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A safety analysis on the potential risks onboard ships that would use ammonia as marine fuel

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A SAFETY ANALYSIS ON THE POTENTIAL RISKS ONBOARD SHIPS THAT WOULD USE AMMONIA AS MARINE FUEL

By

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Declaration

I certify that all the material in this dissertation that is not my own work has been identified, and that no material is included for which a degree has previously been conferred on me.

The contents of this dissertation reflect my own personal views, and are not necessarily endorsed by the University.

(Signature): ....

(Date): September 20, 2022

Supervised by: **Dr.Anish Hebbar**

Supervisor's affiliation**: Assistant Professor, World Maritime University**

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Abstract

Title of Dissertation: A safety analysis on the potential risks onboard ships that would use ammonia as marine fuel.

The shipping industry has to address and achieve, the GHG emission reduction targets as set out in the IMO's strategy for reducing GHG emissions and eventually phasing out as soon as possible. The decarbonisation of maritime transportation has apparently, no single pathway towards attaining a 'zero carbon' fuel at this stage. Various research projects are currently underway, to identify the most suitable alternate fuel considering all aspects including namely, the cost, scalability, availability, safety, performance, etc.

This research is an attempt to understand and acquire a wider perspective on the matters of safety and risks, pertinent to ships that select ammonia as the alternate marine fuel. The industrial accidents that have occurred in the sectors such as food processing, chemicals and fertilizers etc. have provided some insights into the potential hazards posed by ammonia and have been used in this research as case-study.

Acknowledging the fact that the uptake of ammonia as a marine fuel will be hugely dependent on the safety performance of the ships that would be the initial movers during this transition period, the researcher engaged with experts from the shipping industry to understand the risk profile and the mitigation measures considered prudent and necessary.

This research also attempts to identify the existing gaps in the current regulatory framework at a time, when the shipping regulators and the industry are still in the process of creating overarching guidelines for ship's use of ammonia as a marine fuel. The research outcomes are demonstrated with the aid of two diagrams namely, a fishbone diagram showing the cause and effect of an ammonia accident and a bow tie diagram incorporating the identified safety barriers in the concluding chapter of this research.

Keywords: Risk assessment, safety analysis, hazard identification, toxicity, corrosivity, pollution, safety barrier

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List of Abbreviations

ABS	: American Bureau of Shipping
ACGIH	: American Conference of Governmental Industrial Hygienists
AEGL	: Acute Exposure Guideline Level
BV	: Bureau Veritas
CAS	: Chemical Abstracts Service
CDC	: Centre for Disease Control
CoC	: Certificate of Competency
GHG	: Green House Gas
GHS	: Globally Harmonized System of Classification and Labelling of Chemicals
CoP	: Conference of Parties
CO_2	: Carbon dioxide
DNV	: Det Norske Veritas
EPA	: Environmental Protection Agency (United States of America)
ERPG	: Emergency Response Planning Guideline
ESD	: Emergency Shutdown
HSE	: Health and Safety Executive (UK)
IACS	: International Association of Classification Societies
IATA	: International Air Transport Association
ICE	: Internal Combustion Engine
IDLH	: Immediately Dangerous to Life and Health
IGF	: The International Code of Safety for ships using gas or other low flashpoint fuels

IGC	: The International Code of the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk
ILO	: International Labour Organization
IMDG	: International Maritime Dangerous Goods
IMO	: International Maritime Organization
IPCC	: Intergovernmental Panel on Climate Change
ISM	: International Management Code for the Safe Operation of Ships and for Pollution Prevention
ISO	: International Organization for Standardization
KR	: Korean Register
LEL	: Lower Explosive Limit
LFL	: Lower Flammability Limit
LR	: Lloyd's Register
LNG	: Liquefied Natural Gas
LPG	: Liquefied Petroleum Gas
MARVS	: Maximum Allowable Relief Valve Setting
MARPOL	: International convention for the prevention of pollution from ships
MLC	: Maritime Labour Convention
MSDS	: Material Safety Data Sheet
NH_3	: Ammonia
NIOSH	: National Institute for Occupational Safety and Health
NO_x	: Nitrogen Oxides
OSHA	: Occupational Health and Safety Administration
PEL	: Permissible Exposure Limit

PPE	: Personal Protective Equipment
PPM	: Parts Per Million
PRV	: Pressure Relief Valve
REL	: Recommended Exposure Limits
SCR	: Selective Catalytic Reduction
SDG	: Sustainable Development Goal
SDS	: Safety Data Sheet
SOLAS	: International Convention for the Safety of Life at Sea
STCW	: International Convention on Standards of Training, Certification and Watchkeeping for Seafarers
STEL	: Short Term Exposure Limit
TLV	: Threshold Limit Value
TWA	: Time Weighted Average
UEL	: Upper Explosive Limit
UFL	: Upper Flammability Limit
UK	: United Kingdom
UN	: United Nations
UNCED	: UN Conference on the Environment and Development
UNFCC	: United Nations Framework Convention on Climate Change
USA	: United States of America
WEL	: Workplace Exposure Limit
WHO	: World Health Organization

Chapter 1: Introduction

1.1 Background

Albert Einstein once said, "There are only two ways to live your life. One is as though nothing is a miracle. The other is as though everything is" (Sessions, 2005). The world has acknowledged albeit lately, that the planet earth is warming. The recent statement by the World Health Organization (WHO), Director for Europe (WHO, 2022) on the record-breaking high temperatures and heat wave conditions that prevailed across Europe during the summer of 2022, quoted adjectives from news reports such as “Unprecedented”, “Frightening” and “Apocalyptic” to sum up the disastrous outcomes of climate change.

Historically, the rise in temperatures has been attributed to the increase in human activities and the corresponding increase in the concentration of the Greenhouse gas (GHG) emissions to the atmosphere (Khandekar et al., 2005). In 2015, at the United Nations Framework Convention on Climate Change (UNFCC), an international agreement was adopted which is popularly known as “The Paris Agreement”. This Conference of Parties (CoP) attended by 196 parties set its goal to limit global warming to well below 2, preferably to 1.5 degrees Celsius, compared to pre-industrial levels (UNFCC, 2015). Although international shipping was not included in the Paris Agreement, the International Maritime Organization (IMO), as the industry's regulating authority, has been active in its efforts to decrease greenhouse gas emissions from ships.

Global warming has been a serious concern and with its ever-growing visible impacts to both, nature and human lives, the shipping industry which contributes 2.89 % of the global anthropogenic emission (IMO, 2021), has a serious course correction on hand.

In solidarity with the United Nation’s global fight against climate change and in support of the UN Sustainable Development Goal 13, the IMO had amended the ‘International Convention for the Prevention of Pollution from Ships’ (MARPOL) requiring ships, to combine a technical and an operational approach to reduce their carbon intensity. The maritime industry had been exploring the use of alternate fuels against the now dominant fossil fuels in its efforts to meet the reduction in the levels of Nitrogen Oxide, Sulphur and Greenhouse gases as emission from the ship's exhaust. These changes are being undertaken, both on existing ships as retrofits and in newbuilding (DNV, 2021a).

The initial IMO strategy towards reducing the GHG emissions from ships adopted in April 2018 (IMO, 2019) has set ambitious targets for the maritime industry to adopt, with the ultimate aim of phasing out the GHG emissions from maritime transportation. The IMO has set targets of achieving 50% reduction in GHG emissions from ships on international voyages by 2050 and reducing carbon dioxide (CO_2) emissions by 70% by the year 2030, compared to the 2008 level. To meet the ambition set out in the initial IMO GHG policy, zero-emission vessels must enter the fleet by 2030 and make up a significant share of newbuilds thereafter. It is critical that zero-carbon solutions are not only commercially viable, but also technically possible and can be implemented and run securely (Lloyd's Register and UMAS, 2019). There are serious deliberations and research on the suitability and wider acceptability of a variety of fuels; and as a first step, hybridization of the existing ships is also a viable transitionary process and has the potential to provide a baseline which will lead towards a zero-emission configuration for newer designs (Reusser & Perez Osses, 2021).

The use of gaseous fuels such as Liquified Natural Gas (LNG), Liquified Petroleum Gas (LPG), Ammonia, Hydrogen raises the hazard level especially on the non-tanker ships, which earlier had very limited risk exposure in relation to the fuel onboard. The International Code of Safety for ships using gas or other low flashpoint fuels (IGF Code) was developed by IMO (IMO, 2015) to provide an international standard for ships, using low flash-point fuels other than those ships covered by the International Code of the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk (IGC Code). The toxicity and other hazards associated with most of these alternate fuels, require development of new safety standards (McCarney, 2020) as the current IGF Code focuses only on regulations to meet the functional requirements for LNG as fuel and is silent on other prospective fuels. Until such regulations are in place, approval of ships using fuels other than LNG will be based on alternative design approach, demonstrating that the design complies with the functional requirements of the IGF Code. This risk-based approval process is referred to as the 'alternative design' approach (part A sec. 2.3 in the IGF code), where an equivalent level of safety needs to be demonstrated as specified in SOLAS regulation II-1/55 and approved by the Administration.

Ammonia is an alternate fuel candidate that has the potential to emerge as one of the future alternate fuel options for the shipping industry. Ammonia can easily be liquefied by increasing the pressure to 10 bar at room temperature or cooling to -33 degrees Celsius at atmospheric pressure (MacFarlane et al., 2020). The availability of appropriate production and distribution facilities, as well as adequate bunkering infrastructure, are all prerequisites for launching a new fuel. Ammonia has the potential to have a huge influence in the next decades by enabling the shift away from our worldwide reliance on fossil fuels and contributing significantly to the reduction of greenhouse gas emissions.

1.2 Problem Statement

A majority of the alternate fuels under consideration, necessitate considerable on-board modifications and, therefore, designing a traditional system may not only be difficult but also have cost implications. Although ships have been carrying chemicals such as ammonia as cargo on liquefied gas tankers, there exist huge technical differences in the ships that are being built with the provision of ammonia as marine fuel. Most of the technical differences pose distinct safety challenges which need to be mitigated for ammonia to be considered as a safe fuel onboard.

Finding economical and effective answers to all of these difficulties, as well as establishing technical feasibility, developing suitable legislation, and putting in place safety procedures, will be critical in allowing more flexible routes to a low-carbon energy future on a global scale.

1.3 Aims and objectives of this research

The machinery space of a significant number of newer ships is set for a change, not only in layout but also additional equipment that may have to be fitted, based on the chosen energy conversion methods viz., Internal Combustion (IC) Engine, Fuel cell, battery, etc.

This research aims to assimilate the potential hazards associated with the use of ammonia as marine fuel onboard ships and assess the adequacy of the barriers in place, to control and mitigate those identified hazards. In the historical perspective, ammonia has been used for industrial purposes, and the knowledge of production, storage, transportation and usage is well documented. The research aims to study the available data on industrial accidents involving ammonia and critically assess the same in the shipping context.

Objectives of the Research

The research comprises of the following objectives:

1. To identify potential hazards that would be posed by the use of ammonia as marine fuel onboard ships; and
2. To examine efficacy of the safety standards currently being employed in the design and construction of ships that would use ammonia as marine fuel, in the interim hiatus period of non-existent uniform, international regulations.

1.4 Research questions

The researcher proposes the following research questions to meet the aim and objectives of this research:

1. What would be the causal factors of potential accidents onboard a ship designed to operate on ammonia as fuel?
2. What control measures would be required to be employed, to ensure safety of ship and personnel onboard, protection of marine environment and safe

shipboard operation and maintenance activities when ships use ammonia as marine fuel?

1.5 Structure of this dissertation

This introductory chapter provided a brief background on the trajectory of the international bodies in the pursuit of achieving elimination of the GHG emissions within the targeted period. Further, an insight was provided on the maritime decarbonization scenario and the specific challenges it gives rise to. The remainder of the dissertation is structured under five chapters as follows.

Chapter 2 examines maritime decarbonization and risk mitigation. The chapter commences with a background on the use of ammonia in other allied industries over the past years and provides an update on the data about the ships on order with various alternate fuel options. The researcher discusses the concept of hazard identification, risk assessment and safety analysis with thrust on the chemical processing industry acknowledging the marked hazards of ammonia which are dealt in the subsequent chapters.

Chapter 3 examines material safety data on Ammonia. The chapter introduces the standards governing the design of any 'Safety Data Sheet' and discusses the important sections such as physical and chemical properties, health and environment hazards, etc. The variance in the standards especially those concerning the exposure threshold and flammability limits are explored and tabulated.

Chapter 4 discusses the research methodology. The chapter explains the methodology employed in this research, and introduces the data collection technique, data analysis methods used in the research.

Chapter 5 examines the results and analysis. The chapter assimilates the data collected and starts with analysis of the industrial accident data to understand the underlying risks. The qualitative data acquired by way of interview with the experts in the decarbonization field, were analysed by selecting the themes and categorising them into broad groupings.

Chapter 6 concludes the dissertation with a discussion on the interpretation of the results and recommendations. The cause and effect of an accident is presented using a fishbone diagram and the safety barriers to prevent one, is demonstrated using a bow-tie diagram. The outcome of the research and the scope for future research are discussed in the concluding part of this chapter.

Chapter 2: Maritime Decarbonization and Risk Mitigation

2.1 Maritime decarbonization at crossroads

The transition to zero carbon fuels for the maritime industry is challenging and diverse with no single pathway to decarbonization, as yet. This is inevitable, as different sectors and regions of the world are expected to adopt the decarbonization pathway best suited for them based on the prevailing policy of the respective government(s), and shall surely be influenced by the developments that are taking shape around the world. Historically, the maritime sector has been connecting allied sectors and regions of the world, providing uninterrupted supply of the required product and has always played the role of an enabler. The improvements in technology and the manner in which other sectors prepare and finally make the transition to alternate fuels, shall have a bearing on the shipping industry as well (Müller-Casseres et al., 2021).

The Hellenic Shipping News network (2022) has reported that a record 268 alternate fuelled ships have been ordered in the first half of 2022; out of which 174 ships were non-LNG tanker ships. The remainder of the ships ‘on order’ include 66 ships that will be built on the “ammonia ready” concept and 3 ships on the “hydrogen ready” concept. These types of ships are expected to be initially fuelled by either LNG or other such fuels and shall be upgradeable to use ammonia as fuel, at a later stage as the technology develops and ammonia becomes widely available.

Although, cost and GHG savings are fundamental enablers for the fuel uptake, there are other aspects such as safety regulations, technical maturity, operators’ expertise, etc. which still have to be analysed to allay safety concerns, especially for zero carbon fuel options such as ammonia and hydrogen (Prussi et al., 2021). The most challenging task is to account for all potential failure modes of a system during development and to ensure safe operation under all circumstances (Bozzano et al., 2003).

