – Bosch process to form NH₃. (Wang et al., 2018).

3.1.2 Green ammonia production

Green ammonia is produced when the energy used in the ammonia production process is renewable. Feasible renewable energy sources include wind, solar, and hydropower (Wang et al., 2018; Ikkäheimo et al., 2018).

P2A (power to ammonia) process separates hydrogen from water through electrolysis and nitrogen from the air with a swing pressure system. Both N_2 and H_2 production processes are powered with renewable electricity. The $N_2 H_2$ gas mixture is compressed and fed to the Haber-Bosch system. (Wang et al., 2018).

Other types of green ammonia production processes are under further development. One of these production methods is solid-state ammonia synthesis (SSAS). The process shown in Figure 4 is a direct ammonia production process via a solid electrolyte. In this process, no hydrogen is produced. The ammonia is produced directly from nitrogen and water. (Brown, 2017).

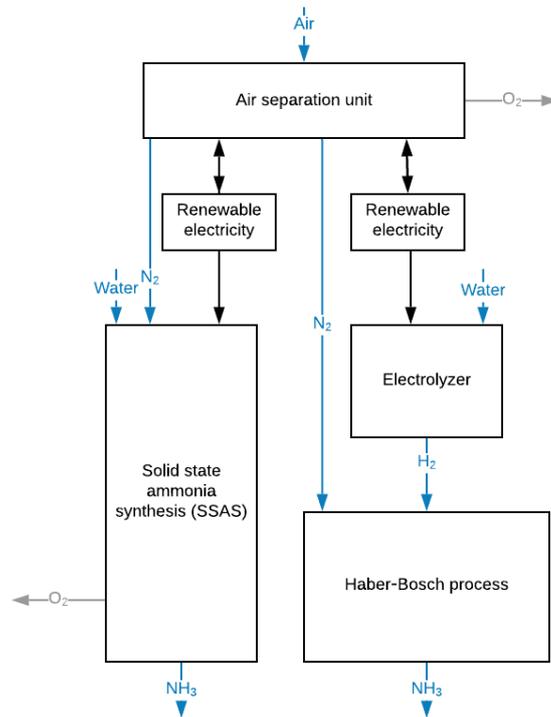


Figure 4. Green ammonia production through electrolysis – Haber-Bosch process and SSAS (modified from Bicer (2017)).

3.1.3 Cost comparison of NH₃ production and economic feasibility

From 2016 to 2018, global ammonia prices have ranged from 160-390 US dollars per ton (The Food and Agriculture Organization, 2018). Bicer et al. (2016) explain that natural gas forms 70-90 % of the ammonia production price. Bicer et al. (2016) further explain that since a significant proportion of ammonia is produced by the steam methane reforming (SMR) method, a rise in natural gas prices will simultaneously increase ammonia production prices. As shown in Figure 5, there has been an apparent connection between monthly ammonia and natural gas price.

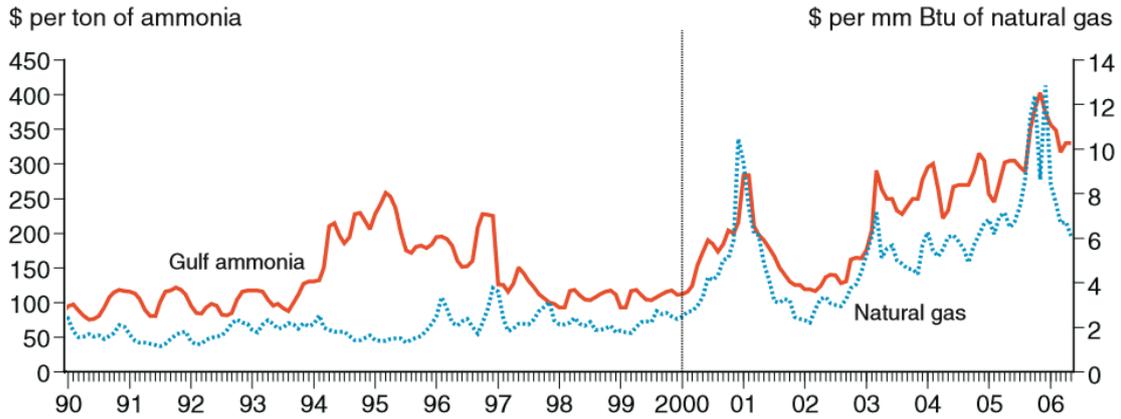


Figure 5. Historical data on monthly ammonia and natural gas prices in the USA. Modified. (Huang, 2007).

When green ammonia is produced, the main element needed in the production process is renewable electricity instead of natural gas. The green ammonia price was estimated to be 670-710 US dollars per ton, when using the cheapest solar PV electricity price tariff of 24 US dollars per megawatt-hour for the case studied by Ash et al. 2019. The same study estimated ammonia price to be 710-790 US dollars per ton of green ammonia when using electricity price USD29/MWh for onshore wind. Armijo & Philibert (2020) found that green ammonia's production cost could be below 500 USD/t on production cost estimates calculated for variable solar and wind energy. The renewable electricity price forms approximately 30 % of the green ammonia price. The price of renewable electricity has been on a downward trend and the electricity industry expects it will decrease further in the future. Therefore, green ammonia is expected to become cheaper in upcoming years. (Ash et al., 2019).

The price of green ammonia is thus estimated to be significantly higher compared to fossil fuel such as liquefied natural gas (LNG) and marine gas oil (MGO). Compared to marine gas oil the price of green ammonia was estimated to be roughly three times higher. Green ammonia would not be able to compete with fossil fuels if the GHG emissions are not acknowledged in price setting. Similarly to renewable electricity in the electricity sector, support policy mechanisms should be developed in this early state to ease

the market entry and to encourage the development and deployment of zero-carbon fuels (Ash et al., 2019).

3.2 Usage

Currently, ammonia is mostly used as fertilizer. Ammonia is the prime element for all nitrogen-based fertilizer products. Almost all produced ammonia is used as raw material for nitrogen products on the production site. In 2016, only 11 % of the globally produced ammonia was traded. Urea production used 53 % of all produced ammonia. The ammonia production process releases CO_2 , which is used in the urea production process on site. Figure 3 illustrates the uses of ammonia on a worldwide scale. Almost half of the ammonia produced is upgraded to urea. Urea contains a high amount of nitrogen, as 46 % of urea is nitrogen. Urea is also inexpensive compared to other fertilizer products. Therefore, urea is the most common nitrogen fertilizer product. As shown in Figure 6, most of the ammonia produced is used as a different type of fertilizer. Only around 20 % ammonia produced is used in other industrial uses, such as a refringent, ingredient in textile industry processes and power plants, waste incinerators, and engines to reduce NO_x emissions. (Yara, 2018).

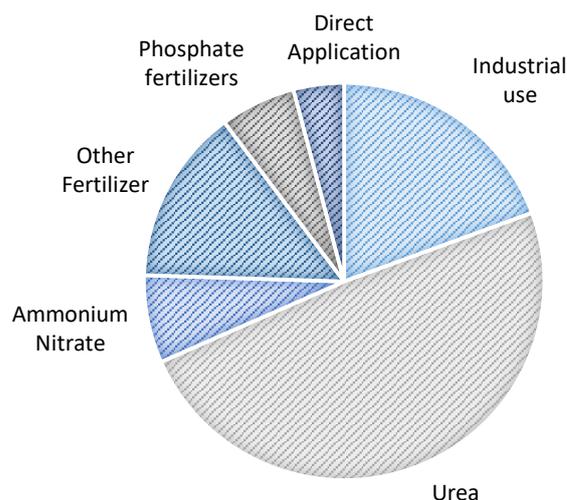


Figure 6. Global ammonia usage 2010-2016 (Reference data from Bicer et al. (2016); Yara (2018)).

4 Ammonia as fuel

This chapter takes a closer look into how ammonia has been used in history as fuel and the characteristics of ammonia fuel. Which kind of devices can adapt to using ammonia as fuel?

