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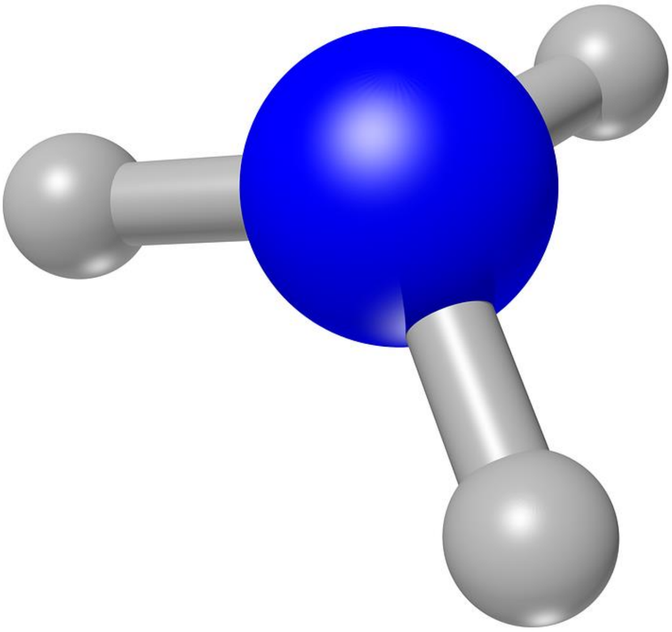

Safety issues regarding the use of ammonia as propellant in marine engine rooms

A case study looking to explore the dangers of ammonia exposure and how to minimize personal injuries

Bachelor Thesis for Marine Engineering Program

JIMMY GERHARDSSON

DEPARTMENT OF MECHANICS AND MARITIME SCIENCES

CHALMERS UNIVERSITY OF TECHNOLOGY
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Cover:
Ammonia (NH3) molecule. Picture was acquired from pixabay.com. Graphic designer: Colin Behrens
https://pixabay.com/illustrations/ammonia-nh3-chemistry-3d-atoms-1117246/

Department of Mechanics and Maritime Sciences
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PREFACE

Studying at Chalmers Institute of Technology’s maritime engineering program has provided a lot of insight on what the future holds for the maritime industry. Learning from a lot of experts in their field, interning aboard commercial vessels, as well as guest lectures from leading developers and innovators from the maritime sector had inspired a closer look at what the future holds for the industry and how to approach this future in a safe and sensible manner. Writing this bachelor thesis have provided an in-depth view of safety regulation procedures and the academic world. I would like to thank Chalmers Institute of Technology as well as Chalmers Library for providing the opportunity and resources needed for this study. Special thanks to Liza Nordfeldt of the Chalmers library for assistance reference handling, Johan Eliasson for mentoring, and Kjeld Aabo at MAN Copenhagen for taking the time for an interview.

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SAMMANDRAG (in Swedish)

Med nya, grönare bränslen på väg in på marknaden för marin framdrift så medför det många nya utmaningar gällande allt från miljö, juridik, ekonomi, säkerhet, etc. Den här fallstudien fokuserar på en sådant bränsle; ammoniak. Ammoniak har visat sig mycket lovande och många större företag har börjat förbereda sig på ett möjligt storskaligt byte till ammoniak från MDO-bränslen (Al-Aboosi et al., 2021; Dimitriou & Javaid, 2020). Det denna studie ämnar få ett grepp om de många personliga hälsoriskerna som medföljer att arbeta i närhet av ammoniak ombord på handelsfartyg. Fokusen ligger på ammoniaks giftiga natur och besättningsmedlemmars säkerhet samt att utforska kemikaliens flammsäkerhet och brandfara jämfört med fossila bränslen. Självklart finns det världsomspännande organisationer som ägnar sig helt åt sådana frågor (International Maritime Organization, 2015). Föreskrifter och säkerhetsstandarder kommer utan tvekan med tiden täcka punkterna som framlyfts av den här tesen. Dock så är denna nya teknologi under utveckling och det anses då rimligt att undersöka dessa frågor från så många perspektiv som möjligt, och det är detta som denna studie vill bidra med. Denna studie kommer dock inte fokusera på bränslets miljömässiga och ekonomiska aspekter. Frågorna som främst kommer framlyftas är: Vad för faror kommer besättningsmän möta med detta nya bränsle, och vad kan göras för att begränsa och/eller motverka dessa faror? De svar som fanns på dessa frågor var att det finns många potentiella hälsorisker vid kontakt med ammoniak, både långvariga och mer akuta, så väl som potentiella brand/explosionsrisker vid längre lagringsperioder av kemikailen. Det blev dock klart att för många av dessa risker finns det sätt att motverka och minimera dessa risker genom att använda sig av, tex, portabel skyddsutrustning, fasta säkerhetsanordningar, skyddsföreskrifter och utbildning av besättning. På grund av bristande data om vad den nya teknologin kommer medföra, så har informationen behövt samlas från vetenskapliga artiklar, säkerhetsdatablad, relevanta IMO-standarder, fallstudier från olika industrier såsom jordbruk, renhållning, och kemisk produktion/transport för att få tag på relevant information om ämnet. Mycket utav datan hittades via Chalmers Tekniska Högskola och Chalmers Bibliotek.

Key Words: Ammoniak, Bränsle, Marin Industri, Maskinrum, Säkerhet, Faror, Brand, Explosion

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ABSTRACT

With new, greener fuels entering the field of maritime propulsion technology, there are countless new challenges ahead regarding everything from economic, environmental, legal, safety, etc. This case study will focus on one such fuel; ammonia. Ammonia shows a lot of promise, and larger companies are already taking steps to prepare for a possible large-scale switch to ammonia from MDO fuels (Al-Aboosi et al., 2021; Dimitriou & Javaid, 2020). This study aims to get a grasp on the many personal safety issues regarding working with ammonia onboard merchant vessels. The focus remains on the toxic nature of ammonia and the safety of crewmembers as well as an examination on ammonias flammability and fire safety issues compared to that of fossil fuels. Of course, there are world-spanning organisations devoted solely to these kinds of issues (International Maritime Organization, 2015). Regulations and safety standards will eventually without a doubt cover the points made in this thesis. However, as this new technology is being developed, it makes sense to look at these issues from as many perspectives as possible, and this is what this thesis aims to provide. This study does not focus much on the economic and environmental aspects of the fuel. The main questions examined here are: What new hazards will engine workers face working with this new fuel, and what can be done to limit and/or prevent these hazards? What was found was that there are many risks regarding the potential health effects of ammonia exposure, both long-term and short-term, as well as the potential risk of onboard fire/explosion and risks regarding the long-term storage of the chemical. It was, however, also concluded that many of these risks can be minimized through protective measures, such as portable safety equipment, Fixed safety equipment, safety regulations and crew education. Due to the lack of data regarding this new technology, the information had to be gathered from: scientific articles, safety data sheets, relevant existing safety regulations from IMO, and case examples from different industries, such as farming, sanitation, and chemical production/transport in order to find relevant information on the subject. Much of the data studied was provided by the Chalmers University of Technology and Chalmers Library.

Keywords: Ammonia, Fuel, Maritime Industry, Engine Room, Safety, Hazards, fire, explosion, Toxicity

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ACRONYMS AND TERMINOLOGY

MDO	Marine Diesel Oil
NH_3	Ammonia (Nitrogen Trihydride)
IMO	International Maritime Organisation
IGC Code	The International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk
W/W	Weight by Weight
TiO_2	Titanium Dioxide
SDS	Safety Data Sheet
GHS	Globally Harmonized System of Classification and Labelling of Chemicals
ppm	Parts Per Million
ppmV	Parts Per Million by Volume
ATE	Acute Toxicity Estimate
ISGOTT	International Safety Guide for Oil Tankers and Terminals
TWA	Total Weight Average
STEL	Short Term Exposure Limit
IDLH	Immediately Dangerous to Life or Heath
IGF Code	The International Code of safety for ships using Gases or other low-flashpoint Fuels
LNG	Liquefied Natural Gas
ESD-System	Emergency Shutdown System
TCS	Tank Connection Space
FPR	Fuel Preparation Room
AEGL	Acute Exposure Guideline Levels
EPA	Environmental Protection Agency (US)
HFO	Heavy Fuel Oil
DWDI	Double Wall Double Insulation
UN	United Nations
NIOSH	National Institute for Occupational Safety and Health
GSP	Green Shipping Programme
IBC-Code	The International Code for the Construction and Equipment of Ships Carrying Dangerous Chemicals in Bulk
ISO	International Organization for Standardization