2.2 Hazard recognition and safety analysis

2.2.1 Recognizing the hazards and the process of risk assessment

An effective safety management (Namian et al., 2018) is fundamentally dependent on the twin factors of hazard recognition and safety risk perception. The state of being considered as 'safe' is often described as the absence of adverse outcomes (accidents, incidents, personal injuries, work loss days, etc.), or more formally as a state in which the risk of harm to persons or of property damage is reduced to, and maintained at or below, an acceptable level (Hollnagel, 2008). This safe state is achieved through a continuing process of hazard identification and risk management.

According to Macdonald (2004), a hazard is 'an inherent physical or chemical characteristic that has the potential for causing harm to people, property or the environment.'

The national chemicals control guidance published by Swedish Chemicals Agency (2020) defines risk as the probability of an adverse outcome.

Risk = Frequency x Consequence of a hazard.

When dealing with the risk assessment of chemicals, the nature of the adverse outcome depends on the intrinsic property of the chemical and the susceptibility of the target organism, while the probability also depends on the degree of exposure to the chemical.

A risk is perceived to be large if the probability of an event is high, or if the loss is severe or both together and vice-versa (Hollnagel, 2008). The ability to identify not only the events that might lead to an adverse outcome, but also the outcome forms the prerequisite for ensuring safety at all times. In fact, this is what risk assessment is all about, and over the years numerous methodologies and techniques have been developed to make this process more reliable and efficient.

An effective risk assessment should comprise of three steps (Adamski & Westrum, 2003):

(a) Recognize the nature of the problem or even to acknowledge that there exists a problem.
(b) Recognize the "mechanisms" or the potential paths which may lead to an adverse outcome, to foresee the consequences, and to distinguish whether the risk posed is small or large.
(c) Consider or identify strategies that can be employed to either lessen or completely eliminate the risk or to safeguard against the outcomes. If any of these stages don't work, the risk might not be identified until an adverse outcome, by which point its usually too late to take any action.

According to Hendershot (2011), the chemical industry employs inherently safe design (ISD) philosophy for addressing safety issues in the design and operation of facilities that use or process hazardous chemicals. However, when one considers the multiple risks associated with any technology, including chemical processing, it is unlikely that any process or plant design can eliminate all hazards and risk. A combination of ISD, engineering and administrative controls will always be required to adequately manage all process risks.

2.2.2 Significance of a safety analysis

Safety analysis can be defined (Harms-Ringdahl, 2013) as a procedure for analysing systems in order to identify and evaluate hazards and safety characteristics. It includes quantitative and qualitative risk analysis, accident investigations, and also some other applications. It can be used to:

- Support efficient accident prevention;
- Contribute to an understanding of how accidents can occur at the specific workplace under examination;
- Increase awareness and communication; and
- Demonstrate systematic safety work.

Pidgeon (1998) had advocated integration of safety risk perceptions while making policies, as perceptions lead to actions with real consequences. The manner in which any worker perceives a risk in their daily activities would have an effect on their performance and, therefore, this factor should be taken into account when making risk-related decisions. The safety evaluation by the ship crew is, therefore, perceived to be an important aspect to ensure shipboard safety (Fenstad et al., 2016).

In addition to the several design requirements identified, any risk elimination or risk reduction process should, therefore, have supplemental requirements such as safety warning devices, personnel training and safe maintenance procedures for further minimizing the safety risk of hazard. The process required to eliminate or control safety risk by the order of hazard precedence as designed by Alberico et al (1999) is presented in the figure 1.

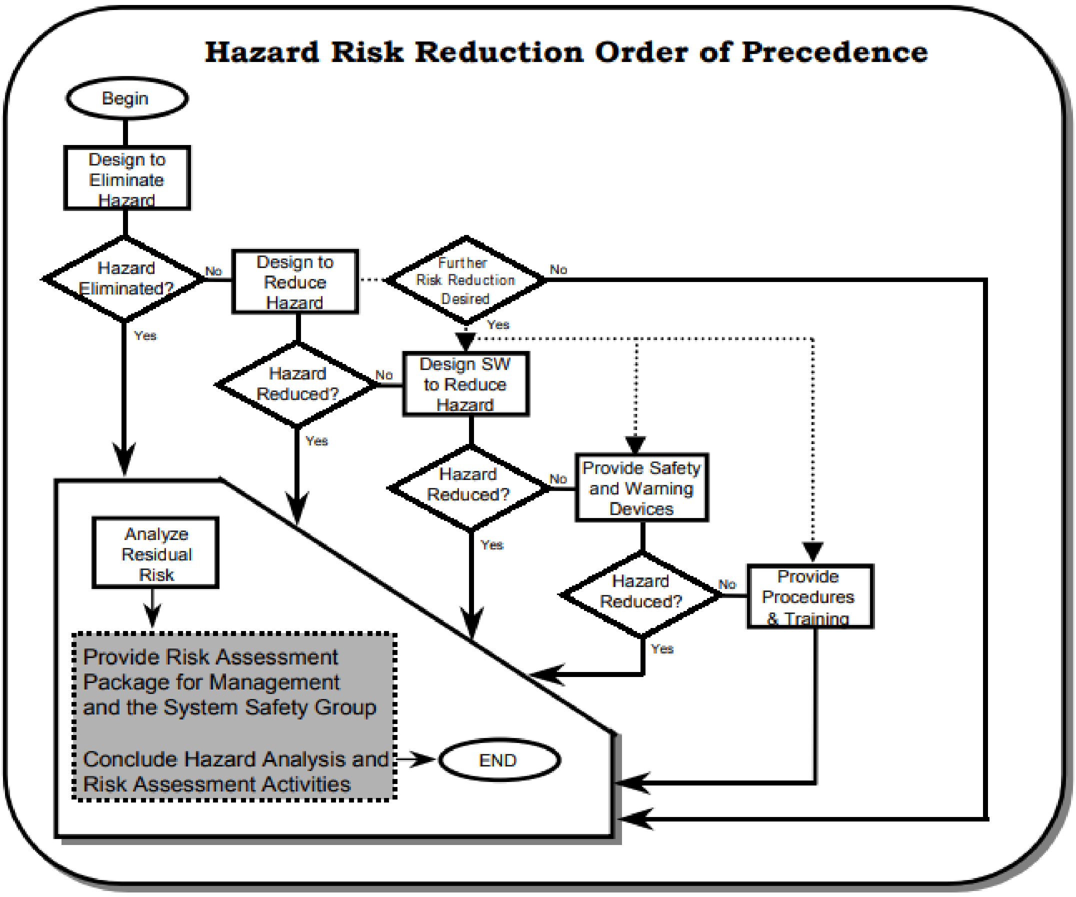

Figure 1: Hazard reduction diagram in the order of precedence

Source: (Alberico et al., 1999)

2.3 Ammonia - a marine fuel option

Ammonia has been known primarily for its use in the agricultural sector and had been produced for over 100 years. As compared to the global production of approximately 300 million tonnes of LPG, approximately 175 million tonnes of ammonia are produced annually worldwide. Most of this ammonia is used in the production of fertilizers, with small amounts going into the production of explosives, chemicals and materials (MacFarlane et al., 2020). Ammonia is also employed as refrigerant in large scale industrial coolers and as a raw material for a variety of industrial goods. Ammonia is a chemical additive used in the thermal power generation sector for Selective Catalytic Reduction (SCR) of Nitrogen Oxides (NO_x) and, therefore, most large thermal power plants have ammonia tanks (Kobayashi, Hayakawa, Somarathne et al., 2019).

The world is also exploring chemical energy storage in the form of carbon free fuels such as hydrogen to meet the decarbonization demands of the various industrial sectors. The renewable sources such as wind energy and solar power are intermittent and requires storage of the energy in batteries or in chemical form in order to cushion the effects of fluctuation in energy production (Kobayashi, Hayakawa, Somarathne et al., 2019). Ammonia is also looked upon as one of the options as a hydrogen carrier (Rouwenhorst et al., 2020).

An Ammonia (NH_3) molecule contains 17.6 wt.% hydrogen and contains no carbon. It can be readily decomposed to a gas mixture of 75% H_2 and 25% N_2, offering a high output and clean hydrogen generation with zero carbon emission (Wan et al., 2021). Ammonia on combustion produces primarily water and nitrogen. The substitution of ammonia for fossil fuels will therefore reduce carbon dioxide emissions significantly.

Ammonia is differentiated based on how it is produced (Ash & Scarbrough, 2019).

Brown ammonia is made using coal gasification, whereas grey ammonia sources the hydrogen from natural gas reforming. Blue ammonia is brown ammonia with carbon capture and storage technology applied to the manufacturing process and green ammonia is made entirely from electricity, water and air; the hydrogen for its synthesis is generated from electrolyser stacks. Green ammonia is not widely produced currently, but holds promise in the sustainability scenario.

2.4 Safety challenges in use of Ammonia as a marine fuel

There are several key barriers to ammonia's wide adoption as a marine fuel (Mallouppas et al., 2022). These include:

(a) high production costs, due to the high capital costs associated with ammonia's supply chain;

(b) availability, specifically the limited geographical locations available for ammonia bunkering;

(c) the challenge of ramping up current ammonia production; and

(d) the development of ammonia-specific regulations addressing issues such as toxicity, safety, and storage.

A ship that would use zero carbon fuel such as ammonia (ABS, 2021) and hydrogen (Bicer & Dincer, 2018) would have to be extremely cautious in the handling of the fuel and the containment/ preparation system due to its unique characteristics. The flammability, corrosivity and the level of toxicity of alternate fuels such as ammonia differ from the conventional fuel and is a safety challenge (Kim et al., 2020).

The industrial use of ammonia as refrigerant, chemicals and fertilizer had resulted in numerous accidents, some of which have been serious with fatalities (OSHA, 2022) (Technical Safety, 2022). A detailed analysis of these accidents provided in the subsequent chapters of this research, provided some significant insights on the hazards posed by ammonia and the mitigation measures that would be required for elimination of the risks.

2.5 Conclusion

The IGC Code regulation 16.9.2 prohibits liquefied gas carriers carrying ammonia to use ammonia as fuel due to its toxicity. The Part A of the IGF Code requires the ships other than liquefied gas carriers intending to use ammonia as fuel, to adopt an alternative design methodology in consultation with the flag administration so as to define the approval process in accordance with the conditions prescribed for installation of machinery, electrical system, fuel storage and distribution systems. The IGF Code, further requires a risk assessment to be undertaken so as to identify possible risks and consider the safety mitigating measures that may need to be implemented during design and operational procedures. In addition to the design of the vessel, specific risks such as bunkering, port operations etc. shall need to be further assessed with the concerned stakeholders.

In order to assess the risk and identify measures to mitigate them, it is vital to understand the physical, chemical and thermodynamic properties of ammonia and the hazards posed by them. The subsequent chapter dwells into these and highlights the inconsistency that exists in the standards applied across the different regions of the world.

Chapter 3: Ammonia: Material Safety Data

3.1 Background

In 1992, the UN Conference on the Environment and Development (UNCED) recommended a globally harmonized system of classification and labelling of chemicals, including safety data sheets as one of the six areas for action on environmentally sound management of toxic chemicals (UNCED, 1992). The Globally Harmonized System of Classification and Labelling of Chemicals (GHS) was developed and issued by the United Nations (UN) in 2003 (Ronald, 2012). GHS regulates the hazard-based labelling and classification of chemicals, and provides the basis for a worldwide harmonization of rules and regulations on chemicals.

GHS was aimed at enhancing the protection of human health and the environment during their handling, transport and use, by ensuring that the information about their physical, health and environmental hazards are available. Further, the United Nations (2007) issued a guidance on the preparation of a Safety Data Sheet (SDS) as an annex to the GHS in the year 2007 with the intention of having a uniform harmonized system, worldwide. This further led to the conduct of a systemic review of the existing standard ISO 11014-1:1994 by the International Organization for Standardization (ISO) and the development of the revised international standard ISO 11014:2009 by aligning the predecessor text with the GHS as regards hazard communication (ISO, 2009). The ISO's objective of this International Standard was to create consistency in providing information on safety, health and environmental matters for chemical products.

SDS's are viewed as an important element of hazard communication in the GHS. The GHS guidelines and the ISO 11014:2009, require the information in the SDS to be presented using the sixteen headings in the order specified in figure 2.

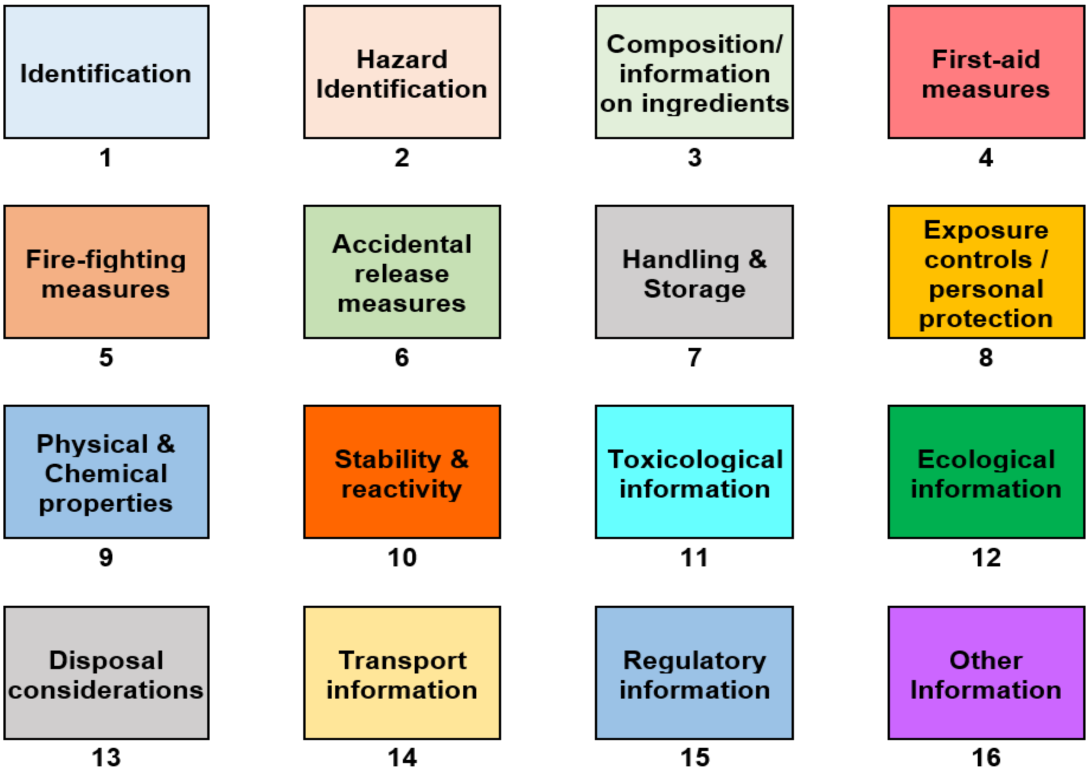

Figure 2: Schematic representation of 16 sections of the Safety data sheet

3.2 Physical and Chemical properties of ammonia

The Safety Data Sheet for ammonia that are being issued by product suppliers worldwide, largely follow the format described above and the particulars are listed in table 1.

