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Risk Assessment of Cryogenic Fuels in Marine Transportation

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The shipping industry has been forced to move towards sustainable fuels. Cryogenic gases, such as Liquefied Natural Gas (LNG), can be a viable solution for fuel storage and transportation even for remote areas. Besides, Liquefied Hydrogen (LH₂) seems to be another, yet long-term solution, where several studies are directed towards this new opportunity. To address the intensive use of these two fuels, a detailed comparison from a technical, economic and environmental point of view is strongly required. Nevertheless, so far, a full understanding of the complex phenomena characterizing the accidental release of LNG and LH₂ in harbour environment has not been assessed. In the current paper, a comparison of the two fuels is presented regarding safety perspective. The hazards and the consequences that will be caused by an accidental release are described considering the specific storage system which can be possibly installed on small ships such as ferries, small cruisers, and small cargos.

Keywords: Alternative fuels, LNG, liquid hydrogen, safety, risk assessment, shipping.

1. Introduction

The European Union is moving towards a neutral climate where Sulfur and Nitrogen Oxides (SOx, NOx), carbon dioxide (CO2) and greenhouse gas (GHG) emissions will be considerably reduced to form environment-friendly industries (European Commission, 2019a, b). The shipping industry operating on the European waterways, has to adapt to such a strict policy which is also in line with the corresponding international restrictions set by the International Maritime Organisation (IMO) (IMO, 2008). New technologies for implying alternative low-flashpoint fuels are being considered to reduce hazardous emissions from ships. Among the most promising alternative fuels are the low-carbon fuels such as Liquefied Natural Gas (LNG), Liquefied Petroleum Gas (LPG) and methanol. The use of these fuels can benefit in the mid-term applying the existing technologies and infrastructure. On the other hand, hydrogen, and electrification are emerging as long-term solutions that will allow a zero-carbon shipping industry in the future.

LNG and hydrogen constitute the most prevalent options for future ship bunkering. LNG is, actually, a ready-to-use marine fuel as the know-how for storage, handling, and distribution is really mature (Aneziris et al., 2020). Hydrogen has very recently begun to be studied as the era of zero emissions has not yet arrived and the knowledge of handling them as marine fuels is insufficient. Nevertheless, the adoption of such fuels also poses significant risk to human health, the environment and the installations, when stored in port areas or during the bunkering process. Indeed, the accidental release of LNG and hydrogen might result in either fires or explosions. Therefore, conducting risk assessment is necessary to ensure safe storage and handling of these substances in port areas.

The current paper investigates and compares safety levels when ships are fuelled with LNG and LH₂. LNG has recently been introduced as a marine fuel, while hydrogen has not been used until now. Therefore, few quantitative safety studies have been performed to ensure that the use of these fuels does not pose significant risks to human life, the environment or the ship. Quantitative risk assessment is performed for the bunkering of the alternative-fuelled-ship from a ship or a truck located at port facilities. The remaining of the paper is structured as follows: Section 2 briefly presents the physical behaviour of the under investigation alternative marine fuels and discusses the environment and economic impact of their use, the hazards imposed, and the relevant regulatory framework of application in the shipping industry. Section 3 presents the technical requirements for storage and transport of LNG and LH₂. Section 4 performs a risk assessment for estimating the risk of alternative fuels release. Finally, section 5 contains the concluding remarks.

2. Alternative Cryogenic Gases

2.1. Uses in Maritime Transportation

As the shipping industry is forced to support the implementation of alternative fuels to comply with European and international requirements for reduced emissions from ships, LNG was initially chosen as the fuel that would drastically reduce the carbon footprint at a relatively low operational cost. Indeed, many LNG-fuelled ships have been built and are currently operating in many countries around the world. The Norwegian passenger ship MV Glutra was the first LNGfuelled ship, built in 2000 and classified by the Norwegian Class Society. In order for this ship to be refuelled with LNG, the first LNG bunkering port was established in the port of Stockholm. Other ports followed, such as the European ports of Rotterdam and Zeebrugge, the ports in the United States, such as the Port of Jacksonville, and the Asian ports in Singapore and Kochi. So far, a total of 39 LNG ports are operating or have confirmed plans to operate worldwide while there are 355 LNG-fuelled vessels in service, and 251 new ones on order (DNV, 2021a).

