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A Comparison of Alternative Cryogenic Fuels for Regional Marine Transportation from the Perspective of Safety

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Marine industry has been forced to move towards sustainable fuels. Cryogenic gases as Liquefied Natural Gas (LNG) and ammonia (LNH_3) can be the solution for fuel storage and transportation even for remote reservoir. Besides liquefied hydrogen (LH_2) seems to be a long-term solution, but several studies are addressed to this new opportunity. To deal with intensive use of these three fuels, a detailed comparison for the technical, economic and environmental point of view is strongly needed. Nevertheless, so far, a full understanding on the complex phenomena characterizing the accidental release of LNG, LH_2 and LNH_3 in harbour environment has not been assessed. In this paper, a comparison of the three fuels for the safety perspective, i.e., the hazards and the consequences of accidental release, is shown, considering storage systems which can be possibly installed on small ships such as ferries, trailers, cabin cruiser, small cargos, and leisure.

1. Introduction

The European Union is moving towards a neutral climate where Sulfur and Nitrogen Oxides (SO_x, NO_x), carbon dioxide (CO_2) 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 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 LNG, LPG and methanol. The use of these fuels can benefit in the mid-term applying the existing technologies and infrastructure. On the other hand, ammonia, hydrogen, and electrification are emerging as long-term solutions that will allow a zero-carbon shipping industry in the future.

LNG, ammonia 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). Ammonia and hydrogen have very recently been studied but the adoption of these fuels poses risks to human health. Indeed, the accidental release of LNG and hydrogen may cause fires or explosions, while the release of ammonia may cause severe toxic effects. 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 achieved when ships are fueled with LNG, ammonia and hydrogen. Quantitative risk assessment is performed for the bunkering of alternative-fueled-ships, via tanks installed at port facilities. The remaining of the paper is structured as follows: Section 2 briefly presents the physical behavior of the under investigation alternative marine fuels, 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, ammonia, and hydrogen. Section 4 performs a risk assessment for estimating the risk of alternative marine fuels. Finally, section 5 contains the concluding remarks.

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2. Alternative cryogenic gases

LNG is natural gas, consisting mainly of methane, which is liquefied at atmospheric pressure to -162 °C. Its reduced volume, achieved by liquefaction, enhances its storage and transport in large quantities. Cold LNG is, commonly, stored in pressurized tanks at a pressure 0 to 4 bar and temperature -160 to -138 °C. All components that come into contact with the LNG, including tanks and pipes, are made of cryogenic materials to withstand excess temperatures that can significantly affect both the infrastructure and the people who come in contact with it. Hydrogen is produced either from fossil fuels, biomass or from the electrolysis of water. To store and transport hydrogen in large quantities, it needs to be liquefied at -253 ℃. Its low density requires storage tanks with volume 5 times larger than petroleum-based fuels and therefore it would be practical only for small ships that travel short distances. As long as ammonia is concerned, it can be stored and transported either pressurized at 8.6 bars or refrigerated at -33.6 °C or lower.

2.1 Hazards

LNG is a flammable and in case of an accidental release may cause vapor cloud flash fire, jet fire, pool fire or vapour cloud explosion (Aneziris et al., 2014; Mokhatab et al., 2014). Hydrogen is also flammable, especially when mixed with pure oxygen. When hydrogen is released into the open air, a flammable gas mixture is formed that produces invisible flames posing serious hazards (ABS, 2021a). The result is a jet fire or an explosive gas cloud and leads to deflagration or detonation of the gas. Hydrogen, when stored outdoors, is considered safer than LNG due to its ability to diffuse faster into the air reducing the available amount to be ignited. In addition, human exposure to extreme hydrogen temperatures poses a cryogenic risk. Although it is not a toxic substance, at high concentrations it may lead to oxygen depletion and asphyxia.
In contradistinction to LNG and hydrogen, ammonia is a less flammable, yet it is significantly toxic and reactive. Indeed, its ignition temperature reaches approximately 650°C, which, combined with its significantly low burning rate, makes ammonia a low fire risk fuel (Yadav & Jeong, 2022). Nevertheless, ammonia is a highly toxic gas and has a strong characteristic odor. Exposure to ammonia at low concentrations can be irritating to the eyes, lungs and skin, while at high concentrations or through direct contact it poses risk to life. Moreover, it is toxic in water as it forms ammonium (non-toxic) and hydroxide (toxic) ions when it reacts with it.