4.1 History

Using ammonia as fuel for ICEs is not an entirely new concept. Kobayashi et al. (2019) explain that the first-time ammonia was used as fuel was during world war II. During the war, ammonia was used to power omnibuses. Ammonia was mixed with coal, which was used more commonly as fuel. Lhuillier et al. (2019) states that the first real wave of interest using ammonia as fuel was in the 1960s. A study carried out by Pearsall and Garabedian in the '60s concluded that ammonia could be used as a fuel in a compression ignited engine if a very high compression ratio is used. Gray, Dimitroff, Meckel, & Quillian reported similar results a year earlier. Kobayashi et al. (2019) explain that ammonia has not been utilized as a fuel since war times in combustion systems; it has been used to study NO_x formation and reduction chemistry in combustion systems, particularly in the 1970s. The second wave of interest in using ammonia as an energy source rose in the 1990s due to the ongoing discussion about global warming.

4.2 Suitability of ammonia as fuel

Recent years the interest using ammonia as fuel has been steady. Many researchers have recognized that ammonia is suitable fuel and is suitable for fuel cells, gas turbines and ICEs.

4.2.1 Fuel cells

A fuel cell is an electrochemical "factory" that converts a fuel into electricity. Batteries also operate through electrochemical reactions, but unlike batteries, a fuel cell requires a continuous fuel flow to operate (O'hayre et al., 2016).

Ammonia can be used as a fuel in solid oxide fuel cells (SOFC) and alkaline fuel cells (AFC). Ammonia can also be used as a fuel proton exchange membrane fuel cell (PEMFC) through hydrogen cracking. SOFCs are considered to be the most suitable fuel cells for ammonia. (Zamfirescu & Dincer, 2008).

4.2.2 Gas turbines

A turbine is a machine that operates with a continuous flow of fluid. In a turbine, energy is exchanged between the working fluid and rotating blades. In a gas turbine, the working fluid is the gas produced through the combustion of fuel and compressed air. (Dick, 2015).

Ammonia is seen as a potential fuel for gas turbines. Ammonia-air blends for gas turbine operation are challenging since the laminar burning velocity of ammonia-air blends is slow. Fifty-fifty ammonia-hydrogen blend for gas turbine study showed that such blend could produce stable flames. However, the operability range was very narrow compared with hydrocarbon fuels. (Valeria-Medina et al., 2017).

Early studies concluded that ammonia could be used as a substitute fuel for gas turbines optimally sized for hydrocarbon fuels. When ammonia pre-decomposition to nitrogen and hydrogen was 28 %, ammonia had approximately the same minimum ignition energy and flame stability properties as methane (Verkamp et al., 1967).

Using ammonia or ammonia mixtures with other fuels as fuel for gas turbines is a potential solution to reduce GHG emissions in power generation applications. However, for marine applications, such technologies are unlike, since gas turbines are not commonly used in marine applications due to the low efficiency and high fuel cost.

4.2.3 Internal combustion engines

Internal combustion engines (ICE) are engines where a burning fuel's chemical energy is converted into mechanical energy. In ICE, the fuel-air mixture can be ignited by an electric spark or compressing the fuel-air mixture, causing an increase in temperature to ignite the mixture (Wärtsilä, 2020c). Internal combustion engines are seen suitable for using ammonia or ammonia mixtures as fuel.

Suitable engine types

Ammonia or ammonia blends are recognized in Wärtsilä to be feasible fuel for most of Wärtsilä's engines (Figure 7). In 2018, Wärtsilä launched the 32LG engine developed to run on liquefied petroleum gas as the main fuel and LFO as a back-up fuel. Liquid ammonia is also considered to be suitable fuel for Wärtsilä 32LG engines. Similarly to LPG, which is mainly liquid propane, liquid ammonia is also low viscosity fuel and with alike handling properties.

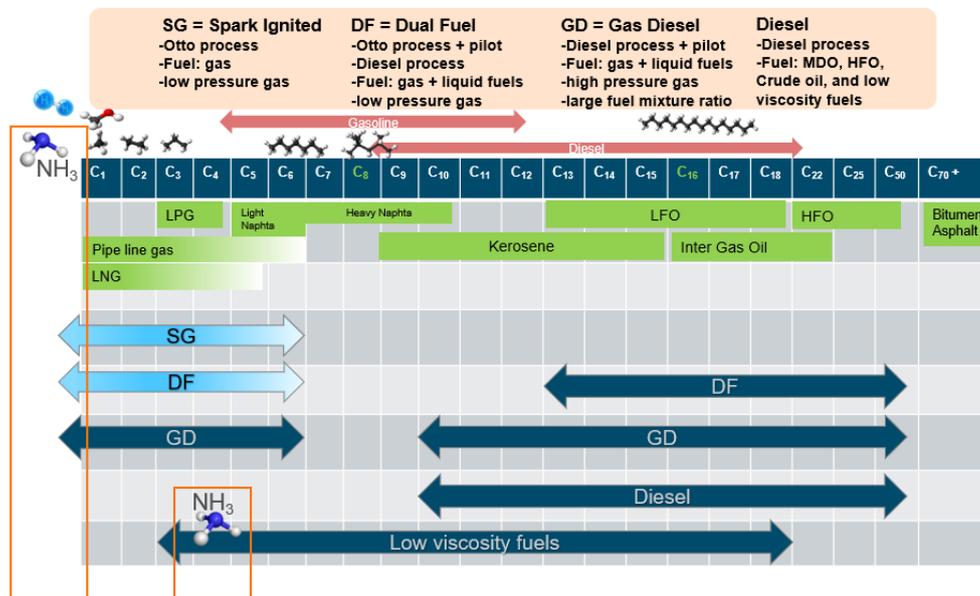


Figure 7. Wärtsilä engine types that are suitable for ammonia or ammonia mixture fuels. Modified. (Portin, 2020)

Wärtsilä 32GD gas-diesel engines are also considered to be suitable engines to run on ammonia. Wärtsilä GD engines operate on diesel process with a pilot fuel. The main fuel

in these engines is in the gas phase, and the pilot fuel used to ignite the fuel is liquid fuel. The gas enters the combustion chamber under high pressure.

Wärtsilä's fuel experts have estimated that ammonia would also be a suitable fuel for Wärtsilä dual-fuel (DF) engines. The DF engine was initially developed for gaseous fuels with pilot fuel ignition. This type of engines can also operate on liquid fuels with pilot ignition. Wärtsilä spark-ignited gas (SG) engines are, as well, seen as suitable to run on ammonia or ammonia mixture.

5 Ammonia safety

In this chapter, the general safety of the chemical ammonia is discussed. First, the hazards of ammonia as fuel are compared with other types of fuels. After understanding the hazards of ammonia as fuel, the health hazards ammonia pose to humans and hazards for the environment are discussed in more detail. Furthermore, general safety precautions and regulations concerning ammonia were studied.

5.1 Hazards of ammonia as fuel

hazard diamond is a guideline introduced by the United States national fire protection federation to quickly assess the hazards to rescuers in spill and fire situations. The health hazard to rescuers is assessed on a scale of no specific danger - very dangerous (0-4). The fire hazard is assessed on the same type of scale by a non-combustible substance - at all temperatures a flammable substance (0-4). The evaluation also includes the reactivity of the substance and special instructions. (Työterveyslaitos, 2020c).

According to the NFPA classification, the health hazard of ammonia is 3 (dangerous). The health hazards of natural gas (NG), methane, liquefied natural gas (LNG), liquefied petroleum gas (LPG), methanol, and gasoline are 2 (irritant). Hydrogen does not pose any health hazard.

The fire hazard of ammonia is the lowest of the evaluated fuels (Table 2). Level 1 fire hazard chemicals require considerably preheating before ignition or combustion is possible. Level 3 fire hazard substances can ignite under all ambient temperature conditions. Hydrogen at level 4 fire hazard vaporizes rapidly under normal atmospheric pressure and temperature and will burn readily. It can be seen from Table 2 that the overall hazardous level of these fuels is similar. (Työterveyslaitos, 2020b).

