Nordic Roadmap

Future Fuels
for Shipping

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Foreword

DNV and partners Chalmers, IVL Swedish Environmental Research Institute, MAN Energy Solutions, Menon, and Litehauz have been tasked by the Norwegian Ministry of Climate and Environment on behalf of the Nordic Council of Ministers to develop a Nordic Roadmap for the introduction of sustainable zero-carbon fuels in shipping. The overall aim of the project is "to reduce key barriers to implementation and establish a common roadmap for the whole Nordic region and logistics ecosystem towards zero emission shipping".

To support this overall aim, DNV is responsible for task 1-B Technical and regulatory analysis and has prepared this report. MAN Energy Solutions has contributed with valuable input.

Nordic Roadmap Publication No.1-B/2.3/2023 is a third version with an update in chapter 5.2.2.

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4th September 2023

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NORDIC ROADMAP FOR THE INTRODUCTION OF SUSTAINABLE ZERO-CARBON FUELS IN SHIPPING

Fuel properties and their consequences for safety and operability

The Norwegian Ministry of Climate and Environment on behalf of the Nordic Council of Ministers

DNV

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Objective: This report reviews the physical properties and related safety risks of natural gas, for which the IGF Code has put internationally recognised safety barriers in place to ensure safe use of LNG as a fuel onboard - and compare them to the physical properties and related safety risks of hydrogen, ammonia, and methanol.

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EXECUTIVE SUMMARY

This report is developed as a part of the project "Nordic Roadmap for the introduction of sustainable zero-carbon fuels in shipping"[1,2]. The overall aim of the project is to "to reduce key barriers to implementation and establish a common roadmap for the whole Nordic region and logistics ecosystem towards zero emission shipping". Lack of international safety regulations has been identified as a key barrier against implementation of zero-carbon fuels.

To reduce this barrier, one objective of the project is to provide stakeholders in the Nordic countries with a technical knowledge base for selected zero-carbon fuels to facilitate submissions to IMO with proposals for regulations on the use of ammonia and hydrogen as ship fuels. Hydrogen, ammonia (both pre-selected by the customer) and methanol (selected based on the screening in Task 1-A) are subject to further analysis in Task 1-B Technical and regulatory analyses.

What we did:

This report assesses the physical properties and related safety risks of natural gas[3], for which the IGF Code has put internationally recognised safety barriers in place to ensure safe use of natural gas as a fuel - and compares them to the physical properties and related safety risks of hydrogen, ammonia, and methanol. The aim is to map differences in behaviour between the fuels that may warrant a different approach to safe ship design when hydrogen, ammonia or methanol is used as a fuel. The overall approach is illustrated in Figure A.
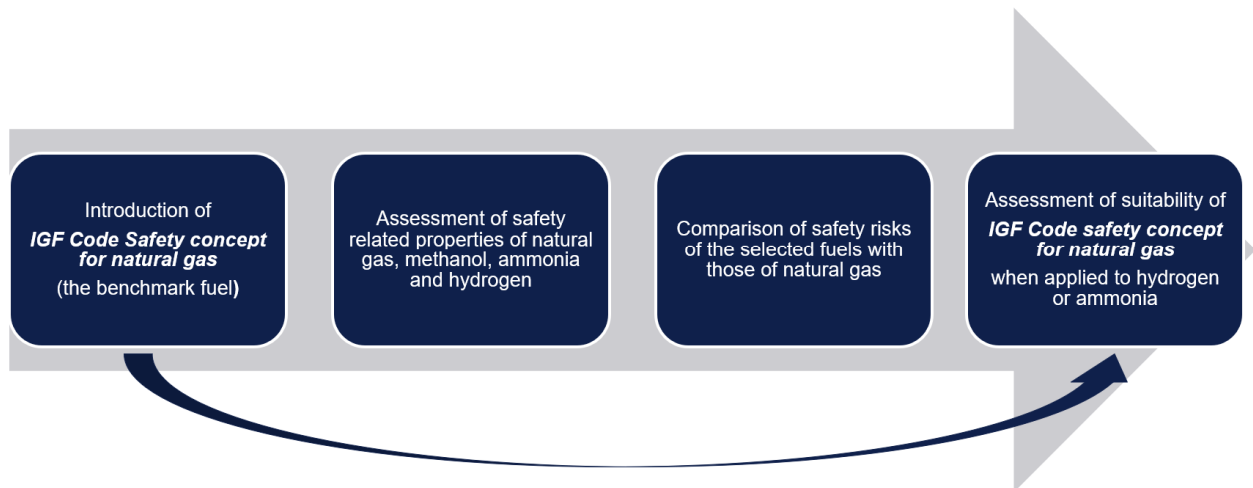
Figure A Illustration of the stepwise approach of the study.

We find that:

Natural Gas – the benchmark fuel

Natural gas is a naturally occurring mixture of gaseous hydrocarbons consisting primarily of methane. In ambient conditions, methane is ignitable in a 5-17% mixture with air, with a minimum ignition energy of 0.27 mJ[4]. Consequently, any leaks or discharges from the fuel system will introduce a significant fire and explosion risk onboard a ship.

The volume of methane is reduced by 600 times when it is liquefied by cooling at atmospheric pressure to form LNG. Due to space constraints methane is usually stored in its liquefied form, making the low boiling temperature at -161°C a

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[1] The term sustainable zero-carbon fuels is used to indicate fuels with potential zero climate impact throughout their lifecycle.
[2] https://futurefuelsnordic.com/
[3] Natural gas fuel in the context of the IGF Code is either in its liquefied (LNG) or gaseous state (NG). Its composition varies, but the primary component is methane.
[4] mJ; millijoules

safety challenge. Normal ship steel is not suited for such low temperatures. It will become brittle and crack. Leakages of liquid natural gas may therefore damage load carrying structure and compromise gas tightness of safety barriers. Additionally, large, pressurised storage tanks have a high energy content which will be released if the tank has a substantial rupture.

Hydrogen

Hydrogen has a 6-7 times wider flammability range and a significantly lower minimum ignition energy over most of its flammability range compared to methane. Consequently, there is a significantly higher risk of ignition of hydrogen leakages compared to a corresponding methane leakage. The higher burning velocity of hydrogen is linked to more severe explosions which can transition to detonation.

Due to the extreme flammability properties of hydrogen, any hydrogen discharge on open deck, in semi-enclosed or enclosed spaces onboard constitutes an additional safety risk compared to methane. Hydrogen releases in confined spaces are particularly dangerous since the rapid pressure build-up after an ignition in many cases will be sufficient to cause structural damage and thereby potentially escalate hydrogen leakages and destroy existing safety barriers.

Having a normal boiling point of -253°C, liquefied hydrogen (LH_2) is stored at temperatures more than 90°C lower than liquefied methane (LNG). This result in additional safety challenges in onboard hydrogen storage and distribution, like boil-off gas management and possibilities for condensation and solidification of other gases (oxygen, nitrogen).

Gaseous hydrogen can be compressed to very high pressures (250-700 bar). Under such pressures, the hydrogen has considerable potential (stored) energy, like any other gas. The release of this energy can generate strong pressure effects depending on the release rate, even without a subsequent combustion (ISO, 2015). Also, a sudden hydrogen release from high-pressure systems into air can be spontaneously ignited without any apparent ignition sources present, such as spark, hot surface, fire, etc. As hydrogen can cause a significant deterioration in the mechanical properties of metals (referred to as hydrogen embrittlement), the choice of material for hydrogen systems is an important part of hydrogen safety.

Bunkering high-pressure hydrogen from shore can be challenging. Consequently, several projects are looking towards swappable compressed hydrogen storage units which can be re-charged at shore facilities. This concept is not in line with current shipbuilding practice, where gas fuel storage tanks are permanently onboard and are certified in accordance with the requirements of the IGF Code, and will also result in more frequent coupling and de-coupling of leak-prone equipment.

Ammonia

Ammonia has a much higher lower flammability limit (LFL) compared to methane, and the minimum ignition energy is also significantly higher. This means that a higher gas concentration in air and more energy is needed for ignition of a flammable gas cloud. Further, its burning velocity is well below that of methane, which leads to a lower rate of pressure rise for an explosion in confined spaces. There are no reports of any anhydrous gaseous ammonia explosions in open air.

Although gaseous, anhydrous ammonia is lighter than air, the rapid evaporation following a sudden release of pressurized, liquid ammonia may cause liquid carry-over to the gas cloud. The ammonia droplets may disperse in the gas, forming a cloud that is heavier than the ambient air. Ammonia may behave in buoyant, neutral, or dense fashion depending on the circumstances of its escape into the atmosphere. Kaiser et al. (1982) shows that the crucial parameter which determines whether the ammonia is likely to form part of a buoyant, neutral, or dense mixture is the airborne liquid fraction. For ammonia releases with a content of airborne liquid fractions below 4% (by mass), a buoyant mixture is always formed, while for high liquid fractions (>20%), the mixture is always dense. In between, the mixture may be buoyant, neutral, or dense, depending on the atmospheric humidity.

Toxicity is in many ways the key hazard related to ammonia, and the property that separates it most from methane; it is harmful to personnel at concentrations well below its lower flammability limit and can be life-threatening in concentrations of 0,5% in air. Introduction of ammonia as fuel in the maritime sector poses challenges that are different from the ones seen in the onshore industry, including situations with personnel near operations with a relatively high probability of leakages, such as bunkering, more frequent coupling and de-coupling of equipment and also the limited possibility of escaping the consequences of an ammonia release when at sea.

The fact that harmful concentrations range down to a fraction of a percentage makes even small leakages hazardous, and the extent of a hazardous gas cloud potentially very large. This hazard must be considered in all aspects of ammonia fuelled ship operation, including ship design, with respect to passenger and crew areas, escape ways, mustering stations and location of, and access to, life rafts and Personal Protective Equipment. Ports, as a focal point for ammonia fuelled ship calls, bunkering operations and shore storage facilities may represent a risk for exposure for people in the vicinity. Port layout and bunkering infrastructure must also be designed to ensure the safety of people in the vicinity of potential leaks.

Unlike the other fuels described in this report, whose primary risks are related to fires or explosions, the risks related to ammonia toxicity cannot be reduced by measures that reduce the chance of ignition; ammonia has a direct effect when released close to personnel.

The United States National Institute for Occupational Safety and Health (NIOSH) specify that the Immediately Dangerous to Life or Health Concentrations (IDLH) value is 300 ppm. The Occupational Safety and Health Administration (OSHA) operates with a Permissible Exposure Limit of 50 ppm time-weighted average (TWA).

Ammonia is transported in liquid state, either compressed, refrigerated, or a combination of the two. Fully refrigerated ammonia at atmospheric pressure is stored at -33°C, whilst ammonia liquefied by pressure requires tanks and equipment designed for 18 bar, which corresponds to the vapour pressure at 45°C.

Ammonia's atmospheric boiling point, -33°C, is significantly higher than those of LNG and LH_2. Still, materials must be selected with care to avoid brittle fracture when ammonia is stored and handled in a fully refrigerated condition.

Unlike methane, ammonia is corrosive, which must be accounted for in the selection of materials in direct contact with ammonia, including materials likely to be exposed to ammonia in the case of leakages.

Methanol

Methanol is a liquid at normal conditions and can therefore be stored in integral hull tanks comparable to conventional fuel oil tanks. Having a flashpoint at 11°C implies that it will create ignitable vapours above this temperature. It is reasonable to assume that the ambient temperature onboard normally will be above 11°C. The lower flammability limit (LFL) of methanol vapours is comparable to methane, implying that the risk of ignition arises at the same range of concentration in the atmosphere. The upper flammability limit (UFL) is significantly higher, meaning less oxygen is required for ignition. The maximum burning velocity is around 20% higher. The minimum ignition energy is about 50% lower than that of methane, hence a methanol vapour cloud is easier to ignite than a methane gas cloud.

This means that methanol is highly flammable and constitutes a fire risk in enclosed spaces and on open deck. Accumulation of methanol vapours in confined spaces may lead to explosion if ignited. Hence, a methanol leakage will introduce fire and explosion hazards, and the methanol tank atmosphere will be explosive.

Unlike methane, methanol is toxic and poisonous to the central nervous system, and may cause blindness, coma, and death if ingested in large quantities. Methanol in the human body (either ingested or by skin absorption) oxidizes and produces formic acid and formaldehyde. At high vapour concentrations, methanol can also cause asphyxiation.

The United States National Institute for Occupational Safety and Health (NIOSH) specify that the Immediately Dangerous to Life or Health Concentrations (IDLH) value is 6000 ppm. The Occupational Safety and Health Administration (OSHA) operates with a Permissible Exposure Limit of 200 ppm time-weighted average (TWA).

Comparison of physical properties and related safety-risks

The safety risks related to the physical properties of methane, methanol, ammonia and hydrogen when used as fuel onboard are rated below. They are split in two groups: safety risks related to properties affecting the flammability of a fuel, and safety risks related to properties relevant for storage, release, and dispersion phenomena, shown in Figure B and Figure C, respectively.

Figure B shows that the flammability properties and related safety risks of hydrogen are extreme compared to methane, those of methanol are comparable to methane and those of ammonia have lower flammability and related safety risks than methane.

Relatively low	Medium	High	Very high

	Flashpoint (°C)	Flammability range (%vol. fraction)	Minimum ignition energy (mJ)	Auto-ignition temperature (°C)	Laminar burning velocity (m/s)
Methane	-*	5.3-17	0.274	537	0.37
Methanol	12	6-36.5	0.174	385	0.48
Ammonia	-*	15-28	40-170	650	0.07
Hydrogen	-*	4-77	0.017	585	2.7

*The gaseous fuels do not have a defined 'flashpoint' like the liquid fuels, but will instead transfer fully into gaseous form at ambient conditions, due to the low boiling temperatures.

Figure B Safety risks related to flammability properties for methane, methanol, ammonia, and hydrogen when used as fuel onboard.

Figure C shows that hydrogen has similar, but more extreme storage, release and dispersion properties compared to methane. Ammonia and methanol introduce new safety risks related to toxic properties. Toxicity challenges will be more difficult to manage for ammonia, being a gaseous fuel, than for methanol which is stored as a liquid at ambient conditions.

	Relatively low	Medium	High	Very high

	Normal boiling point (°C)	Density (kg/m³)		Expansion ratio liquid NBP/gas NTP	Toxicity IDLH (ppm)
		(G,NBP)	(G,NTP)		
Methane	-162	1.819	0.6594	600	Asphyxiation
Methanol	64.9	-	1.11*	-	6000
Ammonia	-33.4	0.89**	0.610**	850	300
Hydrogen	-253	1.312	0.0827	847	Asphyxiation

G – gas
L - liquid
NTP - normal temperature and pressure
NBP - normal boiling point
IDLH – Immediately Dangerous to Life or Health Concentrations specified by the United States National Institute for Occupational Safety and Health (NIOSH)
* Specific gravity of methanol vapour
**Due to hygroscopic properties ammonia vapours reacts with moisture in air resulting in a density that is heavier than air.

Figure C Safety risks related to storage, release and dispersion properties for methane, methanol, ammonia and hydrogen when used as fuel onboard.

Suitability of the safety principles in the IGF Code

Having considered the safety risks illustrated in Figure B and C, the report addresses the safety principles in the IGF Code and whether those principles would be suitable and provide sufficient risk reducing measures if applied to ammonia or hydrogen as ship fuels. Safety barriers applied to LNG systems by the IGF Code can broadly be divided into five categories related to segregation, system integrity, double barriers, leakage detection and automatic isolation of leakages.