1. INTRODUCTION

The search for new, greener fuels in the shipping industry has been a long road of ambitious innovation and relentless research. The fossil fuels have been dominating the field as propellant ever since we moved on from harnessing the wind, and this has in turn had severe environmental consequences. Commercial marine vessels are a massive contributor to the global greenhouse emissions and work is being done to limit, if not eliminate these emissions. Through the 'Tier III' International Maritime Organization 2020 or 'IMO 2020'-convention on sulphur emissions, it will no longer be possible on a global scale to use Heavy Fuel oils (HFOs) without using scrubber technology (Chu Van et al., 2019). This will result in innovations over the coming decades bringing many, more carbon neutral contenders to the traditional fossil fuels (Al-Aboosi et al., 2021; Hansson et al., 2020). One such fuel being Liquid Natural Gas (LNG), which has already developed to an acceptable standard, and regulations have been developed for it in the 'International Code of safety for ships using Gases or other low-flashpoint fuels', or IGF Code (Green Shipping Programme, 2021; International Maritime Organization, 2015). Although LNG complies with the current IMO-standards, many consider LNG to be a "steppingstone" on the road to even greener fuels (Dimitriou & Javaid, 2020; Hansson et al., 2020). A promising contender for the future market of low carbon fuels is ammonia (NH_3), it is already being produced on a massive scale for use, mainly in agricultural fertilizer, but also in refrigerants and cleaning chemicals, among other fields, around the world (Al-Aboosi et al., 2021; Pattabathula, 2019). Ammonia on its own, if produced with renewable energy, will leave an incredibly small carbon footprint, especially for long distance shipping (although it is likely to be used in dual fuel systems and thereby not completely erasing the carbon pollution from shipping). Using ammonia, however, opens many questions regarding the overall health and safety of the marine engine workers due to the toxic and corrosive nature of the chemical. Working in close proximity to such a chemical carry with it quite a few health risks for crewmembers, and exposure to the chemical can have dire consequences for the victim and could lead to permanent injury or death (Ryer-Powder, 1991). In a growing industry with over 1.6 million seafarers, the cause for looking into the health and safety issues of a new element such as this is well justified (Senčila, 2018). This study aims to investigate the risks of working around NH_3 and explore safety measures in order to minimize injuries.

1.1 Background

The basis of the study comes from an incentive to identify and understand the risks regarding the future of the maritime engineering field. It is a fact that the switch to more eco-friendly alternatives to Marine diesel oils (MDOs) is inevitable since the IMO global sulphur limit caps since January 2020 are set at a maximum 0.5% (Chu Van et al., 2019). This means that traditional fossil fuels can no longer measure up to the standards and must be replaced with alternatives. It is also a fact that many of these alternative fuels have very different properties to that of traditional fossil fuels (Al-Aboosi et al., 2021; Green Shipping Programme, 2021). Ammonia was chosen for this study as it is an incredibly versatile chemical that is quite likely to play a major part in the future of marine propulsion (Dimitriou & Javaid, 2020). Ammonia is, however, corrosive to the touch and toxic to inhale, this means understanding the safety-issues is imperative in order to protect workers and avoid personal injuries in the work environment onboard commercial vessels. Ammonia being produced today has many uses, the most common one being fertilizers for agriculture, it has, however, never been used specifically as a propellant on any larger scale and this market is very new (Pattabathula, 2019). This means that there is a lot to look at regarding health and safety issues. The chemical has been used in plenty of fields for a great many uses, so there is much research data to look at for the purposes of this study.

1.2 Aim of the study

This case study aims to explore the hazards we may face working with the toxic chemical ammonia as a fuel for marine vessels and what steps are to be taken to help keep the crewmembers safe in the foreseeable future. In order to proceed safely into the change to greener fuels, it is important to get a grasp on what dangers one might face going forward. Looking at current research, regulations, and safety data, it will hopefully paint a clearer picture on what needs to be considered moving into the future.

1.3 Research questions

- What hazards will crewmembers face going forward with ammonia used as a fuel?
  - What happens when a person is exposed to ammonia?
  - What are the risks of storing ammonia?
  - What are the fire/explosion-hazards regarding ammonia?

- What can be done to prevent these hazards and keep the crewmembers safe?
  - What kind of safety equipment is needed?
  - Are there existing regulations regarding ammonia?
  - How does crew-training help limit the risks of working with toxic gases?

1.4 Delimitations

The thesis will focus on the personal safety issues for crewmembers regarding working with ammonia as a propellant for marine vessels. The environmental and economic development issues, most other experimental fuels as well as any in-depth review of ammonia propulsion-technology, other than the safety aspect, will not be examined here. The thesis will not go into great detail about the process of how safety regulations are written and evaluated by the safety organisations. SOLAS regulations will be mostly left out, because even though they are relevant and can be applied to many of the topics in this study, they are quite unspecific to the case and a detailed description of what the convention states on every subject may just take up space and be quite distracting from the specific points of the thesis.

2. THEORY

There is a push for change on a global scale regarding what we as a society put into the atmosphere. The commercial marine transport fleet is responsible for 2.7% of the annual CO2 emissions (Mersin et al., 2019). This push for change is bringing new innovations and introducing many new players into the energy sector. A promising candidate for greener propulsion is ammonia (Al-Aboosi et al., 2021; Dimitriou & Javaid, 2020; Green Shipping Programme, 2021). However, ammonia is both a toxic and corrosive substance (United Nations, 2019; World Health Organization., 1988). If this becomes a standard fuel it will require a different way of thinking and acting when it comes to the safety of the people working in the engine rooms. Further safety precautions must be taken to prevent exposure as well as locate leaks before it becomes a danger to crewmembers. There are limited studies on the matter regarding safe handling of ammonia as a fuel in engine rooms since the technology is currently being developed, making it hard to find direct sources of information. There are, however, studies on the toxicity and health hazards of ammonia in other fields, short and long-term health issues with ammonia exposure as well as data on the flammability of the chemical (Amshel et al., 1999; Czuppon et al., 2000; Lamberg et al., 2015; NIOSH, 1994; Ryer-Powder, 1991). There are also established safety regulation on handling ammonia in an industrial setting along with transport of the substance in the form of safety data sheets (SDS) and the IGC Code as well as current regulations for low-flashpoint fuels in the IGF Code (Air Liquide, 2020; International Maritime Organization, 1993, 2015). Studying the data from these areas will provide a basic idea on solutions to the safety issues ahead.

2.1. POSSIBLE HAZARDS AND HEALTH EFFECTS

This segment describes the various risks, hazards and health effects of exposure to ammonia.

What is Ammonia?

Ammonia, or nitrogen trihydride (NH_3), is a molecule consisting of one nitrogen atom in combination with 3 hydrogen atoms. In its gas form, it is lighter than air, colourless, and has a very intense, pungent odour (Czuppon et al., 2000). Small doses of ammonia are not inherently dangerous as proven by the fact that people get exposed to about 20 mg/day of the chemical through ammonium salts in food, drinking water, or cigarettes and traces in urban air quality (Ryer-Powder, 1991). the human body even has a daily ammonia production of approximately 17 mg/day through metabolic processes. Globally, ammonia is among the most widely used chemicals (World Health Organisation, 1986). On an industrial scale it can be quite hazardous to be around in large volumes and concentrations, and much caution must be used while handling it in order to avoid personal injuries and/or environmental damages. It is a colourless gas that has a very distinct odour, it is applied by many industries for a wide range of uses all around the world, mainly as a key ingredient fertilizer production for agriculture in the form of ammonium nitrate. There are established guidelines regarding how to handle the chemical, found in documents such as safety data sheets. The following information derives from Air Liquide's SDS No. NOAL_0002 (2019), According to regulation (EC) No. 1272/2008 [CLP], which is based on the Globally Harmonized System of Classification and Labelling of Chemicals (GHS). It states that, on physical hazards, ammonia is GHS-classed as a 'category 2 (H221) flammable gas'. This means that the gas has a flammable range while mixed with air at atmospheric pressure as well as having a temperature of 20°C. It is also classed under 'Gases under pressure, Liquefied Gas (H280)'. Meaning that containment vessels containing the chemical may explode while heated. Furthermore, on health hazards, the SDS states that ammonia has 'category 3 (H331) acute toxicity as an inhaled gas'. The acute toxicity estimate (ATE) of a category 3 gas is between 500 and 2500 ppmV. It has a 'category 1B (H314) skin corrosion/irritation'. This is explained in the GHS as a substance that *"produces destruction of skin tissue, namely visible necrosis through the epidermis into the dermis"*, specifically category 1B shows corrosive responses between 3 minutes to one hour of exposure. Additionally, it has 'category 1 (H318) serious eye damage/eye irritation', a damage to "*the iris, cornea or conjunctiva that are not expected to reverse or have not fully reversed within an observation period of normally 21 days"* (United Nations, 2019).