In contrast to LNG, ships powered by LH_2 are not yet in operation anywhere (Ustolin et al., 2022). Two installations offering LH_2 bunkering solutions have been established in two ports in Japan and Australia. The first LH_2 -fuelled ship is the Ro-Pax ship MF-Hydra which is being prepared under a research project investigation. It is currently undergoing tests and is going to be in operation soon. Moreover, another three ships are under construction or at the design stage. It is therefore obvious that the shipping industry is moving towards adopting hydrogen, in addition to other fuels, as an alternative marine fuel.

2.2 Production and Environmental Impact

Natural gas is an extracted fossil fuel consisting mainly of methane, and a small amount of nitrogen, ethane, propane, iso-butane, and other alkanes. It is a rather clean fuel regarding CO₂ emissions. It is preferred to be used in shipping in liquefied form to achieve reduced volume enhancing their storage and transportation in large quantities. Natural gas is converted to a liquid state at normal atmospheric pressure by cooling down to -162 °C. Cold LNG is, commonly, stored in pressurized tanks at a pressure 0 to 4 bar and temperature -160 to -138 °C. At the same time, not all emissions from LNG combustion are eliminated as greenhouse gases (GHGs) are still produced, making LNG a transition fuel.

Hydrogen, on the other hand, is an almost zero-carbon alternative as its combustion merely produces hydrogen or water depending on the production method. Liquefied hydrogen is a pure substance that, to be used as a fuel, is obtained by applying steam reforming of methane or electrolysis of water. Depending on its production method, it is roughly distinguished using some typical colours accounting its carbon footprint (Ustolin et al., 2022). Gray, blue and green hydrogen are the most acknowledged. Gray hydrogen is produced via methane steam reforming whereby methane and water are heated at high temperatures generating hydrogen and, inevitably, CO₂. This technique is great for energy efficiency, yet quite harmful to the environment as an increased amount of CO_2 is released. Blue hydrogen is produced similarly to gray hydrogen, except that most of the CO₂ is captured and stored for other uses. It is of course more sustainable. however it increases costs due to the further infrastructure and energy required to capture CO₂. Green hydrogen is CO₂-neutral as it is produced via water electrolysis in which hydrogen and oxygen are produced. It is obvious that the production of green hydrogen requires highenergy processes that increase the expected cost of production as well as the indirect emissions due to its production process, which is currently based on fossil fuels. However, in the cases where renewable sources are applied for green hydrogen production, the indirect emissions are eliminated. To store and transport hydrogen in large quantities, it needs to be liquefied at -253 °C. Its great energy density requires storage tanks 5 times larger in volume compared to petroleumbased fuels. This means that hydrogen would only be practical for small ships that travel short distances and require more frequent bunkering. Furthermore, it is common for hydrogen-fueled ships to generate the hydrogen on board by implementing the hydrogen fuel cells. Fuel cells directly convert the chemical energy of hydrogen into energy and produce merely water and heat, thus providing clean, zero-emissions power.

2.3 Hazards

Nevertheless, regardless of the environmental sustainability, the use of LNG and LH₂ can pose a significant risk to human life and infrastructure. Primarily. human exposure to extreme temperatures of these two fuels poses a significant cryogenic risk. It is therefore important that all components in contact with them, including tanks and pipes, are made of cryogenic materials to withstand excess temperatures that can significantly affect both the infrastructure and the people in contact with them.

In addition, they are both flammable substances that require major measures to be taken to prevent large-scale accidents. Indeed, an accidental LNG release in combination with a nearby ignition source may cause vapour cloud flash fire, jet fire, pool fire or vapour cloud explosion which can lead to catastrophic consequences (Aneziris et al., 2014, Mokhatab et al., 2014). In case there is no nearby ignition source, LNG vaporizes, spreads and eventually forms a vapours cloud that disperses in the atmosphere. Similar to LNG, LH₂ is considerably flammable especially when mixed with pure oxygen. When LH₂ is released into the open air, a flammable gas mixture forms that produces invisible flames posing a serious fire hazard (ABS, 2021). The result is jet fire that creates an explosive gas cloud and leads to a deflagration and possible detonation of the gas. LH₂, when stored outdoors, is considered safer than LNG due to its ability to diffuse faster into the air reducing the available amount for ignition.