The suitability of these safety barriers if applied to ammonia or hydrogen is summarized in Figure D. Methanol is not included, as IMO has already provided an international standard by the non-mandatory interim guidelines for methyl/ethyl alcohols (methanol/ethanol).

	Segregation		System integrity		Double barriers				Leakage detection	Automatic isolation of leakages
	Mechanical damage	External fire	System design	Operational and emergency discharges	Piping	ESD machinery space	Double barrier spaces	Ventilation	LEL	ESD valves
Ammonia			corrosivity pressure toxicity	toxicity	toxicity	toxicity	toxicity	toxicity	toxicity	toxicity
Hydrogen			leakage prone, flammability	flammability	flammability	flammability	flammability	flammability	density, flammability range	flammability

Legend: IGF can be used | IGF minor changes | IGF major changes | IGF questionable

Figure D Suitability of using safety concept of the current regulations in the IGF Code for natural gas fuel also for ammonia and hydrogen.

As indicated in Figure D, many of the safety principles in the IGF Code for natural gas can be applied to ammonia with substantial modifications to account for the additional toxicity risk upon loss of containment. The IGF Code requirements for natural gas fuel do not account for fuel toxicity, which necessitates stricter barriers to protect against ammonia exposure during normal operation and in emergency situations. This is supported by EMSA (2022) where many additional safeguards, not found in the IGF Code, due to the inherent risks of ammonia are identified.

Due to extreme flammability and reactivity, adoption of IGF safety principles is less obvious for hydrogen as a ship fuel. The existing LNG safety barriers are likely not sufficient to suppress the extreme flammability of hydrogen. This identifies the need for further regulatory development, where the findings from this report can be used to investigate ways of containing the new safety challenges.

1 INTRODUCTION

DNV, together with partners Chalmers, IVL, MAN Energy Solutions, Menon, and Litehauz, have been assigned the Nordic Roadmap project by the Norwegian Ministry of Climate and Environment on behalf of the Nordic Council of Ministers. The project has an overall aim "to reduce key barriers to implementation and establish a common roadmap for the whole Nordic region and logistics ecosystem towards zero emission shipping". Hydrogen, ammonia[5] (pre-selected by the customer) and methanol (selected based on the screening in Task 1-A) are subject to further analysis in Task 1-B Technical and regulatory analyses. This is the second report resulting from Task-1B. The results from the first part of this task are summarized in the report "State of play – status on regulatory development for zero-carbon fuels".

The International Maritime Organization (IMO) has established an internationally recognised safety standard - "The International Code of Safety for Ships using Gases or other Low-flashpoint Fuels" (IGF Code) where equivalent safety with conventional oil-fuelled ships is a functional requirement. The current version of the Code includes regulations to meet the functional requirements for natural gas fuel. Through the development and introduction of the IGF Code, the industry obtained a set of requirements providing the required level of safety when introducing new, and at the time unconventional, technology and marine fuel. Major accidents have been avoided, and the significance of that cannot be underestimated. Accidents associated with new technology can halt the development and implementation of alternative fuels for years and must be avoided also when introducing the fuels discussed in this report.

For ships using other fuels falling under the scope of the Code, like ammonia and hydrogen, flag state approval is based on the alternative design approach of the Code, which does not provide the support and predictability designers and shipyards are used to when working with established rules and regulations. The alternative design approach is a time consuming and unfamiliar way of working for shipyards, designers, and shipowners, resulting in significantly increased cost, and added business risk for any conversion or newbuilding project - and is therefore a barrier against the uptake of alternative fuels.

The intention with this report is to provide the Nordic countries with a technical knowledge base on the fuels analysed and use the existing IGF Code, providing internationally recognized and accepted regulations for natural gas fuelled ships, as a benchmark for safety level when evaluating hydrogen, ammonia and methanol. Methanol is included in this study for future reference, even though IMO has provided an international standard by the non-mandatory interim guidelines for methyl/ethyl alcohols (methanol/ethanol).

This report has the following structure: Chapter 2 briefly describes the method, and chapter 3 introduces the safety concept applied in the IGF Code. Chapter 4 presents an overview of safety-related properties of hydrogen, ammonia, methanol and natural gas (methane) - and assesses how these properties affect the safe use of a fuel onboard a ship. In chapter 5 the safety risks of ammonia, methanol and hydrogen are compared to those of methane, and additional safety risks arising from differences in physical properties are discussed. Chapter 6 evaluates to what degree IGF safety principles introduced in chapter 3 would be suitable for hydrogen and ammonia, which are not currently covered by prescriptive requirements. Our findings are summarized in chapter 7.

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[5] Ammonia when used as fuel is anhydrous ammonia (less than 0.2% water).

2   OUR APPROACH

This chapter briefly describes the methodology used in this study to assess the suitability of the IGF Code safety concept for the selected fuels. Figure 2-1 illustrates the overall approach.
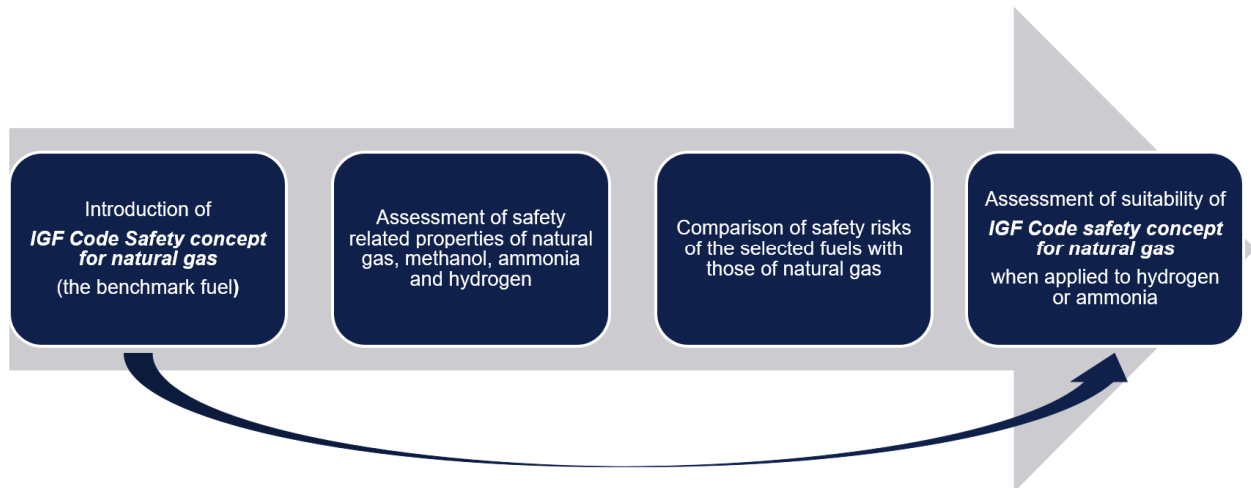

Figure 2-1 Illustration of the stepwise approach of the study.

This study is divided in four steps. In step 1 (chapter 3), we introduce the safety concept applied in the current regulations in the IGF Code for natural gas fuel. In the 2nd step (chapter 4), an overview and explanation of safety-related properties of hydrogen, ammonia, methanol and natural gas (methane) is presented, based on available literature, previous experience and studies performed by DNV. The safety related fuel properties discussed in this report are split in two groups: properties affecting the flammability of a fuel (flashpoint, lower and upper flammability limit, minimum ignition energy, auto-ignition temperature, burning velocity) and properties relevant for storage, release, and dispersion phenomena (normal boiling point, expansion ratio liquid-to-gas, gas density and specific gravity and toxicity).

In step 3 (chapter 5), the additional safety risks from the onboard storage, distribution and use of the selected fuels (ammonia, hydrogen and methanol) have been analysed and compared to methane. In step 4 (chapter 6), the safety concept of the existing IGF Code, providing internationally recognized and accepted regulations for natural gas fuelled ships, is used as benchmark for safety level when evaluating hydrogen and ammonia used as fuel onboard. The safety principles are discussed to address to what degree they also would be suitable for ammonia and hydrogen currently not covered by prescriptive requirements.

3   SAFETY CONCEPT FOR ALTERNATIVE FUELS

Fire is a major hazard onboard ships and handling flammable fuels in spaces with ignition sources and hot surfaces is one of the risk factors. Fuel vapour may ignite spontaneously without any secondary ignition source if it is heated up to its auto-ignition temperature. Leaking oil contacting high-temperature surfaces is by far the most common reason for engine-room fires. With an ignition source present, fuel vapours may also be ignited when the fuel is heated to a temperature at which the fuel will give off enough flammable vapour to be ignited. This temperature is referred to as the flashpoint of the fuel. The flashpoint, the amount of energy required to ignite the vapour mixture (minimum ignition energy (MIE)) and the ratio of air to fuel vapour (flammability range) are specific to each fuel type. To limit the risk of tank explosions and vapours being ignited, IMO has generally prohibited the use of fuel oils with a flashpoint below 60°C.

Most alternative fuels are gases or liquids with a significantly lower flashpoint than conventional fuel oils and will, unlike conventional fuel oils, create an explosive gas atmosphere at the right conditions. Some alternative fuels are also toxic to humans in small quantities and in low concentrations, and some are stored at very low temperatures, adding to the challenge of integrating a safe storage and distribution system. On the positive side, many have a substantially higher auto-ignition temperature than fuel oils. Storage of gaseous fuels in liquefied form will require control of temperature and/or pressure in the storage tanks. Due to the high energy content and the resulting discharge of large amounts of flammable/toxic fuels, damage to storage tanks can have potentially catastrophic consequences. The differences in properties and associated hazards for alternative fuels require additional safety barriers to maintain the safety level when compared with conventional oil fuel. Each alternative fuel has its unique properties and associated hazards requiring special consideration. Figure 3-1 illustrates the safety concept applied to mitigate these risks in the current regulations in the IGF Code for natural gas fuel. It consists of five main principles:

1. **Segregation**: The fuel tank and installation must be protected from mechanical damage and fire.

2. **Integrity**: The fuel system must be designed to minimize leakages from the fuel installation.

3. All parts of the fuel system must have **double barriers** to protect the ship against leakages.

4. **Leakages** in the system must be **detected** to give warning and enable automatic safety actions.

5. When a leakage is detected the fuel supply system must be **automatically shutdown** to reduce the consequence of a leakage.

We anticipate that the same principles can be applied to other alternative fuels in the development of prescriptive fuel-specific rules and regulations. However, other fuel properties like toxicity and extreme flammability will require additional safety barriers. Having a clear understanding of the unique properties of each fuel and their effect on the risk picture is essential to put effective safety barriers in place to mitigate risks of using hydrogen or ammonia as fuels. This forms an important basis for the development of efficient safety regulations.

Segregation
Protect fuel installation from external events

| **System integrity** | **Double barriers** |
| Minimize leakages from fuel installation | Protect ship against leakages |

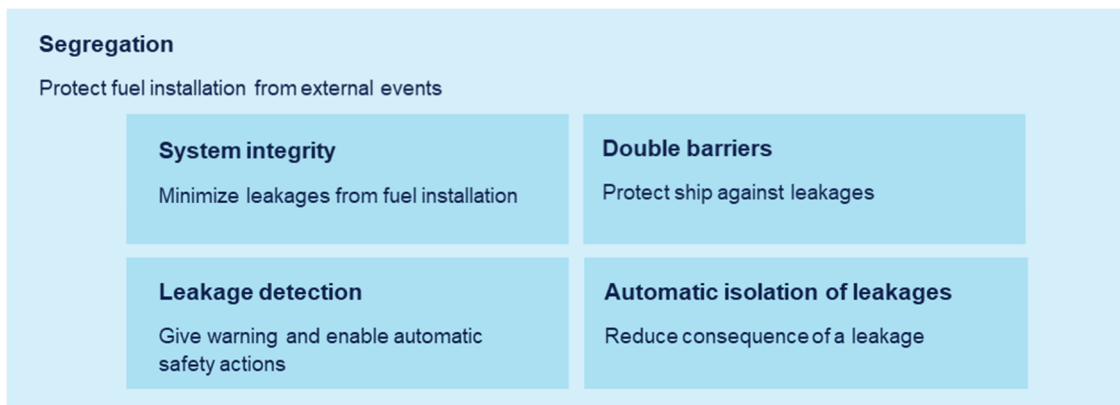| **Leakage detection** | **Automatic isolation of leakages** |
| Give warning and enable automatic safety actions | Reduce consequence of a leakage |

Figure 3-1 Safety concept of the current regulations in the IGF Code for natural gas fuel.

4 FUEL PROPERTIES RELEVANT FOR SAFETY

This chapter presents an overview of safety-related properties of hydrogen, ammonia and methanol compared to natural gas and how these properties affect the safe use of a fuel, summarized in chapter 4.1. Since the physical properties of natural gas can vary slightly with its composition, the physical properties used are for methane which is the main component of natural gas. They are split in two groups: properties affecting the flammability of a fuel and properties relevant for storage, release, and dispersion phenomena, further discussed in chapter 4.2 and 4.3, respectively.

4.1 Overview of selected properties of methane, hydrogen, ammonia and methanol

For comparison purposes, selected physical properties of methane, hydrogen, ammonia and methanol are shown in Table 4-1.

Table 4-1 Selected physical properties of fuels relevant for safety

Fuel property	Methane (CH₄)[1]	Hydrogen (H₂)[1]	Ammonia (NH₃)[2]	Methanol (CH₃OH)[1]
Flashpoint (°C)	-	-	-	12[6]
Lower & upper flammability limit (LEL and UEL) (% vol. fraction)	5.3-17*	4-77*	15-28[3]	6-36.5*
Minimum ignition energy (mJ)	0.274*	0.017*	40-170[3]	0.174*
Auto-ignition temperature (°C)	537*	585*	650[4]	385*
Laminar burning velocity (m/s)	0.37*	2.7*	0.07[3]	0.48*
Normal Boiling point (°C)	-162	-253	-33.4	64.9[5]
Expansion ratio liquid NBP/gas NTP	600**	847	850	-
Density (kg/m³)	422.5 (L, NBP) 1.819 (G, NBP) 0.6594 (G, NTP)	70.8 (L, NBP) 1.312 (G, NBP) 0.0827 (G, NTP)	679 (L, NBP) 0.89 (G, NBP) 0.610 (G, NTP)	786.9 (L, 25°C)[5]
Specific gravity (Air: 1)	0.547 (G, NTP)	0.069 (G, NTP)	0.51 (G, NTP)	1.11 (V)[6]

Remarks: * Ignition and combustion properties for air mixtures at 25°C and 101.3 kPa
         ** varies slightly depending on LNG composition

L – liquid, G – gas, V – vapour, NTP - normal temperature and pressure, NBP - normal boiling point

1 Unless specified otherwise, source of data is ISO/TR 15916 Basic considerations for the safety of hydrogen systems
2 Unless specified otherwise, source of data is INERIS Work study N°10072 Ammonia Large-scale dispersion test
3 Harris, MacDermott (1977)
4 EPA
5 Molkov (2012)
6 https://www.methanol.org/wp-content/uploads/2016/06/Physical-Properties-of-Pure-Methanol.pdf

4.2 How does the physical properties define the flammability of a fuel?

4.2.1 Flashpoint

The flashpoint is used as a main indicator of the flammability of a liquid product. It is defined as the lowest temperature at which there will be enough flammable vapour from a liquid to induce ignition when an ignition source is applied.