Table 2.1:

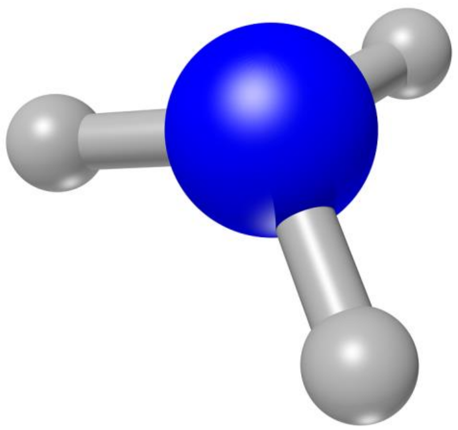
Basic Properties of ammonia (NH_3)

Properties	Values
Boiling point (1 atm)	-33.42 °C
Melting Point	-77.74 °C
Density (Liquid at 1 atm)	0.6818 g/cm^2
Density (Gas)	0.7714 g/litre
Viscosity (-33 °C)	0,254 centipoise
Vapour Pressure at 25 °C	10 atm
Critical Temperature	132.45 °C
Critical Pressure	112.3 atm

Note: Data taken from World Health Organisations Environmental health criteria 54(1986) p. 15/16

Figure 1:

Model of the Ammonia (NH_3) Molecule



Note: Ammonia (NH3) molecule. Picture was acquired from pixabay.com. Graphic designer: Colin Behrens https://pixabay.com/illustrations/ammonia-nh3-chemistry-3d-atoms-1117246/

2.1.1. Acute Exposure to Ammonia Gas

Sudden exposure to ammonia gases is always an underlying risk when working in the vicinity of systems containing the chemical. It can be, for instance, from a burst pipe, safety equipment failure such as gasmask containment breach, or any number of human error scenarios or malfunction of equipment associated with the fuel system. The National Institute of Occupational Safety and Health (NIOSH) state that the Immediately Dangerous to Life or Health (IDLH) concentration value is between 300 and 500 ppm (NIOSH, 1994). The study 'Acute respiratory effects of exposure to ammonia on healthy persons' by Sundblad et al. (2004) examined the effects by exposing healthy human test subjects to varying levels of ammonia up to 25 ppm inside an exposure chamber. The study concludes that *"During ammonia exposure in an exposure chamber, symptoms related to irritation and central nervous effects increase and are constant with no sign of adaptation" (2004, p.1).* The harmful effect of the gas depends on the concentration of the gas, the duration of the exposure as well as the tidal volume (Amount of air displacement within a person's lungs) (Sundblad et al., 2004). The study, however, was aiming to get data on ammonia exposure within swine confinement chambers, not engine rooms on large sea vessels. Yet, it covered ammonia exposure in confined spaces, so the research remains relevant to this study. Another study suggests that if high enough concentrations of ammonia are inhaled, it may cause severe tracheobronchitis and respiratory failure (Leduc et al., 1992). If the victim survives, the effects may cause significant damage to the lungs and long-term respiratory impairment.

2.1.2. Long Term Exposure to Ammonia Gas

NIOSH recommends that the maximum exposure limit of ammonia is 25 ppm (18 mg/m³) Total Weight Average (TWA) over 8 hours and 35 ppm (27 mg/m³) Short Term Exposure Limit (STEL) over 15 minutes (NIOSH, 1994). Low concentrations of ammonia gases inhaled over an extended period of time, especially when combined with the inhalation of different harmful particulates, may have negative effects on a person's lung capacity and increase the risk of contracting certain respiratory illnesses (Pawar et al., 2011). Though data on long term exposure effects are scarce, ammonia exposure has not been connected with carcinogenicity in humans as opposed to the traditional fossil fuels, which have well known cancer inducing properties (Lamberg et al., 2015; Rengarajan et al., 2015; Ryer-Powder, 1991).

2.1.3. Direct Contact with Anhydrous Ammonia

Ammonia is alkaline by nature and has a pH value of approximately 11, making it a corrosive chemical (Brown, 2018). It will corrode, among other substances, galvanized metals, copper, brass and/or copper alloys, and cast iron. Which means that it is important to use the proper material quality in ammonia systems (Green Shipping Programme, 2021). In the case of an explosion or other source of immediate direct contact with anhydrous ammonia (Ammonia that contains no water) on a person, the victim will be subjected to extreme chemical burns on all areas exposed to the chemical. The most common areas of exposure are the skin, respiratory system, and eyes, and the damage is mainly due to the effect of ammonium hydroxide, or ammonia dissolved in water (Amshel et al., 1999). The solubility of ammonia is 1300 units of ammonia to one unit of water. As a hydroscopic compound, ammonia seeks water from the nearest source to bind with (Green Shipping Programme, 2021). Another reason for concern is that the temperature of liquid ammonia is -33° C and the chemical freezes on skin contact at room temperature, this will cause frostbite of the same nature, but more intense than that of dry ice. Being subjected to frostbite can, in severe cases, cause substantial tissue damage in the affected areas as the tissue freezes and may cause circulatory obstruction and necrosis (Gao et al., 2021; Zook et al., 1998). The severity of the frost- and chemical-burns depends on the amount of ammonia and how quickly one is able to wash the exposed areas with water to dilute the corrosive chemical as well as heat up the frost-burned areas.

2.1.3.1 High Risk Operations

High risk operations are situations where exposure or fire hazards are greater than during normal operations, such as bunkering, where there are strict rules and regulations that dictate the operating procedures and documentation of bunkering standards (International Maritime Organization, 1993, 2015). For LNG, the international organization for standardization (ISO) have released a document providing detailed descriptions regarding transfer system design, bunkering processes and procedures, management system/quality assurance, personnel training, and risk assessment (International Organization for standardization, 2017). Such regulations must be followed in order to be allowed to proceed with bunkering operations in port states which implement them. As of this moment, there are no official documents specific for ammonia bunkering. The closest regulations regarding the transfer of ammonia and other toxic and flammable chemicals can be found in the IGC Code.

2.1.4. Engine Room Fire/Explosion

Compared to marine diesel, which today is the most common fuel used in the maritime industry, ammonia has a much higher auto-ignition temperature (Dimitriou & Javaid, 2020). The autoignition temperature of ammonia is at 924K while diesel lands at 504K,meaning that a leak dripping down on a hot surface is not likely to ignite ammonia without a kindling element such as a spark or a flame. This suggests that the risk of fire in an engine room using ammonia as fuel will be much lower than that of an engine room using diesel. However, the autoignition temperature is only the temperature at which the substance self-ignites, if a kindling source would be present, there is a chance that the gas will ignite (Jishin Jayan et al., 2021). Ammonia has a boiling point of -33°C, which means that if the chemical were to escape the closed system through a leak, it would immediately start to evaporate and mix with air and hence become a fire hazard. The various types of flame that can be caused by a leakage with kindling present includes flash fire, vapour cloud explosion, pool fire and jet fire. However, while the gas is considered flammable, the flammability limits are quite narrow and the fire hazard of ammonia is very low (Karabeyoglu & Evans, 2012). On the other hand, ammonia is not likely to be used on its own as a fuel as ammonia alone is difficult to ignite and would have extremely high compression ratios (35: 1 – 100: 1) (Dimitriou & Javaid, 2020). For ammonia to be realistically implemented as a fuel you would need a dual fuel system with another substance with a high cetane number for the initial ignition. The high cetane number of the additional fuel would imply that, wherever this fuel is involved, the risk of fire would be high, perhaps even higher than an engine room using regular MDO depending on what fuel would be used as a secondary fuel. Combining this with the fact that ammonia tanks when heated up has a high risk of exploding creates a very real danger that needs to be considered (Green Shipping Programme, 2021).

2.1.4.1 Flammability of ammonia

Ammonia is not considered a highly flammable gas as ammonia-air mixtures are difficult to ignite and the ignition temperature is approximately 650°C (Czuppon et al., 2000). Its in-air flammability limits are 16-25% by volume and the oxygen range needs to be within 15-79%. However, if these air mixtures were to be ignited, they can have explosive capabilities, which is why it is being considered as a fuel to begin with.