Last but not least, although these are not essentially toxic substances, at high concentrations where large amounts of LNG or LH_2 vapours are released, they significantly displace air (i.e. oxygen) from the area and cause loss of consciousness and possibly injury or death.

2.4 Regulatory Framework for Application in Maritime Sector

As the use of LNG as a marine fuel is well established in the shipping industry, a wide range of international and national regulations and guidelines have been developed to enhance its application and safe use (Aneziris et al., 2020). IMO, classification societies and organizations requirements have issued for both the construction and operation of LNG-fueled ships, as well as for the demanding, in terms of safety, bunkering procedures (IMO, 2015; DNV, 2015; ABS, 2017; IACS, 2017). In particular, the most main and most useful regulation is the code of safety for ships using Gases or other lowflashpoint Fuels that must be applied for construction and bunkering of LNG-fueled ships (IGF code: IMO, 2015). Moreover, of great interest is the European Seveso III Directive 2012/18/EC concerning the safety of port facilities handling LNG (European Commission, 2012), the agreement concerning International Carriage of Dangerous Goods by Road concerning the safe transport of LNG (ADR, 2017), as well as the advisory standards for safe LNG bunkering solutions issued by the International Organization for Standardization, such as ISO 16901, 18683 and 20519 (ISO, 2015a; ISO, 2015b; ISO, 2017).

The IMO through the IGF code allows also the application of other alternative fuels, including hydrogen (IMO, 2015). Nevertheless, IMO does not currently assess detailed requirements for its application, thus the vessels that use LH_2 as a fuel shall be designed with the specific requirements contained in the SOLAS alternative ship design regulation (IMO, 2009). In order for this alternative fuel to become a commercially viable fuel, relevant infrastructure for both transport and storage as well as bunkering need to be built and new safety regulations be developed and implemented.

Some guides have been already developed very recently by classification societies that encourage the use of LH₂ (DNV, 2021b; IMO, 2021; ABS, 2021). Moreover, there are some recommendations applied for ships carrying LH₂ as cargo to supply LH₂-fuelled ships (these are the so-called bunker ships) (IMO, 2016; ClassNK, 2017). Nevertheless, there is an extensive regulatory framework for the safe use of hydrogen in the chemistry industry, where the shipping industry would be influenced and assisted (LaChance et al., 2009; NFPA, 2019; ISO, 2008). Specialised documents for providing guidelines for safe LH_2 bunkering have not published yet (Ustolin et al., 2022).

3 Requirements for Storage and Bunkering

Principally, the bunkering of ships with the alternative fuels can be carried out in any of the next three ways: (a) tank-to-ship through fixed storage tanks; (b) truck-to-ship through a truck; and (c) ship-to-ship through a bunker ship (Aneziris et al., 2020). The first bunkering mode requires the establishment of fixed tanks in the port area, while the other two require a truck or a bunker ship to reach the port only during bunkering.

Assuming a small-scale LNG installation, fixed tanks are, typically, pressurized cylindershaped tanks with a volume of 1000 to 3,500 m³. They are permanently placed, either horizontally or vertically, in a special pier serving LNG bunkering whereby unloading is accomplished through a fixed cryogenic loading arm or a hose at a rate of 50 to 750 m³/h, depending on the size of the tank of the fuelled ship. On the other hand, an LNG truck is used when small quantities of LNG are required, since a typical truck tank has a volume of 40 to 80 m³ and supplies a fuelled ship at a rate of 40 to 60 m³/h. Many trucks in a row can also be applied for slightly larger bunkering quantities. On the other hand, a bunker ship serves much larger LNG quantities. A typical LNG ship tank in case of small-scale installations is capable of supplying the ship with LNG through a flexible hose or fixed arms at a rate of 60 to $3.000 \text{ m}^3/\text{h}$.