The flashpoint of a liquid is related to its vapour pressure. A liquid's specific vapour pressure is a function of the temperature and is subject to Boyle's Law. As the temperature increases, vapour pressure increases. With increasing vapour pressure, the concentration of vapour of a flammable or combustible liquid in the air increases. Hence, the temperature will determine the concentration of vapour of the flammable liquid in the air.

How does the flashpoint affect the safe use of a fuel?

If a liquid fuel with a flashpoint below the ambient temperature is leaking out of its containment, it will according to the above start to evaporate, creating an ignitable atmosphere around the leakage.

To prevent this from happening, SOLAS has until 2017 prohibited the use of fuel oils with a flashpoint below 60°C, which is generally accepted to provide a sufficient safety margin against an explosive atmosphere considering the ambient temperatures typically encountered by ships in operation. With the IGF Code, an acceptance of fuels with a lower flashpoint was introduced. Such fuels are typically referred to as low flashpoint liquid fuels or LFL-fuels.

A leakage of low-flashpoint liquids in an open space will create a fire risk, while in confined spaces the additional risk of explosions must be accounted for.

Flashpoint for gaseous fuels?

Gas is by the IGF and IGC[6] Codes defined as a fluid having a vapour pressure exceeding 0.28 MPa absolute at a temperature of 37.8°C. The gaseous fuels (natural gas, ammonia, hydrogen) do not have a defined 'flashpoint' like the liquid fuels (e.g., methanol) but will instead transfer fully into gaseous form at ambient conditions, due to the low boiling temperatures (see Table 3-1). Also see Chapter 4.3.1

4.2.2 Lower and upper flammability limit

Flammability limits refer to the range of gas or vapour concentrations in air which will burn or explode in the presence of an ignition source. The flammability limits are usually given as the percent by volume of the gas or vapour in air.

Lower flammability limit (LFL): the lowest concentration of gas or vapour which will burn or explode if ignited.

Upper flammability limit (UFL): the highest concentration of gas or vapour which will burn or explode if ignited.

In the range between LFL and UFL, the air/gas mixture is flammable/explosive. Below the LFL, the mixture is too lean to burn. Above the UFL, the mixture is too rich to burn. Concentrations above the UFL are still very dangerous because, if the concentration is lowered (for example, by introducing fresh air), it will enter the flammable/explosive range.

How does the lower and upper flammability limits affect the safe use of a fuel?

Consideration of the LFL and the UFL is the background of several well-known and established safety barriers, e.g.:

- Locating leakage sources in open air or in well-ventilated spaces to keep the concentration below the LFL.

- Displacing air containing oxygen with an inert gas prior to filling tanks and piping systems with flammable substances to keep the concentration above the LFL at all times.

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[6] IGC Code; International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk

Similarly, double-walled piping may be fitted with ventilation to dilute the concentration in case of leakages, or they may be inerted to keep the flammable compound to air-ratio above the UFL. Hence, consciousness of the LFL and the UFL of the fuel is important when designing the safety barriers.

4.2.3 Minimum ignition energy

The minimum ignition energy (MIE) determines the ignition capability of fuel-air mixtures, where the fuel may be a combustible vapour or gas. It is defined as the minimum electrical energy stored in a capacitor, which, when discharged, is sufficient to ignite the most ignitable mixture of fuel and air under specified test conditions. The MIE value is used to assess the likelihood of ignition during processing and handling.

The curve in Figure 4-1 shows within which concentrations of gas in air there is an explosive atmosphere. All flammable gases and vapours have their own specific "explosion curve". If the air-gas ratio is below or above the explosion limits explained above, there will not be an explosive gas atmosphere. The lowest point of the explosion curve is the optimal concentration of the gas or vapour in air, i.e., when the minimum amount of energy is required to ignite the atmosphere.
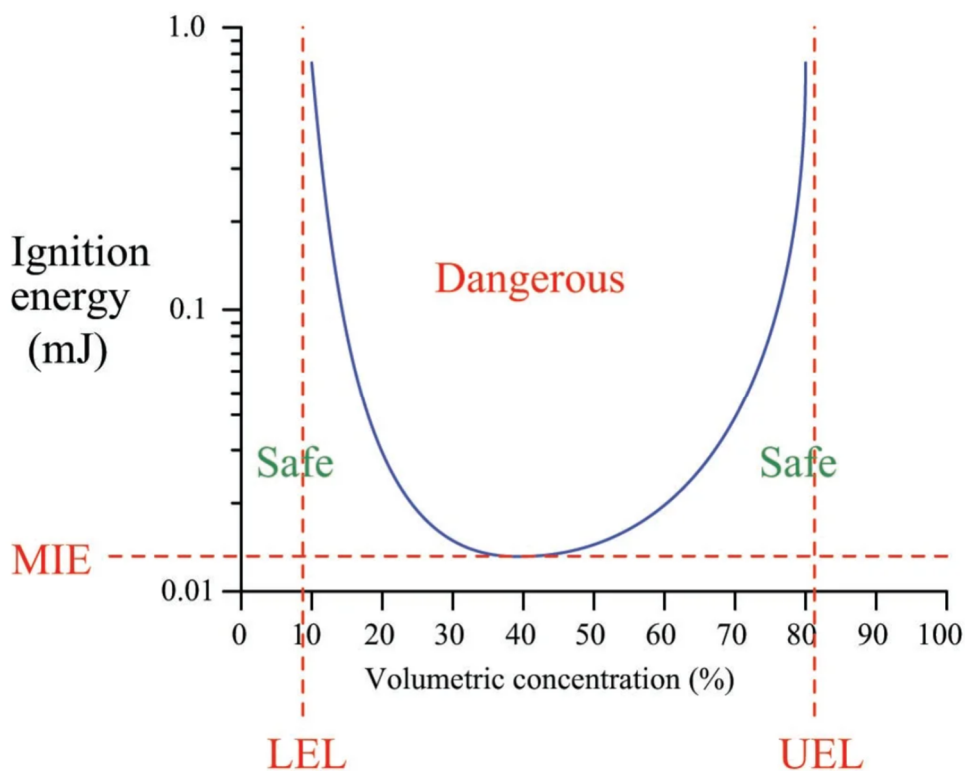

Figure 4-1 "Explosion curve" (Source: Lessons in Industrial Instrumentation, control.com).

How does the minimum ignition energy affect the safe use of a fuel?

A fire triangle is often used to illustrate the three elements a fire needs to ignite: heat (ignition source), fuel and an oxidizing agent (usually oxygen). A fire risk reduction strategy commonly applied in ship design is to prevent scenarios where all elements are present and combined in the right mixture, typically by attempting to remove one or more of them.

Irrespective of safety barriers, a fuel that has a very narrow flammability range and requires a lot of heat to ignite will pose less of a fire risk than a fuel with wide flammability range requiring little energy to ignite.

Electrical equipment are potential ignition sources in case of leakage and formation of a flammable or explosive atmosphere. Sparks, short circuits and arches from switches or electric motors are examples of ignition mechanisms from electrical sources. Static discharges can also carry enough energy to ignite an explosive atmosphere of methane or hydrogen. Hot surfaces, open flame (hot work), and exhaust are other typical sources of ignition.

A lower minimum ignition energy means that less energy from e.g., electrical equipment is required to cause ignition. It should however be noted that most ignition sources generate more than 10 mJ, which would be sufficient to ignite most common fuels in mixture with air if their concentration exceeds the lower flammability limit.

4.2.4 Auto-ignition temperature

The auto-ignition temperature of a substance indicates the lowest temperature at which it may spontaneously ignite without the presence of an ignition source such as a flame or spark. At the auto-ignition temperature, the temperature alone provides sufficient energy to induce combustion. The auto-ignition temperature depends on pressure and availability of oxygen and is typically given at standard pressure and temperature, with ideal oxygen concentration.

How does the auto-ignition temperature affect the safe use of a fuel?

Between 30 and 50% of fires on merchant ships start in the engine room, and most of these fires are caused by oil leaks from pressurised systems. Oil fires usually occur when oil from a large leak or a smaller but persistent leak comes into contact with a nearby hot surface at a temperature that exceeds the auto-ignition temperature of the oil. The sources of heat most likely to start a fire in an engine room are hot exhaust pipe and engine surfaces, bearings of rotating machinery heating up and defunct electrical equipment.

High pressure sprays comprising fine droplets of fuel can ignite immediately on contact with the hot surface, and liquid leaks can ignite after a short period of time sufficient to evaporate the fuel and generate a flammable concentration of fuel vapour. Under certain circumstances, such as where flammable concentrations of vapour form in confined spaces, the fire may be preceded by an explosion.

The gases and low-flashpoint liquid fuels covered by the IGF Code typically have higher auto-ignition temperatures than fuel oils. Gaseous fuels will be in gaseous form or in most cases instantly vaporise upon leakage and will therefore represent a different fire and explosion hazard than liquid fuels. In a scenario where a gas fire fades out due to lack of oxygen, materials heated by the fire could be the source of auto-ignition if oxygen is somehow reintroduced to the space.

Low flashpoint liquid fuels like methanol can cause engine room fires in the same way as oil fuels but require higher surface temperatures than oils to ignite.

It should be noted that most energy converters using alternative fuels are dual fuel engines using oil as a pilot fuel, so the risks associated with the IGF Code fuels comes in addition to the risk of engine room fires due to having oil under pressure.

4.2.5   Burning velocity and detonability

The severity of an explosion will depend on many factors, but in general, the more 'reactive' the fuel the worse the explosion. Reactivity in this sense relates to how fast a flame moves through a flammable cloud. At its worst, hydrogen flames can burn about an order of magnitude faster than natural gas and much faster than most commonly used hydrocarbons. To add to this, when a flame travels very fast, going supersonic, the explosion can transition to a detonation. A detonation is a self-sustaining explosion process with a leading shock of 20 bar that compresses the gas to a point of autoignition. The subsequent combustion provides the energy to maintain the shockwave. Detonability varies from fuel to fuel and detonations would not occur in any realistic situation with natural gas but are entirely credible for hydrogen (DNV, 2022).

Detonation limits are the range of composition within which detonations have been observed in laboratory and field experiments. Detonation limits are a strong function of mixture composition, initial pressure and temperature but usually considered to be narrower than the flammability limits. In addition, detonability is much more strongly dependent on the ignition source, confinement, and the physical size of the environment than flammability limits. The ability to initiate and propagate a detonation requires a set of critical conditions to be satisfied and despite extensive research into the subject, the limits are empirical in nature.
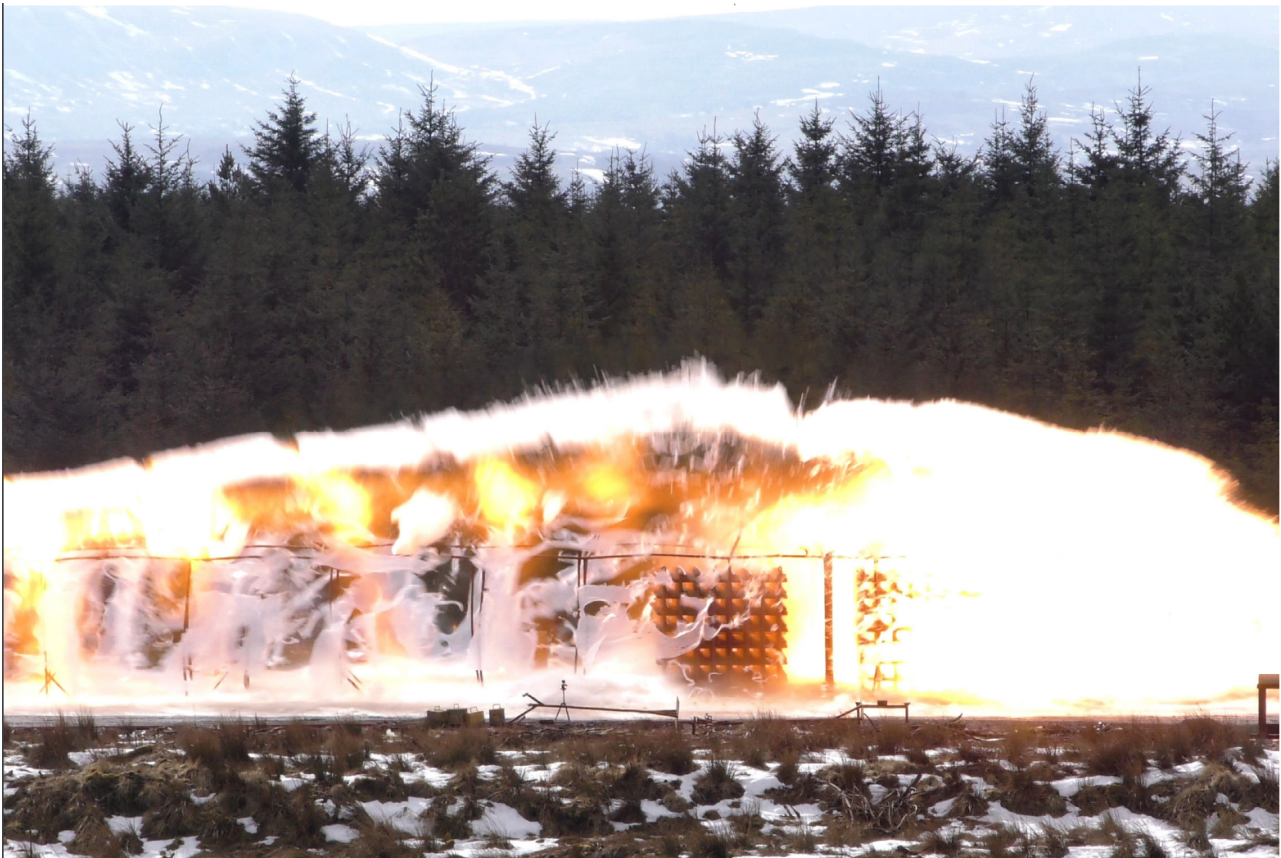

Figure 4-2 *Detonation of hydrogen is entirely credible at scales representative of many scenarios where it is not for traditional hydrocarbons. This image shows a still image from a 15 m^3 (approx. 1,3 kg) hydrogen detonation conducted as a demonstration at DNV's Spadeadam Research Centre in the UK (DNV, 2022)*

4.3 How does the physical properties of the fuel affect storage, release and dispersion phenomena?

4.3.1 Normal boiling point and saturation temperature

The boiling point of a liquid is the temperature at which its vapour pressure is equal to the surrounding pressure and the liquid changes into a vapour.

When the external pressure is

- less than one atmosphere, the boiling point of the liquid is lower than its normal boiling point

- equal to one atmosphere, the boiling point of a liquid is called the normal boiling point

- greater than one atmosphere, the boiling point of the liquid is greater than its normal boiling point.

Liquids may also change to a vapour at temperatures below their boiling points through the process of evaporation. Evaporation is a surface phenomenon in which molecules located near the liquid's edge, not contained by enough liquid pressure on that side, escape into the surroundings as vapour. On the other hand, boiling is a process in which molecules anywhere in the liquid escape, resulting in the formation of vapour bubbles within the liquid.