2.1.5. Risks of Storing Ammonia

The storing of anhydrous ammonia is on its own something that comes with a risk. The International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk, the IGC Code, is an amendment to the IMO convention Safety of Life at Sea (SOLAS) implemented in 1993, §17.13.1 of the IGC Code states that:

> *Anhydrous ammonia may cause stress corrosion cracking in containment and process systems made of carbon-manganese steel or nickel steel.*

This means that if the tanks and systems are not built for ammonia, there is a high risk of leakage over time. How to prevent these issues will be addressed in chapter 2.2.3.1.

2.1.5.1. Long-Term Storage

Storing ammonia on board a ship means constant relative proximity to the toxic chemical. This means that leaks occurring is more or less a constant risk. There are many faults that could lead to incidents with long term storage, including: tank over pressurization, pressure relief system failure, failure of refrigeration system, compressor failure, external fire, etc. (Jishin Jayan et al., 2021). Having containment failure happen when confined to the limited space of a ship can potentially be very dangerous. There are safeguards for this which will be addressed in 2.2.2.

2.1.6. Areas with Significant Risk of Ammonia Exposure

The IGF Code §15.8 covers areas where permanent gas detectors are to be installed. These are spaces where exposure to the gas is a non-negligible possibility and must be protected in order to minimize crewmember exposure to harmful gases. The spaces mentioned are:

> .1 the tank connection spaces;
>
> .2 all ducts around fuel pipes;
>
> .3 machinery spaces containing gas piping, gas equipment or gas consumers;
>
> .4 compressor rooms and fuel preparation rooms;
>
> .5 other enclosed spaces containing fuel piping or other fuel equipment without ducting;
>
> .6 other enclosed or semi-enclosed spaces where fuel vapours may accumulate including interbarrier spaces and fuel storage hold spaces of independent tanks other than type C;
>
> .7 airlocks;
>
> .8 gas heating circuit expansion tanks;
>
> .9 motor rooms associated with the fuel systems; and
>
> 10. at ventilation inlets to accommodation and machinery spaces if required based on the risk assessment required in 4.2 (International Maritime Organization, 2015).

These spaces cover most of the engine room, as well as open air spaces through vents, meaning that engine workers will be spending much of their time in areas considered having a risk of exposure. In the Green Shipping Programme (GSP) ‘Ammonia as a marine fuel safety handbook’ it is said that venting of ammonia vapours to open air during normal operation could prove a significant risk unless handled properly in compliance with the IGC Code and IBC Code. These risks, however, may be countered with a variety of different safety measures which will be examined in 2.2.

2.2. POSSIBLE SOLLUTIONS AND SAFETY MEASURES

This segment explores possible solutions to, and protection from, the many hazards involving ammonia in the engine room.

2.2.1. Portable Safety Equipment

Portable safety equipment should be used for protective or reactive purposes that is meant to be carried on person, either at all times, or to be placed within reasonable vicinity of areas where there is a high risk for injury or other incidents. The following chapter will explore different types of portable equipment that can be made available onboard ships to provide increased safety for the crew.

2.2.1.1. Personal Gas Sensors

A very effective way of protecting yourself from exposure to toxic gases is detecting them before they can do any damage. In recent years there have been a lot of innovation regarding gas sensors and there are a large variety of sensor types to choose from (Capone et al., 2003). Having engine room personnel always carry a personal gas sensor while working is today a fairly cheap and very viable option. There are many varieties of sensors that are suited for different concentrations, mixes, and temperatures. In order for a sensor to be carried on a person it will have to be viable for room temperature measurement, very low concentrations, and be durable enough to withstand being worn by engine room personnel. One candidate for this task is the polyaniline-TiO_2 nanocomposite sensor (Pawar et al., 2011). It combines the properties of the polyaniline sensor, which is a very precise, yet fairly fragile sensor material with that of the nanocrystalline Titanium Dioxide (TiO_2), which is a very popular material for modern gas sensors, in order to increase the mechanical strength of the sensor while keeping a high accuracy. This has proven to be a very suitable sensor for gas detection in room temperature. Given the fact that large scale use of ammonia on ships is still several years away, it is appropriate to look at some of the more cutting-edge sensor technologies. Namely graphene-based wearable gas and chemical sensors (Singh et al., 2017). The research regarding graphene sensors shows that the material has much promise and incredible flexibility. Graphene is an immensely versatile material that consists of a 2-Dimensional sheet of carbon molecules. It is both extremely durable, transparent, and thermally stable. It is being discussed that graphene can be used to develop “flexible and stretchable wearable electronic devices” such as wearable gas and chemical sensors for, among many other chemicals, ammonia. This could mean that a chemical gas sensor would not need to be carried as a bulky brick-like device, but rather something flexible to be attached to work clothes or to some other gear crewmembers would always be carrying.

2.2.1.2. Personal Gas Mask and Breathing Apparatus

If there were to be a leak in an engine room space, the only way to be able to move about inside that space would be to wear a respiratory protection. Of course, one should avoid moving through these spaces unless absolutely necessary. In an interview with MAN, a company developing ammonia propulsion for ships, it was said that a personal gas mask should be carried by engine crew at all times while in engine spaces in case of an emergency. The mask should be a full-face mask complete with a filter (Air Liquide, 2020). Should there be a toxic leak inside an engine room space, the environment within that space would in many ways become similar to that of an enclosed space. In the International Safety Guide for Oil Tankers and Terminals (ISGOTT) 10.6 Emergency Procedures, it is stated that:

> *"When an accident involving injury to personnel occurs in an enclosed space, the first action must be to raise the alarm. Although speed is often vital in the interests of saving life, rescue operation should not be attempted until the necessary assistance and equipment have been mustered."*

And

> *"Whenever it is suspected that an unsafe atmosphere has been a contributory factor to the accident, breathing apparatus and, where practicable, lifelines should be used by persons entering the space."* (International Chamber of Shipping, 2006).

Having this in mind, carrying a personal gas mask on your person may not only help speeding up the rescue of injured crewmembers, but also help a person escape a suddenly toxic environment before succumbing to/getting injured from the gas. A filtered mask does not, however, protect against oxygen deprivation (Air Liquide, 2020). Depending on the severity of the leak, a self-contained breathing apparatus will be required and should be kept readily available in case of emergency situations. A self-contained breathing apparatus should also be kept close during maintenance activities on installation systems.

2.2.1.3. Protective Gloves

The hands are the most likely part to be subjected to unwanted substances, so it is important to wear proper hand protection while working with high-risk chemicals (Air Liquide, 2020). Wearing Standard EN 374 gloves while risking exposure to ammonia is recommended in order to avoid chemical burns. Additionally, when in contact with transfer lines, cold insulating gloves of standard EN 511 will help protect from the freezing temperatures of the medium when risking direct exposure.

2.2.1.4. Eye Protection

Whenever there is a risk of a person's eyes getting exposed to any dangerous chemicals, such as when breaking transfer connections, it is imperative to use eye protection (Air Liquide, 2020). Since ammonia is severely damaging to the eyes it is incredibly important to shield oneself from it, or risk being permanently blinded. Standard EN 166 eye protection along with a face shield is recommended for these situations.

2.2.1.5. Chemically Resistant Clothing

There may be situations, such as emergency situations, where gas masks, gloves, and goggles will not be enough to protect a person from getting in contact with ammonia. In these cases, or when these situations have a risk of developing, chemically resistant, protective clothing should be worn or kept readily available (Air Liquide, 2020). The standard EN-943-1 is a full protective suit that shields from both liquid, solid and gaseous chemicals.

2.2.2. Fixed Safety Equipment

Fixed safety equipment in this instance means stationary equipment which is easily accessible and readily available for use in the event of an accident. As opposed to portable safety equipment which is safety equipment that one may carry on their person. The chapter also includes leak prevention measures and fixed gas detection installations.

2.2.2.1. Chemical Wash Stations

When exposed to ammonia, especially in its liquid state, it is, as mentioned in 2.1.3., crucial to have the exposed areas rinsed and washed with water as soon as possible to limit the tissue damage from the chemical burns (Green Shipping Programme, 2021). The person exposed should be moved to a safe place and the exposed areas should be rinsed for a minimum of 15 minutes. This means that water must be readily available in close proximity to wherever there is a risk of ammonia exposure. The most effective way to provide this is through decontamination showers and eye wash stations. These should at the very least be placed close to bunkering stations, exits from tank connection spaces, exits from fuel preparation rooms, and in engine rooms.