Since the behaviour of LH2 resembles that of LNG, its introduction to shipping as an alternative fuel can easily be achieved by establishing LH₂ bunkering stations capable of providing all three key bunkering modes (tank, truck and bunker ship) (Georgeff et al., 2020). The solutions of tank-to-ship and ship-to-ship bunkering have already been examined (Kamiya et al., 2015). A storage tank of 2500 m³ has been installed in the first existing unloading terminal at port of Kobe in Japan (Nishimura et al., 2021). The first existing bunker ship carries 1250m³ LH₂ (Ustolin et al., 2022). Considering the existing LH₂-fueld ships, capacities between 15 and 80 m³ are applied. A hydrogen truck is used when small quantities are required, since a typical truck tank

has a volume of 50 m^3 and supplies a fuelled ship at a rate of 1000 to 4000 kg/h.

4 Risk Assessment

Handling alternative fuels in port areas is hazardous, as already noted. The methodology to be followed for the quantification of risk from installations handling flammable substances can be distinguished into three major phases, as already presented by Papazoglou et al. (1992), which are the following: a) assessment of damage states and their frequency of occurrence, b) assessment of consequences of flammable or toxic substances release, and c) risk integration. This methodology is consistent with the quantitative risk analysis recommended in the Formal Safety Assessment issued by IMO (IMO, 2018).

In the first phase, the master logic diagram (MLD) technique is used to identify the initiating events which create a disturbance in the installation and have the potential to lead to alternative fuel release, as presented by Papazoglou and Aneziris (2003). In addition, event trees may be developed to describe the accident sequences starting from the occurrence of an initiating event and followed by the failure of safety systems. Finally plant damage states are defined and the associated accidental release of toxic or flammable fuel. The frequency of the major accident scenarios is calculated by exploiting available failure rate data and the Fault Tree-Event Tree method. In cases where failure rate data of accidental scenarios exist, they may also be used.

The second major step involves the assessment of the consequences owning to the release of the alternative fuel. In case of LNG and LH_2 release, fires and explosions are taken into account. Consequence assessment is performed by using specially designed methods, such as those developed by Papazoglou et al. (1996).

Finally, the third major step involves the integration of the results of all previous phases to estimate the total individual risk. Risk is evaluated by combining the frequencies of the various accident scenarios with the corresponding consequences resulting in individual risk.

The current paper performs risk assessment for truck to ship (TTS) and ship to ship (STS) bunkering at a port taking into account the two alternative fuels. Two main critical areas are considered, which are the following: a) truck area in the port and b) hose or loading arm area in the port, where bunkering is performed. Table 1 presents the considered capacities and bunkering rates for LNG and LH₂.

4.1 Initiating Events and Accident Sequences

In the first phase of the risk assessment, MLDs are constructed to determine the initial events that are likely to occur during truck or ship to ship bunkering. MLDs initiate with the top event "Loss of Containment" which is decomposed into simpler events. Corrosion in tanks, pipelines and other parts, excess external heat owing to nearby external fire, high level, external loading and natural phenomena (such as high winds) are identified initial events in case of LNG storage and bunkering (Aneziris et al. 2021). On the other hand, inadequate purging or ventilation, external heat owning to external fire, tank rupture owning to corrosion, embrittlement or weld failures, and overfilling are some of the most critical initial events resulting in LH2 leakage during storage or bunkering (Ringland, 1994; NASA, 2005).

Table 1. Bunkering rates in small-scale stations for LNG and LH_2 .

Alternative fuel	Bunkering rate or quantity
LNG - STS	750 m³/h
LNG - TTS	50 m ³ /h
LNG truck	50 m ³
LH ₂ - STS	400-1000 m3/h
LH ₂ - TTS	4000 kg/h
LH ₂ truck	50 m ³

As soon as the initial events are identified, the safety functions and systems for preventing fuel release, such as emergency shut-down system (ESD) and pressure safety valves (PSV), are determined. Three damage states were identified in the case of the LNG release, which are the following: a) tank rupture, b) tank rupture and BLEVE, and c) hose rupture. The frequency of occurrence of each of these damage states can be calculated by the Event Tree and/ or Fault Tree methodology, or by using accident frequency data from the literature.