Saturation temperature refers to the temperature at the boiling point. The liquid can be said to be saturated with thermal energy. Any addition of thermal energy results in a phase transition. A saturated liquid contains as much thermal energy as it can without boiling (or conversely a saturated vapour contains as little thermal energy as it can without condensing).

If the pressure in a system remains constant, a vapour at saturation temperature will begin to condense into its liquid phase as thermal energy is removed. Similarly, a liquid at saturation temperature and pressure will boil into its vapour phase as additional thermal energy is applied.

How does the boiling point and saturation temperature affect the safe use of a fuel?

Gases are normally liquefied by pressurization or cooling for ease of storage and transportation. Prismatic fuel tanks are generally more space efficient than cylindrical pressure vessels. However, due to their tank shape they cannot withstand high pressures (their design vapour pressure is limited to 0.7 bar according to IGF/IGC). When a fuel gas is stored in prismatic tanks it will necessarily have to be cooled close to the boiling point as the design pressure of the tank is close to atmospheric pressure. Hydrogen and methane must be cooled to cryogenic temperatures[7] in order to be stored in atmospheric tanks, while ammonia is liquefied at atmospheric pressure at -33°C. Safely handling such low-temperature liquefied gases generates challenges in design:

- Tanks and piping systems holding cold fluids must be made of materials with mechanical properties unaffected by cold temperatures.

- Safety barriers and safety systems which may be exposed to low temperatures from leakages must be designed accordingly. When steel is cooled down to cryogenic temperatures, its mechanical properties will be changed. If ordinary steel typically used in shipbuilding is exposed to leakages from cryogenically stored fuels, the fracture toughness will be reduced, increasing the risk of brittle fracture.

- Personnel must be kept safe from direct contact and inhalation of cold fluids and indirectly from low surface temperatures of equipment. A leakage of cryogenically stored fuel in the vicinity of personnel could lead to cryogenic burns, internal damage due to cold vapour inhalation and asphyxiation due to displacement of oxygen. Also, the evaporation of liquids and the dispersion of low temperature vapours might prevent

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[7] Cryogenic temperatures; very low temperatures (-150°C to -273°C)

personnel to access main escape routes and refuge areas. Therefore, a cryogenic leakage event could restrict safe evacuation.

- The fuel must be prevented from boiling off through the vent mast. Fuel gases being stored at the boiling point will constantly go from liquid to gas due to heat influx to the storage system. This boil-off gas (BOG) will increase the tank pressure, and unless the tank is able to handle a pressure build-up in the tank by containing the BOG at an equilibrium (as is the case for some properly insulated pressure vessels), systems to safely manage the BOG must be arranged.

4.3.2 Expansion ratio liquid-to-gas

The expansion ratio (ER) of a liquefied gaseous fuel is the volume of a given amount of that substance in liquefied form compared to the volume of the same amount of substance in gaseous form, at room temperature and normal atmospheric pressure.

How does the expansion ratio affect the safe use of a fuel?

If liquefied gaseous fuel is spilled and vaporised within an enclosed space, the pressure inside the room will increase. Depending on the possibilities for pressure relief and the vaporisation rate, the pressure increase may or may not be sufficient to damage the structure. The structure surrounding the leakage will typically be a safety barrier against further spreading of flammable or toxic gas in the ship and maintaining the integrity and gas tightness of the bulkheads in a leakage scenario is essential.

The liquid-to-gas expansion ratio is also important to estimate consequences of a liquid leak with respect to flammability and toxicity. When the space volume, evaporation rate and flammable range is known, it is possible to evaluate if ventilation can be used to keep the atmosphere below LEL, and what rates that would be required to provide the necessary dilution.

4.3.3 Gas density and specific gravity

Density is defined as the amount of mass present in a given volume. For solids and liquids, this is a fairly straightforward measurement. However, gases are very responsive to temperature and pressure (more so than solids or liquids), which can cause their densities to change rather quickly. The densities at normal boiling point (NBT) and normal pressure and temperature (NTP) are shown in Table 4-1 for comparison.

Specific gravity for gases is defined as the ratio of the density of the gas to the density of air at a specified temperature and pressure. If a gas has lower specific gravity than air (<1), it is said to be "lighter" than air, and if it has a higher specific gravity it is said to be "heavier" than air (>1). The specific gravity at NTP is used in Table 4-1.

How does the gas density and specific gravity affect the safe use of a fuel?

Accounting for the density of any released gas is important for proper design of many safety barriers. Examples are location of gas detectors, arrangement of ventilation systems and the geometrical shape of spaces where gas leaks may occur, which all need to account for the density of the leaking gas.

If a propane tank leaks, the gas can accumulate near the floor because it is denser than air. If a natural gas pipe leaks, the methane can accumulate at the ceiling because it is less dense than air. However, once the leak is stopped and the air is mixed, the gases distribute uniformly throughout the room. If the gas source is small or leaking slowly, resulting in

ppm[8] levels of contaminants, the air never becomes stratified in the first place. Gases tend to diffuse and mix quickly, so even if the gas starts out stratified, it cannot stay stratified for a long time in a small, confined space.

From a safety point of view, early gas detection is essential to enable fast response to a leakage which must be alarmed and isolated as rapidly as possible. Consequently, the placement of fixed gas detectors should to a certain extent be dictated by the density of the gas it tries to detect. Likewise, if the location of ventilation inlets and outlets accounts for the gas density, a more effective ventilation of the room can be obtained.

4.3.4   Hygroscopic compounds

A hygroscopic compound has the ability to attract water molecules from the surroundings.

How does hygroscopic properties affect the safe use of a fuel?

The related safety risks depend on how hygroscopic the compound is. For ammonia it has direct health effects upon exposure, has impact on dispersion behavior and is relevant for emergency response strategies, while it has no direct safety impact for methanol.

4.3.5   Asphyxiation

Asphyxiant gases displace and dilute oxygen from air and people can suffocate as a result. Asphyxiants with no other health effects are referred to as simple asphyxiants. Examples of simple asphyxiants include methane, hydrogen nitrogen, helium, and carbon dioxide.

How does the asphyxiation risk affect the safe use of a fuel?

Most asphyxiation incidents occur when entering confined spaces and many injuries and deaths are reported each year from such accidents. A large part of the fatalities has been among the would-be rescuers. Consequently, it is essential to always verify that the air quality is acceptable before entering a space where there is a potential for fuel leakages. It is worth noting that a leakage of small quantities of liquefied gas will expand upon vaporisation and displace the oxygen inside.

4.3.6   Toxicity

Toxicity is a chemical substance's ability to damage an organism. Toxicity is dose-dependent; even harmless substances, such as water, can lead to intoxication if taken in too high a dose, and very poisonous substances can be harmless if the dose is negligible. In the context of this study, toxicity is the fuel's ability to cause harm to humans in realistic scenarios when used as a fuel.

How does the toxicity affect the safe use of a fuel?

With the introduction of LNG as a ship fuel, ways to relate to the risk of releases of highly flammable gaseous fuels had to be found. Trying to limit leakage sources by design, limiting operational releases and introducing secondary barriers were parts of this solution.

However, the toxicity limits of ammonia and methanol are significantly lower than their flammability limits (and the flammability limits of methane). The ammonia gases and vapours are an immediate threat to people onboard, as opposed to flammable gases which have to be ignited upon release to cause damage. This implies that releases of toxic fuels may have to be viewed differently than flammable fuels from a regulatory point of view.

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[8] ppm; parts per million

5 COMPARISON OF FUEL PROPERTIES AND RELATED SAFETY RISKS

In the following sub-chapters, the fuel properties and related safety risks of hydrogen, ammonia and methanol are compared to those of methane, and the difference in safety risks are discussed.

5.1 Hydrogen vs methane

5.1.1 Flammability

For hydrogen, as for methane, ignition of accidental releases can result in fires and explosions. This is discussed in the following sub-chapters.

Lower and upper flammability limit

As shown in Table 5-1, the flammable range of hydrogen in air is 4-77%, which is a considerably wider range than 5.3-17%, for methane. The lower flammability limits are comparable, meaning that smaller leakages of the two fuels pose similar risks of creating flammable or explosive atmospheres. However, hydrogen is ignitable in a much wider range of richer mixtures compared to methane – meaning less oxygen is required for ignition. This implies that in instances where inerting is used to suppress the ignition risk, a hydrogen atmosphere will be more sensitive towards ingress of air than methane.
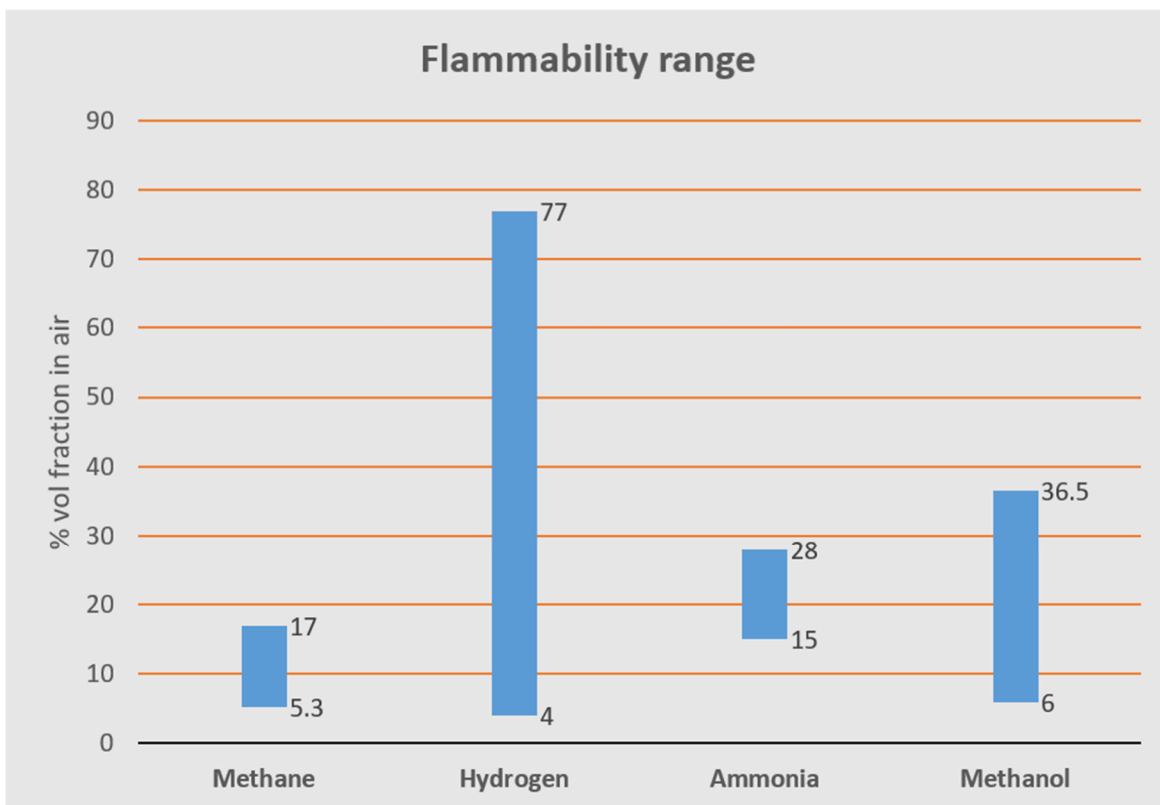

Figure 5-1 Flammability range of methane, hydrogen, ammonia, and methanol.

Minimum ignition energy

Hydrogen requires significantly less energy to be ignited than methane (MIE for methane is 16 times that of hydrogen), and this applies over a wide range of hydrogen concentrations as shown in Figure 5-2.

A source able to generate a spark having the energy of 1 mJ will ignite hydrogen-air mixture with hydrogen content ranging from 6 to 64 vol. %. At the limits of flammability, the ignition energy is similar to methane (Figure 5-2). Its value is relatively high compared to the MIE, and many ignition sources would be able to provide this level of energy. Less energy is needed to ignite a mixture that is closer to its lowest point on the explosion curve.

Relevant ignition sources include mechanical sparks induced from rapidly closing valves, electrostatic discharges occurring in ungrounded particulate filters, sparks from electrical equipment, catalyst particles, heating equipment, lightning strikes near the vent stack, etc (HyResponse, 2015a).
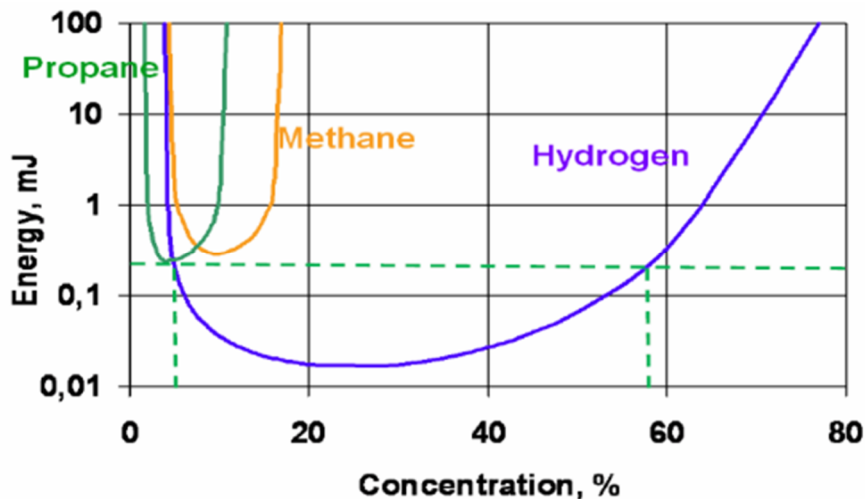

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Figure 5-2 "Explosion curve" for methane, hydrogen (and propane) (HyResponse, 2015a).

Auto-ignition temperature

The auto-ignition temperature of LNG is 537°C, slightly lower than for H_2, which auto-ignites at 585°C. In practical terms, the risk of auto-ignition is similar for the two fuels.

Burning Velocity

The burning velocity of hydrogen is 265-325 cm/s, which is more than 7 times that of methane (37-45 cm/s) (MarHySafe, 2021). The higher burning velocity results in a greater flame acceleration in congested areas and higher pressures in confined spaces due to the resistance in venting ducts and openings through which the pressure must escape.

Ignition of a flammable gas cloud does not always result in an explosion. Pressure is generated when either the gas cloud is confined within an enclosure, or the flame accelerates to high speed (or both).

In sum, hydrogen has a 6-7 times wider flammability range and a significantly lower minimum ignition energy over most of its flammability range compared to methane. Consequently, there is a significantly higher risk of ignition of hydrogen leakages compared to a corresponding methane leakage. The higher burning velocity of hydrogen is linked to more severe explosions which can transition to detonation.

Due to the extreme flammability properties of hydrogen, any hydrogen discharge on open deck, in semi-enclosed or enclosed spaces onboard constitutes an additional safety risk compared to methane. Hydrogen releases in confined spaces are particularly dangerous since the rapid pressure build-up after an ignition in many cases will be sufficient to cause structural damage and thereby potentially escalate hydrogen leakages and destroy existing safety barriers.