2.2.2.2. Fixed Gas Detection Installations

The safest way to detect toxic gas leaks is by having stationary sensors placed in at-risk areas and spaces of the engine room. There are many types of sensors with different methods of detecting toxic gases (Capone et al., 2003). For instance, we have the solid-state method, which use metal oxide or conducting polymers, the optical method using tuneable diode laser spectroscopy, and other methods such as electrochemical sensors, surface acoustic wave sensors, and field effect transistor sensors. (Kwak et al., 2019) Whichever sensor works best depends on where the gas is being measured, what temperature the gas is expected to be, what other gases might be present, etc. These factors will vary across the many spaces within an engine room. The important thing is to cover the at-risk areas (covered in 2.1.6.) with sufficient detection to keep the crew as safe as possible at all times.

2.2.2.3. Purging for Maintenance Operations

Doing maintenance on ammonia systems means that the lines should be purged before any disassembly can take place in order to minimize exposure to the chemical, and to minimize environmental pollution. In in the interview with MAN, it was said that before doing maintenance on the fuel system, due to the fact that it will most likely be a dual fuel system, the lines and equipment may be flushed and purged with the other, less toxic fuel being used. Meaning that there would be no need to bring in a separate purge medium and the maintenance would be similar to that of today's diesel systems. For LNG carriers there is an inert gas/dry air plant in a segregated part of the engine room to provide purging and aerating of cargo tanks and related piping systems (Pentatech CO, 2005). However, co2, which is a common inert gas used for inerting cargo and fuel tanks with fossil fuels, cannot be used as inert gas for ammonia systems as it will form solid ammonium carbamates inside the fuel lines when reacting with ammonia (Kim et al., 2008). Nitrogen, on the other hand is an ideal purging medium as it is considered a non-reactive non-flammable gas. It can be supplied either from liquid nitrogen gas containers on board, or from pipelines when moored in a dock with nitrogen supply capabilities.

2.2.2.4. Double Walled Piping

Double walled piping is a fairly effective way to protect from sudden leaks in lines and connection points that transport toxic or in other ways dangerous substances (Green Shipping Programme, 2021). The pipes have an internal pipe wall, where the inner diameter is used for transport of a substance, as well as an additional, protective pipe wall on the outside with a duct containing controlled atmosphere inside equipped with gas sensors and air ventilation. The IGF Code, §9.5.1. states that:

> "*Where fuel pipes pass through enclosed spaces in the ship, they shall be protected by a secondary enclosure. This enclosure can be a ventilated duct or a double wall piping system. The duct or double wall piping system shall be mechanically under pressure ventilated with 30 air changes per hour, and gas detection as required in 15.8 shall be provided. Other solutions providing an equivalent safety level may also be accepted by the Administration.*"

Having the ducts ventilated ensures that airflow helps the sensors pick up potential leaks, protects crewmembers from exposure and activate the Emergency Shutdown System (ESD).

2.2.2.5. Emergency Shut Down Systems

Emergency Shut Down (ESD)-systems are there to protect machinery spaces from potential leaks, power failures, or explosion hazards. IGF Regulations dictate that arrangements such as gas detectors, shutoff valves, redundancy, and efficient ventilation shall be provided for machinery spaces certified for periodically unattended operation (International Maritime Organization, 1993, 2015). This is used in situations such as bunkering or loading of toxic or flammable cargo in bulk.

2.2.2.6. Gas Leak Prevention

In order to prevent gas leakage in areas where it would be impractical to use double walled piping, tank connection spaces (TCS) and fuel preparation rooms (FPR) should be arranged (Green Shipping Programme, 2021). Equipment to process the fuel should all be located within a FPR and tank connections should be located within a TCS that is mounted on the tank. Due to the toxic nature of Ammonia, both these kinds of spaces should be gastight and equipped with airlocks to keep vapours inside and to make it easier to escape/rescue injured personnel from within the spaces. The spaces should also be equipped with continuous ventilation creating an under-pressure with ventilation outlets placed in areas where the risk of subjecting crewmembers to toxic gases is as low as possible.

The tanks need to be of a certain type and quality in order to minimize tank rupture incidents. Based on quantitative risk assessment (in an industrial setting), it is recommended to use double wall double insulation (DWDI) tanks instead of single wall tanks due to the failure rate being nearly on hundredth in comparison (Pattabathula, 2019). The tanks should also be equipped with at least two pressure relief valves along with two vacuum relief valves to make sure maintenance can be performed on a valve without losing the tanks protection. A permanent nitrogen connection should be present for each tank instead of air ingress to avoid stress corrosion of the tank material. Being aboard a ship in proximity to a failing storage tank can be potentially lethal and regular safety inspections would need to be performed in order to minimize these risks.

2.2.2.7. Ammonia Vapour Ventilation

Minimizing venting ammonia vapours to open air should always be high priority, both from a safety, and an environmental perspective. It will be impossible to completely prevent open air ventilation of ammonia, but systems can be put in place to reduce discharge as much as possible, and certain toxic hazard zones on outer deck will need to be established to ensure the vapours stay clear of air intakes and other openings to enclosed spaces. Since there are no case studies on ships using ammonia as propellant, the next best thing is to look at the IGC- and IBC (The International Code for the Construction and Equipment of Ships Carrying Dangerous Chemicals in Bulk)-Codes for regulations regarding toxic cargo venting (Green Shipping Programme, 2021). The IGC Code mentions that mechanical ventilation systems should be fitted within spaces which contain cargo handling equipment. This ventilation should, in order to ensure that toxic or flammable fuels does not accumulate, have the capacity of at least 30 changes of air per hour (International Maritime Organization, 1993). Note that this regulation relates to *cargo* handling, and not specifically fuel operations. The IGF code also has regulations regarding hazardous area zones on deck. However, these regulations only focus on fire and explosion prevention and not so much the toxicity of the chemical, which is necessary to cover the risks of ammonia. In order to achieve proper guidelines for ammonia fuel handling, the IGF code would need to be amended with chapters specifically focusing on ammonia.

2.2.3. Existing Safety Regulations

This segment will cover what existing regulations may be relevant for the study. As there are no current regulations regarding the use om ammonia as a propellant, the regulations examined are largely relating to ammonia transport through the IGC Code, and LNG systems through the IGF Code.

2.2.3.1. The IGC Code on Storing Ammonia

The IGC Code is there to set an international standard for safe operation and handling of liquefied gases on gas carriers. It has a separate chapter covering the use of liquefied gas cargo as fuel, however, it does not permit the use of ammonia, as a toxic chemical, to be used as fuel on gas carriers. Meaning that until the code is amended, the use of ammonia as fuel is prohibited for gas carriers (Green Shipping Programme, 2021). The IGC Code does, however, contain a chapter regarding the guidelines in safely storing ammonia relating to the type of tank-material to use as well as safe storage temperatures and oxygen content. It states that in order to avoid stress corrosion cracking on piping and storage tanks made from carbon-manganese steel, the material should be fine-grained steel with a minimum yield strength of below 355N/mm² and an actual yield strength of below 440N/mm² (International Maritime Organization, 1993). Another measure should be taken as well, such as: the use of a lower strength with a minimal tensile strength below 410 N/mm², post-weld stress relief heat treatment should be applied to storage tanks, the storage temperature of the chemical should be close to its boiling point of -33°C, but never above -20°C, and/or the ammonia should at least contain 0,1% w/w water. Where the yield properties of carbon-manganese tanks and pipes exceed 355N/mm² minimum and 440N/mm² actual, a post-weld stress relief heat treatment should be applied to the system. If nickel steel with a below 5% nickel content is used, the storage temperature should also be kept at around -33°C and not above -20°C. Finally, it is also recommended that the dissolved oxygen content is kept below 2.5 ppm w/w.

2.2.3.2. The IGF Code

The SOLAS convention was amended in 2015 in order for ships to be allowed to use low-flashpoint fuels as long as they would comply with the International Code of safety for ships using Gases or other low-flashpoint Fuels, or the IGF Code. The code is meant to, as the title suggests, set an international standard for ships using low-flashpoint fuels, extended beyond that which is provided by the IGC-Code. So far, the safe use of ammonia is still being investigated and there are not yet any official standards for the use of the chemical as fuel. The code covers basic functional requirements for all fuels included in the code. Yet, specific design requirements are so far only covered for LNG. Other low-flashpoint fuels need to be developed further before specifics can be added into the code. What has been established by the IGF code and the DNV-GL regarding safe handling of LNG fuel, is that it mainly revolves around concepts like segregation, where you keep the sensitive installations clear of external dangers such as collisions or fires, double barriers, meaning having a second layer of protective barrier, such as dual layer piping, around areas with a risk of leaking, leakage detection, normally in the form of fixed gas detection installations, and automatic leakage isolation, for instance in the form of automatic shut-down valves where the gas detectors indicate a leak (Green Shipping Programme, 2021).