Table 2. Selected fuels are classified according to the NFPA hazard diamond.

Fuel	Health hazard	flammability
ammonia	3	1
gasoline	2	3
NG/methane/LNG/LPG	2	4
methanol	2	3
hydrogen	0	4

5.2 Hazards of ammonia for humans

Ammonia is classified as a highly toxic chemical. It is highly water-soluble and can be easily absorbed through mucous membranes. The alkalinity of ammonia causes local irritation when dissolved in body fluids. A cold burn may occur when skin or eyes are exposed to liquid ammonia. Liquid ammonia is highly corrosive and causes extreme cooling. Ammonia does not accumulate in the body and does not cause permanent symptoms. Ammonia has not been found to cause cancer and is not classified as a carcinogenic agent. (Meulenbelt, 2012; Työterveyslaitos, 2019). The ability to detect ammonia varies from person to person, and prevailing atmospheric conditions may affect. It has been found that some individuals can detect ammonia at values as low as 0.5-3 ppm (Appl, 2011a). At concentrations 50 ppm, the odour can be detected by most individuals. Occupational exposure is generally regulated in national laws to a limit of 25-57 ppm. Values between 50-72 ppm do not cause significant symptoms to the respiration system. At concentration over 72 ppm, ammonia causes irritation in the eyes and upper respiratory tract. Values over 100 ppm cause a burning sensation on the eyes and rapid and shallow breathing, at 200 ppm, nausea, and headaches. Difficulties in breathing normally and abnormally fast heartbeat may occur at values 250-500 ppm. An immediate burning sensation occurs on concentration more than 700 ppm, and immediate coughing occurs in concentrations over 1000 ppm. Acute respiratory distress can occur in minutes in concentrations of more than 1500 ppm. An immediate threat to life occurs in concentrations of more than 2100 ppm. Concentrations over 5000 ppm are fatal. (Meulenbelt, 2012; Appl, 2011a).

5.3 Hazards of ammonia for environment

Ammonia, although it occurs in nature, causes air pollution when realised into the atmosphere in large quantities. When realised into the atmosphere, ammonia quickly reacts with other molecules and turns into particulate matter. Ammonia generally stays in the atmosphere less than a day. (Stokstad, 2018).

Ammonia emissions cause long-term damage to the soil, waterways, and air quality. When realised in large concentrations to the atmosphere, Ammonia is linked to have an effect on acidification, eutrophication, and biodiversity loss on a local scale. (Spranger et al., 2009).

5.4 General safety precautions

Although ammonia as fuel is relatively unknown, it has been used and manufactured on an industrial scale since the early 20th century. Consequently, information on the dangers of ammonia and the necessary safety requirements for using the chemical is well known. Hazard statements for anhydrous liquefied and gaseous ammonia under the EU Classification, Labelling, and Packaging of substances and mixtures (CLP) regulation (CE) 1272/2008 are set out in Table 3 (Työterveyslaitos, 2020a).

Table 3. Hazard statements and pictograms for anhydrous ammonia according to the CPL regulation (Työterveyslaitos, 2020a).

Hazard statement	Hazard pictogram	Signal words: Danger
H221 Flammable gas		
H331 Toxic if inhaled		
H314 Causes severe skin burns and eye damage		
H400 Very toxic to aquatic life		

Safety precautions for ammonia are listed in the list below. The list is based on Työterveyslaitos (2020a) guidelines and Lamberg et al. (2015) safety guide for ammonia refrigeration systems.

- **Ventilation**

If ammonia is used indoors, there must be adequate ventilation.

- **Personal protective equipment (PPE)**

When handling ammonia, protective gloves, protective clothing, and a gas mask with an ammonia filter should be used.

- **Gas detectors**

If ammonia is used indoors adequate amount of ammonia gas detectors need to be installed.

- **First aid**

Washing with water is an emergency first aid when skin or eyes have come into contact with anhydrous ammonia. Eyes should be rinsed with warm water for at least 20 minutes. Use an emergency shower and strip off ammonia contaminated clothing. Skin exposed to liquid ammonia should be rinsed under running water for at least 15 minutes.

- **Fire protection**

Ammonia tank and pipes are an additional risk if a fire breaks out nearby. In a fire situation, the supply of ammonia should be stopped immediately. Clear the danger zone. Stay above the wind. An ammonia tank can explode due to the heat caused by the fire. Because of this, ammonia tanks are cooled with water. Burning ammonia can be extinguished with all fire-extinguishing agents.

- **Maintenance**

With regular and pre-scheduled maintenance, it is possible to ensure that the tank, pipes, and valves can safely handle the liquefied ammonia and gas under pressure. Daily visual inspection of the equipment is essential so that any defect can be detected in time.

5.5 Regulations

Currently, there is no regulation allowing the use of ammonia as a fuel. The IMO's international code of construction and equipment of ships carrying liquefied gases (LG) in bulk (IGC Code) only permits the transport of LG on board and the use of non-toxic liquefied gases as a fuel. The use of such gases as fuel was only allowed a few years ago when interest in using fuels such as methane arose. Since ammonia is a toxic chemical, its use is not allowed as a fuel today. (DNV GL, 2020).

Using ammonia as a fuel in ammonia tankers and other vessels impose additional requirements to ensure safe use. In collaboration with engine manufacturers, various classification societies are currently working on rules that allow ammonia to be used as fuel.

6 Material requirements

Ammonia reacts readily with several substances without specific catalysts. Metals such as copper and zinc are incompatible with ammonia, and if these substances come into contact, corrosion of these metals will occur. Even copper-based alloys are not recommended due to the corrosive properties of ammonia. However, some journal bearings, thrust washers, and piston rings used in ammonia compressors can contain copper-bearing materials. This is acceptable since constant lubricant prevents any chemical reactions with ammonia. Most mineral lubricant oils are unmixable with ammonia, although liquid ammonia carries oil with it when flowing. (IIAR, 2008).

6.1 Compatibility with elastomers

Ammonia has a varying degree of compatibility with elastomers. Typical elastomer compatibility with ammonia is described in Table 4. (IIAR, 2008). Of the elastomers shown in Table 4 for most purposes, Perfluoroelastomer (FFKM/FFPM) is probably the most suitable. It is flexible and suitable to use with ammonia and suitable for use with other common fuels. Fluoroethylene Propylene-Perfluoroalkox (FEP/PFA) and Polytetrafluoroethylene (PTFE) known as teflon, although suitable for use with ammonia as well as other fuels studied here, are more rigid material and are therefore not suitable for use at most parts of the fuel system.

Table 4. Elastomer compatibility with ammonia and other fuels (Iar, 2008; Novotema, 2020).

Material	Compatibility				
	Ammonia	LPG	LFO	Natural gas	
Elastomer					
FKM/FPM (Fluoroelastomer or Fluorocarbon)	Do not use	Excellent	Excellent	Excellent	Commonly used in fuel systems, cylinder o-ring seals and well known by the brand name Viton.
EPR/EPDM (Ethylene-Propylene)	Excellent	Do not use	Do not use	Do not use	Not suitable with mineral oils or petroleum-based fuels.
FFKM/FFPM (Perfluoroelastomer)	Excellent	Excellent	Excellent	Excellent	Suitable with a wide range of chemicals and fuel oils and oils.
FEP/PFA (Fluoroethylene Propylene-Perfluoroalkoxy)	Excellent	Excellent	Excellent	Excellent	Excellent chemical resistance. These chemically treated fluoropolymers appear more like plastic than rubber. Continues temperature range from -100 to 250 Celsius degrees.
PTFE (Polytetrafluoroethylene)	Excellent	Excellent	Good	Excellent	Technically not an elastomer. Well known by the brand name Teflon. Hard and lacks elasticity. For this reason, it is not used generally as an elastomeric sealing ring material, but it is often used as a back-up ring material.
IIR (Butyl)	Excellent	Do not use	Do not use	Do not use	Suitable with a variety of fluids, except for petroleum and mineral oils.
CR (Chloroprene)	Excellent	Good	Doubtful	Good	Medium resistant to high molecular weight oils. Commonly used as sealing or gasket material with refringent.