Hydrogen leakages in enclosed spaces onboard a ship can play out in different scenarios depending on the circumstances. This has been thoroughly described in (Molkov, 2012) and in (HyResponse, 2015b) as summarised below:

An unignited hydrogen release will lead to accumulation of hydrogen within the space. If the hydrogen leakage rate exceeds the ventilation rate in the space, a hydrogen concentration above LEL will be produced, creating a possibility for delayed ignition in a layer and a resulting deflagration. Larger leakages can also create an overpressure in the leakage space unless proper pressure relief through ventilation is arranged. If hydrogen is leaking at a lower rate than the space ventilation, not resulting in a layered hydrogen concentration above LEL, it can still result in a delayed ignition in a jet.

Both types of delayed ignition can result in deflagration of hydrogen-air mixture with overpressure, which can potentially destroy the enclosure.

- For a space completely filled with a stochiometric hydrogen air mixture, the flame temperature is such that a confined deflagration (excluding detonation) can cause a pressure peak of more than 800 kPa, which is more than enough to destroy the integrity of bulkheads and decks forming secondary barrier spaces.

- If the enclosure was only partly filled, the pressure would be less, as only the hydrogen layer would increase in temperature, not the whole volume.

- Venting of hydrogen explosions is not simple because the flame speed is high, giving a rapid rate of pressure rise. This makes it difficult to vent the combustion products fast enough. There are significant uncertainties unless venting is from very simple, mostly empty volumes.

- Pressure is not just governed by flame temperature, but also flame speed. This can produce higher pressures than quoted here. In some cases, deflagration can result in a transition to a self-sustaining detonation. Due to the higher flame propagation velocity and higher levels of overpressure, detonations present greater hazards compared to deflagrations.

An ignited hydrogen release can develop into a *well-ventilated fire* or an *under-ventilated fire*. In a well-ventilated fire there is sufficient oxygen present in the enclosure for complete combustion of the hydrogen.

The heat load from a well-ventilated fire may damage essential safety components in the space, structural failure of load bearing construction elements due to direct flame impingement, etc.

A well-ventilated fire may transform into an under-ventilated fire where oxygen is consumed at a faster rate than it can be replenished (e.g., if leakage rate increases or ventilation rate is reduced/ventilation stops). This could lead to a scenario where the hydrogen burns out through the ventilation openings, but without sufficient air to have combustion inside the space, or to a full self-extinction within the enclosure. The self-extinguished under-ventilated fire may re-ignite when a fresh supply of air enters the enclosure. It can potentially lead to a localized deflagration and a diffusion flame in the zones containing hydrogen above LEL.

Safety related phenomena and potential consequences associated with indoor incidents are summarized in Figure 5-3:
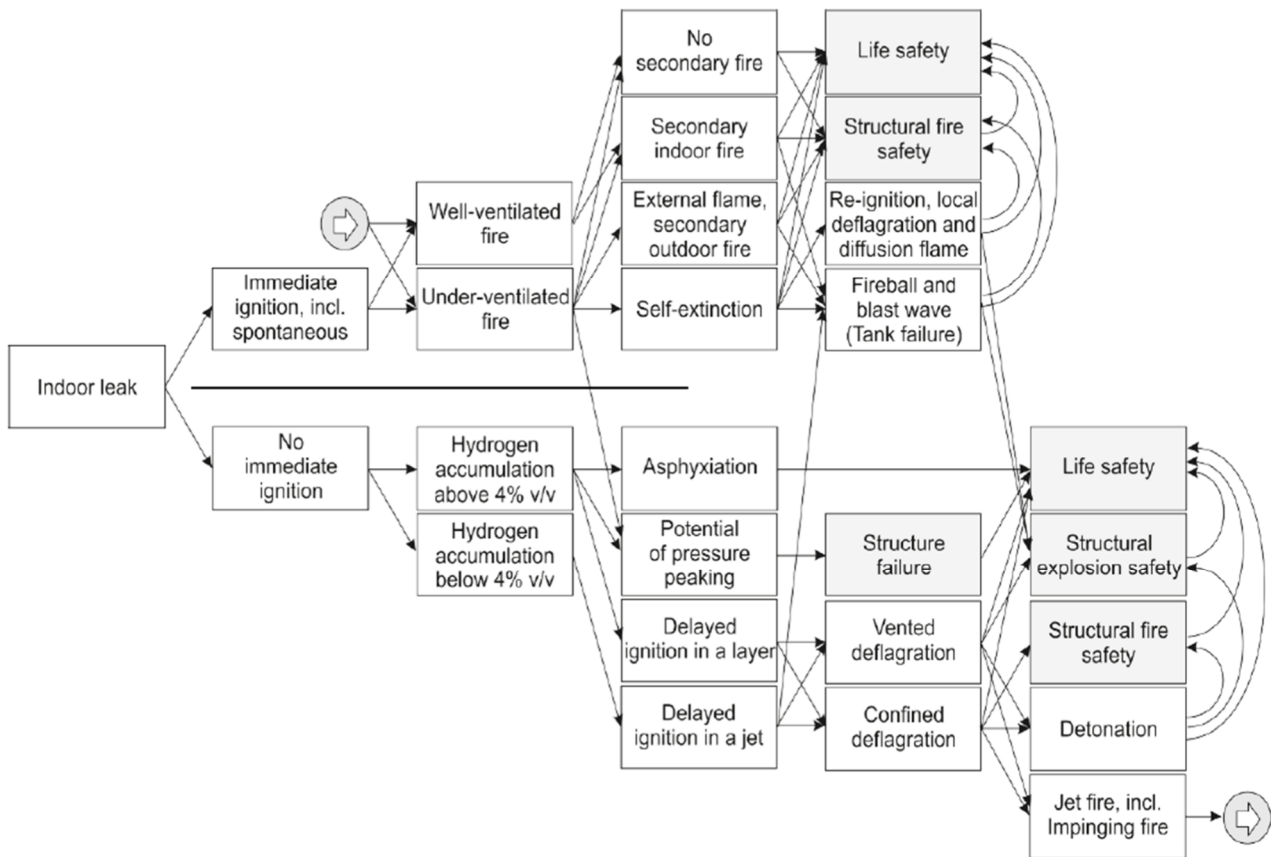
Figure 5-3 Safety related phenomena and consequences. White boxes correspond to hydrogen phenomena; grey boxes – to the consequences (HyResponse, 2021b).

5.1.2   Storage, release, and dispersion properties

Normal boiling point and saturation temperature

Having a normal boiling point of -253°C, liquefied hydrogen (LH2) is stored at temperatures more than 90°C lower than liquefied natural gas (LNG). This results in additional safety challenges in hydrogen storage and distribution.

Like smaller LNG tanks, LH2 is stored in vacuum insulated tanks to minimise the heat input from the surroundings. The boil-off gas due to heat input is accumulated in the ullage space above the liquid, increasing the tank pressure. This increases the boiling point of the liquid, allowing it to be stored for extended periods. When the vapour pressure reaches the set-point of the tank's pressure relief valves, the hydrogen vapour is released automatically. Having a constant discharge of hydrogen from the tank is not favourable from a safety point of view. The large temperature differences between the stored hydrogen and the ambient makes boil-off gas management more challenging than for LNG.

Both fuels are stored at temperatures that will cause embrittlement if carbon steel (normal ship steel) is exposed to a leakage. However, LH2 evaporates more easily and quickly, requiring less energy from its surroundings. Hence, comparison of the substance's cooling effects is not straightforward. Large-scale experiments investigating and comparing the effects are limited. The cooling down to brittle transition temperature of a structural element directly exposed to cryogenic leakages will be almost instantaneous. In a scenario where the temperature in an enclosed space is lowered due to leakages, the cooling of the surrounding structure will be slower.

An additional safety concern with cryogenically stored hydrogen is that due to its very low temperature, all gases (except for helium) will be condensed and solidified in contact with it. If air or other gases enters a LH2 system, the solidified gases can create restrictions in the piping system and interfere with normal operation of valves. Surfaces not properly

insulated can be cooled to below the normal boiling point of oxygen (-183°C), thus condensing the air around it. This condensed air will be enriched with oxygen and can significantly increase the flammability of any organic materials it comes into contact with, or embrittle materials.

In a process known as cryo-pumping the reduction in volume of condensing gases may create vacuum that can draw in yet even more gas, e.g. oxidant like air. Large quantities of condensed or solidified materials can accumulate if the leak persists for long periods of time. At some point, should the system be warmed for maintenance, these solidified materials will vaporise, possibly resulting in high pressures or forming explosive mixtures. These other gases might also carry heat into the liquid hydrogen and cause enhanced evaporation losses or "unexpected" pressure rise.

It may be necessary to have liquefied hydrogen tanks warmed and purged periodically to remove accumulated oxygen.

Expansion ratio liquid to gas

The volume increase associated with the phase change from liquid to gaseous hydrogen is larger than for methane. The ratio from liquid to heated gas is 847 (600 for methane). Liquid hydrogen will rapidly boil or flash to a gas if exposed to or spilled into an environment with normal temperature. Warming liquid hydrogen to ambient temperature can lead to very high pressures in confined spaces. As for LNG, an assessment of leaked volume and time for evaporation is necessary to verify that the pressure limiting measures provided for an enclosed space are sufficient to prevent damage of ship structures and safety barriers. Leakages of liquefied gas also have the potential to rapidly create an explosive atmosphere in enclosed spaces.

Rapid evaporation of LH_2 poses a risk of pressure build-up in confined spaces. To avoid detrimental pressure build-up in hold spaces, enclosures, and venting systems, they must be designed and dimensioned to cope with rapid evaporation.

Gas density

Gaseous hydrogen forms the smallest, lightest molecule of any gas (about 14 times lighter than air). As a result, gaseous hydrogen better permeates through materials, passes through smaller leak paths, diffuses more rapidly in surrounding media, and has greater buoyancy than other gases. The consequences arising from these properties are that released hydrogen has a tendency to rise and diffuse, but if confined, it can accumulate in high spots and reach ignition sources located there (e.g. ceiling lights). Hydrogen vessels and piping systems require good seals, and leaks are always a concern (ISO, 2015).

Gaseous hydrogen has a density of 0.0827 kg/m3 (at NTP[9]), which is more than 14 times lower than that of air (1.205 kg/m3) at the same conditions, whilst methane is 2 times lighter than air but almost 8 times heavier than hydrogen gas. The specific gravities of hydrogen and air at NTP are 0.07 and 1.0, respectively. Therefore, hydrogen gas is lighter than air, and in ambient conditions it will rise and disperse in an open environment. With a proper ship design the significant buoyancy of hydrogen gas can be a safety asset, i.e. in case of hydrogen releases into the open atmosphere allowing released hydrogen to rise and disperse rapidly.

However, one should be careful in applying gaseous hydrogen buoyancy observations to the releases of hydrogen vapours at cryogenic temperatures. Saturated hydrogen vapour is heavier than air and will remain close to the ground until the temperature rises. Usually, the condensation of atmospheric humidity will also add water to the mixture cloud, firstly making it visible, and secondly increasing the molecular mass of the mixture even more.

Gaseous storage

Gaseous hydrogen can be compressed to very high pressures (250-700 bar). Under such pressures, the hydrogen has considerable potential (stored) energy, like any other gas. The release of this energy can generate strong pressure effects depending on the release rate, even without a subsequent combustion (ISO, 2015).

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[9] Normal temperature and pressure (NTP); temperature of 20°C and pressure of 1 bar

Also, a sudden hydrogen release from high-pressure systems into air can be spontaneously ignited without any apparent ignition sources present, such as spark, hot surface, fire, etc. According to Molkov (2012) it is an agreed opinion that the probability of hydrogen spontaneous ignition at sudden release from high-pressure equipment is high if mitigation measures are not undertaken. However, no references to spontaneous ignition problem or engineering design to avoid or promote it can be found in codes and standards for piping, storage and use of high-pressure systems handling compressed hydrogen. Spontaneous ignition of high-pressure hydrogen release is one of the main unresolved problems of hydrogen safety, for which a little fundamental explanation exists.

Bunkering high-pressure hydrogen from shore have challenges, one of them being the time needed for the bunkering process. Consequently, several projects are looking towards swappable compressed hydrogen storage units which can be re-charged at shore facilities. This concept is not in line with current shipbuilding practice, where gas fuel storage tanks are permanently onboard and are certified in accordance with the requirements of the IGF Code. There will be a lack of control over such tanks when they are not onboard, and they will require disconnection and connection of numerous leakage-prone non-permanent connections to the piping system for each bunkering. Lifting hydrogen tanks on and off the ship will introduce an additional risk.

Corrosion

As methane, hydrogen is non-corrosive. However, hydrogen can cause a significant deterioration in the mechanical properties of metals. This effect is referred to as hydrogen embrittlement. Hydrogen embrittlement involves a large number of variables such as the temperature and pressure of the environment; the purity, concentration, and exposure time of the hydrogen; and the stress state; physical and mechanical properties, microstructure, surface conditions, and nature of the crack front of the material. Many hydrogen material problems involve welds or the use of an improper material.

Many metals absorb hydrogen, especially at high pressures. Hydrogen absorption by steel can result in embrittlement, which can lead to fails in the equipment. There is an atomic solution of hydrogen in metals. Permeated through a metal atomic hydrogen recombines to molecules on the external surface of storage to diffuse into surrounding gas afterwards. The choice of material for hydrogen systems is an important part of hydrogen safety (Molkov, 2012).

Asphyxiation

As with methane, significant hydrogen leakages will cause a risk of asphyxiation due to oxygen depletion.

5.2 Ammonia vs methane

5.2.1 Flammability

Lower and upper flammability limit

The flammable range of ammonia is 15-28%, hence a higher concentration of ammonia is required for ignition, compared to LNG (Table 4-1). This will make dilution with ventilation a more reliable safety barrier against possible ignition from minor leakages of ammonia than a corresponding methane leakage.

Minimum ignition energy

Ammonia is flammable but it is relatively difficult to ignite compared to methane. Reported MIE values in the limited literature on the subject varies between 8 mJ and 680 mJ (e.g., Dupont (2009)) and seems to be affected by measurement methods. However, it seems reasonable to conclude that mixtures of ammonia and air are significantly more difficult to ignite than those of methane, with the majority of experimental results supporting a MIE of 40 to 170 mJ (Harris, MacDermott (1977)).

Auto-ignition temperature

With an auto-ignition temperature of 650°C, NH₃ requires hotter conditions to auto-ignite than LNG. Hence, the risk of auto-ignition of a NH₃ leak exposed to a heated surface is less than that of an LNG leakage. However, the risk of auto-ignition must still be assessed e.g., in case of high temperature reforming in production of hydrogen rich gas for use in fuel cells.

Burning velocity

The burning velocity of ammonia is significantly lower than for methane at 0.07 m/s.

In sum, ammonia has a much higher LEL compared to methane, and the MIE is also significantly higher. This means that a higher gas concentration in air and more energy is needed for ignition of a flammable gas cloud. Further, its burning velocity is well below that of methane. It should be noted that oil contamination can increase the flammable properties of gaseous ammonia. Ammonia can ignite and explode under certain conditions of containment, e.g., within enclosures when its concentration is between 15 and 28% vol. in air. The flame temperature is the primary cause of pressure increase from ignited gases in a fully confined space. Ammonia and methane have similar flame temperature and expansion ratio so there is not a big difference in explosion pressure if the volume remains fully confined. However due to the lower burning velocity of ammonia there will be a much lower rate of pressure rise if ammonia is ignited. This means that venting (either deliberate or adventitious due to structural failure) will be much more effective, generally giving lower pressures.