2.2.3.3. Firefighting Measures for Ammonia

Air Liquide's safety data sheet NOAL_0002, mentions that if a leak is discovered, all ignition sources need to be eliminated. When fighting a leaking ammonia gas fire, you should not attempt to extinguish the fire unless the leak can be stopped safely. Doing so could lead to spontaneous/explosive reignition; However, the surrounding area should be sprayed down to help keeping the fire from spreading. If there are storage tanks of volatile chemicals nearby, they should be sprayed with water, if possible, to cool them down until they can be safely removed. The use of water spray is effective in knocking down fire fumes. Suitable Extinguishing media is water spray/fog, or foam. It is not suitable to use carbon dioxide or water jet, these can however be used to control fire in the surrounding area. Gas tight and chemically protective clothing and a self-contained breathing apparatus should be used by anyone attempting to fight an ammonia fire.

2.2.4. Educating Personnel on Hazards

Arguably the most effective way of preventing accidents, especially the ones involving human error, is educating the workforce on the risks and hazards regarding their work environment. Human error is responsible for approximately 80% of global accidents in marine engine rooms (Islam et al., 2020). According to the IGF code, Chapter 17, there should be regular drills and emergency exercises performed on board (International Maritime Organization, 2015). Examples of exercises relating to gas mentioned in the code are:

> *.1 tabletop exercise;*
>
> *.2 review of fueling procedures based in the fuel handling manual required by 18.2.3;*
>
> *.3 responses to potential contingences;*
>
> *.4 tests of equipment intended for contingency response; and*
>
> *.5 reviews that assigned seafarers are trained to perform assigned duties during fuelling and contingency response.*
>
> *Gas related exercises may be incorporated into periodical drills required by SOLAS.*

Having the crew understand the nature of these accidents is the key to preventing them in the future.

2.2.4.1. Risk Assessment

According to the IGF Code, §4.2, a risk assessment is to be made on any reasonably foreseeable scenario affecting persons onboard with regards to low-flashpoint fuels (International Maritime Organization, 2015). It includes issues such as the ships structural integrity, physical layout, operation, and maintenance. Whenever a risk assessment is made, the risks are to be analysed using "*acceptable and recognised risk analysis techniques*". HAZID methodology is a proven technique used to identify hazards and limit loss (Rivera Domínguez et al., 2021). Using such methods is important in order to establish corrective and preventative measures in order to keep workers safe.

2.2.4.2. Treating Ammonia Exposure

With ammonia exposure, there are different symptoms and treatments depending on the area effected and the state of matter of the ammonia, as well as the severity of the exposure (World Health Organization., 1988). Having had the skin contact with ammonia, the symptoms include redness and irritation, and chemical burns are a possibility. With eye contact there is severe irritation and redness as well as temporary or permanent loss of vision. The treatment for both skin and eye ammonia exposure is to immediately rinse them with massive amounts of water for at least 10 minutes in order to dilute the corrosive nature of the chemical. If clothing has been soaked with the chemical, said clothing should be removed from the exposed areas before rinsing with water. Due to the cold nature of anhydrous ammonia, be sure to check whether the clothes have been frozen to the skin below it. If so, rinse it with water before attempting to remove it. Mild inhalation exposure tends to result in irritation of the mouth, nose, and throat. It may also result in shortness of breath, cough and/or a fever. In the case of a more severe exposure, it can lead to breathlessness, pulmonary oedema, wheezing, pain in the chest, and oxygen deprivation throughout the body due to collapse of the circulatory system. It may also lead to Bronchitis. If these symptoms are showing after inhalation exposure, it is important to immediately seek medical advice from experts and try to have oxygen readily available for if the victim displays wheezing breath. It would be reasonable for the ship to carry pure oxygen tanks, salbutamol, and beclomethasone for the treatment of inhalation exposure while awaiting professional assistance.

3. METHODS

The strategy chosen for this study is ‘case study’ (Denscombe, 2014). Reason being to explore the many safety aspects of the new technology and in some ways compare these aspects with traditional ones. Using other methods such as a literature study, interview studies, or surveys were considered. Making a survey, however, would not make sense due to this study revolving around a largely untested and non-existent topic, and not enough people can provide relevant statistics and information. Making interviews was partly used in this study, however, getting in touch with people and being able to get face to face meeting have been challenging due to the COVID-19 pandemic. It would have been preferable to be able to meet with people in person and perhaps visit the locations where ammonia propulsion systems are being developed. One interview with Kjeld Aabo from MAN Energy Sollutions was made possible, however, through online platforms and video communication, but after that, other sources were prioritized. Having the study be a literature study was deemed to be too narrow of an information platform given how new the technology is. A combination of varying methods was used and ‘case study’ was ultimately chosen for the freedom it would bring in gathering information from different sources and being able to perform an in-depth exploration of the many aspects of ammonia propulsion from different perspectives.

The gathered data was mainly acquired from scientific articles and relevant literature on the subject from sources found in the databases ‘Web of Science’ and ‘Google Scholar’, rules and regulations from SOLAS, the IGC and IGF codes, as well as looking at safety data sheets from different industries and collecting information by interviewing people working with the development of the new ammonia-based engines. The articles were found using a combination of specific search phrases in google scholar and web of science such as: ammonia, safety, sensors, fire hazard, health, etc. The articles were then examined for relevant data regarding the subject of the study as well as assessing the credibility of the articles in the form of dating of the article, number of publications and author credentials. The ones containing relevant information and that were deemed credible enough for the study were saved in a research manager program for further study and possible application into the research paper. Regarding the endeavour to perform interviews, several companies and developers were contacted but it was difficult to secure an interview with people working on these projects. The one interview that yielded useful information regarding this study was with Kjeld Aabo of MAN Energy Solutions. He was contacted a few weeks after he held a guest lecture via zoom for Chalmers University of Technology about future fuel alternatives for ship propulsion at the end of 2020. He was quick to reply and was happy to take time to answer questions about the thesis subject. The interview questions were prepared beforehand on a document and later the interview was performed remotely via online video call. No other people were present during the interview on either side. The transcript of the interview is included in the appendix of this thesis. Some information gathered through interviewing was then implemented into a few subchapters of the theory chapter, his advice on where to look for further information was also considered. Having different sources of information provides a broader spectrum and get to look at the issue from several points of view which, again, fits well with the case study approach. Access to the databases and scientific articles was provided by the Chalmers Library and the IGC and IGF code were supplied through Chalmers courses in tanker safety. All the data collected through these means provided a good grasp on what hazards the engine workers might face as well as what can be done to minimize the exposure to the chemical.

The challenges for this study were figuring out relevant information given the cutting-edge nature of the technology. As of now, what the thesis covers is technically a non-existing problem, or at least a not yet existing problem. The fields in which the issues addressed in this study will emerge is as of yet only a hypothetical. It was necessary to provide a clear image of the issue by, in many ways, looking around the issue. The focus had to be on related fields and known facts about the currently known dangers of ammonia exposure and flammability. Another challenge was, as mentioned, the pandemic, which in many ways slowed down and obstructed the research of the topic. In normal times, in person interviews and visits to developers might have been possible. Many interviews were hard to secure, and some companies contacted never replied. Had these been normal times, cooperation with ammonia propulsion developers might have been easier and funding for the study might even have been on the table.

While gathering the data, the study was divided into segments, each tackling the different aspects of identifying the fire-hazards as well as exploring the health effects of acute and long-term exposure, and later what can be/is being done to prevent these hazards. The segment identifying the hazards was divided into subsegments covering acute exposure to ammonia gas, long term exposure to ammonia gas, direct contact with anhydrous ammonia, engine room fire/explosion, risks of storing ammonia, and areas with risk of ammonia exposure. These were studied first in order to get a good measure of the risks that needed to be addressed in the following chapter. The hazard prevention segment called '2.2. Possible solutions and safety measures' is divided into four main subsegments: portable safety equipment, fixed safety equipment, existing safety regulations, and educating personnel on hazards. A conclusion was later made based on information in the different segments in the theory chapter.

The reference management was handled through the use of 'Mendeley Reference Manager', and there were instructions from the institution to use APA7 as a citation method.

4. RESULTS

In this study, the issues regarding the safety of crewmembers aboard ships using ammonia as a propellant were examined. The many different risks and hazards were looked at and ways to minimize these risks along with the consequences of potential accidents were explored. There are not many case studies specific to the safe operation of ammonia-fuelled ships. There are, however, information relating to the risks and hazards of ammonia in existing regulations on handling of the chemical in transport and production along with case studies from other, different industries such as agriculture and the medical field which proved useful for the purposes of this study.