At the current study, literature data was used. As it has already been stated leak and failure frequencies have large uncertainties owing to: a) incorrect information, b) inaccurate assessment of equipment populations, c) selection of relevant incidents and f) inappropriate representation of the release frequency distributions by fitted correlations (IOGP, 2019). The annual frequency of a hose rupture, in case of all cryogenic gases, varies between 5.82x10⁻⁶ and 2.74x10⁻³ with mean 1.01x10-3, according to Gerbec and Aneziris (2022). This analysis was based on all published hose rupture frequencies, as for example by HSE (2019), RIVM (2009), and NFPA 59A (2019). According to the Bayesian analysis of LNG frequencies performed by Mulcahy et al. (2021) the annual frequency of an LNG hose rupture varies between 2.96x10⁻⁶ and 4.34x10⁻¹, with median value 1.1x10⁻³. Limited data exist on the failure of LH₂ leak frequencies. Brooks et al. (2022) performed a Bayesian analysis based on data points of LNG and gaseous hydrogen failure. The annual frequency of an LH₂ hose rupture varies between 2.96x10⁻⁷ and 5.6x10⁻ ², with median value 1.3×10^{-4} .

According to the Bayesian analysis of LNG failure frequencies performed by Mulcahy et al. (2021), the annual frequency of an LNG vessel rupture varies between 1.67x10⁻⁸ and 5.77x10⁻⁴, with median value 3.05x10⁻⁶. In addition, the Bayesian analysis performed by Brooks et al. (2022) provides the annual frequency rupture of an LH₂ vessel, which varies between 6.8x10⁻⁹ and 2.0x10⁻⁴, with median value 1.2x10⁻⁶. According to RIVM (2009) the annual failure of a pressurised tank rupture on a road tanker is expected to be 5.0×10^{-7} , and the BLEVE hourly rate of a road tanker containing either LNG or LH₂ is 5.8x10⁻¹⁰. By assuming 100 hours of operation per year, the annual BLEVE rate of these trucks is estimated to 5.8×10^{-8} /year. Table 2 presents the relevant ranges of the annual failure frequencies proposed in the literature. The median

Table 2. Annual frequencies of damage states

Damage State	LNG	LH ₂
Hose rupture during bunkering	2.96 x10 ⁻⁶ - 4.34 x10 ⁻¹	2.96 x10 ⁻⁷ - 5.6 x10 ⁻²
Truck rupture and BLEVE	5.8 x 10 ⁻⁸	5.8 x 10 ⁻⁸
Truck rupture	1.67 x10 ⁻⁸ - 5.77 x10 ⁻⁴	6.8 x10 ⁻⁹ - 2.0 x10 ⁻⁴

values of these frequencies are considered for the risk analysis of the two alternative fuels, presented in the next paragraph.

4.2 Consequences of Accidental Release

In case of an accidental release of LNG or LH_2 there are two possibilities: a) an immediate ignition will occur at the time of the release thus either a fireball, or a pool fire, or a jet fire will take place, and b) in case an immediate ignition does not occur, LNG (or LH_2) will evaporate, spread and eventually form a vapor cloud dispersing into the atmosphere that may result in flash fire or vapor cloud explosion, if ignited.

Figure 1 illustrates the possible paths, owning to LNG or LH₂ hose rupture. For this damage state, it is assumed that LNG is released at the unloading rate 750 m³/h for five minutes (as shown in Table 1). In case of hose rupture, the result is either immediate ignition which will cause a jet fire, or delayed ignition whereby LNG will vaporize at a rate equal to the release rate producing a cloud denser than air spreading according to the weather conditions. If the cloud reaches concentrations between the upper and lower flammability level (5-15% by volume for LNG) the mixture can be ignited. As a result, if LNG is contacted with an ignition source, either a flash fire or an explosion will take place. The probability of direct ignition depends on the release rate and the type of installation (truck or ship) and varies between 0.1 and 0.7. In case of road tankers, the probability of direct ignition is equal to 0.1 for continuous and 0.4 for instantaneous release, according to RIVM (2009). In case of a ship release direct ignition probability is estimated to 0.7, while for tanks it is estimate to be 0.2 for small releases, 0.5 for medium releases and 0.7 for large releases RIVM (2009). A similar tree is developed for the LH₂ hose rupture. In case