There are no reports of any gaseous ammonia explosions in open air (Dupont, 2009). Even though the explosion risk is low, it must be accounted for in the design of enclosed spaces onboard ships where there is a risk of ammonia leakages. Outside of confined spaces, the fire hazard is lower compared to that of methane, yet not negligible. An ignited ammonia release will most likely cause a fire, whilst the more likely event of an unignited ammonia release will generate a toxic ammonia atmosphere.

5.2.2   Storage, release, and dispersion properties

Normal boiling point and saturation temperature

Ammonia is transported in the liquid state, either compressed, refrigerated, or a combination of the two. Fully refrigerated ammonia at atmospheric pressure is stored at -33°C, whilst ammonia liquefied only by pressure requires tanks and equipment designed for 18 bar, which corresponds to the vapour pressure at 45°C.

Ammonia's atmospheric boiling point, -33°C, is significantly higher than those of LNG and LH₂. Still, materials must be selected with care to avoid brittle fracture when ammonia is stored and handled in a fully refrigerated condition. When selecting materials for secondary barriers, the additional cooling effect of ammonia during evaporation must be accounted for. Experiments have shown that the bulk pool temperature in an ammonia spill can be as low as -70°C (AristaTek 2006).

The low temperatures may also cause chemical freezes on human skin, and cause burns like, but more severe than those caused by dry ice (Schwab, Charles V. et al., 1993).

Due to having a boiling point closer to ambient condition, it can be a challenge to provide ammonia to consumers in the right aggregate condition. For ammonia consumers requiring a supply of gaseous ammonia, it is important to avoid condensation in the fuel supply line. Depending on supply pressure and temperature it may be necessary to arrange heat tracing on supply piping to ensure a 100% gaseous supply.

Expansion ratio liquid to gas

The liquid-to-gas expansion ratio of ammonia is similar to that of hydrogen at 850. As for LNG and liquefied hydrogen, there is therefore a risk of overpressure in enclosed spaces if ammonia is spilled into a space where proper pressure relief is not arranged. Additionally, the toxicity of ammonia causes additional safety challenges, and a leakage of liquefied ammonia will generate a significant amount of toxic gas. Ammonia has an acutely toxic effect at 5.000 ppm, and given the expansion ratio of 850, one litre of spilled liquefied ammonia will generate a 170 m^3 acutely lethal toxic gas cloud.

Gas density

Ammonia vapour at ambient temperature is less dense than air. Its molecular weight of 17 is only just over half that of nitrogen or oxygen. Even at its boiling point of -33°C the density of its vapour (about 0.9 kg/m3) is less than that of air at 20°C (1.2 kg/m3). It follows that ammonia, should it escape to the atmosphere as a pure vapour, will be buoyant. However, the rapid evaporation following a sudden release of pressurized, liquid ammonia may cause liquid carry-over to the gas cloud. The ammonia droplets may disperse in the gas, forming a cloud that is heavier than the ambient air. Ammonia may behave in buoyant, neutral, or dense fashion depending on the circumstances of its escape into the atmosphere. Kaiser et al. (1982) shows that the crucial parameter which determines whether the ammonia is likely to form part of a buoyant, neutral, or dense mixture is the airborne liquid fraction. For ammonia releases with a content of airborne liquid fractions below 4% (by mass), a buoyant mixture is always formed, while for high liquid fractions (>20%), the mixture is always dense. In between, the mixture may be buoyant, neutral, or dense, depending on the atmospheric humidity.

There are well documented accounts of accidents in which ammonia, accidentally released from a pressurized container, formed part of a denser-than-air mixture. For example, in 1976 in Houston, Texas, a road tanker drove off an elevated section of motorway and burst on falling to the ground. Chemical burns of the vegetation in all directions around the crash site clearly indicated that the ammonia had formed a denser-than-air vapour cloud.

Figure 5-4 Photograph of ammonia road tanker accident in Houston, Texas, 1976[10].

Toxicity

Unlike LNG, ammonia is a toxic substance which has a sharp suffocating odour at low concentrations in gaseous form. Acceptable human exposure limits to ammonia are defined by legislation and is typically a function of concentrations

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[10] https://www.houstonchronicle.com/news/houston-texas/houston/article/In-1976-an-ammonia-truck-disaster-claimed-the-12906732.php

and exposure time. The limit is set between 25-50 ppm with dangerous consequences for exposure to concentrations above 300 ppm (Valera-Medina et al., 2018). Examples of exposure guidance are shown in Table 5-1 and Table 5-2 :

Table 5-1 Exposure guidance (Karabeyoglu A, Brian E., 2012)

Effect	Ammonia concentration in air (by volume)
Readily detectable odour	20 – 50 ppm
No impairment of health for prolonged exposure	50 – 100 ppm
Severe irritation of eyes, ears, nose and throat. No lasting effect on short exposure	400 – 700 ppm
Dangerous, less than ½ hours exposure may be fatal	2000 – 3000 ppm
Serious edema, strangulation, asphyxia, rapidly fatal	5000-10000 ppm

Based on Acute Exposure Guideline Levels (AEGL) for airborne chemicals defined by the Environmental Protection Agency (EPA) US, the limits to ammonia exposure can be identified as shown in Table 5-2:

Table 5-2 EPA Acute Exposure Guideline Levels (EPA)

Ammonia 7664-41-7 Expressed in ppm					
	10 min	30 min	60 min	4 h	8 h
AEGL 1	30	30	30	30	30
AEGL 2	220	220	160	110	110
AEGL 3	2700	1600	1100	550	390

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

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

AEGL 3: Life-threatening health effects or death.

An ammonia release within the hull of a ship has the potential to develop fatal concentrations in confined spaces.

An additional concern is the low boiling point of ammonia. The chemical freezes on skin contact at room temperature. It will cause burns similar to, but more severe than, those caused by dry ice.

Toxicity is in many ways the key hazard related to ammonia, and the property that separates it most from methane; it is harmful to personnel at concentrations well below its lower flammability limit of 15% in air. For example, UK HSE indicates a concentration of 0.36% could cause 1% fatalities given 30 minutes of exposure. Concentrations of 5.5% could cause 50% fatalities following 5 minutes of exposure. While ammonia has been widely manufactured for over 100 years and is used in considerable amounts in the manufacture of fertilizers, its potential hazards need now to be

understood in the context use of ammonia as a fuel in the maritime sector. Introduction of ammonia as fuel in the maritime sector poses challenges that are different from the ones seen in the onshore industry, including situations with personnel in close proximity to operations with a relatively high probability of leakages, such as bunkering and during maintenance of ammonia systems, more frequent coupling and de-coupling of equipment and also the limited possibility of safe evacuation when at sea. Ports often represent a high number of people close to the ship, bunkering- and ammonia storage facilities.

The fact that harmful concentrations range down to a fraction of a percentage makes even smaller leakages hazardous, and the extent of a hazardous gas cloud potentially very large. This must be considered in ship design, with respect to passenger and crew areas, escape ways, mustering stations and location of, and access to, life rafts and PPE. Port layout and facilities must also be designed with potential ammonia leaks in mind.

Further, the hygroscopic nature of ammonia may introduce challenges when leaks or releases through vent masts and/or ventilation outlets from secondary enclosures occur in rainy or windy conditions, as ammonia can react with rain- or sea water and form ammonium hydroxide, a moderately toxic compound that can affect crew and passengers.

Unlike the other gaseous fuels described in this report, whose primary risks are related to fires or explosions, the risks related to ammonia toxicity cannot be reduced by measures that reduce the chance of ignition; ammonia has a direct effect if released and comes into contact with personnel. Risk assessment would involve application of standard hazard management methods and would need to consider aspects such as the types of release that could occur, the potential concentrations that could be generated, and the likelihood of personnel being exposed to harmful levels. Mitigation methods would include ammonia release detection and emergency shutdown of ammonia systems and ventilation but could also require the availability of emergency breather units and very well-defined escape routes.

Most deaths from ammonia are caused by severe damage to the throat and lungs from a direct exposure. When large amounts are inhaled, the throat swells shut, and victims suffocate. Exposure to vapours or liquid can also cause blindness.

The United States National Institute for Occupational Safety and Health (NIOSH) specify that the Immediately Dangerous to Life or Health Concentrations (IDLH) value is 300 ppm. The Occupational Safety and Health Administration (OSHA) operates with a Permissible Exposure Limit of 50 ppm time-weighted average (TWA)

Corrosion

Unlike methane, ammonia is corrosive, which must be addressed in the selection of materials in contact with ammonia, including materials intended to contain ammonia in the case of leakages. Ammonia has alkaline properties and will corrode galvanized metals, cast iron, copper, brass and copper alloys. Not all rubbers and polymers typically used for gaskets and sealing are compatible with ammonia use, Hence, careful material selection is required in design of ammonia fuel systems.

Hygroscopic compound

Ammonia is a hygroscopic compound, which means it seeks water from the nearest source, including the human body. Mucous membranes, like the eyes, respiratory system and skin have high moisture contents at especially at risk when put into contact with ammonia. When ammonia dissolve in the body tissue, it causes caustic burns.

The hygroscopic properties of ammonia are also relevant when evaluating the dispersion of released ammonia gases, as the reaction with moisture in the air will affect the density of the ammonia vapour.

In an emergency, a water spray may be used to dissolve ammonia gas from the air to reduce the dispersion. It should be noted that applying water directly into a pool of liquefied ammonia will cause a violent reaction which may subject responders to direct contact with ammonia, and it will also increase the evaporation rate of toxic gases. The water and

ammonia form ammonium hydroxide which is a corrosive liquid, so efforts should if possible be made to control the run-off.

From a safety point of view, drainage of ammonia spills overboard and discharge of ammonia vapour underwater is preferable to keeping ammonia onboard. However, release of ammonia to the sea has impact on the environment. Ammonia is classified as toxic to aquatic life with long lasting effects according to GHS[11].

5.3 Methanol vs methane

5.3.1 Flammability

Flashpoint

As opposed to methane – methanol is liquid at ambient conditions and with a flashpoint of 11°C it will create ignitable vapours above this temperature, and thereby introduce fire and explosion hazards upon loss of containment and in tank ullage spaces.

Lower and upper flammability limit

The flammable range of methanol vapour in air is 6-36.5%. The lower limit is similar to LNG (5.3%), whilst the upper is significantly higher (17% for LNG), meaning less oxygen is required for ignition (Table 4-1).

Minimum ignition energy

The MIE of methanol vapour is about half of that for methane at 0,174 mJ.

Auto-ignition temperature

The auto-ignition temperature of methanol is about 80°C lower than that of LNG at 455°C, which must be considered wherever heated surfaces can be exposed to leaked methanol. As a liquid, leakages will also have other ways of coming into contact with hot surfaces.

Burning velocity

The burning velocity of methanol at 0.48 m/s is higher than for methane at 0.37 m/s.

In sum, the lower flammability limit (LFL) of methanol is comparable with methane, meaning that the risk of ignition arises at the same range of concentration in the atmosphere. The upper flammability limit is significantly higher, meaning less oxygen is required for ignition.

The maximum burning velocity is around 20% higher. The minimum ignition energy is about 50% lower than that of methane, hence a methanol vapour cloud has a higher risk of ignition than a methane gas cloud. Although methanol is a liquid at normal conditions, it's flashpoint at 11°C means that it will create ignitable vapours above this temperature. It is reasonable to assume that that the temperature onboard a ship is normally above 11°C.

This means that methanol is highly flammable and constitutes a fire risk in enclosed spaces and on open deck. Accumulation of methanol vapours in confined spaces may lead to explosion if ignited. Hence, a methanol leakage will introduce fire and explosion hazards, and the methanol tank atmosphere will be explosive.

Methanol flames are particularly hazardous, as they burn at low temperatures with a flame that is nearly invisible in daylight with no smoke. A methanol flame often goes undetected until it has spread to adjacent materials that burn in a

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[11] Globally Harmonized System of Classification and Labelling of Chemicals (GHS). United Nations, New York and Geneva, 2011.

https://www.unece.org/fileadmin/DAM/trans/danger/publi/ghs/ghs_rev04/English/ST-SG-AC10-30-Rev4e.pdf

wider range of light. A methanol-water mixture of at least 25% methanol is still capable of burning, so special fire extinguishing practices need to be followed, including the use of alcohol-resistant foams.

5.3.2 Storage, release, and dispersion properties

Normal boiling point and saturation temperature

Methanol is a liquid at normal conditions and can therefore be stored in integral hull tanks comparable to conventional fuel oil tanks. The normal boiling point of methanol is 65°C. Consequently, safety aspects of methanol boiling are not considered relevant for shipbuilding applications.

Expansion ratio liquid to gas

Methanol is a liquid at ambient conditions and will remain in liquid state after a spill. If the temperature is above its flashpoint (11°C), a toxic and flammable atmosphere will result, but there will not be any significant pressure increase.

Gas density

With a molecular mass of 32 g/mol, or 1.41 kg/m3, methanol vapour is practically neutrally buoyant in air (29 g/mol or 1.28 kg/m^3), and almost twice as heavy as natural gas (16 g/mol) at similar pressure and temperature.

Like gases, the density of methanol vapours is sensitive to pressure and temperature differences. A methanol vapour cloud can be heavier than air if colder, or lighter than air if warmer than its surroundings. Safety measures such as ventilation arrangements, escape routes and fixed gas detection systems should be designed reflecting this.

Toxicity

Unlike LNG, methanol is a toxic substance. Unlike ammonia, the primary risks related to methanol toxicity is through ingestion of the substance in its liquid state. However, harmful atmospheres can be generated, especially if methanol is released as a liquid spray (aerosols).

Methanol exposure can occur by vapor inhalation, by contact and absorption through the skin, and by liquid ingestion.

Based on Acute Exposure Guideline Levels (AEGL) for airborne chemicals defined by the Environmental Protection Agency (EPA) US, the limits to methanol exposure can be identified as shown in Table 5-3

Table 5-3 EPA Acute Exposure Guidelines (Interim) (EPA)

Methanol 67-56-1 (Interim) Expressed in ppm					
	10 min	30 min	60 min	4 h	8 h
AEGL 1	670	670	530	340	270
AEGL 2	11.000	4000	2100	730	520
AEGL 3		14000	7200	2400	1600

AEGL 1: Notable discomfort, irritation, or certain asymptomatic non-sensory effects. However, the effects are not disabling and are transient and reversible upon cessation of exposure.
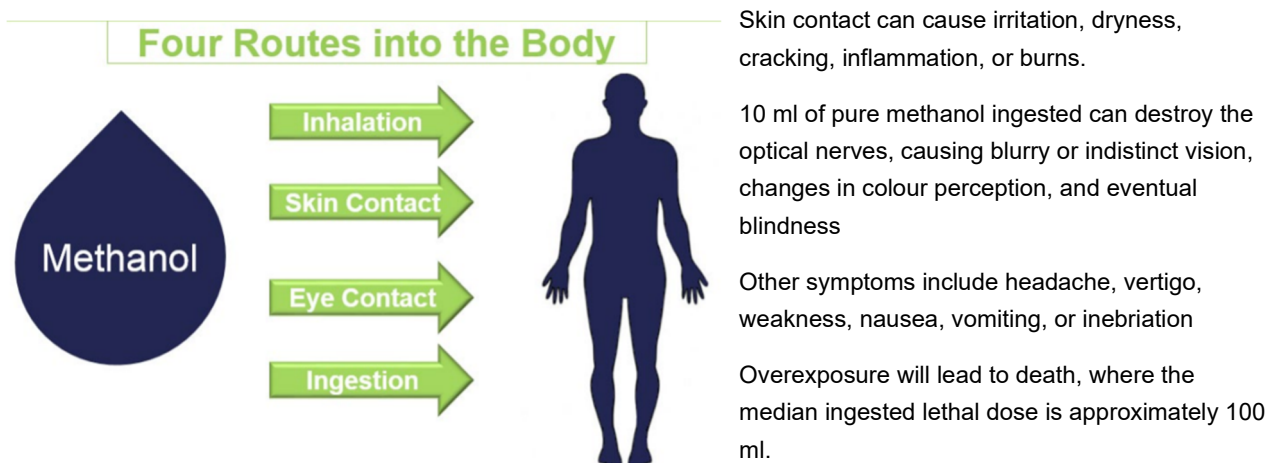
AEGL 2: Irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape.