4.1. Fire Risk/Safety

The main risk with ammonia is its toxicity and corrosive nature, however, it has a non-negligible risk of fire that must be addressed as a safety hazard (Green Shipping Programme, 2021). In the event of fire aboard a ship, it is crucial to keep the ammonia tanks safe from excessive heat or risk fuel tank explosion. Meaning that the fuel should be stored separate from spaces with high fire risk, such as machinery spaces, and be equipped with a water spray system in order to keep them cool and protected. The fire risk of uncontained ammonia in the event of a leak should be quite low considering the high autoignition temperature and the narrow flammability limits compared to diesel oil (Dimitriou & Javaid, 2020). However, in the event of an ammonia leak being set ablaze, attempting to extinguish a burning ammonia leak with waterjet is highly inadvisable as it may produce explosive reignition (Air Liquide, 2020). The highest priority should be to stop the flow in the line if possible, and then use waterjet to cool down the areas around the fire and limit the spread as well as using water mist to knock down the burning fumes.

Table 4.1:
Main properties of ammonia compared to diesel.

Properties	Units	Ammonia	Diesel
Storage Method		Compressed Liquid	Liquid
Storage Temperature	K	298	298
Storage Pressure	Bar	10.3	1
Autoignition Temperature	K	924	503
Flammability Limits	Vol. %	16 - 25	0.6 - 7.5
Min. Ignition Energy	mJ	8	-

Note: The storage temperature in this table is based on room temperature, compressed storage, in atmospheric pressure the storage temperature would be 240 K.

Table data taken from "a review of ammonia as a compression ignition engine fuel" by Pavlos Dimitriou and Rahat Javaid, 2020, International Journal of Hydrogen Energy 45, p 7101.

4.2. Exposure

Exposure to ammonia, both as a liquid and as a gas, can potentially cause serious injuries to a person (NIOSH, 1994). From a safety perspective it is imperative to prevent and minimize this exposure as much as possible. There are existing safety equipment and guidelines available to protect from most hazardous scenarios and these should be implemented in coming regulations and always be in place aboard a vessel. The most effective way to keep crewmembers safe is to prevent leakages and only risk exposure when unavoidable, and even then, it should be done under controlled circumstances with the right safety equipment and precautions and training. Nevertheless, should a crewmember be subjected to ammonia exposure, it is crucial that the right countermeasures are readily available in order to avoid permanent injury or death. Emergency shut down measures should be in place covering a wide range of possible faults in the system during operations (International Maritime Organization, 2015). There should be chemical wash stations for the skin and eyes and self-contained breathing apparatuses in reasonably close proximity to high-risk areas, along with regular emergency training for all crew members. A personal gas mask, as well as gas detectors should be carried at all times when spending time in risk-zones. The medical cabin should be stocked with oxygen tanks, salbutamol, and beclomethasone in the case of exposure by inhalation (World Health Organization., 1988).

4.2.1 Acute Exposure Guideline Levels (AEGL)

The environmental protection agency (EPA) US have developed a guideline table for ammonia gas exposure based on parts per million (ppm) and exposure time (Green Shipping Programme, 2021). This provides an overview of the severity of ammonia exposure over time.

Table 4.2:

Acute exposure guideline levels with regards to exposure time and ammonia ppm:

	10 min	30 min	60 min	4 h	8 h
AEGL 1	30	30	30	30	30
AEGL 2	220	220	160	110	110
AEGL 3	2700	1600	1100	550	390

AEGL 1: Notable Discomfort, irritation, or certain asymptomatic non-sensory effects. However, the effects are not disabling and are transient and reversible upon cessation of exposure.

AEGL 2: Irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape.

AEGL 3: Life-threatening health effects or death.

Note: Table data taken from "Ammonia as a marine fuel safety handbook" by Green Shipping Programme, 2021, p 9.

4.3. Safety Equipment

Even though immense efforts may be made in order to limit crewmember’s exposure to ammonia and prevent leaks, there will still be a need for safety equipment in order to further minimize the risk of personal injury or death during high-risk operations, maintenance, and equipment failures. Even with the ammonia propulsion technology being under development and regulations currently being worked on, tested and approved personal safety equipment is readily available from other industries with experience handling ammonia (Air Liquide, 2020). A ship using ammonia for propulsion should also have fixed safety equipment installed and readily available, such as chemical wash stations, fixed gas detection installations, purging systems, double walled piping, ESD systems, FPR and TCS for leak prevention, and proper ventilation.
This equipment should be used in accordance with safety data sheets, and safety regulations once developed for ammonia propulsion systems.

4.4. Safety Regulations

There are no safety regulations specific for ships with ammonia propulsion. There are, however, a number of IMO safety standards set for related areas, such as the IGC Code for the maritime transport of toxic and flammable gases, or the IGF Code, in which the standards for low-flashpoint gases are handled (International Maritime Organization, 1993, 2015). Before the shipping industry can begin using ammonia as a marine fuel, effective safety regulations must be put in place due to the toxicity of the chemical (Green Shipping Programme, 2021). Such regulations will need to be developed over the coming decades while the technology develops and begins to take shape. The regulatory framework of LNG carries with it similarities to that of future regulations on ammonia in areas such as leakage detection, double barriers, bunkering procedures, segregation, and automatic isolation of leakages.

5. DISCUSSION

5.1 General Discussion

The questions regarding health and safety of persons working in high-risk areas are always an important topic to consider. Over the course of modern history, these questions have more and more frequently been brought to attention and in turn the safety in the workplace have improved greatly for the individual seafarer (Helle A. Oltedal & Margarera Lützhöft, 2018). This thesis strives to continue that trend by exploring the next step in the development of work-related safety at sea. Ammonia carries with it inherent risks given its toxic and corrosive nature, fire/explosion risk as well as low storage temperature. With the development of ship engines using ammonia propulsion and the possible event that it will cover a large part of the maritime industry, the questions covered in this study is more than relevant and one can never overthink issues of health and safety. The two main research questions of this study were "What hazards will engine room crews face going forward with ammonia used as a fuel?" and "What can be done to prevent these hazards and keep the engine room crews safe?".

For the first question, covered in 2.1, the possible risks and hazards were examined in the form of health effects of exposure to ammonia, fire/explosion hazards as well as the areas on board where the risk of exposure is present. During this research it became even more apparent that the occurrences and consequences of accidents are to be avoided as far as possible. What was found researching the second question, covered in 2.2, was that there are many ways to protect people from ammonia exposure, even when working in close proximity to the chemical. To limit exposure as far as possible; double walled piping, fixed gas detection installations, gas sealed fuel preparation rooms and protected tank connection spaces can and should be installed (Green Shipping Programme, 2021). Personal safety equipment such as personal gas sensors, gas masks, eye protection, gloves, and other chemically resistant clothing can be worn when in a high-risk area, or during high-risk operations and maintenance, to further protect oneself from exposure (Air Liquide, 2020; International Maritime Organization, 1993). Safety regulations, while not yet established specifically for vessels using ammonia for propulsion, are in place for ammonia transport and production. These established regulations can potentially be modified and extended to include the safe use of ammonia as marine fuel once the technology has been further developed. When, despite all efforts to prevent it, a person is exposed to ammonia gas or anhydrous ammonia in its liquid form, there are ways to limit the damage suffered by having chemical wash stations close to high-risk areas, a well-stocked medical cabin with treatments for ammonia, and other crewmembers trained in emergency first response with regards to chemical exposure (World Health Organization., 1988).

The validity and reliability of the information gathered through scientific articles should be of decent standard since most of the articles were found on official scientific databases and had been cited many times. If the information found in an article did not fully explain what was being examined, other sources were found and included to confirm and complete a statement made in this thesis. The only questionable reliability would be from older sources and articles, but they mainly focus on the chemical nature of ammonia which has not changed through time and their validity should remain unchanged. The fact that there are few sources on the actual technology being researched may also put the validity in question. However, as mentioned before, the nature of the subject revolves around a technology that is in its very early stages of development and the data simply does not exist yet. The data found in official IMO safety regulations, UN classification documents, and safety data sheets have previously been thoroughly examined by leading experts in their respective fields and the reliability of those sources should be without question. As for the validity of these documents, again, it is as valid as it will get at this point in time. With the development of the technology and new regulations, other documents might be more valid in time. The information gained from the interview should in the authors opinion be considered highly reliable as well as valid due to the person interviewed being a leading developer of the main subject of the thesis.