2.2 Regulatory Framework for Application in Maritime Sector

As the use of LNG as 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. IMO, classification societies and organizations have issued requirements for both the construction of LNG-fueled ships and their operation, as well as for the demanding, in terms of safety, bunkering procedures (IMO, 2015; DNV, 2015; ABS, 2017; IACS, 2017).
The IMO through the IGF code allows also the use of alternative fuels, such as hydrogen and ammonia (IMO, 2015). Since IMO does not provide detailed specifications for their use, hydrogen or ammonia fueled vessels should be designed according to the SOLAS alternative ship design regulation (IMO, 2009). Several safety guidelines have recently been developed by classification societies (DNV, 2021a; IMO, 2016; IMO 2021; ABS, 2021b; BV, 2021; DNV, 2021b). Nevertheless, there is an extensive regulatory framework for the safe use of hydrogen and ammonia in the chemistry industry, which may assist the shipping industry (LaChance et al., 2009; NFPA, 2019; ISO, 2008).

3. Requirements for storage and transport

Bunkering of ships with the alternative fuels can be carried out in any of the following three ways: (a) tank-to-ship through fixed storage tanks; (b) truck-to-ship through trucks; 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 be at the port only during bunkering.
A small-scale LNG installation consists of fixed tanks which are pressurized cylinder-shaped tanks with a volume of 100 to 3,500 m^3. They are permanently placed in a special pier serving LNG bunkering, whereby unloading is accomplished through fixed cryogenic loading arms or hoses at a rate of 50 to 750 m^3/h, depending on the size of the fuelled ship tank. On the other hand, LNG trucks are used when small quantities of LNG are required. A typical truck tank has a volume of 40 to 80 m^3 and supplies a fuelled ship at a rate of 40 to 60 m^3/h. On the other hand, a bunker ship may supply larger LNG quantities. A typical LNG tank in case of small-scale installations, has a capacity of 500 to 3,000 m^3 and is capable of supplying the ship with LNG through a flexible hose or fixed arms at a rate of 60 to 3,000 m^3/h.
Since the behaviour of hydrogen resembles that of LNG, its introduction to shipping as an alternative fuel can easily be achieved by establishing hydrogen 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). The capacity of fixed storage tanks ranges between 2,500 to 3,000 m^3, assuming a small-scale bunkering station, and 50,000 m^3 assuming a large-scale station. The capacity of small bunker ships is 2,500 m^3 and the capacity of the large bunker ships is 160,000 m^3. It is likely that the first ships fuelled with ammonia could be those ships carrying ammonia as cargo, since they do not depend on the available bunkering facilities in the port areas. For all other ships, bunkering can supposedly be carried out by tank, truck, or bunker ship similar to the other two alternative fuels. The most immediate and effective way, however, is to use the existing storage facilities as bunkering stations, which corresponds to tank to ship bunkering. Such tanks can be isothermal and capable of carrying up to 30,000 t of ammonia or spherical pressurized with a storing capacity 1,000 to 2,000 t (Alfa Laval et al., 2020). Moreover, converting small tankers into bunkering barges would be another feasible bunkering solution in the future.

4. Risk assessment

The methodology to be followed for the quantification of risk from installations handling toxic or flammable substances can be distinguished into three major phases, as already presented by Papazoglou et al. (1992), which are the following: a) assessment of plant damage states and their frequency of occurrence b) assessment of consequences of flammable or toxic substances release and c) risk integration. 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 initiating an 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.