AEGL 3: Life-threatening health effects or death.

Methanol is not toxic itself but is metabolized after intake and becomes highly toxic formic acid and its anion formate. Ingestion of methanol causes multiple organ failure, affecting the brain and vision first. As little as 10 mL of pure methanol can cause permanent blindness by destruction of the optic nerve. 15 mL is potentially fatal, although the median lethal dose is typically 100 mL. Extensive skin exposure or breathing in fumes is rarely harmful. However, by entering into fuel tanks or enclosed spaces where methanol leakages may occur one may be exposed to dangerous concentrations of methanol vapours.

Unlike methane, methanol is toxic and poisonous to the central nervous system and may cause blindness, coma, and death if ingested in large quantities. Methanol in the human body (either ingested or by skin absorption) oxidizes and produces formic acid and formaldehyde. At high vapour concentrations, methanol can also cause asphyxiation.

The United States National Institute for Occupational Safety and Health (NIOSH) specify that the Immediately Dangerous to Life or Health Concentrations (IDLH) value is 6000 ppm. The Occupational Safety and Health Administration (OSHA) operates with a Permissible Exposure Limit of 200 ppm time-weighted average (TWA)

Four Routes into the Body

Methanol — Inhalation, Skin Contact, Eye Contact, Ingestion

Skin contact can cause irritation, dryness, cracking, inflammation, or burns.

10 ml of pure methanol ingested can destroy the optical nerves, causing blurry or indistinct vision, changes in colour perception, and eventual blindness

Other symptoms include headache, vertigo, weakness, nausea, vomiting, or inebriation

Overexposure will lead to death, where the median ingested lethal dose is approximately 100 ml.

Since its vapour is heavier than air, it increases the risk of inhaling the vapour by the onboard crew and passengers. During bunkering tank vapours will be displaced by the incoming fuel and discharged trough a vent mast on open deck. Bunkering operations with its handling, connection and disconnection of heavy bunkering hoses is subjecting the crew involved to the risk of being directly exposed to methanol in case of leakage.

Tank entry is another situation where crew can be exposed to toxic levels of methanol vapours. Special consideration should be given to situations where methanol is spilled or leaked in confined spaces like the fuel preparation room or on deck.

Personnel may also be exposed to methanol spills and vapour when breaking into containment for repairs and maintenance.

The Lower Explosive Limit of methanol is 6% by volume, which is 10 times the Immediately Dangerous to Life or Health concentration. Since methanol vapour concentrations in the explosive range are toxic, keeping the air concentration safe for health also makes it safe from fire. However, keeping it safe from fire does not make it safe to breathe.

Methanol has poor warning properties. Methanol vapour is invisible; methanol liquid is clear, colourless and easily mistaken for water; methanol flames are invisible in bright light; and the odour threshold of methanol vapour is high, meaning that the presence of methanol vapour may not be detectable below 5900 ppm. By the time a person detects the odour of methanol vapor, they have already incurred an acute IDLH exposure. A final consideration is that acutely

irreversible exposure can occur without symptoms beyond irritation of the nose, throat and airways, and a feeling of fatigue and disconnected discomfort similar to drunkenness.

Onset of acute methanol exposure symptoms is delayed by 8 to 24 hours following exposure; the body metabolizes methanol slowly. The period of delay between the time of exposure and the time at which health critical symptoms manifest is extended if a victim has consumed alcoholic beverage (ethanol) several hours prior to and after exposure. The human body metabolizes ethanol, an alcohol which is poisonous when ingested in large doses, in preference and prior to metabolizing methanol, an alcohol which is poisonous when ingested, inhaled, or contacted in small doses. The effects of ethanol mask the effects of methanol. If exposure is unrecognized and untreated within the first 12 to 24 hours due to poor sensory warning and/or delayed onset of toxic symptoms, then blindness, brain damage, or even death may occur within 48 to 60 hours (Methanol Institute, 2016).

Corrosion

Unlike methane, methanol is corrosive which must be addressed in the selection of materials in contact with methanol. Typically, methanol fuel tanks would be coated with compatible coating systems (zinc).

6 SUITABILITY OF IGF CODE SAFETY CONCEPT FOR LNG FUEL WHEN APPLIED TO AMMONIA OR HYDROGEN

As referred to in chapter 1, the project will use the existing IGF Code, providing internationally recognized and accepted regulations for natural gas (LNG) fuelled ships, as benchmark for safety level when evaluating regulatory requirements for hydrogen and ammonia.

In this report we discuss physical properties of alternative fuels introducing additional safety risks from storage, distribution and use on-board. Understanding their effect on the overall risk picture will enable an evaluation of the suitability of safety barriers introduced for LNG by the IGF Code, and where such barriers are unsuitable or unnecessary.

Chapter 3 gives a high-level overview of the safety barriers applied to LNG systems by the IGF Code. They can broadly be divided into five categories related to segregation, system integrity, double barriers, leakage detection and automatic isolation of leakages. In addition to this the IGF Code also has requirements for preventing discharges from the fuel storage tanks due to pressure build-up, requirements for ventilation arrangements and fire safety. These safety principles are further discussed below to address to what degree they also would be suitable for other fuels currently not covered by prescriptive requirements.

6.1 Segregation to protect fuel installations

In order to prevent damage to fuel containment systems and fuel distribution lines, limitations regarding the location of equipment containing fuel are put in place by the IGF Code to reduce the risk of external events causing mechanical damage and instigate leakages. The biggest risk factor is obviously damage to the LNG fuel storage tanks, considering the large amount of flammable and cryogenic material they contain, and in the case of pressurised tanks, also a huge amount of potential energy from boiling liquid under pressure. Consequently, sufficient protection from collisions, grounding, external fires and explosions, damage from ship and cargo operations are essential for the ship's survival. Damages to the fuel piping system is also a safety risk, but has the possibility of mitigating consequences by arranging possibilities for isolating the damaged part of the system from the fuel storage tanks and thereby limit the amount of fuel released.

Can these safety barrier principles be utilised also for ammonia?

Recognizing that a substantial damage to an LNG storage system is a catastrophic scenario the ship is not designed to handle, it is reasonable to conclude that the barriers defined in the IGF Code for LNG tank protection will be applicable also for ammonia as fuel. A substantial damage to an ammonia storage tank will also have unacceptable consequences, hence the severity of the requirements in the IGF Code aimed to protect LNG systems should be the right level also for ammonia systems.

Can these safety barrier principles be utilised also for hydrogen?

Recognizing that a substantial damage to an LNG storage system is a catastrophic scenario the ship is not designed to handle, it is reasonable to assume that the barriers defined in the IGF Code for tank protection can be applied for hydrogen as fuel. A substantial damage to a hydrogen storage tank will also have unacceptable consequences. Therefore, it is also reasonable to assume that the severity of the requirements in the IGF Code aimed to protect LNG system against collision damage is the right level for hydrogen systems. Compressed hydrogen is stored under high pressure in pressure vessel tanks. To save weight, such tanks are often made from composite materials. The behaviour of composite tanks in a fire scenario onboard will have to be properly understood and analysed to understand if the current fire protection regulations in the IGF Code will require sufficient protection also for this tank type. A composite tank's ability to withstand impacts must also be assessed to ensure their suitability in an environment where accidental loads on the containment system from cargo and ship operations is a distinct possibility.

6.2 Fire safety measures to protect fuel installation and to reduce consequences of an ignited fuel leakage

Considering the large amount of flammable and cryogenic material they contain; it is important to protect LNG fuel tanks from heat input from a surrounding fire. The fire safety requirements in the IGF Code are to a large extent based on the requirements in the IGC Code for gas carriers, e.g., fire insulation of superstructures facing LNG fuel tanks on open deck aimed at protecting the superstructure from fire on deck. On the other hand, to protect LNG fuel tanks on open deck from an external fire on deck, a water spray system for cooling of the tanks is required. The water spray system is also required to cover spaces facing LNG fuel tanks on open deck. To protect LNG fuel tanks located in enclosed spaces/below deck from exposure to heat input from a surrounding fire, the IGF Code sets requirements to a protected tank location away from high fire risk spaces (e.g., engine rooms and cargo spaces) and equipment representing a fire risk. Bunkering stations and fuel preparation rooms needs fire extinguishing.

Can these safety barrier principles also be utilised for ammonia or hydrogen?

The principle of protecting the fuel tank from external fire is equally important for ammonia and hydrogen tanks. Compressed hydrogen is stored in composite pressure vessels which are less resistant to heat. It should be investigated if current requirements for protection of LNG storage systems provide sufficient protection against fire for such tanks.

Ammonia is less flammable than methane, and ignition of ammonia releases in open air has not been reported. Consequently, the need for fire protection of superstructures due to having an ammonia tank on deck should be considered. The applied means of fire extinguishing should also be considered for ammonia, taking its extreme reactivity with water into account.

6.3 System integrity to reduce the risk of leakages

To ensure that LNG fuel systems are fit for purpose, it is important to use system components manufactured from materials which are compatible with chemical and mechanical stresses they will be subjected to in service. Methane is not particularly corrosive, but the cryogenic temperature of liquefied natural gas creates challenges with choice of materials and thermal stresses. It is also important to minimize the amount of leakage sources by design, e.g., by using

welded connections instead of flanged connections, prohibit the use of leak-prone components like bellows and require full penetration welds for pipe joints. The IGF Code has requirements to ensure proper design, manufacture workmanship and testing. These regulations draw heavily on the regulations in the IGC Code, which has tested the suitability of requirements in the design of LNG tankers for decades.

Can these safety barrier principles also be utilised for ammonia?
The principles of ensuring fit-for-purpose design and minimizing leakage sources are essential for ammonia fuel systems. However, due to the difference in chemical and physical properties between ammonia and methane, such regulations need to address the specific needs of ammonia with respect to corrosivity, pressure and temperature. Also, there is serious health risks involved in being directly exposed to ammonia (ref. 5.2.2). Therefore, it should be considered to have stricter requirements for mechanical screening of leakage points and to have adequate Personal Protective Equipment and emergency eyewashes and showers available for people involved in operations that may directly expose them to ammonia. Design pressure of ammonia piping should be at a level where fitting of pressure relief devices is unnecessary.

Can these safety barrier principles also be utilised for hydrogen?
The principles of ensuring fit-for-purpose design and minimizing leakage sources are especially relevant for hydrogen fuel systems. Because gaseous hydrogen consists of very small molecules, smaller leaks are common. Consequently, one should consider having strict requirements to leakage sources in hydrogen piping systems, avoiding detachable pipe connections, reduce the number of valves and other leakage sources as far as possible.

6.4   Control of operational and emergency discharges from the fuel system

In view of methane being a greenhouse gas and flammable, it is important to minimize discharges of methane from the LNG fuel system. Hence, the IGF Code have requirements for arrangements to control the tank pressure being able to avoid discharges from the tank for a period of 15 days. Venting of fuel vapour to control the tank pressure is not acceptable, except in emergency situations. The activation of the safety system (emergency shutdown - ESD) alone is not considered to be an emergency in this context. A worst-case scenario with respect to discharges from the vent mast is a fire surrounding the LNG fuel tank causing full capacity discharge from the tank's pressure relief valves.

The IGF Code also requires that no gas shall be discharged to the atmosphere during filling of storage tanks (bunkering). However, there are no specified limits to operational discharges from vents in the fuel piping system.

The Code sets requirements to location of the vent mast and surrounding safety zone and hazardous area to limit the consequence of a gas discharge from tanks/systems to the ship/crew.

Can these safety barrier principles also be utilised for ammonia?

The need for controlling operational and emergency discharges from ammonia fuel systems is emphasized by its toxicity which will give an immediate hazardous effect upon release. It should be considered to increase the holding time limit of 15 days to infinity. As opposed to methane, this will be possible for ammonia with pressure accumulation (18 bar) alone, consumption/refrigeration or a combination of both.

It should be considered to avoid all operational discharges from the fuel system.

An unavoidable consequence of storing liquefied gas is the need for pressure relief devices to ensure that a rise in temperature (and therefore pressure) does not damage the tank. It is possible to prevent discharge trough these vents in normal operation by adding a system that can safely handle the boil-off gas. However, in case of a safety valve failure or in a fire scenario a large amount of pressurised gas will be discharged through the vent mast. How to handle a full capacity emergency discharge from ammonia tank's pressure relief valves must be carefully considered. Requiring the incorporation of a "safe haven" onboard for the crew should be evaluated.

Can these safety barrier principles also be utilised for hydrogen?

For hydrogen stored under pressure operational releases from the tanks should not be an issue. However, tanks for compressed hydrogen are often protected against pressure increase from fire load with heat-sensitive opening devices which will release all hydrogen if activated, resulting in a significant gas cloud. Considering the ignition sensitivity and significantly higher reactivity, including the propensity for detonation, it is clear that releases of hydrogen are more hazardous compared to releases of LNG.

Liquefied hydrogen is stored in vacuum insulated tanks at -252°C. The extreme temperature difference to ambient temperatures and the relatively small volumes may cause challenges with holding times, potentially leading to operational releases from the storage tank.

6.5   Double barriers to reduce consequence of leakages

Fuel leakages reaching ignition sources may cause fires or explosions depending on circumstances. In many cases it will be necessary to locate fuel systems in spaces where it is not possible to control the ignition sources, like for instance the fuel supply system to gas fuelled engines in the engine room. To overcome these challenges, the IGF Code require that fuel piping routed through enclosed spaces shall be protected by a secondary enclosure able to contain any gas that may leak from the primary piping system. Where the need for a lot of piping components makes it difficult to fit a secondary enclosure around piping, the IGF Code requires that these components are placed in dedicated gas tight spaces where it is possible to control the ignition sources. Examples of such spaces are Tank Connection Spaces (TCS), Fuel Preparation Rooms (FPR), and Gas Valve Units (GVU).

Can these safety barrier principles be utilised also for ammonia?
The double barrier principle applied for LNG systems to prevent leakages from reaching ignition sources is a principle that can also be applied to prevent leakages of ammonia from reaching areas where personnel may be exposed. It may be necessary to evaluate the requirements for location of openings from double barriers considering that it will be toxic gases being discharged. It should also be considered to keep the requirements for fitting enclosed tank connection spaces to tanks located on open deck to better control release of toxic gases.