What this study establishes is a comprehensive summary of many of the potential risks and safety hazards to expect going forward with ammonia as a future propellant and what can be done to pre-emptively minimize these risks before individuals suffer the damages of toxic exposure. There are areas that can be further explored and information that will be made available once the technology develops further. The aim of this study was to dig deeper and provide a more detailed look at potential hazards and safety measures, and this goal has for all intents and purposes been reached. Many of the conclusions reached were expected, such as the dangers of ammonia exposure or the fact that there is protective gear to protect a person working in close proximity to the chemical, these risks are what brought the incentive for the study to begin with. However, many aspects of the study were interesting to get an in-depth view of, such as double walled piping, gas leak prevention through TCS and FPR, and the fact that, at this time, there are no rules and regulations covering fuels with this type of toxicity. The study also provided a detailed look at the basic properties of the versatile chemical that is ammonia, and the many fields where it is being used. It will be fascinating to see what the future holds for marine propulsion and how the choices made will impact both the workers and the environment as a whole.

5.2. Method Discussion

The case-study method used for this research was chosen to get as clear perspective as possible on the subject of the research. The many angles provided by the different kinds of sources was used to provide a fairly specific and detailed summation of the information gathered. However, this type of method is in many ways tailored for social studies, rather than technical ones. The reason the method was chosen though, was that the main characteristic of the study is that it focuses on one instance of the thing being investigated. In this study, the one instance of the thing being investigated was specifically the safety aspect of specifically ammonia propulsion specifically on ship engines. Other research methods were found to be quite limiting or straying from the purpose of the study.

What could have been done better in the information gathering segment of the study is the interview part of the research. There could have been more perspectives from experts in the field along with follow up interviews with more in-depth questions as more information about the subject was revealed. There were attempts to contact several ammonia engine developers, but in the end, there was only one that took the time for an actual interview. Stronger efforts could have been made in order to secure more interviews with more parties for a more nuanced perspective from different experts. On the literature side, a few of the sources used may be a bit on the older side and there might be more relevant and updated sources to be found on the specific subjects had there been more time and resources to do so. Also, perhaps SOLAS could have been mentioned a bit more on the regulation side of the research as it is one of the main regulatory documents regarding safety precautions used at sea, but at the time it felt excessive to include as it covers a very broad range of regulations, and the study was focusing on very specific circumstances. What shines through in a positive light with this study is that the endeavor to collect a wide variation of data and making a fairly coherent summation of it was, in the authors opinion, a success. The safety issues regarding the use of ammonia as a fuel aboard ships were identified and addressed and solutions and measures were explored in a sufficient manner. All in all, though not worked to perfection, it is a finished study. As the technology develops and more specific safety regulations are written there will be much more to be said about the subject.

6. CONCLUSION

The aim of the thesis was to study identify the risks and hazards regarding using ammonia as a marine fuel and to explore ways to prevent exposure to the toxic chemical going forward with this new technology. Two main hazards were identified to risk the health and safety of crewmembers where the greatest one is personal exposure to the chemical and the lesser one was fire/explosion hazard. Exposure to ammonia in its gas and liquid forms, as well as gas leak fires can be very dangerous and may cause serious damage or fatalities during accidents. However, many of these accidents can be prevented through safety measures and regulations, and the damages can be limited through fixed, and/or portable safety measures and equipment. The conclusions made in this study for the different hazard protections are as follows:

Chemical Exposure:

- The piping and storage tanks need to be the right material and kept to an acceptable standard to avoid rupture and gas leaks.
- Purging of ammonia gas lines should not be made with CO2 due to the reactive formation of solid ammonium carbamates, but instead with nitrogen gas or an alternative fuel in dual fuel systems.
- Proper ventilation of spaces should be in place in order to limit the accumulation of toxic and flammable gases.
- Fixed and portable gas sensors need to be in place and carried to identify possible leaks and minimize damage.
- Ammonia is toxic, corrosive as well as freezing to the skin, lungs, and eyes. Approved safety gear needs to be available and worn, and chemical wash stations should be in close proximity to where there is a risk for exposure.
- A personal gas mask should be carried at all times in case of emergencies or to be worn as extra protection when in a high-risk situation.
- The IGF, IGC and other relevant safety regulations should be considered and followed.
- Crewmembers should be trained in safe handling of ammonia and emergency response regarding corrosive chemical exposure.

Fire safety:

- Ammonia is a mildly flammable chemical that is difficult to ignite on its own, yet ammonia storage tanks may explode when exposed to intense heat.
- In the event of an ammonia leak, any kindling medium such as sparks or open flames should immediately be removed or extinguished.
- Should there be an ammonia gas leak fire, one should not try to extinguish it directly, doing so may cause explosive reignition. Instead, try to stop the flow of ammonia first while keeping the spread of the fire to a minimum.
- Water spray may be used to supress toxic fire fumes.
- Foam or water spray/fog are suitable extinguishing mediums.
- Carbon dioxide or waterjet should only be used on areas surrounding the fire in order to minimize the spread of the fire.

Safety Regulations:

- As of now, there are no specific safety regulations regarding the use of ammonia for propulsion of ships.
- The specific safety regulations mentioned in this study were chosen for their relevance to the field as they cover the safe handling of ammonia as well as liquified gas propulsion.
- The IGC Code covers safe storage and transport of ammonia as well as other toxic chemicals in bulk.
- The IGF Code covers the use of liquefied gases or other low flashpoint fuels for ships.
- GHS is the United Nations classification system for chemicals and many safety data sheets are based on these classifications.
- ISO handle the specifications for safe bunkering of liquid natural gases.

There is much more research to be done and technology and infrastructure to be developed before ammonia can become an established fuel for the maritime industry, and it is too early to say whether it will definitely reach that point in the future. However, if/when that point is reached, it will be at the risk of the health and safety of the workers and it is imperative that matters of work safety are taken seriously.

6.1 Recommendations for further research

If further research is to be conducted on the subject, it is best to wait a few years for the technology and the industry to develop. What could be added today is more of the environmental aspect and environmental health issues outside of the workspace regarding ammonia pollution. Other relevant research might be an in-depth look at the development process of new regulations and safety standards by IMO and the classification societies.
As time passes, the regulations and safety standards for ammonia will be developed. IMO will likely work on conventions for the safe handling of the fuel as amendments of the IGF code and those will be interesting and relevant to this study's research field once that information becomes available.

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APPENDIX

Interview transcript with Kjeld Aabo, MAN Energy Solutions:

1. Are people less likely to be exposed to ammonia with the new systems than being exposed to MDO in current systems, as of before maintenance such as pump overhauls or filter changes?

   - Yes, you can flush the piping and equipment on the engine before maintenance with the other fuel being used. The systems being developed at the moment are dual fuel systems. Pipe bursts are protected with dual layers and alarm systems.

2. What sort of safety equipment will need to be added to an engine room where ammonia is being used as a fuel? Will people need to wear gasmasks? If so, when?

   - Workers will probably always need to carry a gasmask when working. The industry already has measures for transporting ammonia so there will likely be many parallels to their safety standards. I recommend looking at standards for ammonia chemical tankers.

3. Are there any long-term health problems working with ammonia? Is ammonia less cancerous than diesel?

   - Again, this question might be better aimed at chemical tankers and manufacturers. Check regulation on transporting ammonia such as the IGC code.

4. Most health studies I have found so far regarding ammonia are based on the farming and sanitation industry, would you say these studies could be relevant in regard to gas exposure?

   - Yes, I would say so, other relevant industries are chemical tankers, transportation, and manufacturers, I would recommend getting in touch with them.

5. Is there a higher risk of engine room or other on-board explosions with ammonia as a fuel compared to diesel? I understand the fire safety is better with ammonia due to the much higher ignition point.

   - Explosion risks and fire risks are both lower as the pressures are lower and ignition point is higher.

6. How concentrated is the ammonia to be used as a fuel? Are we going to use a dual fuel system? Is it possible to use H2 as a pilot fuel?

   - We will be using pure NH_3 along with a secondary fuel in dual fuel systems, and no there are no plans on using H2 as a pilot fuel at this point.

7. I am assuming there will be new safety-courses regarding ammonia that the crew will need to take before working on these kinds of systems. Is it too early to know any details about that?

   - The safety standards are being developed at the moment so yes, it is too early to go into these details.

8. What can be done to protect from direct contact of the liquid ammonia? Are there special suits one would have to wear while overhauling these engines?

   - Not a big issue due to the fact that pumps and filters can be flushed before maintenance. but

9. Do you have anything you would like to add regarding personal safety issues with ammonia?

   - Not at the moment, no.

10. Do you have any recommendations on anyone else I should contact on these issues?

    - You should try to get in touch with danish ammonia producer Haldor Topsoe.

11. May I quote you on these answers in the thesis?

    - Yes

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