6.2 Compatibility with metals

Aluminium, steel, and stainless steel are compatible with ammonia. Some high tensile steels can be vulnerable to stress cracking due to corrosion if the ammonia is entirely anhydrous. The sensitivity to stress corrosion cracking (SCC) increases with carbon steels, the higher the steel strength. Susceptibility to stress corrosion increases when the oxygen concentration is only 0.5 ppm. On the other hand, stress corrosion can be prevented with a water content of 0.2%. For this reason, even anhydrous ammonia usually contains about 0.2% water. (IIAR, 2008). Compatibility of ammonia with different metals Table 5.

Table 5. Metal/Ammonia compatibility (Cole-Parmer Instrument Company, 2020).

Material	Compatibility
Aluminium	Excellent
Brass	Poor
Bronze	Poor
Carbon steel	Good
Cast iron	Excellent
Copper	Poor
Stainless steel 304	Excellent
Stainless steel 316	Excellent

Stainless steel is already widely used as a pipe material for fuel systems due to its good corrosion resistance. As seen in this chapter, stainless steel is well suited for use with ammonia. Copper and its alloy are commonly used in pipelines, especially as coating

materials. However, it was found that copper or its alloys are not suitable for ammonia due to ammonia's corrosive properties.

Ammonia's new use as fuel raises questions about finding suitable materials for fuel systems. It was seen in this chapter that many commonly used elastomeric materials used in O-rings are not chemically compatible with ammonia. New fuels set new requirements for the fuel compatibility of the materials. This sets a challenge also for the manufacturers to develop and provide new materials that are more suitable for the industry use.

7 The existing test cell configuration

In this chapter, the existing test cell configuration in Wärtsilä's engine testing laboratory is described. The current fuel system was designed for LPG fuel, mainly for liquefied propane. The existing fuel system compatibility needs to be reviewed because of the added elements of ammonia's toxicity and corrosivity.

7.1 Vaskiluoto engine testing laboratory

The Vaskiluoto engine testing laboratory is located in the Vaasa harbour area. The Wärtsilä Smart Technology Hub under construction, the Vaskiluoto power plant, the Port of Vaasa, and residential buildings are located in the same area. The Vaskiluoto engine testing laboratory is located next to the Smart Technology Hub (Figure 8).



Figure 8. Vaskiluoto engine testing laboratory and Smart technology Hub (Honkela, 2020).

7.1.1 Engine testing cell

The Vaskiluoto engine testing cell has been used in recent years to test the LG engine. The test cell was then updated to handle liquefied propane. The engine test cell's strong ventilation is currently routed to the roof of the laboratory building, which is about four meters high. Exhaust air is also collected in the same roof area from the safety valves

and breather air from the crankcase. Currently, also air ventilation in the area of fuel pipe flange connections is collected and guided to the laboratory roof area. This ventilation from the floor area was added to prevent leaking propane from accumulating in the testing cell area. In addition, the floor wells of the engine test cell are blocked to prevent heavier-than-air propane gas from accumulating in the test cell in the event of a leak and causing an explosion hazard. Figure 9 shows the ventilation outlet from the testing cell on the roof of the laboratory. Figure 10 crankcase breather removal on the same roof. The engine exhaust is directed to a height of several tens of meters from the ground with a long exhaust system. Figure 11 shows the tower to which the engine exhaust is directed.



Figure 9. Test cell air ventilation outlet on the laboratory roof.



Figure 10. Crankcase breather air outlet.



Figure 11. Engine exhaust outlet location.

The untreated exhaust gases are directed to the exhaust outlet. Exhaust gas in the pipeline is not currently treated by a selective catalyst reduction (SCR). However, studies suggest that ammonia in the engine could produce more nitrogen oxides than conventional fuels. It should be noted. However, engine testing in the laboratory and regulations on vessels or power plants can be significantly more stringent in exhaust gas content. Suppose unburned ammonia is present in the exhaust gases. In that case, future regulations may require a simple oxidizer as part of the exhaust system that oxidizes the ammonia into nitrogen oxide.

7.1.2 Storage

Ammonia will be stored in pressurised tanks outside the engine laboratory in Vaskiluoto, Vaasa, Finland. Similar storage tanks is used also with LPG. Ammonia is stored in C-type tanks used to transport ammonia. A flexible hose connection is connected to the tank to facilitate the tank's connection to the pipeline. Immediately after the tank, an automatic control valve is installed to close the tank if necessary. As ammonia is toxic, it must be possible to cut off the ammonia supply with an automatic valve to prevent the entire tank from being depleted.

7.1.3 Pipeline

The pipelines are made of 316L stainless steel. Stainless steel 316 is ideally suited for use with ammonia (Table 5). Stainless steel types 304 and 316 are commonly used as material for tanks to transport and store ammonia. The latter is required if the material is exposed to coastal or marine conditions. Since the most likely leakage points are the piping joints, such as flange joints and welds, the piping should be made as uniform as possible in the design of the piping.

7.1.4 Heat exchanger

If ammonia is to be supplied to the engine in the gas phase, an evaporator must be included in the fuel system. Liquid ammonia under pressure evaporates when the pressure

drops below 10 bar at 25 °C. As ammonia evaporates, heat absorbed, and the environment cools to the low boiling point of ammonia (-33°C). The cooling property of liquid ammonia evaporation could be utilized to cool other equipment.

7.2 Fuel system

7.2.1 External fuel system

The laboratory fuel system for the LG engine consists of two separate fuel systems. One system handling LFO fuel, and one is handling LG fuel. The LG fuel system was initially designed for LPG, which is the lowest viscosity LG fuel. Similarly to ammonia, LPG is also stored at pressurised tank roughly at 10 bar pressure. Other requirements for the fuel system, designed for the use of different fuels are controllable fuel flow rate. This is important since heating values of fuels may vary. To maintain the same engine output power when using fuel with a low heating value, the fuel feed pressure is increased accordingly. The compatibility of the systems materials with the fuel is also to be considered (Okhotnikova, 2020).

A high-pressure pump (Hammelman) delivers through common fuel line fuel to each cylinder in the common rail system. The Hammelman high-pressure pump is an electrical engine driven, and it has already been used for methanol and LPG testing. In Figure 12, the Hammelmann high-pressure pump in its place in the test cell.

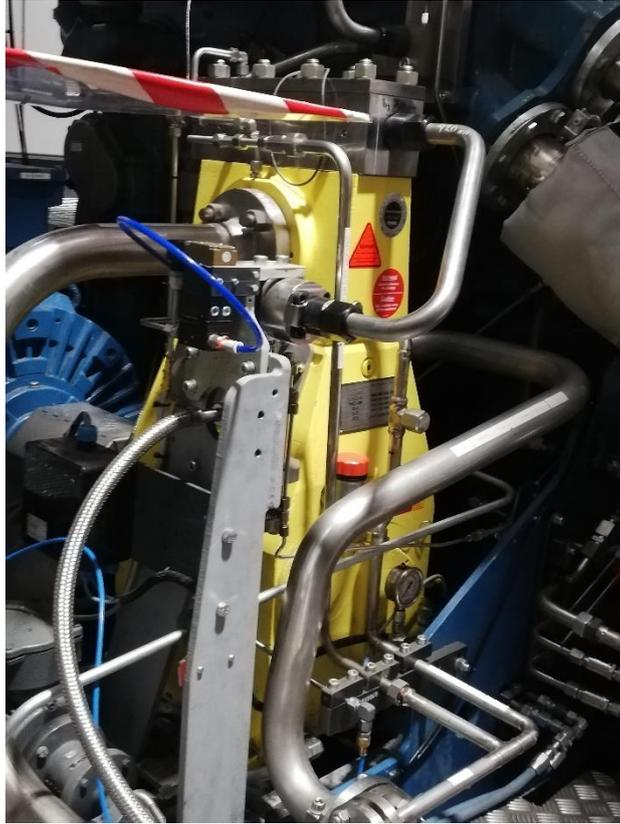


Figure 12. Hammelmann high-pressure pump.