Damage state	Immediate Ignition		Delayed Ignition		Physical phenomenon	
	YES	Immediate ignition				Jet fire
Hose Rupture						Flash fire
	No	Dispersion	YES	Delayed ignition		Explosion
			No			Safe

Fig. 1. Consequence event tree for LNG and LH2 accidental release, following hose rupture.

of immediate LNG or LH₂ release from tanks BLEVE may also occur.

Assuming the LNG or LH_2 release and the associated physical phenomena, heat radiation or the maximum overpressure is calculated by using specially designed simulation models. Heat radiation and overpressure are assessed over time and the dose an individual receives is estimated. Lastly, appropriate dose-response models are exploited to eventually estimate the probability of

Table 3. Distances where individual risk is equal to $1.0 \ 10^{-6}$.

Damage State	Frequency	Distance
	/у	(m)
LNG hose rupture - STS and jet fire	7.70 10-4	90
LNG hose rupture - STS and flash fire	1.65 10-4	110
LNG hose rupture - STS and explosion	1.65 10 ⁻⁴	50
LNG hose rupture - TTS and jet fire	1.10 10-4	90
LNG hose rupture - TTS and flash fire	4.95 10-4	45
LNG hose rupture - TTS and explosion	4.95 10-4	30
LNG truck rupture and BLEVE	5.80 10-8	-
LNG truck rupture and flash fire	1.53 10-6	10
LNG truck rupture and explosion	1.53 10-6	45
LH ₂ hose rupture - STS and jet fire	9.10 10 ⁻⁵	150
LH_2 hose rupture - STS and flash fire	1.95 10-5	100
LH ₂ hose rupture - STS and explosion	1.95 10-5	270
LH ₂ hose rupture - TTS and jet fire	1.30 10-5	55
LH ₂ hose rupture - TTS and flash fire	5.85 10-5	10
LH_2 hose rupture - TTS and explosion	5.85 10-5	145
LH ₂ truck rupture and BLEVE	5.80 10-8	-
LH ₂ truck rupture and flash fire	6.00 10-7	-
LH ₂ truck rupture and explosion	6.00 10-7	-

4.3 Risk Results

fatality of an individual receiving the assessed dose.

The main results of the risk assessment involve the calculation of individual risk. This is performed by combining the frequencies of the various accidents with the corresponding This consequences. paper utilizes the computational program "SOCRATES" to achieve this integration, and also to calculate heat radiation and overpressure at any point in the area where a release takes place (Papazoglou et al., 1996). SOCRATES estimates the individual risk taking into account the existing uncertainties, such as the distance of ignition in case of delayed ignition and the meteorological conditions. Meteorological conditions include the wind speed and direction, the atmospheric stability class according to Pasquill A-F, ambient temperature, and relative humidity.

Table 3 shows the damage states as well as the distances where individual risk equals to 10^{-6} for the considered LNG and LH₂ installations. The most serious accidents in the present case study are the following: a) hose rupture during LH₂ bunkering STS and explosion and b) hose rupture during LH₂ bunkering and jet fire.

5 Conclusions

This paper presented a Quantitative Risk Assessment (QRA) methodology for the study of alternative fuels, namely LNG and LH₂, for ship bunkering. FSA consists of the basic steps of QRA, which are identifying initial events lead to accidents, determines accident sequences and damage states and quantifies risk. The probability of LNG or LH2 release was calculated based on literature data. Finally, consequences assessment in case of flammable LNG and LH2 were estimated in a case of truck to ship and ship to ship bunkering. The damage states with the most serious risks for and bunkering phases are the following: a) hose rupture during LH2 STS bunkering and explosion and b) hose rupture during LH₂ STS bunkering and jet fire. In the first case, individual risk is equal to 10^{-6} at a distance of 270 m and in the second case the same risk level is reached at 150 m from the release.

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