Table 1. Physical and chemical properties of ammonia

Identification

Product name	: Ammonia, anhydrous
Chemical formula	: NH_3
CAS. No	: 7664-41-7
UN-Number, IMDG, IATA	: UN 1005
EC No.	: 231-635-3

Physical and Chemical Properties

Physical state:	:	Gas
Form:	:	Liquefied gas
Colour:	:	Colourless
Odour:	:	Pungent suffocating odour
pH:	:	10.6 - 11.6 (0.02-1.7% aqueous ammonia solution)
Melting Point:	:	-77.7 °C
Boiling Point:	:	-33 °C
Critical Temp. (°C):	:	132.0 °C
Flash Point:	:	Not applicable to gases and gas mixtures.
Flammability (solid, gas)	:	Flammable gas
Flammability limit - upper (%):	:	25 ~28 %
Flammability limit - lower (%):	:	15~16 %
Vapour pressure:	:	8.5737 bar (20 °C) Experimental result, Key study
Vapour density (air=1)	:	0.59 AIR=1
Relative density:	:	0.8
Solubility in Water:	:	531 g/l (20 °C)
Partition coefficient (n-octanol/water):	:	<1
Autoignition Temperature:	:	651 °C Experimental result, Key study
Decomposition Temperature:	:	> 450 °C
Dynamic viscosity:	:	0.7 mPa.s (48.9 °C)
Molecular weight:	:	17.03 g/mol (NH_3)

Ammonia is a flammable gas with a low flame speed (0.07 m/s), low flame temperature and is hard to ignite. The flammability limits are LFL = 14% vol and UFL = 32.5% vol at 25 °C (Europe - Chemsafe) or LFL = 15% vol and UFL = 28% vol at 20 °C (USA – NFPA) (Tan et al., 2020). The minimum ignition energy is generally estimated to be in the range of 12 ~ 50 MJ. Flashpoint as a physical property is applied only to material in liquid phase and, therefore, the flashpoint of ammonia has not been consistently identified in relevant publications such as the Safety Data Sheet (Japan et al., 2021). Such properties together with the possible dependence of the flashpoint on the method used to determine it (e.g., ISO 1523, ISO 2719, ISO 2592, ISO 3679, ISO 13736) have introduced uncertainty in determining the flashpoint of ammonia (reported with different values between 11°C and 650°C); but being a combustible gas at standard conditions, most of the methods and definitions for flashpoint are not applicable (International Association of Classification Societies (IACS), 2022).

The IMO has defined *Low-flashpoint fuel* as "gaseous or liquid fuel having a flashpoint lower than otherwise permitted under paragraph 2.1.1 of SOLAS regulation II-2/4."

Irrespective of the above, the IACS had vide paper submitted to the Maritime Safety Committee (MSC) (MSC 105/2/2) proposed that

> *"While it is a consolidated knowledge that ammonia may create explosive atmosphere when its concentration in the air is between 15% (LEL) and 28% (UEL), regardless of the definition of low flashpoint fuel given in the SOLAS regulation II-1/2.30, precautions should be taken in respect of the possible formation of both toxic and explosive atmosphere for its safe use as a fuel."*

3.3 Hazards associated with ammonia

Ammonia has a history of being used in various sectors worldwide and, therefore, there is ample understanding of the physical dangers, health and environmental hazard it poses.

3.3.1 Physical dangers

Ammonia gas is a flammable gas, lighter than air. However, under certain conditions, when compressed liquified ammonia gas initially escapes and comes into contact with moisture in the air, it tends to form an ammonia fog (CDC, 2011). These dense aerosol clouds caused due to the flashing phenomenon is likely to remain low to the ground, and could prevent ammonia gas from rising in the air. There exists a risk of these clouds getting transported by the winds to a populated area (Crolius et al., 2020). Dangerous concentrations of ammonia gas will occur quickly in enclosed or poorly ventilated spaces.

3.3.2 Health Hazards

According to the Classification, Labelling and Packaging Regulation of the European Union (Ash & Scarbrough, 2019), ammonia is classified as having an acute toxicity rating of 3 (with 1 being the highest level of danger). It is corrosive and hazardous when inhaled. This corrosive effect can result in acute eye injury, severe skin burns, and damage the respiratory tract. There is risk of frostbite or freezing of the skin on account of any contact with evaporating liquid, in the event of a leak.

The ammonia that has been in use in the various industries as fertilizers, refrigerants etc. have clearly defined safety procedures to prevent any exposure. For instance, the stipulated ammonia exposure limits at workplace (WEL) in the United Kingdom (HSE, 2018) are at table 2.

Table 2. UK HSE workplace exposure limits for Ammonia

	LTEL (8 hours reference period)		**STEL (15-minutes reference period)**	
	ppm	mg/m^3	ppm	mg/m^3
WEL	25 ppm	18 mg/m^3	35 ppm	25 mg/m^3

LTEL: Long Term Exposure Limit STEL: Short Term Exposure Limit

Areas where workers are regularly carrying out activities need to be monitored to ensure that these limits are not exceeded. The immediately dangerous to life and health (IDLH) level for ammonia is 300 ppm (CDC, 2011), which is substantially lower than the lower explosive limit (150,000 ppm). However, its odour can be detected by humans at concentrations below 1.5 ppm (Ash & Scarbrough, 2019), significantly lower than concentrations that produce eye, nose or throat irritation.

The protection of employees from hazardous chemicals has long been acknowledged by the International Labour Organization (ILO), as key to maintaining health of the personnel employed and sustainable landscapes. However, employees are still disproportionately exposed to chemicals in practically every industry (ILO, 2021). The occupational exposure limits for ammonia derived from the International Chemical Safety Card (ICSC) which was prepared by an international group of experts on behalf of ILO (ILO, 2013) and the WHO, with financial assistance of the European Commission are at table 3.

Table 3. ILO occupational exposure limits for ammonia

	Threshold Limit Value (TLV)	**EU-Occupational Exposure Limits**	
TWA	25 ppm	20 ppm	14 mg/m^3
STEL	35 ppm	50 ppm	36 mg/m^3

The Occupational Health and Safety Administration (OSHA) was formed in 1970 in the United States of America (USA). The National Institute of Occupational Safety and Health (NIOSH) was later created in the year 1970. The NIOSH issued the first Toxic Substances List in 1971, followed by publishing of the IDLH values in 1974. In the USA, the professional organizations had predated the formation of the governmental bodies; with the effect that governmental bodies such as the OSHA have not been able to update the exposure limits of the hazardous chemicals unlike organizations such as the NIOSH and the American Conference of Governmental Industrial Hygienists (ACGIH) (Bobst, 2017). A comparison of their respective standards is presented at table 4.

Table 4. Comparison of TWA and STEL of NIOSH, OSHA and ACGIH

	NIOSH - REL		**OSHA - PEL**		**ACGIH - TLV**	
TWA	25 ppm (10 hours)	18 mg/m^3	50 ppm (8 hours)	35 mg/m^3	25 ppm (8 hours)	17 mg/m^3
STEL	35 ppm (15 minutes)	27 mg/m^3	35 ppm (15 minutes)	27 mg/m^3	35 ppm (15 minutes)	24 mg/m^3

The Safety Data sheet issued by the product supplier in the USA consists all of the above-mentioned standards for the exposure limits related to ammonia as mandated by the OSHA (2014). The exposure limits prescribed in the SDSs issued, varies according to the legislation of the receiving State (Crolius et al., 2020) and is an area of concern. These thresholds are an important factor to appropriately design the emergency plans and may prove detrimental in case of a sudden release or an accident (Crolius et al., 2020).

The acute guidance values are intended to give decision support during planning, preparedness and response on potential human health consequences of chemical releases (Öberg et al., 2010).

The two internationally most frequently used guidance values are the Acute Exposure Guideline Levels (AEGL), developed by the U.S. National Advisory Committee for the Development of Acute Exposure Guideline Levels for Hazardous Substances (AEGL Committee) and the Emergency Response Planning Guidelines (ERPG) developed by the Emergency Response Planning Committee of the American Industrial Hygiene Association (AIHA). The AEGL and the ERPG systems are similar in that they have three comparable threshold levels (Tiers). Thus, inhalable exposure above the Tier 1 level causes slight, reversible effects such as discomfort and/or irritation. When the exposure exceeds Tier 2 the health effects are disabling. The effects may be non-reversible and/or impair the ability to escape but they are still non-fatal. Exposure above Tier 3 is deemed to be life threatening or fatal.

The ERP guidelines were issued to aid Emergency Response and to evaluate possible health effects to the public or emergency response personnel. The maximum values of ammonia that can be exposed in the three tiers of the Emergency Response Planning Guideline (ERPG) are at table 5.

Table 5. Emergency Response Planning Guideline (ERPG) values

Values → / ERPG Classification ↓	Listed value (ppm)	Calculated value (mg/m^3)
ERPG-1: *Maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to 1 hour without experiencing other than mild transient adverse health effects or perceiving a clearly defined, objectionable odour. Odour should be detectable near ERPG-1*	25	18
ERPG-2: *Maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to 1 hour without experiencing or developing irreversible or other serious health effects or symptoms which impair an individual's ability to take protective action.*	150	105
ERPG-3: *Maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to 1 hour without experiencing or developing life threatening health effects.*	1500	1050

Source: (Crolius et al., 2020)

AEGLs represent threshold exposure limits (EPA, 2008) for the general public and are applicable to emergency exposure periods ranging from 10 minutes (min) to 8 hours (h). The three levels viz. AEGL-1, AEGL-2, and AEGL-3 were created for five different exposure durations (10 min, 30 min, 1 h, 4 h, and 8 h) and have varying levels of the severity of the toxicity effects. The three AEGLs are defined as follows: AEGL-1 is the airborne concentration (expressed as parts per million [ppm] or milligrams per cubic meter [mg/m^3]) of a substance above which it is predicted that the general population, including susceptible individuals, could experience 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 is the airborne concentration (expressed as ppm or mg/m^3) of a substance above which it is predicted that the general population, including susceptible individuals, could experience irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape. AEGL-3 is the airborne concentration (expressed as ppm or mg/m^3) of a substance above which it is predicted that the general population, including susceptible individuals, could experience life-threatening health effects or death. The AEGL levels and the maximum ammonia concentration levels for the different time duration are specified at table 6 and conceptualised by the author in figure 3.

Table 6. Threshold ammonia exposure limits at AEGL 1, 2 and 3 vis-à-vis different time durations

	Ammonia concentration (ppm)				
	10 min	30 min	60 min	4 hrs	8 hrs
AEGL-1	30	30	30	30	30
AEGL-2	220	220	160	110	110
AEGL-3	2700	1600	1100	550	390

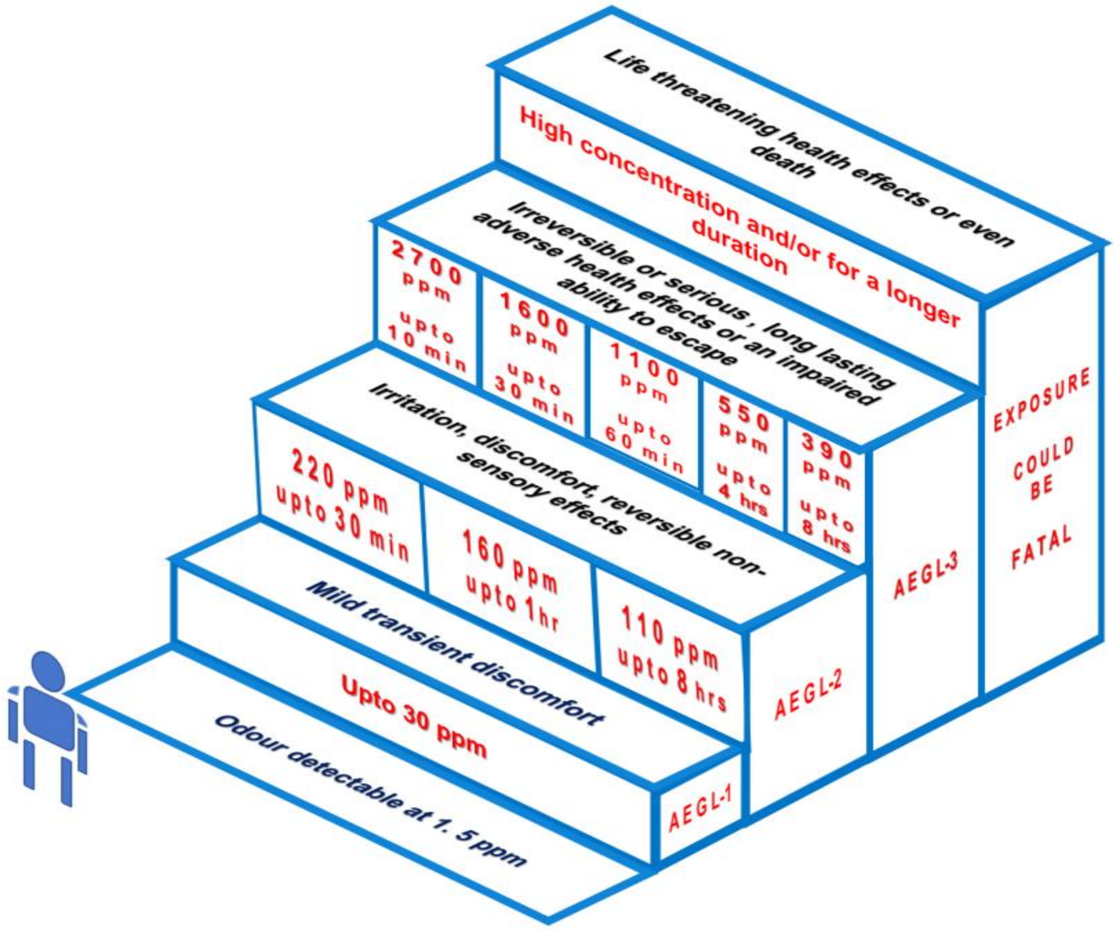

Figure 3: Threshold levels diagram conceptualized by the author based on Acute Exposure Guideline Levels (AEGL)

3.3.3 Environmental hazards

The United States Environmental Protection Agency (EPA) (EPA, 2022) have concluded that based on the nitrogen content, ammonia has two forms: the ionized form (ammonium, NH_4^+) and the un-ionized form (ammonia, NH_3). An increase in pH favours formation of the more toxic, un-ionized form (NH_3), while a decrease favours the ionized (NH_4^+) form. Temperature also affects the toxicity of ammonia to aquatic life.

Research by the EPA has showed that ammonia is a common cause for fish kills. However, the most common problems associated with ammonia relate to elevated concentrations affecting fish growth, gill condition, organ weights and haematocrit

(Milne et al., 2000). Exposure duration and frequency strongly influence the severity of effects (Milne et al., 2000). These chronic hazards posed by ammonia to the aquatic environment have long lasting effects (Ayvali et al., 2021).