7.2.2 Injection system

The initial testing using ammonia as a fuel LG injection system could be used since the Wärtsilä LG fuel injection systems were designed for low viscosity fuels. The Wärtsilä LG fuel injection system injector is a twin-needle type (Figure 13). This enables the injection of two different fuels; one needle injects the main fuel and the other a pilot fuel. (Okhotnikova, 2020)



Figure 13. LG fuel injector (Okhotnikova, 2020).

Since the LG injector was developed for LPG fuel, its sealant materials are incompatible with ammonia (Figure 14). FKM is used as a sealant material for the injection nozzle is incompatible with ammonia. Similar to the injector, the Hammelmann high-pressure pump has unsuitable material with ammonia used as sealing. FPM used as a material for solenoid seal is not suitable for ammonia, but with solenoid cooling oil, the sealant material would not come into contact with ammonia. Before using the LG injector for ammonia, these unsuitable sealant materials should be replaced.

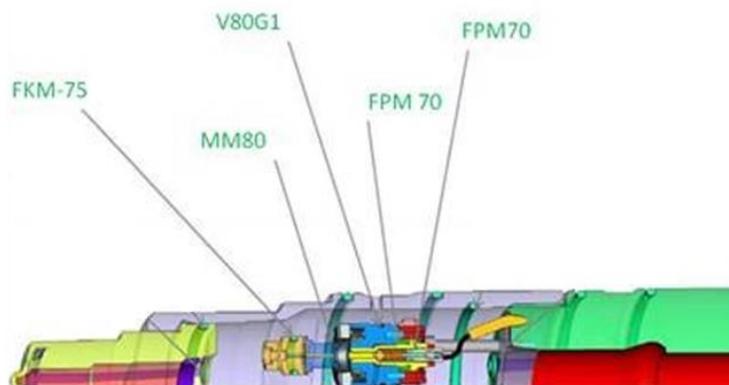


Figure 14. LG injector sealants.

8 Ammonia as ICE fuel safety

This chapter discusses engine safety issues when ammonia is used as fuel. The risk assessment is divided so that each system risk assessment is done individually. The safe use of the test cell has also been evaluated. Due to ammonia's toxicity, the training of test cell staff and protective equipment needs to be updated.

8.1 Assessing risks

The risk assessment was performed with the experts involved in the project. Risks were assessed by conducting a hazard identification study (HAZID). The risk assessment sought to identify risk factors and risk locations, identify causes and consequences, and identify a safeguard measure or eliminate risk by changing operation.

8.2 Storage and fuel system

The most significant single risk to the ammonia storage and fuel system is that toxic ammonia can leak. To prevent such an event, the risk assessment has identified potential leak locations so that the leak can be detected immediately, as well as the causes of the leak. A potential leak can be prevented entirely or prevented from causing a hazard to the environment. The aim was to identify all potential hazards and risks associated with the use of ammonia as a fuel in the Vaskiluoto engine testing laboratory. Table 6 shows the potential risks in the ammonia storage and fuel system. The aim was also to find safeguards for each identified potential hazard to minimize the risks.

Table 6. Hazard identification liquid ammonia storage and fuel system.

No	Type of event	Potential hazard	Cause/Consequences	Initial risk	Safeguards	Residual risk	Recommendations
1	leak	Pipe connection leaking	Small leakage of liquid ammonia. Liquid ammonia evaporates into gaseous ammonia.	Moderate risk	leak basin should be placed under the pipe connection. Automatic main closing valve directly after tank connection Gas detection outside to alert of the gas leak.	Low risk	Test the tightness of connection before use. Dispersion study to be conducted to the area in case of big leak. Water spraying system in case of big leak.
2	leak	Safety valve above the tank opens (22 bar in 55°C)	External fire near the tank. Large amount gaseous ammonia leaks. The BLEAVE-risk of ammonia tank.	High risk	Connection from the relief valve to 3m ³ safety tank and after that to burner or scrubber.	Moderate risk	Water jet system to cool the exposed parts of the tank.
3	leak	Damage to the tank	The tank will be damaged during lifting. The truck collides with the tank. Liquid ammonia leaks into the leak basin/ ground. Liquid ammonia evaporates into gaseous ammonia cloud.	High risk	Prevent collision with the tank with a guardrail.	Moderate risk	A protection zone is assigned to the tank. Access to the protection area by truck is prevented by mechanical barriers.
4	Flexible hose from tank to feed pump is damaged	Hose connection loosens or comes loose. Hose breakage.	Poorly connected or external impact. Liquid ammonia leaks into the ground and evaporates into ammonia cloud.	High risk	Automatic valve after the tank. Flow meter to detect changes in the feed.	Moderate risk	Welded connections should be favoured. Alarm system to detect the leakage and system shut down.
5	leak	Leak from the feed pump	Leaking connection. Liquid ammonia leaks into the ground and evaporates. Gaseous ammonia cloud is formed.	Moderate risk	Gas detectors installed to the vicinity of the leak basin.	Low risk	Level and temperature monitoring to provide additional indication of leakage.
6	leak	Pipeline leakage	External impact. Liquid ammonia leaks to the test cell floor or ground and evaporates.	High risk	Outside pipeline located in the pipe bridge above the road. Indoors, the piping must be double-walled or there must be enough gas detectors to prevent the formation of dead spots.	Low risk	
7	Ammonia leak inside of the test cell	Failure of gaskets or connections.	Poor connection. Ammonia evaporates inside on the test cell and is vented outside through the test cell ventilation.	Moderate risk	Gas detectors installed to the vicinity of each flange connection.	Low risk	In case of alarm normal ventilation is closed. Emergency ventilation through the scrubber. Under pressure at the test cell to prevent toxic gases from entering other spaces.

Safeguards make risks to storage and the fuel system acceptable. Protective measures are intended to prevent large leaks from occurring by quickly limiting the leak utilizing control valves. It is also vital that a leak is detected quickly to prevent a large leak from occurring in the event of a leak. Placing gas detectors in risk areas such as pipe connection areas ensures that if a leak occurs, it can be detected quickly from the control room. As a limit, 300 ppm can be considered closure level for the automation valves.

8.3 Engine system

Leakages

Three separate leak lines can be identified in the LG test engine fuel injection line. The leak lines are shown in Figure 15. The LG test engine's high-pressure fuel supply system is double piped. This is a requirement for all high-pressure systems to collect leaks and act as protection in a pipe breakage event.