The second major step involves the assessment of the consequences owing to the release of the alternative fuel. In case of LNG and hydrogen release, fires and explosions are considered, while in the case of ammonia evaporation and dispersion models assess the toxic consequences to people. 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 a risk assessment for tank-to-ship bunkering at a port taking into account the three alternative fuels. Two main critical areas are considered, which are the following: a) the tank area in the port and b) fuelled ship area at the pier, where bunkering is performed. In addition, for each critical area, one operating phase is considered and therefore the phases which are analysed are the following: (i) Storage of the alternative fuel in the tank in the port area; and (ii) Transfer of the alternative fuel from the tank to the fuelled ship. Table 1 presents the considered capacities and bunkering rates of the storage tank for LNG, LH_2 and LNH_3.

Table 1: Fixed storage tank capacities and bunkering rates in small-scale stations

Alternative fuel	Tank capacity	Case study capacity	Bunkering rate
LNG	500-1,000 m^3	1,000 m^3	750 m^3/h
LH_2	2,500-4,500 m^3	2,500 m^3	600 m^3/h
LNH_3	1,477-2,954 m^3	1,477 m^3	750 m^3/h

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 tank-to-ship bunkering: a) for storage of LNG, LH_2 or NH3 in tank and b) for transfer of fuels from the tank to the fuelled ship. 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). In case of ammonia, the identified initiating events, as presented by Papazoglou and Aneziris (2003), are the following: excess external heat, high level, external loading, and high winds.

As soon as the initial events are identified, the safety functions and systems for preventing fuel release, such as the emergency shut-down system (ESD) and pressure safety valves (PSV), are determined. Three damage states were identified, which are the following: a) tank rupture, b) tank rupture and BLEVE for pressurised tanks (LNG and LH_2), and c) hose rupture. The frequency of occurrence of each of these damage states can be

calculated by quantifying by the Event Tree and/ or Fault Tree methodology, and/ or using accident frequency data from the literature. At the current study, literature data was used. As it has already been stated (IOGP, 2019) leak and failure frequencies have large uncertainties owing to: a) incorrect information, b) inaccurate assessment of equipment populations, c) selection of relevant incidents and d) inappropriate representation of the release frequency distributions by fitted correlations. The annual frequency of a hose rupture, in case of all cryogenic gases, varies between 5.82×10^{-6} and 2.74×10^{-3}, according to Gerbec and Aneziris (2022). This analysis was based on the most comprehensive 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 rupture varies between 2.96×10^{-6} and 4.34×10^{-1}, with a median value 1.1×10^{-3}. Limited data exist on the failure of LH_2 leak frequencies. Brook et al. (2022) performed a Bayesian analysis based on data points of LNG and gaseous hydrogen failure. The annual frequency of an LH_2 hose rupture varies between 2.96×10^{-7} and 5.6×10^{-2}, with a median value 1.3×10^{-4}. The annual frequency of an ammonia loading arm rupture has been estimated to 3.8×10^{-3}, in a QRA study of an ammonia plant by Papazoglou et al. (1992).
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 1.67×10^{-8} and 5.77×10^{-4}, with median value 3.56×10^{-6}. In addition, the Bayesian analysis performed by Brooks et al. (2022) provides the annual frequency rupture of an LH_2 vessel, which varies between 6.8×10^{-9} and 2.0×10^{-4}, with a median value 1.2×10^{-6}. According to RIVM (2009) the annual failure frequency of a pressurized tank rupture is expected to be 5.0×10^{-7}, while the BLEVE annual frequency of a tank containing LNG or LH_2 5.8×10^{-10}. In case of rupture of an ammonia atmospheric tank, the annual failure rate is estimated as 1.0×10^{-8}, according to RIVM (2009). Table 2 presents the relevant annual failure frequencies, which may be used for the risk estimation of the plant damage states of three alternative fuels and Table 3 the corresponding quantities released.