3.4 Conclusion

Currently there is no single, acute guidance values for the exposure limits of ammonia, globally. There have been individual attempts by various nations which are comparable but not consistent. This poses practical difficulties in evaluating and benchmarking a common standard that shall be acceptable across the world. This lack of harmonization has the potential to affect the risk management and communication amongst the stakeholders in the event of any accident or may prove to be a stumbling block for an international collaboration. The variance in exposure limit stipulation may also have a bearing on the adoption of a common standard for the personal protective equipment and other such emergency equipment.

Chapter 4: Research Methodology

4.1 Introduction

Research methodology is the structured approach adopted by the researcher in order to find answers to the research questions, assimilating useful information in the process. The basic methodology used are qualitative, quantitative or a mixed method (Goundar, 2012). In this chapter, the methodology employed in this research is described, followed by other key elements viz., data gathering techniques, data analysis, ethical consideration, choice of participants, and the limitation of this research.

4.2 Methodology and design

The research method used in this research is qualitative research methodology. It can be classified as exploratory from the research objective viewpoint as there was very limited data available on the subject at the time of writing this dissertation.

A qualitative research approach relies on observations, informal interviews, and the researcher's own experience of events and processes (Rossman & Rallis, 2016). According to Jones (1995) qualitative research begins by accepting that there is a range of different ways of making sense of the world and is concerned with discovering the meanings seen by those who are being researched and with understanding their view of the world rather than that of the researchers.

In most qualitative studies, the researcher is the primary instrument for data collection and data analysis (Merriam, 2002). Although the qualitative method is generally undertaken using a relatively small but focused sample base, data collection can be rather time consuming.

This study was conducted in two parts:

(a) Firstly, accident data obtained from industrial accidents database were analysed as case study for understanding the causal factors of such accidents involving ammonia.

(b) Secondly, exploratory interviews were undertaken with the participation of experts that included members representing the shipping regulators, flag States, shipping industry associations, classification societies, and other important stakeholders who have been involved in the risk assessment, hazard identification (HAZID) and such studies for projects that not only include ships but other ancillary shore infrastructure such as bunkering facilities, ports etc.

Overall, figure 4 presents the author's conceptualisation of the research methodology.

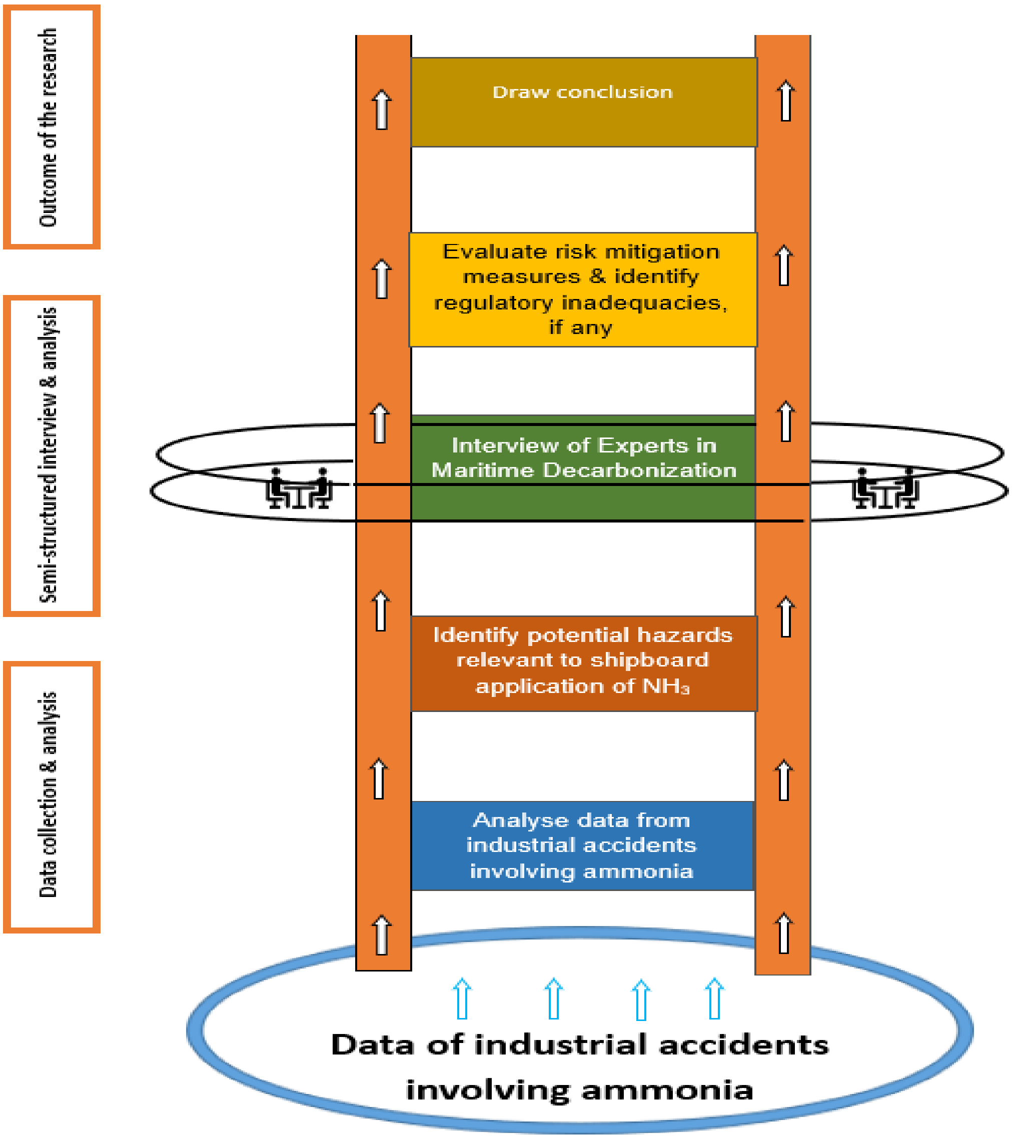

Figure 4: The Research Ladder (as conceptualized by the author)

4.3 Data gathering techniques

The data collection methods employed in this research include the following:

(a) *Industrial accidents data involving ammonia as case study*: collection of data on industrial accidents involving ammonia from authentic sources viz., US Department of Labour, OSHA (https://www.osha.gov/) and an independent, self-funded organization 'Technical Safety BC, Canada' (https://www.technicalsafetybc.ca/case-study-ammonia-release-incidents-2007-2017) which has been involved in overseeing safe installation and operation of technical systems, risks assessment studies, education, and research;

(b) *Document review*: collection of documented materials such as Material Safety Data Sheets, Classification Rules and Guidelines issued on the subject of ammonia as marine fuel;

(c) *Semi-Structured interview*. Qualitative researchers usually employ "semi-structured" interviews which involve a number of open-ended questions based on the topic areas that the researcher wants to cover (Hancock et al., 2001). The interview is a unique method of data collection as it involves a direct face-to-face interaction. The interview provides the researcher with an opportunity to follow up on the verbal leads and thus achieve higher degree of success in data collection and greater clarity. A semi-structured interview enables exploratory discussion that help the researcher to understand the what and the how but also to grasp and explore the internal dynamics of the research topic (Annan, 2019).

    The interviews were scheduled after the participants were provided with a set of initial questions on the subject. The interviews of the participants were conducted during the period July 20, 2022 till August 31, 2022 on the remote mode.

4.4 Choice of participants for the research

The participants for the interview, forming part of the qualitative method of data collection were chosen based on their expertise in the field of maritime decarbonization with the aim to establish a purposive sample. The participants have been working in different capacities as subject matter experts or specialists within their respective organization's as well as in other industry coalitions for the risk assessment studies and development of guidelines for ships that would use ammonia as a marine fuel. Few of the experts also have the exposure of working with the equipment manufacturers which include the risk assessment at the design and trial stage.

4.5 Data analysis

Data analysis is the most vital aspect of any research. The approach to data analysis essentially includes, organizing the collected data, reading and coding them, organizing the themes and interpreting the data (Cypress, 2018).

The data collected from the industrial accidents involving ammonia were analysed using the 'Root Cause Analysis' methodology and causes identified during the review of the data were assigned to three main categories, namely,

(a) Human factor

This includes four themes related to deficient safety awareness, deviation from safe working practices, lack of knowledge and human error.

(b) Management factor

This includes causes attributable to ineffective maintenance, lack of or ineffective supervision, ineffective or lack of adequate training and non-adherence to standard operating procedures (S0P).

(c) Technical factor

This includes technical causes such as mechanical defects, lack of adequate protection to critical machines, lack of physical barriers in potentially hazardous areas and failure to the automation and control system.

The findings were interpreted using the 'Fishbone diagram' which provides a visual interpretation of how the different facets of the problem interact and helps in identifying the cause-and-effect relationship.

The interview data were analysed using content analysis and manual coding. The data was divided into select categories and each was assigned the most appropriate theme derived from the data.

4.6 Limitations

The research was conducted at a time when the IC Engine for ammonia combustion was in its advanced stage of development and the trials had not commenced. Moreover, the risk assessment and feasibility studies by different industry groupings for different regions of the world on the specific aspect of ammonia bunkering has not been concluded and the research did not have access to any such inputs.

The intended validation study of the research outcome by way of a workshop with the participation of subject matter experts could not be materialized due to paucity of time.

Chapter 5: Results and analysis

The research further progressed using the methodology detailed in the previous chapter and in the order, a detailed analysis of the results obtained from the qualitative data is presented in this chapter. The first section of this chapter examines the industrial accident data and presents the causal factors; whereas, the second section analyses the qualitative data from the interview of maritime experts.

5.1 Accident data analysis

This research analysed as case-study, a total of ninety-six (96) industrial accidents that were retrieved as described in section 4.3. The aim was to identify the underlying causes that resulted in these accidents, which should prove to be useful in identifying potential risks, that ammonia would pose in its new role as a fuel, in the maritime decarbonization context. The case study data was limited to the period 2000 – 2021, with the sole intention of having a data that is not outdated and is relevant. It is believed that considering the technological advancement in the recent years, a rather old database will not provide a true assessment on the effectiveness of the safety barriers employed by other industrial sectors that have been using ammonia for over hundred years.

The extracted data was organized using worksheets and further classified based on multiple criteria such as severity of the injury caused to the people in the vicinity; and, the status of the industrial plant or the concerned equipment at the time of accident. The cause and effect of the accident was analysed for understanding the root cause of the accident and its consequence.

5.1.1 Status of the industrial plant at the time of the accident

The analysis of the accidents revealed that a majority (75%) of the accidents had taken place while the plant was 'in operation'. Maintenance activities accounted for 23% of the accidents and 2% of the accidents had occurred during transportation of ammonia.

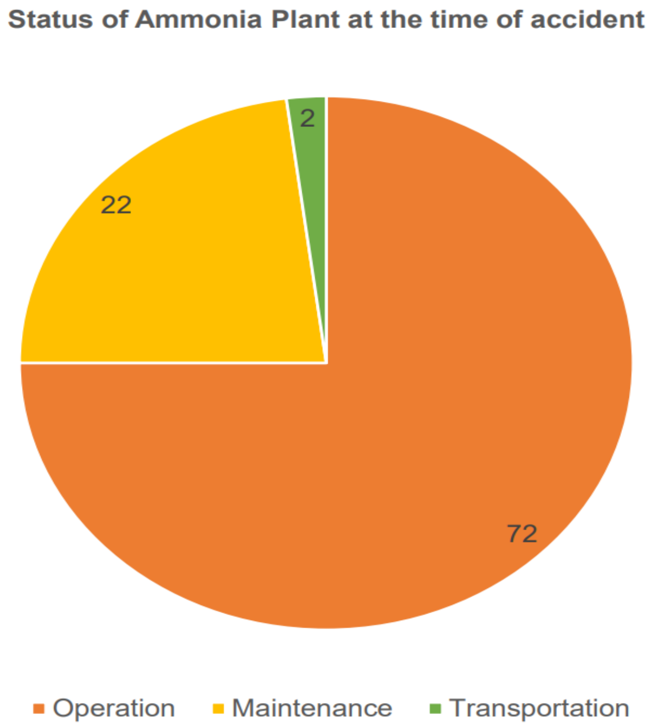

Figure 5: Pie chart depicting the number of accidents and status of the ammonia plant at the time of the accident (N = 96 accidents)

5.1.2 Impact of the accident on the industrial workers

The hazards of ammonia are well known and the exposure thresholds have been defined, documented by the ILO and most member State and/or the other international groupings. These have been discussed earlier, in the Chapter 3 of this research. For the purpose of analysing the severity of the accidents, the data has been classified into three categories:

(a) very serious,
(b) serious, and
(c) less serious.

An accident which has resulted in at least one fatality has been designated as 'very serious accident'.

An accident in which at least one person has been seriously injured, requiring hospitalization and no one had suffered a fatal injury, has been designated as 'serious accident'.

An accident in which a person or person(s) suffered minor injury or tolerable exposure to ammonia vapours which did not require hospitalization has been designated as 'less serious accident'.

Figure 6 provides a graphical representation of the number of accidents in each of the above-mentioned categories.

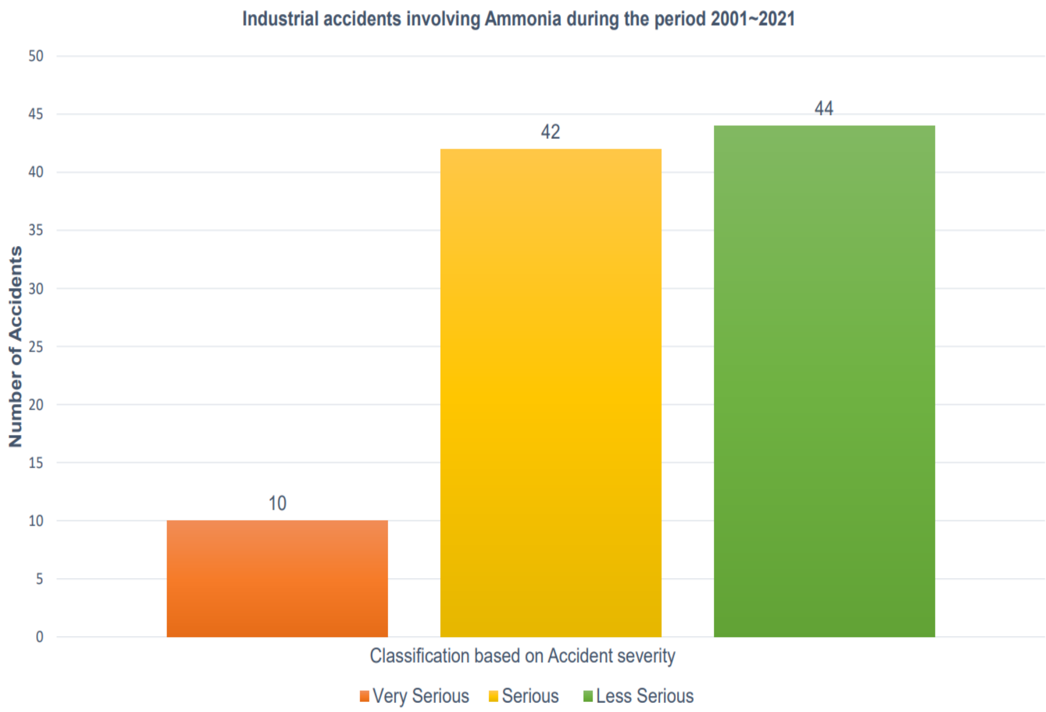

Figure 6: Classification of ammonia accident data based on the severity of the accident (N = 96 accidents)

The analysis of the accident data revealed that out of the total 96 accident cases, 10 cases of 'very serious accidents' had resulted in fatalities to the industrial workers and this amounted to 10.4% of the total accidents studied for the purpose of this research. 43.7% of the accidents (42 cases) were of 'serious' nature and required the affected person(s) to be hospitalized. The remainder of the cases were less severe and did not require hospitalization.