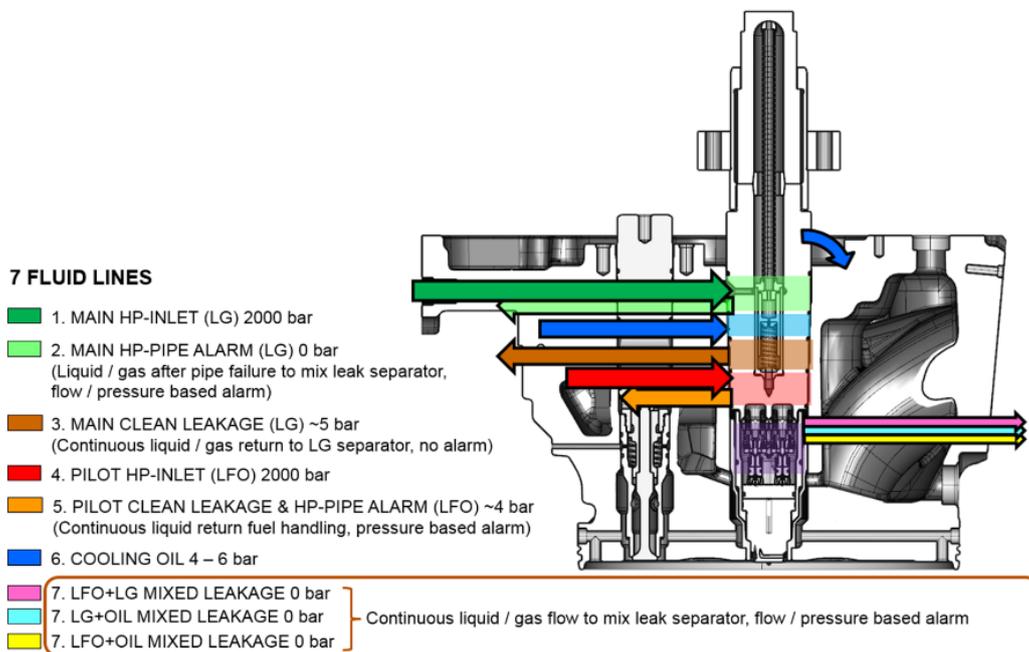


Figure 15. Leak lines in the LG test engine.

As it stands, fuels used in the existing system have been LFO and LPG. In this system, the main clean leak treatment depends on the fuel used. LFO, as a liquid fuel, is recycled back into the fuel tank. LPG leaks are gaseous and are directed to a separate container

from which it can be diverted to the burner. The pilot clean leak is directed back to the fuel tank. The LFO and oil mixed leak is addressed to the separator, where oil is removed. In LPG mode, mixed leaks are directed to the burner. (Okhotnikova, 2020).

In the ammonia test, the main leakage line leak is a mixture of LFO and gaseous ammonia. Such a leak is collected in a separate tank, from which the liquid fuel can be collected back to the fuel tank, and the gaseous ammonia is diverted to the burner for processing. The pilot leak line can also, in this case, be diverted back to the tank. The mixed leak is directed to the burner.

During regular engine operation, unburned ammonia can accumulate in the crankcase. However, if the constant concentration of ammonia in the crankcase ventilation exceeds the limit of 30 ppm, it should be treated. One possibility is to direct the gases from the crankcase to the scrubber.

8.4 Exhaust gas system and ventilation

The main risk for the exhaust gas system is toxic gases may be present in the exhaust gas. If a failure occurs during the test, ammonia may be present in the exhaust. In the first part of the engine tests, the liquid ammonia is mixed with the LFO, so the ammonia proportion in the exhaust gas is assumed to be small. However, the amount of ammonia in the exhaust gas must be possible to measure and monitor. If the amount of ammonia in the exhaust gas rises high, the LFO can be used as a back-up fuel, in which case the amount of ammonia can be reduced quickly. The Vaskiluoto engine laboratory is located near the residential area and the port. Therefore the amount of ammonia in the exhaust gases must be kept low under all conditions during the test. The amount of continuously measured ammonia in the exhaust gases should not exceed 10-30 ppm. To prevent high instantaneous ammonia concentrations in the exhaust gases, it is recommended that the test engine be started and stopped with back-up fuel. In this way, ammonia is also flushed from the fuel pipeline.

During normal operation, the air ventilation blows untreated air from inside the test cell into the laboratory roof. The risk of air ventilation operation is that the air ventilation blows ammonia gas out in the event of a leak. In the event of a significant leak, normal air conditioning must be shut off so that ammonia does not pose a danger nearby areas. As a safety precaution, if the gas detectors inside the test cell alarms, the test cell air should be treated before venting it out. A simple water scrubber is suitable for this purpose (Figure 16).

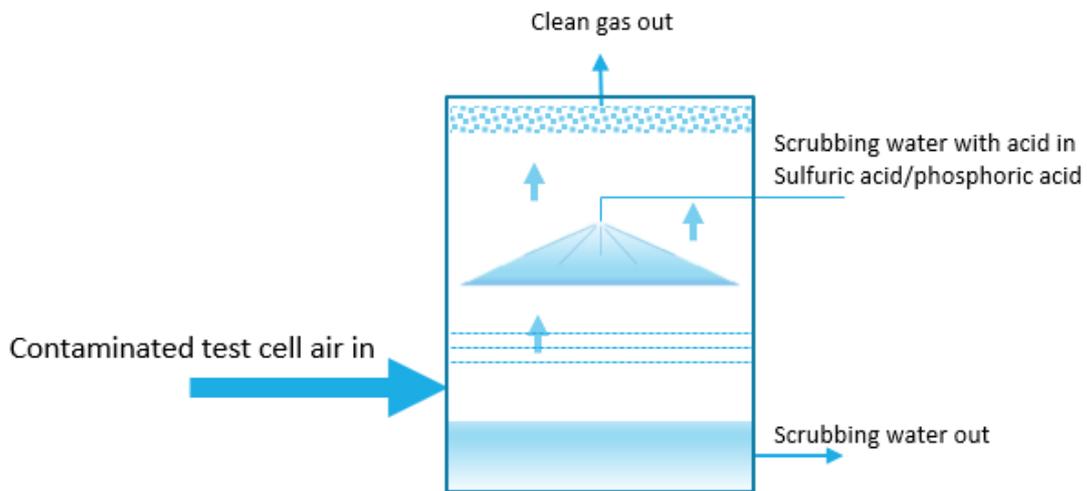


Figure 16. Schematic drawing of an ammonia scrubber.

8.5 Test cell safety

Accumulation of toxic ammonia gas inside the test cell is possible despite efficient conditioning. To ensure the safest use of the test cell, it must always be possible to detect whether ammonia has leaked into the test cell. There should be a gas detector in the vicinity of any pipe connection area. If ammonia is present in the systems inside the test cell, it should be possible to verify that there is no ammonia at the breathing air's height with a personal gas detector. Because ammonia is a toxic gas, the recommendation is that no persons are allowed to be inside the test cell during testing.

9 Proposed test cell configuration and actions

The safe use of ammonia as a fuel in an engine testing laboratory requires several changes. This chapter presents the measures that have to be done before ammonia can be used. However, ammonia is a toxic gas when inhaled, and because of this, safety actions should be improved. In addition to this, ammonia is an unknown substance for the Vaskiluoto engine laboratory staff.

9.1 Fuel system

The laboratory's current fuel system has been developed to meet the needs of low-viscosity fuel LPG. The high-pressure pipes in the fuel system are double piped. However, the inside of the test cell, except for high-pressure piping, other fuel pipes are single pipes. In the vicinity of the single-walled piping, ammonia detectors must be installed. Ammonia detectors should be installed specifically at each pipe connection area. Ammonia detectors should have a dense network so that one detector's failure does not pose a danger. The gas detectors currently present in the test cell are calibrated propane for gas (Figure 17). Propane is heavier than air. Therefore the gas detector is installed below the pipe connection. These detectors should be calibrated to ammonia and change the installation place because ammonia is lighter than air. The pipes in which the ammonia is should be clearly labelled as ammonia piping.



Figure 17. Gas sensors calibrated for propane in the engine testing cell.

Failure of the pipe should be able to be spotted without delay. Indoors, this can be ensured by a dense gas detector network that leaves no dead zones. Outside the test cell, pipe failure can be noticed as a drop in pressure using pressure sensors. A pipe that vents air near the flange connection can be installed and address the vented air to gas detectors. There are a few precautions to prevent the maximum leakage that would occur if an entire fuel tank deflated. The automatic main gas valve closes if a leak is detected in the system. The outlet of the relief valve of the fuel tank is directed to the scrubber. If the pressure increases too high, and the safety valve opens, the spread of ammonia to the nearby area can be prevented.