Table 2: Annual frequencies of all damage states and associated quantities

Damage State	LNG	LH_2	LNH_3
Hose rupture during bunkering	9.6×10^{-6}- 2.2×10^{-4}	2.9×10^{-7}- 5.6×10^{-2}	5.82×10^{-6}- 2.74×10^{-3}
Tank rupture and BLEVE	$5.8\ 10^{-8}$	$5.8\ 10^{-8}$	
Tank rupture	1.7×10^{-8}- 5.77×10^{-4}	6.8×10^{-9}- 2.0×10^{-4}	$1.0\ 10^{-8}$

Table 3: Quantities released for all damage stated

Damage State	LNG	LH_2	LNH_3
Hose rupture during bunkering	750 m^3/h	600 m^3/h	750 m^3/h
Tank rupture and BLEVE	1,000 m^3	2,500 m^3	-
Tank rupture	1,000 m^3	2,500 m^3	1,477 m^3

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, a pool fire, or a jet fire will take place, and b) if an immediate ignition does not occur at the time of the release thus 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 LH_2 hose rupture. For this damage state, it is assumed that LNG is released at the unloading rate 750 m^3/h for five minutes (as shown in Table 1). In case of hose rupture, the result is either immediate ignition which will cause a pool or 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. A similar tree is developed for the Hydrogen hose rupture. In case of immediate LNG or LH_2 release from pressurized tanks BLEVE will 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 fatality of an individual receiving the assessed dose.

4.3 Risk results

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 consequences. This paper utilizes the computational program “SOCRATES” to achieve this integration (Papazoglou et al., 1996), and also to calculate heat radiation and overpressure at any point in the area where a flammable release takes place, as well as the toxic effects, in the case of the ammonia release. 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 4 shows the damage states as well as the distances where the probability of fatality equals to 10^{-2} for the considered LNG, ammonia, and hydrogen port installation. The most serious accidents in the present case study are the following: a) ammonia tank rupture, b) LNG tank rupture and BLEVE, c) ammonia hose rupture and d) hose rupture during LH_2 bunkering and explosion.

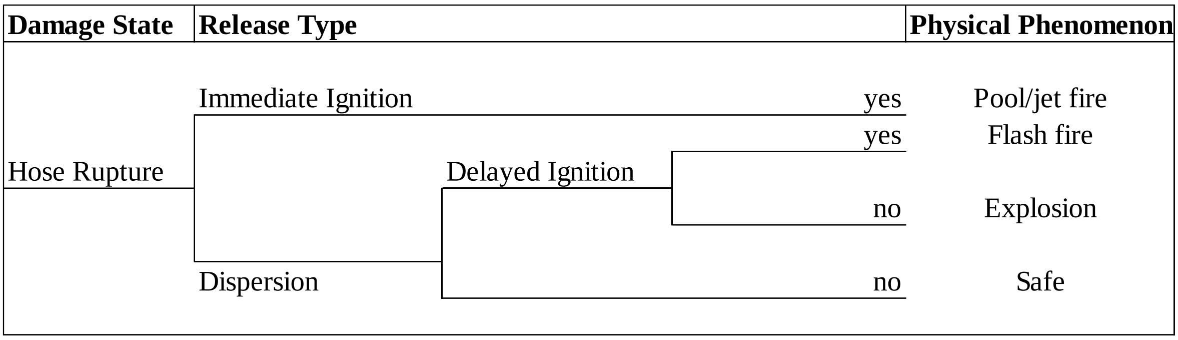

Figure 1: Consequence event tree for LNG and LH_2 accidental release owning to hose rupture

5. Conclusions

This paper presented a Quantitative Risk Assessment (QRA) methodology for the study of alternative fuels, namely LNG, hydrogen and ammonia, for bunkering. QRA starts by identifying initial events which may lead to accidents and determines accident sequences and damage states. The probability of ammonia, LNG or Hydrogen release was calculated based on literature data. Finally, consequences assessment in case of toxic ammonia and flammable LNG and Hydrogen were estimated in a case of tank to ship bunkering. The damage states with the most serious consequences for storage and bunkering phases are the following: a) LNH_3 tank rupture b) LNG tank rupture and BLEVE, c) ammonia hose rupture and d) hose rupture during LH2 bunkering and explosion. In the first case, individual conditional risk reaches a distance of 2,500 m, in the second 730 m and in the last two 500 m respectively.

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