The exposure to ammonia vapour has been found to affect the respiratory tract and cause severe damage to the eyes and the skin of the person(s) in the vicinity of the leak.

5.1.3 Accident causal factors

The industrial accident data that was available for this research had limited detail and were not as elaborate as normally presented consequent to a maritime safety investigation. The proximate cause determined by the author is represented as an infographic in the figure 7.

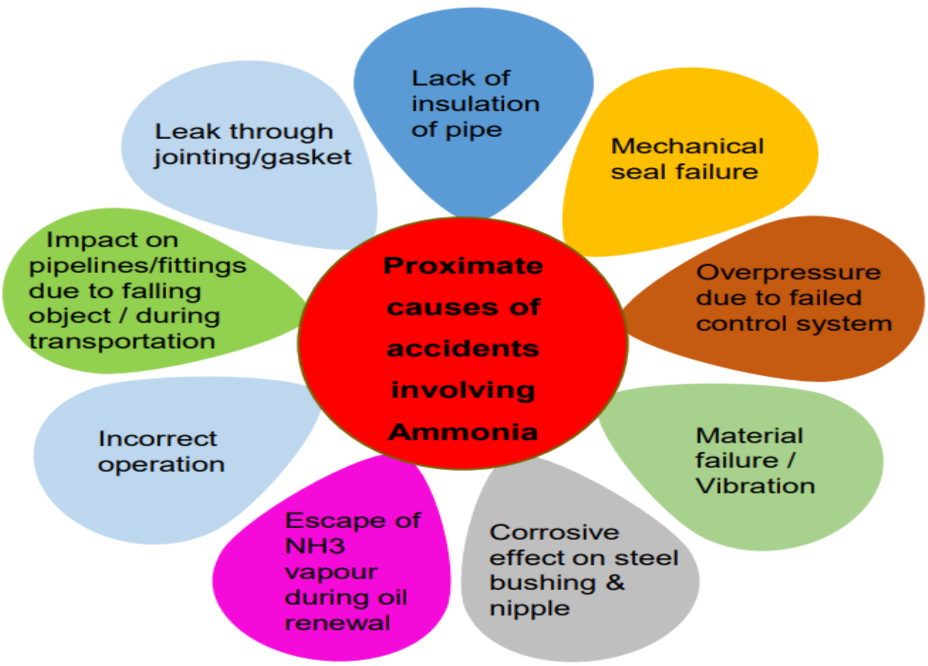

Figure 7: Infographic showing the proximate causes of industrial accidents (N=96 accidents)

The factor(s) that appeared to be instrumental in the sequence of events, leading to the accident are broadly classified into three main categories, namely, the human factor, the management factor and the technical factor. These are further subdivided into four themes in each category and are discussed below.

The frequency distribution of the ammonia accidents causes (N_c=187) and the weighted contribution of each of the factors is at table 7.

I. Human factor

The accident causation factors attributable to human error have been grouped under this category and had a contributory role in 33% of the accidents. Frequent causes of accidents due to the human factor include operator error or incorrect operation (9.09%), lack of safety awareness (5.88%), deviation from safe working practices (13.37%) and lack of knowledge, familiarization (5.35%) etc.

Wearing appropriate personal protective equipment (PPE) when working within a plant that uses ammonia, should definitely lower the number of fatal accidents in most cases. This safety philosophy has to be inculcated so that the personnel are better prepared and equipped to face any unforeseen leak of ammonia, especially during maintenance activities which are planned and normally are not an emergency task.

The data had ammonia leak incidence while undertaking routine work such as renewal of oil and the researcher therefore, attributes deviation from safe working practice as one of main causes of industrial accidents within the human factor.

II. Management factor

The management factor has also been a significant contributor in over 33% of the accidents. More than 10% of the accidents has been caused on account of an ineffective preventive maintenance practice. Failure to adhere to the standard operating procedures as also lack of it has been attributed as the cause in 11% of the accident cases.

Lack of a structured training and familiarization programme for personnel working with the risk of exposure to Ammonia and lack of proper supervision has also been identified as other contributory sub-factors within the management factor. There have been accidents that resulted from rupture of pipelines that carried ammonia due to the impact of a falling object which indicates negligence and most of the above-mentioned contributing factors.

III. Technical factor

The technical factors had contributed to over 33% of the accidents with significant contributions (20.8%) being attributed to mechanical damage, which in a majority of the cases were found to be material failure of the tank shell or piping system. The corrosive action of ammonia which include Stress Corrosion Cracking (SCC) and its non-compatibility with certain materials are key accident contributory factors. This underlines the importance of material selection when using ammonia.

There were accidents caused due to circumferential crack in the stainless-steel tubing within the compression fitting which was attributed to the metal fatigue along with vibration and initial metal stress. Absence of protective guard around critical machines or equipment that contain ammonia has also been identified as a contributor within this factor.

The failure of the control system which include timely activation of the pressure relieving devices and alarm monitoring and alerting devices were also identified to be a factor in 7.49% of the accident causes.

Table 7. Accident causation factors with their weighted contributions, analysed by the author (N = 96 accidents)

Accident causation factors		Code	Number of	%
Human factor	Deficient safety awareness	H1	11	5.88
	Deviation from safe working practices	H2	25	13.37
	Lack of knowledge, skill and familiarization	H3	10	5.35
	Incorrect operation	H4	17	9.09

Management factor	Ineffective preventive maintenance	M1	20	10.70
	Ineffective or Lack of supervision	M2	12	6.42
	Ineffective or lack of adequate training and familiarization of staff	M3	09	4.81
	Ineffective or non-adherence to Standard operating procedures	M4	21	11.23
Technical factor	Mechanical failure	T1	39	20.86
	Lack of adequate warning signs / physical barrier in potentially hazardous areas	T2	03	1.60
	Lack of protective guard in the vicinity of critical machines & auxiliary equipment's/fittings	T3	06	3.21
	Failure of automation or control system	T4	14	7.49
	TOTAL →		187	100%

5.2 Qualitative data analysis

As described in section 4.4, the experts for the interviews were chosen from varied backgrounds and included risk specialists, engine manufacturers, shipping regulators, flag State representatives, members of Classification societies, etc. The perception and experience gathered from these interviews and the existing literature such as the rules or the guidelines formulated by the Classification societies formed the basis of the analysis as real shipboard data on ammonia as marine fuel, is not available at this stage.

A total of ten interviews were conducted on the electronic mode, as the interviewees were from different continents of the world. In most instances, the interviewees were contacted by email for follow-up questions subsequent to the first interaction, as the ideas and theories evolved during the interaction with the other experts. The interviews were recorded and completed in the time range of approximately 40~55 minutes.

5.2.1 Analysis of the interview with experts

The experts that were nominated by the respective organization for the qualitative interview belonged to a diverse maritime background, as may be seen at table 8:

Table 8. Organizational background of the experts who participated in the interview

Participant Ref. No.	Organization represented	Credential
R1	Energy major	Hydrocarbon exploration, refining, chemical manufacturing. Member participant of key industry coalitions on decarbonization.
R2	International Shipping Regulator	Instrumental role in the GHG emission reduction and adoption of alternate fuel in the maritime sector.
R3	Flag State	High stake in bunkering and maritime activities. Active participant and contributor to the development of guidelines for ammonia at IMO and other studies.
R4	Flag State	Active member of the CG and key driver of development of guidelines for ammonia at the IMO. Conduct of HAZID study and risk assessment for ammonia fuelled ships.
R5	Classification Society	Member of the IACS. Active in HAZID studies, dispersion analysis, Risk assessment study during ammonia fuelled engine development and for granting approval in principle.

R6	Classification Society	Member of the IACS. Key expertise are rule development, involved in fuel cell and carbon capture projects, HAZID and HAZOP studies, Risk assessment study during ammonia fuelled engine development and for granting approval in principle.
R7	Classification Society	Member of IACS. Developing safety regulations for ships using gas or low-flash point fuels such as LNG, LPG, methyl/ethyl alcohol, and ammonia
R8	Classification Society	Member of IACS. Key expertise are risk assessment studies during engine development, port bunkering studies including dispersion analysis, fuel cell development, rule development.
R9	Shipping industry association	Represents the voice of the shipping industry. Active in development of guidelines for ammonia fuelled ship at the IMO.
R10	Engine manufacturer	Development of new engines that can burn ammonia and retrofitting the existing ones, testing of various methods of treating ammonia, N_2O emissions mitigation trials.

The interviewees were provided with a set of 12 initial questions for the exploratory interviews (refer Appendix 'A'). These questions and those that followed during the in-camera interview were based on the exclusive context of safety and the barriers that are being currently contemplated by the designers, classification societies, ship-owners, flag State(s) etc.

The respondents had expertise in a wide range of aspects, both safety and technical, that are vital for a safe maritime transportation industry and included:

(a) marine engineers who have years of work experience on merchant ship,
(b) risk specialist with experience in the chemical, oil and gas industry,
(c) experts in the field of Hazard Identification (HAZID) studies,
(d) experienced surveyors involved in formulations of rules and guidelines,
(e) professionals from the maritime law background,
(f) experts who are part of marine engines development and testing,

(g) members of the IMO's correspondence group on amendments to the IGF Code and development of guidelines for low flashpoint fuels.

The interview was transcribed using "otter", the audio file transcribing tool. The final data was arrived only after reading and listening to the interview transcripts multiple times. The transcribed text was, thereafter, corrected as necessary for obtaining the accurate interpretation of the participating expert's viewpoint.

According to Philip Burnard (1991) any analysis of interview transcripts, in qualitative research should aim to create a thorough and systematic record of the themes and topics raised in the interviews; and connect the themes and interviews using a relatively comprehensive category system. The challenge in this method was to compare the utterances of the participants in a reasonable and accurate manner.

After each interview, the researcher read the transcripts and made notes on general themes that appeared. In the next stage the themes were grouped into appropriate headings or categories; and in the process some of the similar headings were collapsed into a common category.

5.3 Qualitative interview results

The interpretation of the results of the interview was undertaken by examining the data relevant to each theme and the participating interviewee has been cited using the unique participant identity code that was referred in table 8. The thematic analysis of the interview transcripts led to fifteen (15) themes which were later categorised into five (5) broad categories and are at table 9.

Table 9. Categories and themes extracted from the interview transcripts by the author

	Category	**Theme**
I	Decarbonization standpoint	1. diesel engine to burn ammonia 2. retrofit option for existing engines 3. bunkering infrastructure
II	Risk and Hazards	4. understanding the physical hazards 5. risk to marine environment

		6. treating ammonia leak
III	Health and Safety of seafarer	7. exposure threshold 8. safe location of muster station 9. permit to work system
IV	Human factor	10. shipboard operations 11. shipboard maintenance
V	Regulatory gaps	12. IGC or IGF conundrum 13. lack of standardization 14. pollution preparedness, response 15. STCW convention

5.3.1 Decarbonization standpoint

This is the first category referred in the table 9 and comprises three themes which were related to the development of 'diesel engine to burn ammonia', determining the 'retrofit option for existing engines' and the readiness of the 'bunkering infrastructure' which are detrimental to the uptake of ammonia as a zero-carbon marine fuel.

5.3.1.1 Diesel engine to burn ammonia

Marine diesel engines that can burn ammonia are currently at various stages of development and trials. Ammonia is not easy to ignite in the engine due to rather high lower flammability limit (R6). It has a very slow flame propagation with the effect that it burns rather slowly (R8). The auto-ignition temperature of ammonia is approximately 651°C, whereas the corresponding value for diesel oil is 210°C. The trials of the diesel engine that can use ammonia as fuel are currently ongoing, and the results are expected to emerge in the year 2023 (R8). Although there are apprehensions on the Nitrous oxide emissions which has more adverse GHG impact than CO_2, engine makers and other technology suppliers are developing catalyst for removing N_2O emission (R8). The engine makers are trying to keep the N_20 emission as 'low as possible' by optimizing engine combustion and the temperatures, so that it not only arrests the escalation of cost but also reduces the complexity of the design (R10).

5.3.1.2 Retrofit option for existing diesel engines

The engine makers are into research and development of not only ammonia fuelled engines but are also exploring the possibility of retrofitting the existing diesel engines for enabling combustion of ammonia (R10). The classification societies have commenced issuance of class notation such as ‘ammonia ready’, ‘ammonia prepared’, ‘fuel ready’ etc. for new built ships, on meeting certain prescribed criteria. Further, these indicate that a vessel has been designed and constructed in a certain way that enables retrofitting to ammonia at a later stage (R8). This mandates the fuel tanks, piping system and the equipment to be designed and fitted in such a way that they can possibly migrate to newer alternate fuels such as ammonia at a later stage depending on the availability of the fuel and the cost effectiveness of such an exercise. There are recent successful examples of LPG tankers undergoing retrofit for enabling use of LPG as fuel (DNV, 2021b).

5.3.1.3 Bunkering infrastructure

The development of ammonia bunkering in all likelihood should be similar to the pathway that was followed earlier for LNG and should account the additional layer of challenge that ammonia presents, due to its toxicity (R1). There are various studies that are currently underway at major bunkering hubs which includes inter alia risk assessment and the safe distance from a bunkering location (R8). The impact on the port and surrounding population if there is an accidental rupture of a pipe or hose leading to a release of ammonia are also concerns that are being looked into (R8). A dispersion modelling software is used to analyse the release rate for different scenarios such as a jet or pool fire so that extent of the leak and toxic cloud can be quantified (R5).

5.3.2 Risks and hazards

This is the second category which comprises of three themes related to ‘understanding the physical hazards’, the ‘risk to the marine environment’ and the ways to ‘treating an ammonia leak’.