9.2 Ventilation

The use of ammonia in an internal combustion engine is not a closed system, from which, in normal operation, ammonia can be released through air ventilation. The air ventilation canal must be able to detect the presence of ammonia. If ammonia is detected in air ventilation, its spread in the laboratory's vicinity must be prevented. Air ventilation must be able to close to avoid the ammonia leak to spread out from the test cell. The test cell is also underpressurized, to avoid the leak spreading through doors to other

rooms. In such a situation, the leak can be ventilated in a controlled manner by rescue personnel. Alternatively, the leakage can be vented from the test to the ammonia scrubber. The scrubber dissolves ammonia in water. The water ammonia mixture is alkaline, but it can be neutralized by adding acid. The gas exiting the scrubber has a harmless amount of ammonia.

The ventilation air vented from the test cell floor area, and the proximity of the pipe connections should lead to an ammonia detector. It is important if ammonia is reached into the ventilation system due to leakage that it can detect the gas with a detector without delay. In case of failure, the ammonia gas that ends up in the ventilation system is directed to the ammonia scrubber. This ammonia scrubber is intended for use in case of defects. Therefore, before starting the test, the operation of the ammonia scrubber should be verified. Its operation should be tested regularly.

9.3 Ammonia testing in gas mode

The supply of ammonia to the engine as a gaseous fuel causes the additional modification necessary for ammonia fuel testing. Storing ammonia when liquefied is more economical, so even if the engine is fed ammonia as a gas, it will be stored as a liquid. Because of this, liquid ammonia will be vaporized into ammonia gas. When vaporized, ammonia absorbs heat, and without heating, it cools its environment to $-33\text{ }^{\circ}\text{C}$. Therefore, when using gaseous ammonia, heat exchanger should be installed in the system.

As a gas, the properties of ammonia are different; most significantly, the volumetric energy density is significantly lower than that of liquid ammonia. In Table 7 is a comparison between the volumetric energy density of ammonia gas and other gaseous fuels under STP conditions. It can be observed from Table 7 that the volumetric energy density of ammonia is more than six times lower than that of propane. The comparison of methane is about 2,5 times that. Due to the lower energy density, ammonia gas should be fed more to obtain sufficient power output.

Table 7. Gaseous ammonia volumetric energy density at STP compared to other fuels.

Gas	LHV [MJ/kg]	Volumetric energy density at STP
Ammonia	18,6	0,14
Propane	46,4	0,93
Methane	50	0,36

In terms of gas supply, low volumetric energy density means a higher volumetric flow rate. The volumetric flow rate can be increased by increasing the pressure or increasing the size of the pipe.

In addition to the unsuitable FKM sealing material, the gas supply system of the main gas valve film material is unsuitable for use with ammonia. Finding a suitable material requires more research from the main gas valve manufacturer.

9.4 Exhaust gases

Since the engines of this size and type have not undergone comprehensive ammonia testing as fuel to ensure safety, the exhaust composition must be monitored. The continuous amount of unburned ammonia shall not exceed the limit value of 30 ppm. This limit value has been defined on the basis of this study, and the rules established by authorities or classification societies in the future deviate mildly from this value.

In this initial testing, in order to avoid the hazards of unburned ammonia in the exhaust gas, its concentration in the exhaust must be detected. Also, the exhaust gases are directed to a height of several ten meters, from which the hot lighter-than-air ammonia gas rises upwards.

Chapter 2.2. stated (Figure 3) that NO_2 may also be produced as a combustion product of ammonia. For climate, N_2O emissions pose a high risk, as its impact on climate is hundreds of times worse than CO_2 . If N_2O is formed as a result of some stage of combustion in the exhaust gases, post-treatment of the exhaust gas is necessary with an oxidation catalyst. A large amount of ammonia or NO_x would also require the use of a catalyst from an environmental standpoint.

9.5 Operation safety

This chapter provides measures for ensuring the safe use of ammonia as a fuel and reducing an accident's risk. An investigation into the causes of accidents has found the accident to be often caused by the four following causes. The user of the system is not trained at all or is not adequately familiar with the system's operation. System design errors; system equipment is improper, or system equipment is damaged. The fourth cause leading to accidents is mechanical failure. (Lamberg et al.,2015).

System design

- Rooms containing ammonia equipment, the air ventilation should be adequate. Classification agency DNV GL has set the minimum value for ventilation in engine rooms at 30 times during an hour. There should be an easy escape route from the rooms. In spaces that can be filled with toxic gas, it must be possible to exit quickly.
- Pipes and equipment containing ammonia should be clearly marked. The piping and the condition of welding seams and equipment should be checked regularly.
- Ammonia equipment and pipe locations should be designed in such a way that the risk of collision is minimized. In terms of pipelines, this can mean placing them high or protecting piping and other equipment with collision barriers.
- Drawings describing the system must be updated to reflect actual installations. Staff members must easily find the updated drawings.

Safety systems

- Gas sensors should be adequately and correctly installed. Dead zones are not allowed to remain. The principle should be that the gas sensor should be in each possible area of the leakage site, or the pipeline must be protected by a double pipe.
- The gas alarm should be able to be heard clearly in and near the laboratory.
- The doors of the rooms should be opened freely from the inside.
- Pressure release valve outputs should be collected in a safe place. The safe place may be a separate tank from which the gases can be diverted to the scrubber.
- Normal air exchange between the test cell and other rooms should be stopped if there is an ammonia leakage.
- The exchange of air in auxiliary systems should be sufficient to prevent the formation of explosive concentrations.

Training

- Staff should be trained in the safe use of ammonia. An employee who has not undergone training on the safe use of ammonia should not be allowed to operate the system.
- Staff should have good knowledge of the dangers of ammonia and know how to act in the event of an accident, as well as know-how to provide first aid in an ammonia accident.
- The local fire department should take part in training to learn how ammonia is stored and used at the site.

Maintenance and operation

- Test cell and auxiliary system rooms, as well as storage areas, should always be kept neat, and the passage must be unobstructed.
- When operating, the system should be monitored at all times.

Safety equipment and emergency preparedness

- Personal protective equipment must be readily available and quickly found in case of ammonia leakage.
- The operation of the alarm system should be checked regularly.
- Emergency jets should be ammonia in the vicinity of pipelines and systems.
- An evacuation plan must be made in case of possible ammonia leakage or fire.
- The wearing of personal protective equipment should be practiced at regular intervals.
- All incidents and close calls must be studied and reported.

10 Discussion

To protect the Earth's climate and combat global warming, policymakers are pushing through increasingly stringent regulations on how much carbon dioxide, sulfur oxides, nitrogen oxides, and particles from engine are allowed to release into the air. For engine manufacturers, strengthening emission targets means that research has to be made to look for ways to manufacture engines suitable for changing regulations.

More significant targets for global warming today are to reduce carbon emissions (European Commission, 2019). Burning fossil fuels associated with energy production and consumption generates almost all of the world's annual carbon dioxide emissions. One way for engine manufacturers is to find fuels that release less emissions when they burn or so-called green fuels, like hydrogen, methanol, and ammonia. Ammonia is quite interesting because it does not contain any carbon.

As a chemical, ammonia has been used for more than a century, but for very different uses than fuel. In the present day, the ammonia produced in the world ends up as fertilizer to grow our food. And even this ammonia, often used in the manufacture of nitrogen fertilizers, is produced from fossil fuels using the Haber-Bosch process. Like engine manufacturers, fertilizer manufacturers also aim for cleaner products and emissions reduction in the sector. Today, blue ammonia, or GHG neutral ammonia, made from fossil fuels, has only been produced in individual batches for clean ammonia projects. However, engine manufacturers, as well as the fertilizer sector, need green ammonia to reach their target of fuel or fertilizer, the production, and use of which does not release carbon emissions into the atmosphere. This study found that green ammonia is estimated to cost roughly three times more than fossil fuel MGO. Today, green ammonia is not produced in industrial scale.

Can ammonia pass fuel safety requirements?

Using ammonia as fuel in engines, one challenge is safety. Ammonia is a very toxic substance for humans when inhaled. Liquid ammonia can cause severe injuries to the skin in the rattles, such as cold burns. Due to ammonia's toxicity, one goal of this thesis was to find ways to determine whether ammonia could be safely used as fuel in internal combustion engines.