Can these safety barrier principles be utilised also for hydrogen?
The double barrier principle applied for LNG systems to prevent leakages from reaching ignition sources is a principle that can also be applied to prevent leakages of hydrogen pipes. However, it needs to be investigated to what degree the higher flammability of hydrogen will require additional safety measures to prevent ignition in annular spaces of double walled piping systems. The extreme flammability of hydrogen may prove challenging with respect to store hydrogen in liquefied or compressed form in enclosed spaces. Whether it is possible to store hydrogen below deck with sufficient safety level will also affect the need for regulation of enclosed spaces with hydrogen leakage potential. In shore-based industries, the main safety barrier w.r.t hydrogen storage is to locate hydrogen leakage points in open air, using its buoyancy as a way to keep leakages out of harm's way.

ESD Machinery space. The early 4-stroke gas fuelled engines were not available with a double barrier fuel system. To facilitate the use of these engines, the IGF Code allows the use of fuel systems without double barriers if this is compensated for with extended requirements to ventilation, engine room arrangement, gas detection and automatic shut-down of fuel supply to engine room. The philosophy is that high ventilation rates, early detection, and isolation of leakages will prevent leakages from generating gas mixtures above the lower explosion limit range.

Can this safety barrier principle be utilised also for ammonia or hydrogen?
Considering the toxicity of ammonia at ppm-level and the extreme flammability of hydrogen, the ESD Machinery concept is not suitable for these fuels.

Access openings between hazardous and non-hazardous spaces. As stated above, the IGF Code require that fuel

system equipment and piping shall be arranged within gastight secondary enclosures. Where these enclosures are arranged as rooms, they must necessarily be provided with some form of access for inspection and maintenance. Access openings obviously have the potential for compromising the gas-tightness of tank connection spaces, fuel preparation rooms, gas valve unit enclosures and other hazardous enclosures with a need for access. To remedy this problem, several approaches are possible. One solution can be to require that the access to a hazardous space must be from open deck in an area where potential gas release through the door will be manageable and safe. Where this is not possible due to the ship arrangement, one can arrange access via a double door arrangement, creating a new room between the two doors where a gas leakage can be handled safely (air lock). In cases where the consequence of a leakage is deemed unacceptable, one can prohibit the arrangement of accessways between two spaces (e.g., between tank connection space and engine room). In some instances, it can be feasible to gas free the complete system before opening, like for gas valve units arranged in the engine room, thereby not needing any other precautions for prevention of gas leakages.

The IGF Code applies all of the principles above to ensure that access openings to hazardous spaces does not provide a way for methane leakages to spread to non-hazardous spaces where potential ignition sources are not controlled in the same way.

Can this safety barrier principle be utilised also for ammonia?

Due to the toxicity of ammonia, it is not immediately clear that the principles in the IGF Code related to access between hazardous and non-hazardous spaces provide sufficient protections against toxic gas leakages spreading throughout the ship. Further restrictions on type and location of openings may be required. Among other things, there may be reasons to evaluate other solutions for access to tank connection spaces than what is specified in the IGF Code for LNG storage (where entry through a bolted manhole is prescribed). Bolted manhole access was introduced on the assumption that entry into TCS would be a rare occurrence. Experience from operation of LNG fuelled ships shows that access to TCS is more regular than initially assumed when the first regulations were made. It may be argued that it will be easier to escape through a door (gastight self-closing) and easier to close the door behind you to limit the amount of gas escaping compared to escape through a manhole and fit a bolted manhole to stop the gas from spreading.

One should also consider taking advantage of the hydroscopic properties of ammonia by providing water curtains at exits from spaces where ammonia leakages can occur. This may help catching gaseous ammonia escaping from the enclosure. This principle could also be applied in other situations to reduce the dispersion of toxic gases in an emergency (at bunkering station, hi-fog in fuel preparation rooms etc.).

Can this safety barrier principle be utilised also for hydrogen?

Before this question can be addressed one needs to consider whether it is technically possible to store hydrogen safely in the ship interior.

6.6 Ventilation arrangements to control fuel leakages and protect against overpressure

Apart from providing a habitable atmosphere in enclosed spaces onboard, ventilation systems on ships with alternative fuels can provide safety barriers mitigating loss of containment, but also be a risk factor in a leakage scenario. On the risk factor side, a ventilation arrangement can result in cross-contamination to other spaces served by the system, it can introduce oxygen to an oversaturated or inerted gas atmosphere taking the gas mixture into the explosive range, the ventilation outlets will discharge a contaminated atmosphere in a leakage scenario, and the integrity of ventilation ducts is important to prevent spreading leaked gas to presumably non-hazardous spaces. Ventilation of spaces with cryogenic equipment can lead to excessive icing on cold surfaces by constantly supplying moist air.

The ventilation system can also improve the ship safety in several ways. Provided that the ventilation capacity is sufficient, it is in many cases possible to dilute a gas leakage in an enclosed space to below the lower explosion limit. With a correctly calibrated ventilation system it can be possible to maintain a pressure differential between spaces,

ensuring that any change of atmosphere is going from a non-hazardous space to a hazardous space. Ventilation ducts of sufficient size can serve as pressure relief in enclosed spaces where there is a possibility for leakages which may create a destructive overpressure (e.g., discharge of large amounts of liquefied gas which rapidly expands upon evaporation). Finally, ventilation systems may assist in a more rapid transfer of hazardous gases from the internals of the ship to a presumably safer discharge in open air.

The IGF Code have introduced safety barriers to prevent that gas is spreading to non-hazardous spaces by requiring that hazardous spaces are served by a separate ventilation system. Outlets from these systems are regulated with respect to location and closeness to ignition sources and other openings in the ship, and ventilation ducts shall be constructed from substantial materials to prevent leakages. It is also required that hazardous spaces are served with extraction ventilation to ensure a lower pressure than the surroundings to control direction of flow.

Can these safety barrier principles also be utilised for ammonia?

For ammonia fuel installations the same principles can be applied in some form, but detailed design may have to be re-evaluated in light of the toxicity, density and flammability of ammonia. Due to its toxicity at low concentrations, it should be considered whether it is acceptable to ventilate two spaces where personnel can be present with the same ventilation system. A common ventilation system could harm someone in a fuel preparation space when there is a leakage in the tank connection space. Suitable ventilation rates for an ammonia space will be dependent on factors that are different from similar spaces where methane is a fuel.

Can these safety barrier principles also be utilised for hydrogen?

Before this question can be addressed one needs to consider whether it is technically possible to store hydrogen safely in the ship interior. The main safety barrier applied in other industries is to ensure that hydrogen leakages are occurring in open air. Ventilation systems and space arrangements should account for the high buoyancy of hydrogen in air by locating vent outlets high and avoid designs where hydrogen can be trapped and isolated from ventilation outlets. Ventilation as a possible risk mitigation measure is further described in MarHySafe (2021).

6.7 Leakage detection and automatic isolation to reduce consequences of leakages

As opposed to a leakage from the tank containment system, a leakage in the fuel piping system can be isolated to limit the amount of fuel being released to the surroundings. To achieve this, it must be possible to detect that there is a leakage in the system and the system must be arranged in such a way that strategically located valves can close and segregate the leakage point from large reservoirs of fuel. The IGF Code has applied the above safety barrier to limit the consequences of an LNG leakage. It requires that leakage detection devices are arranged everywhere there is a possibility for fuel leakages, as in the bunkering station, annular space of double-walled piping systems, in tank connection spaces, in fuel preparation rooms, and in GVUs in the engine room. Further, these detectors shall send signals to emergency shut-down valves placed on tank connections and in the fuel system, leading to a stop of fuel supply to the leakage point. This type of shut-down will necessarily result in a stop of fuel supply to the engine and therefore the Code require a redundancy on fuel supply or some other arrangement to prevent an unacceptable loss of power generation and propulsion power.

Can these safety barrier principles be utilised also for ammonia or hydrogen?

An arrangement enabling detection of leakages, which communicates with a system designed to stop the system flow and thereby reduce the amount of fuel that can escape, will be equally important for ammonia and hydrogen fuel systems. Detector alarm level and detector location must be adjusted for the specific properties of each fuel. For ammonia, the IDLH value of 5-10000 ppm is very much lower than the Lower Explosive Limit (LEL) of 15 vol. %. Monitoring and alarming toxicity and fire concentrations separately should be considered.

6.8   Hazardous zones to control ignition sources

In the event of a gas leakage, it is essential that the escaping gas mixture is kept away from ignition sources. Area classification is a method of analysing and classifying the areas where explosive gas atmospheres may occur. The object of the classification is to allow the selection of electrical apparatus able to be operated safely in these areas. It will also be a tool to ensure that gas is not spreading to areas where ignition sources are not controlled by ensuring that ventilation openings and accesses are kept outside hazardous areas. The IGF Code require area classification of gas fuelled ships, and the method is based on principles laid out in IEC-standards for area classification for hydrocarbons.

Can these safety barrier principles also be utilised for ammonia?

Ammonia leakages will be more of a toxicity hazard than a flammability hazard, even though the flammability aspect cannot be ignored from a design perspective. It should be considered to define two separate zone requirements addressing the two hazards separately.

Flammability:

Ammonia's flammability range is from 15 to 28 per cent mixture in air. Ammonia requires minimum ignition energy of 8 mJ, which is 30 times more energy than methane needs to ignite and 470 times more energy than for hydrogen. Ammonia can self-ignite if the temperature is above 651°C. Ammonia burns with difficulty in open air and will generally need a supporting flame to keep burning. In confined spaces ammonia constitute an explosion risk, and it should be noted that oil contamination can increase the flammable properties of ammonia vapours. Considering the above, the need for hazardous zone definitions on open deck should be evaluated. In enclosed spaces, electrical equipment should probably be of certified safe type.

Toxicity:

To protect people onboard from exposure to ammonia vapours, the primary focus should be to avoid venting of ammonia vapours during normal operation. It should be considered if vent systems can be provided with arrangements to reduce the amount of ammonia being discharged to open air. However, it will not be possible to eliminate all discharge of ammonia vapours from vents and ventilation systems to open air. It will therefore be necessary to define toxic zones around sources of ammonia vapour on open deck to avoid that ammonia vapours are spreading to enclosed spaces through air intakes, air outlets or other openings to enclosed spaces on the vessel.

Can these safety barrier principles also be utilised for hydrogen?

Given the significant differences between hydrogen and methane with respect to densities and flammability/reactivity one should probably be careful in adapting the IGF approach for methane to hydrogen fuel installations. The Code considers enclosed and semi-enclosed spaces to be safe if the equipment inside is certified accordingly. The ignition mechanisms for hydrogen are less well understood, the flammable range is significantly wider, and the energy required to ignite a hydrogen/air mixture is an order of magnitude lower.

7 CONCLUDING REMARKS

This chapter presents a summary of the safety risks related to the physical properties of hydrogen, ammonia and methanol (chapter 4) when used as fuel onboard and compare them to those of methane including additional safety risks arising from differences in physical properties (chapter 5). Further, we summarize the suitability of the safety barriers in the IGF Code for LNG fuel (chapter 3) if applied to ammonia or hydrogen (chapter 5).

Figure 7-1 rates the safety risks related to the flammability properties of methane, methanol, ammonia and hydrogen when used as fuel onboard. In general, it shows that the flammability properties and related safety risks of hydrogen are extreme compared to methane, those of methanol are comparable to methane and those of ammonia have lower flammability and related safety risks than methane.

| | | | Relatively low | Medium | High | Very high |

	Flashpoint (°C)	Flammability range (%vol. fraction)	Minimum ignition energy (mJ)	Auto-ignition temperature (°C)	Laminar burning velocity (m/s)
Methane	-*	5.3-17	0.274	537	0.37
Methanol	12	6-36.5	0.174	385	0.48
Ammonia	-*	15-28	40-170	650	0.07
Hydrogen	-*	4-77	0.017	585	2.7

*The gaseous fuels do not have a defined 'flashpoint' like the liquid fuels, but will instead transfer fully into gaseous form at ambient conditions, due to the low boiling temperatures.

Figure 7-1 Safety risks related to flammability properties of methane, methanol, ammonia and hydrogen when used as fuel onboard.

Figure 7-2 rates the safety risks related to storage, release and dispersion properties of methane, methanol, ammonia and hydrogen when used as fuel onboard. It shows that hydrogen has similar, but more extreme properties compared to methane. Ammonia and methanol introduce new safety risks related to toxic properties. Toxicity challenges will be more difficult to manage for ammonia, being a gaseous fuel, than for methanol which is stored as a liquid at ambient conditions.

	Normal boiling point (°C)	Density (kg/m³)		Expansion ratio liquid NBP/gas NTP	Toxicity IDLH (ppm)
		(G,NBP)	(G,NTP)		
Methane	-162	1.819	0.6594	600	Asphyxiation
Methanol	64.9	-	1.11*	-	6000
Ammonia	-33.4	0.89**	0.610**	850	300
Hydrogen	-253	1.312	0.0827	847	Asphyxiation

G – gas
L - liquid
NTP - normal temperature and pressure
NBP - normal boiling point
IDLH – Immediately Dangerous to Life or Health Concentrations specified by the United States National Institute for Occupational Safety and Health (NIOSH)
* Specific gravity of methanol vapour
**Due to hygroscopic properties ammonia vapours reacts with moisture in air resulting in a density that is heavier than air.

Figure 7-2 Safety risks related to storage, release and dispersion properties of methane, methanol, ammonia and hydrogen when used as fuel onboard.

As illustrated in Figure 3-1, the safety barriers applied to LNG systems by the IGF Code can broadly be divided into five categories related to segregation, system integrity, double barriers, leakage detection and automatic isolation of leakages. The suitability of these safety barriers for ammonia and hydrogen, discussed in chapter 6, is summarized in Figure 7-3. Methanol is not included, as IMO has already provided an international standard by the non-mandatory interim guidelines for methyl/ethyl alcohols (methanol/ethanol).

	Segregation		System integrity		Double barriers				Leakage detection	Automatic isolation of leakages
	Mechanical damage	External fire	System design	Operational and emergency discharges	Piping	ESD machinery space	Double barrier spaces	Ventilation	LEL	ESD valves
Ammonia			corrosivity pressure toxicity	toxicity	toxicity	toxicity	toxicity	toxicity	toxicity	toxicity
Hydrogen			leakage, embrittlement, flammability	flammability	flammability	flammability	flammability	flammability	density, flammability range	flammability

Figure 7-3 Suitability of using safety concept of the current regulations in the IGF Code for natural gas also for ammonia and hydrogen when used as fuel onboard.

As indicated in Figure 7-3, many of the safety principles in the IGF Code for natural gas can be applied to ammonia with substantial modifications to account for the additional toxicity risk upon loss of containment. The IGF Code requirements for LNG fuel do not account for fuel toxicity, which necessitates stricter barriers to protect against ammonia exposure during normal operation and in emergency situations. This is supported by EMSA (2022) where many additional safeguards, not found in the IGF Code, due to the inherent risks of ammonia are identified.

Due to extreme flammability and reactivity, adoption of IGF safety principles is less obvious for hydrogen as a ship fuel. The existing LNG safety barriers are likely not sufficient to suppress the extreme flammability of hydrogen. This identifies the need for further regulatory development, where the findings from this report can be used to investigate ways of containing the new safety challenges.

This report focuses on onboard regulations for ships using potential zero carbon fuels, i.e., international IMO regulations and class rules. It should however be noted that different onshore safety regulations and criteria may apply in the Nordic countries. This will be further considered in other project tasks.

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