5.3.2.1 Understanding the physical hazards

The hazards associated with anhydrous ammonia have been examined in detail in chapter 3 of this dissertation. Ammonia is toxic and should be handled with care. Historically, fatal accidents have occurred due to ammonia leakage. It is, therefore, important that safety aspects are addressed thoroughly when considering ammonia as marine fuel (R7). It has to be acknowledged that the risk of toxicity being the physical property of ammonia can never be eliminated and, therefore, awareness of the hazards is very important and should never be downplayed (R1).

Corrosivity is the second most significant hazard of ammonia. Ammonia forms a high pH corrosive solution in contact with water. This corrosive solution may react with the moisture in the skin, eyes and the respiratory tract to cause burn injury which could be fatal (R5). Selection of material is another key aspect as some materials, like copper, nickel, elastomer, some paints etc. are not suitable for an ammonia fuelled ship (R10). The engine makers are in continuous engagement with additives manufacturers to identify suitable additives that could be added to the lubricating oil for protecting the engine parts (R10).

High concentration of ammonia, especially in areas such as the machinery spaces poses a risk of fire or explosion if ammonia vaporizes rapidly (R7). It is, therefore, warned that a water jet should never be directed at such accumulation of ammonia (ILO, 2013). Anhydrous ammonia has a strong affinity for water. A mixture of gaseous ammonia and water, in an enclosed or partially enclosed space may create a vacuum which could lead to the containment's structural collapse (LR, 2021).

In the gaseous state, ammonia is lighter than air and depending on conditions such as humidity it becomes heavier than air and, this in turn affects the dispersion characteristics of ammonia vapour (R6). Ammonia, when it is first released will be denser than air, so the placement of detectors becomes a critical factor and is a design consideration (R5).

5.3.2.2 Risk to the marine environment

The risk of ammonia to the marine environment is posed by the discharge of ammonia to the sea either directly or as a result of the fire water used as a water spray flowing overboard (R5). The other risk is the pollution of the air on account of venting of ammonia through the vent mast or exhaust either during normal operation or in an emergency (R7). The development of ammonia capturing systems, to capture even the small amounts of ammonia that will be emitted or released during normal operation is in progress. Currently, there is no unanimity on the degree of venting that should be permitted and whether it should be limited to the emergency situation only (R8).

The discharge of ammonia into the sea is governed by the provisions of MARPOL Annex II. However, it was stated (R4) that there is a recognition amongst the members of the correspondence group regarding a lack of information, such as:

· Guidance for dilution or neutralization of ammonia solution;

· Capacity of storage or method of recovery for effluents containing ammonia; and,

· Toxicity to marine life well.

5.3.2.3 Treating an ammonia leak

The likelihood and consequences of fuel releases are to be minimised by ventilation, detection and safety actions. These safeguards can seem innocuous; however, their reliability is critical to reduce the risk to at least a tolerable level (R5).

Methods to treat ammonia in the event of a release are scrubbers, vent stacks (inherently safer if dispersion can be achieved), and thermal oxidation (e.g., flares, incinerators) (R5).

5.3.3 Health and safety of seafarer

This is the third category referred in table 9 and comprises of three themes which were related to the ‘exposure threshold’, the ‘safe location of muster station’ and the prospective changes to ‘the permit to work system’.

5.3.3.1 Exposure threshold

The requirements specified in the safety data sheet are different in different parts of the world (R5) and the variations have been explained in section 3.3.2 of this dissertation. Toxicity and corrosivity of ammonia have led to fatal industrial accidents and, therefore, it is important that safety aspects should be addressed thoroughly when considering ammonia as a marine fuel (R7).

Multiple barriers will have to be in place, whether it is from technological perspective or from a health, safety and environment (HSE) perspective for protection of the seafarers (R1). In normal circumstances, the target is to have ammonia concentration much below the odour threshold; and at all the places where the personnel are expected to be present without any personal protective equipment, the concentration should be below 30 ppm (R10). There will have to be a wide and detailed knowledge of the safety precautions before the world starts using ammonia as a fuel (R10). The exposure to ammonia may have direct and very quick consequences on humans which is not acceptable and, therefore, in the interest of standardization, it is expected that the IMO should be able to issue guidelines by the end of 2023 (R6)

In the meantime, (R5) indicated that it would be helpful if some industry body could bring the various parties together and reach a consensus on these threshold numbers and believed that it would prove helpful to a lot of people including equipment manufacturers and others. Further, on the impact of these threshold limits on the management of different scenarios onboard, (R5) elaborated:

> *"There may also be an impact on how one manages the systems in different scenarios. For e.g., in a scenario of abandonment of the vessel in the event of catastrophic ammonia failure, based on the exposure threshold limit determined, there may be other additional requirement for the emergency breathing apparatus or similar protection, for boarding lifeboats."* (R5)

5.3.3.2 Safe location of muster station

To secure an evacuation route in emergency, it is necessary to determine the diffusion behaviour of ammonia and the requirements for arrangement/ design of vent post for which there is insufficient information at this stage (R4). The location of a muster point becomes important in a scenario where there is a catastrophic leak of ammonia and the crew need to safely muster before considering abandonment of the vessel, if so required (R5). This location has to be defined considering all aspects of crew safety when developing the guidelines on ammonia.

5.3.3.3 Permit to work system

The risk associated with the fuel is completely different from what the crew is currently accustomed with and, therefore, the permit to work system would have to evolve after guidelines are issued by IMO (R9).

In recognition of the risks from potential release of toxic ammonia from pressure relief valves, hazardous space ventilation exits, bunker stations and other potential release sources protected by drip trays, certain areas are to be considered as toxic areas and are required to be located at minimum distances as prescribed in the class rules, from the nearest air intake, outlet or opening to accommodation spaces, service spaces and control stations or other non-hazardous areas (ABS, 2021).

With the experience of having undertaken engine development and trials, (R10) believed that:

> *"For ammonia you will always have handheld sniffer systems before you start to open, for e.g., crankcase doors, exhaust pipes etc. Here we are learning all the time on how to do it in a safe way. Own personal protection equipment and detection system plus good instruction on how to work, what to be inerted, what to be emptied and so on. It will take some time to learn."* (R10)

5.3.4 Human factor

This is the fourth category which comprises of two themes which were related to the 'shipboard operations' and the 'shipboard maintenance'.

5.3.4.1 Shipboard operations

Fuel handling and the entire engine room layout are key challenges onboard a ship that would use ammonia as fuel. Eventually, it is reasonable to expect that there would be some leaks during operation and the challenge is to design the right system that is capable to handle those leaks (R1).

Any single failure in the fuel piping system should not release the toxic ammonia in the machinery space (R7). This has been the philosophy that has been adopted earlier for LNG as fuel in the IGF Code. The fuel pipes are, therefore, required to be of double wall design and outer pipe or duct is to be continuous to prevent any gas being discharged even when the inner pipe has a leak (Korean Register, 2021). Automatic ammonia gas detection at the ppm level and automatic response such as alarm, increased ventilation, and line shutdown are technologies that can enable safe operation of ammonia handling systems (R7).

As the studies are still being undertaken, there is a thought whether the double wall piping is required everywhere in the machinery space or whether it should include spaces such as the fuel preparation room, gas valve unit spaces and the tank connection spaces, where the personnel do not enter during normal operation (R6). There are also alternate concepts being debated such as running fuel pipes in a gastight duct which provide equivalent protection and on how far it should extend (R5).

The toxicity of ammonia provides no allowance for any leak to be permitted, however small the quantity may be and, therefore, instead of the “ESD protected machinery spaces” concept “gas safe machinery space” concept is selected for an ammonia fuelled ship (R4, R7).

The fuel handling system, lube system should look very different on an engine using ammonia as fuel. Ammonia comes with a lot of intricacies, and it is important for the crew to understand why systems, processes and interlocks are in place, so that they can use them properly when working onboard (R1). The perceived changes in the safety habits of a seafarer as expressed by the expert during the interview, can be summarized as:

> *“The natural response of a seafarer today is to rush to the engine room when there is a leak or an alarm to find out and sort it out but, with ammonia the first thing one needs to do is exit the engine room, ventilate, shutdown and only then to go and attend to the problem.”* (R1)

The use of water curtain as a safety barrier against ammonia leak at spaces like the bunker manifold, needs to be handled carefully as the water falling on a refrigerated ammonia pool can have disastrous effects. The vaporisation can turn worse due to the heat transfer to the pool which negates the very purpose for which the water spray system was fitted (R5). The risk of toxicity shall require the crew designated for bunkering operation to wear breathing apparatus (R6).

The human factor is also being looked into in the various HAZID studies that are being undertaken and a safety critical task analysis also would be required to be done at a later stage (R5).

5.3.4.2 Shipboard maintenance

As revealed by interviewee (R10), during maintenance, even after inerting, the odour of ammonia would be experienced as it is the result of the ammonia mixed in the lubricating oil. This is dependent on the oil temperature and was described by the expert:

> *"When the engine is running and the oil is warm, the ammonia in the oil will evaporate. If the oil is cold, there is a possibility of the presence of ammonia in it, especially if the engine has been running."* (R10)

The awareness of the hazards is very important and should not be downplayed and therefore the expert (R1) believes that the seafarers who are working onboard need to have a very good understanding of the fuel handling complexities, and other procedures prior responding to leaks and alarms. Further, it was stated that:

> *"Regular maintenance practices like scavenge cleaning will be a safety challenge as there will be ammonia mixed with the lubricants in these spaces. Even taking a sample of lubricating oil may prove to be a challenge."* (R1)

Safety during maintenance is also one of the aspects being examined in the risk assessment studies that are currently being undertaken (R5) and it was emphasized that:

> *"Perhaps something needs to be learnt from the tanker experience of handling ammonia as cargo, especially the approach towards maintenance activities."* (R5)

The use of compatible materials, appropriate PPE which should include the sniffer system and handheld systems are mandatory before considering opening of the crankcase door, exhaust pipe etc. and should form part of important safety procedures to be followed on an ammonia fuelled ship (R10).

5.3.5 Regulatory gaps

This is the fifth category which comprises of four themes which were related to 'IGC or IGF conundrum' that exists during the design of a vessel, 'lack of standardization' especially with respect to the safety data and the exposure thresholds, 'pollution, preparedness, response', and the 'STCW' convention.

5.3.5.1 IGC or IGF conundrum

The IGC Code regulation 16.9.2 prohibits use of a toxic gas like ammonia as a marine fuel. The safety regulations to be considered when applying the IGF Code for an alternate gaseous fuel like ammonia, are not clear (R7) in the current scenario, any ammonia fuelled vessel in the next few years will need to go through the alternative design approach (R8). Ammonia is currently not part of the IGF Code and the discussions taking place at the IMO is summarized by the author at table 10.

Table 10. Summary of key discussions at the IMO on the amendments to the IGF Code and development of guidelines for the use of ammonia as a marine fuel.

Symbol and Title	Originator	Summary
CCC 7/INF.8: Forecasting the alternative marine fuel: ammonia	Republic of Korea	Introduced the outline of the outlook of ammonia as green ship fuel.
CCC 7/3/9: Amendments to the IGF Code and development of guidelines for low flashpoint fuels	European Commission and 28 member States	Proposed inclusion of the development of two separate guidelines for the safety of ships using ammonia and hydrogen as fuel.

MSC 104/15/9: Development of non-mandatory guidelines for safety of ships using ammonia as fuel	Japan, Singapore, ICS and INTERCARGO	Proposed a new output to develop non-mandatory guidelines for the safety of ships using ammonia as fuel
MSC 104/15/10: Hazard Identification of ships using ammonia as fuel	Japan	Presented result of the HAZID study of ships using ammonia as fuel.
MSC 104/15/30: Necessity of deliberations on operational safety measures and fire safety measures	Japan	Proposal to deliberate on operational safety measures and on the effectiveness and negative impact of fire safety measures, in particular those for limitation of explosion consequences
MSC 105/2/2: The development of safety requirements at the needed pace and detail to support the achievement of the decarbonization goal	IACS	Presents preliminary views on the risks associated with the options currently researched and trialled including ammonia to deliver a safe zero-CO2-emitting ship.
MSC 105/20: Report of the Maritime Safety Committee on its 105th Session	IMO Secretariat	The committee agreed to include in the biennial agenda of the CCC for 2022-23 & provisional agenda for CCC 8 an output on "Development of guidelines for the safety of ships using ammonia as fuel" with a target completion year of 2023.
CCC 8/2/1: The development of safety	IACS	Presents a discussion on the risks associated with ammonia and the

requirements for alternate fuels and technologies at the needed pace and detail to support the achievement of the IMO's decarbonization goals		areas of regulatory development. Emphasizes on the need to set up an overarching Committee considering the complexity involved in the development of safety requirements to support the decarbonization goal.
CCC 8/INF.10: Development of guidelines for the safety of ships using ammonia as fuel	Japan	Presents a summary of comments provided to the Correspondence Group (safety information for the use of ammonia)
CCC 8/13: Development of guidelines for the safety of ships using ammonia as fuel	Japan	Presents a discussion on collection of information on the safe use of ammonia.
CCC 8/13/1: Development of guidelines for the safety of ships using ammonia as fuel	Japan, Singapore, ICS and INTERCARGO	Provides information on possible issues to be considered for developing guidelines for the safety of ships using ammonia as fuel including establishing a CG to prepare draft guidelines.
CCC 8/13/2: Development of guidelines for the safety of ships using ammonia as fuel	Republic of Korea	Proposes a review of the environmental effect for future discussions.

The IGC Code provides a good basis to start with and it is known that certain aspects such as the effect of toxicity, material selection against the corrosivity of ammonia, etc. will need further consideration within the framework of the IGC Code (R3). The IGC Code, therefore, offers a relatively easy way to incorporate concerns pertaining to the use of ammonia.

There was also an opinion that the basic requirements can be referenced to the IGF Code. The main purpose of the IGF Code is to provide countermeasures against fire and explosion of combustible fuels and, therefore, it needs to develop and consider countermeasures for toxicity of ammonia (R4).

5.3.5.2 Lack of standardization

The IMO and the IACS are yet to develop any universal guidelines for use of ammonia as a marine fuel. At this point of time there is no consensus between classification societies or any port or flag authorities. It will be necessary to have a general agreement on safety measures which can be applied to ammonia fuelled ships (R6).

Currently, even for the aspect of toxicity there are different points of view coming from different sources (R10). The workplace exposure limits for short term or long term, and the training of the seafarers do not have a common standard at this point of time (R3). Also, for the personal protective equipment for the crew onboard a ship, the industry seemingly is not ready to agree on a common standard yet (R5). While it is unanimously stated by almost all the interviewees that there are lessons to be learnt from the way the shipping industry has been handling ammonia as cargo it has to be acknowledged that the tanker ships are subjected to additional inspections by oil majors such as vetting and/or Tanker Management Self-Assessment (TMSA[1]) audits. The non-tanker ships such as bulk carriers and container ships that will be using ammonia as fuel would need to have these kinds of systems to promote safety (R5).