The study finds the degree of hazardousness of ammonia to be the same level as other fuels. All fuels contain hazard factors. With most fuels, the most significant hazard factor is flammability. It is important to note that the danger factors of toxicity and flammability are very different. Furthermore, for this, it is necessary to study how toxicity risk can be minimized. However, in other sectors, ammonia has been successfully utilized, despite toxicity, for a long time. Because of the solid experience in other sectors of ammonia utilization, while conducting this study, one could not avoid reading studies on how to safely use ammonia as a refrigerant or fertilizer (i.a. studies of Lambert et al., (2015)). These also provided valuable information about the safe use of ammonia and the different sector; a number of principles seemed to suit engines as well.

The toxicity of ammonia is an acceptable risk. Despite the toxicity, about 20 million tonnes of ammonia is transported by ships, trains, and trucks each year. Ammonia is used in the cold storage and transport of food, as well as in ice rinks as a refrigerant. Safely using ammonia as a fuel is a technical challenge, but answers to this challenge are partly already in place in other sectors.

How to remove or minimize safety risks?

How ammonia can be safely used as a fuel? Many accidents are caused by human error. When toxic gas leaks, it is essential to know about its dangerousness. By organizing safety training for the individuals who operate these systems, one can minimize risks arising from ignorance of danger. Training to understand how the system works are also important. Such training can prevent accidents caused by improper operation of the system.

Another common cause of the accident is the failure of equipment. The reason for the failure of the equipment may be a faulty device, leakage from the flange connections, which may be caused by the rupture of the pipe seal, failure due to corrosion, or relief valve malfunction.

The risk of an accident caused by equipment failure can be reduced by conducting regular visual inspections as well as regular maintenance. Gas sensors allow potential leaks to be detected and prevent a more significant leak by shutting down the nearest control valve before the leak site.

The key target is to try to prevent leaks with various safety precautions before they happen. With a toxic substance, the spread of a potential leak is important to prevent leakage spread, double piping can be made or use gas detectors to detect leakage and control valves to limit the leak to a minimum.

What needs to be changed in order to use ammonia?

Several materials normally used in engines and engine auxiliary systems are incompatible for use with ammonia. The study revealed that, especially in sealant materials, there are currently inappropriate materials in use. FKM/FPM known for the Viton brand name, is not suitable material for use with ammonia. However, even today, at least one alternative material can already be found. FFKM/FFPM is suitable as an o-ring material, as well as it is well suited for use with ammonia and also with fuel oil. This is important because due to the weak combustion of ammonia and high ignition temperature, it is natural to start fuel with a mixture of well-known and better combustible fuel. It is also good to realize that ammonia as a fuel is still taking its first steps. In the event of increased ammonia fuel use, elastomer manufacturers will develop new materials designed to fit ammonia requirements. Gaskets readily used in fuel pipes are found to be also compatible with ammonia.

Similar to propane, clean leaks of ammonia can also be directed to the burner. In addition to the burner, the ammonia scrubber can be used to safely dispose of clean leaks that form in normal operation of the engine in the fuel system. Ammonia gases that have ended up in the crankcase can be directed in the pipe to the scrubber.

Ammonia stored as a liquid has a higher energy density per volume. Due to cost, ammonia is better to store in liquid form, even if ammonia is desired to be utilized as a gas. Because of this, the ammonia should be vaporized before feeding it to the engine. Because in its vaporization, ammonia absorbs energy, it freezes its environment to its vaporization temperature of -33 degrees Celsius. To prevent vaporization from causing equipment damage, there should be a vaporizer for vaporization.

With this research, there has been a gained lot of information about ammonia's properties and how to use ammonia as fuel in the test laboratory safely. However, the test environment differs from the environments in which engines are used. Particularly in ships, the engine's space and its auxiliary systems are desired to be minimized. Additional equipment means expenses and less space for transporting commodities. As such, the solutions provided by this study to test conditions are not entirely suitable for transfer to ship engine rooms.

11 Conclusions and recommendations

The aim of this study was to determine whether ammonia could be safely used as fuel in engines and under what conditions. Another objective was to identify the needs for changes the Wärtsilä's engine testing laboratory at Vaskiluoto and in the LG engine used as the test engine.

One of the properties of ammonia is a strong pungent odor. This can be seen as an advantage, as already extremely low concentrations as low as three ppm can be detected based on odor. Ammonia is toxic but does not accumulate in the body and has not been found to cause cancer.

In terms of safe use, ammonia properties were examined. The risk level of ammonia was also compared with other fuels. The result was that the overall hazard rate is the same as with other fuels. The risk for most fuels is flammability. With ammonia, the main risk is toxicity. Another relevant characteristic of ammonia is its corrosiveness.

Based on this study, the most commonly used elastomer materials are not compatible with ammonia. Options for sealant materials were also limited by the fact that the material must also be adapted for use with other fuels such as LFO and natural gas. This condition was imposed because of the desire to utilize ammonia with other fuels as a mixture. However, of the currently existing elastomer materials, FFKM/FFPM was found compatible with ammonia and the other selected fuels. Most commonly used metals in fuel systems such as cast iron, stainless steel 304 and 316 were found to be suitable to use with ammonia.

In many accidents, the cause of the accident is human error. Therefore, it is very important to provide adequate training for staff on the operation of the system and the characteristics of ammonia.

A HAZID study was conducted to determine the risks associated with using ammonia as a fuel. Changes were made so that risks were minimised or completely eliminated. In HAZID, efforts were made to come up with a safeguard for each identified risk. The following required changes and additions were noticed:

- Relief valves should be connected to the safety tank. From the safety tank possible gaseous ammonia can be addressed to the ammonia scrubber. An automatic valve after the ammonia storage tank should be installed. The valve should be closed automatically if 300 ppm level of ammonia is observed.
- Additional control valves should be installed. After the ammonia tank, an automatic control valve should be installed, which closes automatically in the event of an emergency. With control valves, any leakage may be limited to a minimum when the control valve preceding the leakage area is closed.
- A gas leak must be able to be detected from the operating room. Gas sensors should be installed in such a way that there is one for each connection. As a basic principle, the gas sensors must be installed so closely as not to form dead points, unless the double pipe is present.
- Normal ventilation should be closed in case of an emergency. Emergency ventilation is directed to go through an ammonia scrubber. The under pressure in the test cell prevents the spread of toxic gases to other spaces.
- Continuous ammonia in exhaust gases should not exceed the level of 30 ppm. This ensures the safety in the surrounding areas. Exhaust gases should be monitored in real-time. The exhaust gases measurement should include ammonia, nitrogen oxide, and nitrous oxide measuring.

12 Summary

This study was conducted to find out whether ammonia is safe to use as fuel and what protective precautions should be taken. The study's purpose was to identify modification needs in the Vaskiluoto Engine Laboratory and the test engine. Since ammonia is toxic and corrosive, the study sought to establish ammonia properties, constraints in material compatibility, and necessary safety requirements.

Ammonia was accepted as safe fuel to use in engines, but changes will be required in the fuel-, engine-, and exhaust systems. These changes are mainly to ensure safe use: Gas detection to detect potential leaks. Control valves to limit the leakage. Changes in the ventilation system; in an emergency, stopping normal ventilation and directing emergency air conditioning to the scrubber. Relief valve ventilation is gathered in the safety tank. Monitoring of the exhaust gas content; ammonia, NO_x and N_2O should all be monitored. For the continuous ammonia in exhaust gases, the maximum level was set to 30 ppm. This ensures safety in the surrounding areas.

Safety risks in using toxic ammonia can be minimized if the personnel operating the system know the operation of the system well, the dangers of ammonia and the operation in the event of an emergency. With good training and various safety measures, the risks can be minimized. The risks of ammonia as fuel are at acceptable level. However, ammonia is yet to be approved to be used as a marine fuel.

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