The concentration of ammonia within the double wall piping is a critical parameter since it is the first place where a leak can be identified by the detectors. There is, however, a difference in this threshold value published by different Classification societies. Although the engine makers are very eager to have some kind of unified

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[1] Tanker Management and Self-Assessment (TMSA) is a guideline to measure and assess tanker operators' management system developed by Oil Companies International Marine Forum (OCIMF).

approach, one of the reasons for the different approaches is that the manufacturers are all still learning and trying to figure out what is the best one. (R8)

5.3.5.3 Pollution, preparedness and response

The physical properties of ammonia are different from that of fuel oil. Ammonia is a gaseous fuel that will dissolve in water and cause damage to the marine environment, and therefore needs a different treatment (R2). Ammonia when discharged to the atmosphere poses risk to the human body and is another source of air pollution (R7).

Recognising the long experience that the shipping industry has in operating ammonia carriers it is believed that the risks associated with ammonia can be controlled by having trained and competent crew compared to other sectors. However, it is necessary to consider the newer risks which include consideration of the fact that the ammonia gas carriers have been used only on specific routes and ports, whereas the ammonia fuelled ships will be operating in a much wider range of ports and routes. Therefore, additional safety measures need to be researched and developed. (R4)

The response to any emergency including responding to any technical failure onboard a ship, whether from the ship or from the shore will need some upskilling (R1). The capabilities for emergency preparedness and response exists in the ports that have been handling ammonia as cargo, but a rise in the number of ships would merit a scaling up of resources (R3).

There is a concern on the use of water curtain to deal with an ammonia leak and is explained by the expert (R5) as:

> *"If we try to deal ammonia leak with a water system, then you need to consider how to handle the effluent. The ammonium hydroxide will be caustic and whether spill off the side of the vessel is permissible. Need a containment system for the fire water run off or something of that sort."* (R5)

5.3.5.4 Standards of Training, Certification and Watchkeeping for seafarers

Seafarers would require additional knowledge on the ability to handle leaks during transfer, storage, handling and maintenance of equipment, emergency response scenarios and related equipment (R1).

Acknowledging the significance of the seafarers who would operate the ships that would use ammonia as fuel, the expert (R3) stated:

> *"Seafarer of the future might be quite different from the seafarer of the past, in terms of what they have to deal with, whether it is the safety, environment protection or the technological aspects. In consideration of the upcoming alternate fuel, it is acknowledged that the seafarers are not equipped in terms of the standards and it is something the IMO is going to consider while they are in the process of reviewing the STCW convention. The IMO definitely needs to come up with model courses for ammonia and other alternate fuel options."* (R3)

5.4 Conclusion

This chapter has presented the collected data in different ways which included tabular and graphical representations. The themes identified from the qualitative interview, grouped into five different categories were elucidated in this chapter and shall be used to discuss the research question and obtain meaningful answer to the research questions in the concluding chapter.

Chapter 6: Discussion and conclusion

This chapter discusses the interpretation of the results of the qualitative data and provides an assessment on how successful it has been in finding answers to the research questions. The chapter ends with a conclusion that synthesizes the findings of this research.

6.1 Discussion

This research was undertaken to seek answers to the two pertinent research questions, concerning the safety aspects of ships that would use ammonia as a marine fuel in the maritime decarbonization scenario. During the process of this research, the accident data from the industrial accident databases were analysed and interview with experts from the field of maritime decarbonization were conducted to seek the answers to the research questions.

6.1.1 Causal factors of potential accidents on an ammonia fuelled ships

The research question 1 of this dissertation related to finding the causal factors of potential shipboard accidents when using ammonia as a marine fuel.

A ship has a different work ecosystem when compared to any shore-based industry. The seafarers who work on the modern ships are adequately trained and certified for their role designated onboard a ship. These are more stringent on a tanker ship to fulfil the additional requirements of the oil major, charterer etc. However, accidents occur on ships at regular intervals even with all the technological advancements and enhanced management of safety.

Ammonia has been carried as cargo on ships for decades and has an enviable safety record. But the ships that would use ammonia as fuel will have the toxic ammonia leading into the machinery space and the fuel tank space which can be close to the living quarters depending on the design of the ship, size etc. The potential causal factors of accidents onboard a ship using ammonia as fuel, derived from the study of industrial accidents and from the qualitative interview of experts is synthesised in the form of fishbone diagram at figure 8.

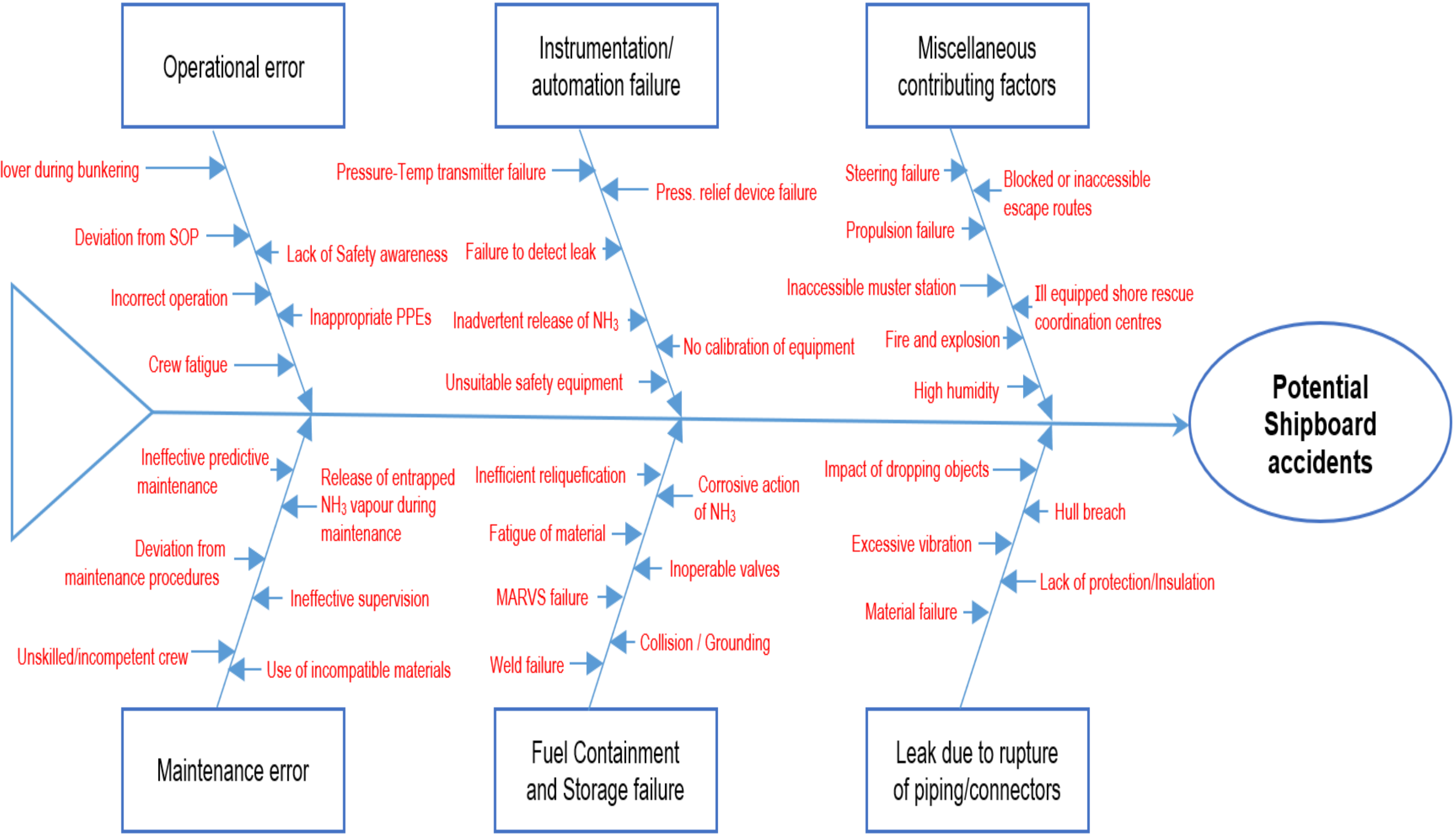

Figure 8: Fishbone diagram depicting the potential causal factors of an accident onboard ship using Ammonia as fuel

Each of the six identified overarching causes of a potential accident onboard a ship is further divided into several contributory factors that are linked to each of the six bones of the fishbone diagram. The causal factors that lead to a shipboard accident on a ship that use ammonia as fuel is further described in detail by discussing each of the key factors.

1. **Operational error**

   The human element in any shipboard accident can be a result of fatigue, lack of safety awareness, deviation from standard operating procedures (SOP) which individually or collectively can cause roll over during bunkering of ammonia. Any leak or dripping of ammonia can lead to formation of a toxic cloud with a rapid impact on the health of the persons in the vicinity. Therefore, the significance of wearing the appropriate PPE cannot be emphasised further.

2. **Maintenance error**

   Periodic maintenance is a vital cog in the wheel for a trouble-free operation of any ship. Every maintenance needs to be undertaken as per the maker's instruction and the safety procedures established by the company's safety management system, which is a requirement of the International Safety Management (ISM) code. Any deviation from these, coupled with the use of spurious and incompatible materials would prove to be disastrous for a ship using ammonia as fuel. The corrosivity of ammonia which have been discussed in the preceding chapters, is a cause for pre-mature failure in certain materials, resulting in sudden release of toxic Ammonia.

   The accident data has highlighted how accidents have occurred while draining and refilling the lubricant from a compressor and the same has been explained in section 5.1.3 and section 5.3.4.1. Onboard a ship, this risk shall have to be mitigated while undertaking activities such as crankcase inspection, scavenge cleaning and inspection etc. for the same reason (R1, R10). Effective supervision and adhering to the prescribed safety procedures during maintenance are, therefore, very significant and need to be emphasized in the safety management system onboard such ships (R1).

3. **Fuel containment and storage failure**

   The fuel storage system is designed to withstand the pressure within the tanks depending on the type of tank and method adopted to have the pressure within the pressure relief valve (PRV) set point. Moreover, the ships with reliquefication system should have a back-up arrangement so that the tank pressure is maintained within the PRV limit at all times (R8). However, any unforeseen emergency situation such as a fire, collision or grounding can lead to the inoperability of the reliquefication unit and, therefore, an increase in pressure inside the fuel storage tanks.

   The corrosive action of ammonia may lead to a rupture or failure of the tank structure if not captured during the maintenance process. Selection of material at the design stage and thereafter is important for example, steel such as 9% Nickel steel which is suitable for LNG cannot be used for ammonia because of corrosiveness (R8).

4. **Instrumentation or automation failure**

   The industrial accident analysis has had many instances where the pressure relief valves or the pressure transmitters had failed to activate or had error in their operation. In order to ensure reliability of safety-critical systems, numerous in-depth reliability analysis must be carried out, particularly during the design stage (Rausand, 2014) and in the shipping context it is key to ensuring safety of personnel and prevention of damage to the environment.

5. **Leak due to rupture of piping or the connectors**

   Ammonia, by its physical property, is highly reactive and incompatible with a number of materials. The industrial accidents had a number of cases wherein the connectors or the adaptor nipple fitted were acknowledged to be the weakest link leading to the ammonia leak. Several accidents were a result of a rupture of a pipe containing ammonia due to the impact of a falling object that was being lifted or shifted within the machinery space.

The double wall ammonia pipelines in the machinery space, which is a protective measure required as per the IGF code, however, does not insulate such accidents from occurring on a ship. The safety management system onboard should be reviewed to have essential safeguards in place for such potential accidents. Although the design of modern ships that will use ammonia as marine fuel have a nearly uniform specification amongst the classification societies regarding minimum distance of about 800 mm from the ship side, breach of the ship's hull on account of a collision or grounding may cause damage to the pipelines depending on the extent of the damage and cannot be ignored.

Ships have different operational conditions (R4). There are both internal and external factors that can induce vibration. The vibration if unattended or timely remedied can lead to a shearing of the pipes or fittings which may cause release of ammonia as seen in the industrial accident data referred in section 5.1.3.

6. **Miscellaneous contributing factors**

The release of toxic ammonia can have a rapid impact on the personnel working in the vicinity especially, if the cause was not anticipated. Moreover, a leak of ammonia, for example, within the confines of an engine room may cause the ammonia to absorb the moisture making it denser than air. This combined with an ignition source can cause a fire or even an explosion.

The location of a muster station for the crew to safely assemble in the event of an emergency due to leak of ammonia is something that has to be well thought off, as it is dependent on various factors such as wind direction, temperature and the dispersion analysis result for the specific ship. The master of the ship has to be conversant about these factors while co-ordinating any evacuation operation both, within and with the shore. Most common ship accident causes such as collision, grounding, steering and propulsion failure shall continue to be a concern despite all the safeguards on account of the physical properties of ammonia and its effects on the humans. Any accident that becomes uncontrolled needs shore intervention and since ammonia has unique properties such as toxicity and corrosivity, the response unit ashore also needs to be suitably equipped and trained. Else, the rescue, relief and pollution prevention efforts will not be purposeful with a likelihood of casualty on the shore side as well and this may prove to be a deterrence.

6.1.2 Discussion on the control measures and safety barriers

The research question 2 of this dissertation related to establishing the control measures and safety barriers that would ensure safe operation and protection of marine environment when ships use ammonia as a marine fuel.

The best way to avoid any accidents is to prevent them from happening by creating safety barriers against the identified threats. The physical properties of ammonia as detailed in chapter 3 of this dissertation and the study of accidents in the other industrial sector has identified the 'toxicity' of ammonia as the most significant contributor to any accident.

As highlighted in section 3.3.2 and section 5.1.2 of this dissertation, ammonia's property of corrosivity is also a concern, as the exposure affects the human eye, skin and the respiratory tract leading to very serious casualties, which can be fatal at times. The underlying significance is, therefore, to prevent any leakage from happening in the first place.

The deployment of effective safety barriers and control measures against the identified risks would define the trajectory of ammonia as a marine fuel. The measures that have emerged from this research are as follows:

1. **Prevention of leakage**

   The design of an ammonia fuelled ship should be based on the philosophy of zero leak with secondary containment for the tanks and double wall protection for the piping. Regular inspection and monitoring shall provide pre-warning of any imminent breakdown.

2. **Effective detection of leakage**

   The selection of appropriate sensors and detectors together with their location is key to detect any leakage of ammonia. The double wall annular space should be fitted with leak detection system for an early detection of any damage to the inner piping. Handheld detection system capable of detecting ammonia should be mandatorily available in sufficient numbers for use of the personnel working onboard a ship.

3. **Treatment of ammonia leakage**

   There are various methods to treat ammonia if a leak is detected namely scrubbers, vent stacks and thermal oxidation (e.g., flares, incinerators) (R5). There is however lack of guidelines on the degree of dilution or neutralization of the ammonia solution (R4); and the capacity of the containment system that may be required on the ships for collection of the effluent generated as a result of the deluge system or water curtain used to deal with an ammonia leak (R5). Remote isolation of fuel systems for isolation in the event of a leak should also be mandated and periodically tested.

4. **Development of ammonia capturing system**

   The development of an ammonia capturing system in the future, should ensure successful capture of even the small amounts of ammonia that will be emitted or released in normal operation.

5. **Transformational changes in the work procedure**

   The maintenance activities should be undertaken with strict adherence to the standard operating procedures to limit the toxic exposure to ammonia. Activities such as opening of the crankcase door, exhaust pipes, cleaning of filters etc. should be handled with extreme caution and appropriate personal protective equipment should be worn. Risk assessment should be performed prior undertaking such tasks and it should be approved by the competent person.

6. Selection of material

According to the chapter 17.12 of the IGC Code *"Anhydrous ammonia may cause stress corrosion cracking in containment and process systems made of carbon-manganese steel or nickel steel."* The IGC Code further requires constructional and operational measures such as limiting the water and dissolved oxygen content in the tanks and the piping, so that the risk of stress corrosion cracking is minimized.

7. **Emergency preparedness**

The toxic nature of the ammonia would require a dispersion analysis to be done, to ascertain the most appropriate location for the crew to safely muster in the event of any leakage of ammonia. The personal protection equipment should include an appropriate suit that provides adequate protection to the skin, face and the feet. In the event of any evacuation, the crew should mandatorily don the breathing apparatus with a respirator that is suitable for the purpose. In a deviation from the other alarms, any ammonia leak alarm should cause the personnel to immediately vacate the place and muster as instructed. The shore rescue teams also need to be equipped to deal with the varied threat posed by ammonia fuelled ships, as currently such preparedness measures are limited to a few ports that handle ammonia as cargo.

8. Developing standards, guidelines and amendments to the instruments

At this stage the ship designers, engine makers, classification societies and other stake holders are deliberating various hazards, identifying the risks and analysing the best method to mitigate them. Safety construction and safety management aspects which need to be considered for harmonization of the standards should include the following as a minimum:

(a) the protective location of the containment system and pipelines;

(b) the design criteria for a fuel tank and minimum time a refrigerated storage tank should withstand the pressure within without causing a relief and release;

(c) location, type and minimum number of detectors and sensors that would be required;
(d) type of sub-division and insulation;
(e) extent of the double-wall piping system;
(f) fire-fighting system;
(g) ventilation type, capacity, suitable location of the vent mast, permissible concentration of Ammonia that can be vented;
(h) standard procedure for sampling of fuel;
(i) limit of NO_x, N_2O and ammonia emission;
(j) defining toxicity threshold for the workplace;
(k) improved standard for monitoring the health of seafarer;
(l) developing guidelines and approving technology that will be required to contain, treat and discharge the effluent resulting from the fire wash water used as a water spray; and
(m) definition of toxic zones similar to the hazardous zones on tanker ships in consideration of the trade-off between toxicity and flammability.

The casual factors which were described in section 6.1.1 and the safety barriers described in the section 6.1.2 are key to ensuring safety of the ship, the seafarers, protection of the marine environment and avoidance of any damage to the adjoining areas, considering the toxic effects of ammonia. The cause to consequence correlation is demonstrated as a bow-tie diagram at figure 9.

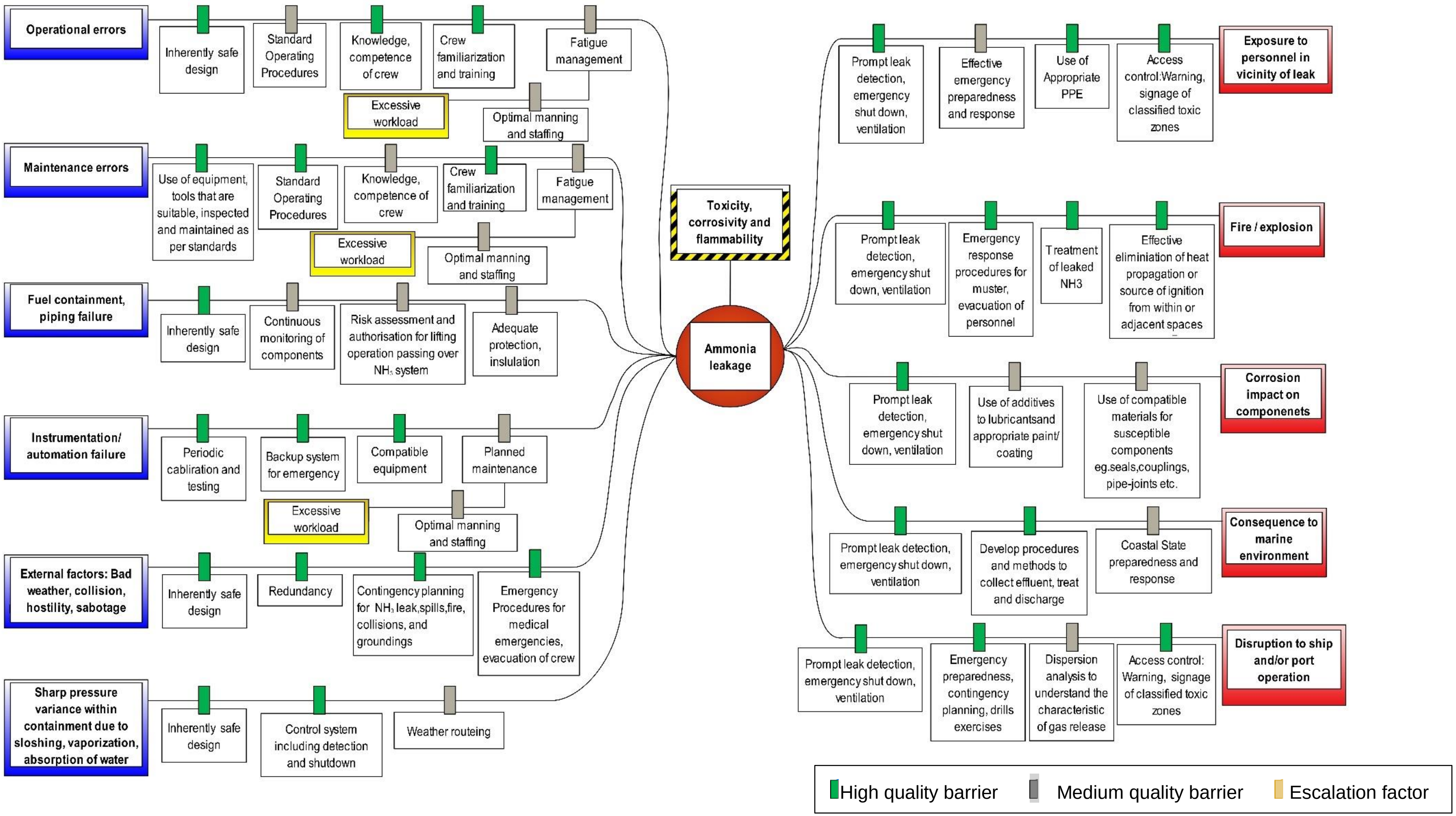

Figure 9: A Bow-tie diagram illustrating the desirable safety barriers against the potential threats on an ammonia fuelled ship

6.2 Conclusion

In pursuit of a suitable replacement for the fossil fuels, there are a number of alternate fuel candidates with no clear winner or loser emerging at this stage. Ammonia has been safely and efficiently transported on ships for the last many decades; and has been used in the fertilizer and other agriculture-based industries for over a century. There is very little unknown about ammonia and that is a huge fillip for ammonia's take-off as a potential marine fuel.

This research had been fairly successful in meeting the research objectives set in section 1.3 of chapter 1. The hazards posed by ammonia in its new manifestation as a marine fuel has been elucidated in this chapter, incorporating the lessons learnt from the industrial accidents and the valuable inputs received from interview with experts. The current standards that are being followed in the design and construction of ships that would use ammonia as fuel are based on the alternate design principle wherein the flag State together with the Recognised Organisation (RO) prescribes the rules for design, construction and trial, recognizing all the hazards based on the risk assessment and HAZID studies undertaken.

There are no uniform international standards that exist today as ammonia was not until recently, a serious alternate fuel option. The material safety data sheet (MSDS) that is currently being used for maritime transportation of ammonia across different regions of the world needs to be standardized with detailed data, including permissible concentration of ammonia for the benefit of the engine and other equipment makers, and the end-user. Currently, the engine that can burn ammonia as fuel is under development and the industry is awaiting results of the initial engine trial to see the level of success that could be achieved in the combustion of ammonia in an IC engine. The abatement technology for nitrogen oxide (NO_x) which include the selective catalytic reduction (SCR) system is in existence and being used on many ships, but the main apprehension is regarding the nitrous oxide N_2O emission which is a greenhouse gas that is much bigger concern than CO_2.

The research could capture a sentiment from the shipping industry wherein the industry is viewing the developments with caution and restrained in their action, to ensure that their investments are not stranded. The industry's apprehension is understood to have been based on their earlier experience with non-universal acceptance of alternative technology such as the exhaust gas cleaning system. The reason is the realization at a later stage that geographically in certain areas around the world a particular option cannot be used owing to issues that were identified after the investment was made.

The industry is, therefore, eagerly awaiting the lifecycle analysis of ammonia before making the first move. There are, however, many ships that are being ordered on the dual fuel concept wherein the classification society has issued them a notation denoting their level of readiness in adapting to a new alternate fuel as it becomes available later. These are basically limited to the construction of fuel tanks, fuel piping system, etc.

The classification societies have developed their own rules for the design and construction of ships with periodic review and amendments as the results of the risk assessments and the engine development, emerge and evolve. The sub-committee on carriage of cargoes and containers (CCC) at its seventh session in September 2021 had tasked the correspondence group that was working on amendments to the IGF code and development of guidelines for low-flashpoint fuels, to 'collect information on the safety of ships using ammonia as fuel.' The information collected together with the HAZID study undertaken by Japan shall be presented before the CCC at the eight session which is scheduled during September 14-23, 2022. CCC-8 is also likely to establish a correspondence group to prepare the draft guidelines which could then be expected to be finalized at the subsequent meeting of the CCC.

The concerns for the shipping industry are the availability of ammonia, development of engines to burn ammonia as fuel and establishing a safety shield against the known hazards of ammonia. It is very vital to the acceptance of ammonia as a marine fuel, that the first movers have a smooth transition without encountering any unmitigated risk and challenges. This has been highlighted by almost all of the experts who were interviewed for this dissertation, as it is feared that a serious accident with threat to life, property and the environment shall influence and drive the public perception in a manner similar to the negative impact it has earlier created in the use of nuclear energy. The development of Ammonia as a fuel will also need further training of the seafarers who would be operating these ships.

The international bodies such as the IMO, ILO, WHO and the ISO have to develop uniform standards and regulations for ensuring safety of shipboard operations keeping in mind the safety, health of the seafarers and the other stake holders so that the uptake of ammonia as a marine fuel receives no set back in the ships that would be early movers.

Ammonia which scores with its low global warming potential (GWP) and ozone depletion potential (ODP) is one of the better candidates to become an alternative to the fossil fuels. In the future, with the development of safety regulations and its adaptation, ammonia could not only be transitional but a transformational alternative to fossil fuel.

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Appendices

Appendix ‘A’

Initial Questions for exploratory interviews

My name is Praveen Raghavan Nair, an ex-chief engineer who is currently working with the Directorate General of Shipping, Mumbai (*Maritime Administration of India*). In partial fulfilment of my Masters programme at the World Maritime University (WMU) at Malmo, Sweden, I am undertaking research on the safety analysis of potential risks onboard ships that would use ammonia as marine fuel. As part of the interview with industry experts, seafarers and stakeholders, I intend to get answers for questions related to the risks and safety barriers arising from the application of ammonia as a marine fuel. Few of the key question are as listed below and based on the discussion, the interviewer may pose further questions for purposeful research on the topic mentioned above.

Details of the participant

<table>
<tr><td>Name</td><td></td><td></td><td>Current Organization</td><td></td></tr>
<tr><td>Designation</td><td></td><td></td><td>Qualification & Training</td><td></td></tr>
<tr><td>Areas of Expertise</td><td></td><td></td><td>Experience in shipping industry (Years)</td><td></td></tr>
<tr><td colspan="5">If the participant is a seafarer, the following additional details may also be provided:</td></tr>
<tr><td>Grade of Certificate of Competency held</td><td></td><td></td><td>Type of Ships sailed</td><td></td></tr>
</table>

Highest rank attained on merchant ships			Have you sailed on ships carrying LPG, LNG, or Ammonia as cargo? If yes, please specify.	

Introductory (sample) questions

1. Could you briefly describe your association (both, current and past) with any maritime decarbonization projects. What is the current status of these projects?
2. In the context of ammonia being one of the alternate fuel candidates for the shipping industry in its search for a zero-carbon fuel, could you please share your views about ongoing projects globally that are being undertaken with ammonia as fuel?
3. On a scale of 1 to 10, how would you rate the degree of risk associated with ammonia as marine fuel? Could you please justify the rating.
4. In the background of your association with the decarbonisation projects, could you please share the outcome of safety assessment undertaken on the use of ammonia as a marine fuel?
5. In your view, to what extent does the 'The International Code of Safety for ships using gases or other low-flashpoint fuels' (IGF Code) address the risks associated with the ships that use ammonia as fuel?
6. As the IMO's mandatory regulatory criteria are still in the evolving stage, could you please describe the safety benchmarking adopted by the industry in the design and construction of ships with ammonia as fuel?
7. In your opinion, what are the specific role(s) played by the flag State and the Recognised Organization (RO) to ensure safe design, construction and operation of ships that are being built on the alternate fuel platform such as ammonia, until adoption of a common regulatory standard by the IMO?
8. In your view, what are the distinctive features of the rules that have been framed by the major classification societies viz. LR, ABS, KRS, NKK, BV etc.

for use of ammonia as marine fuel and are they addressing the identified risks? Are there any aspects that distinguishes these rules from each other?

9. Could you share your opinion on how the shipping industry can mitigate the risks associated with the use of ammonia as a fuel, during operation and maintenance; and whether the existing safety management systems would be adequate to meet the additional challenges?
10. What are the risks and complexities involved in the supply of ammonia as bunker fuel to ships? Could you share your insights on the level of preparedness by the bunker suppliers worldwide, in supplying ammonia to ships as bunker and the steps being undertaken to mitigate the attendant risks?
11. In your opinion what additional skills, competencies and expertise would be required for a seafarer serving on a ship, or a bunker supplying company's personnel to mitigate these risks? What would be the additional training needs for these personnel?
12. What is your opinion on uptake of ammonia as a marine fuel in the mid-term and long term? What would be the likely costs to the industry in terms of additional risk mitigation measures?