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A comparison of the toxicity and asphyxiation risk during bunkering of LH_2, LNG and NH_3 by means of a quantitative risk assessment

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Abstract. To achieve the greenhouse gas (GHG) reduction goals set by the International Maritime Organization (IMO), hydrogen, natural gas and ammonia are considered as marine fuel in their liquefied form. Nevertheless, concerns regarding their safety have been raised. Thus, the overarching aim of this investigation is it to addresses these concerns by conducting a comparative analysis of the safety of bunkering these fuels, with a particular focus on toxicity and asphyxiation hazards. A quantitative risk assessment is thus conducted in two steps: first, to identify the probability through a frequency analysis and second, to identify the severity through a consequence analysis. The present study will utilize the requisite safety distance as the threshold for the severity. The calculation of the safety distance necessary for the different fuels is performed utilizing a Gaussian dispersion model. Subsequently, both the necessary safety distance and the frequency of harmful events of all three fuels are then compared. The findings indicate that the frequencies of the toxicity/asphyxiation case are of comparable order magnitude for all fuels. However, the safety distance of ammonia is one order of magnitude larger than that of the other fuels.

1. Introduction

According to the International Maritime Organization (IMO), the shipping industry is responsible for approximately 3 % of global CO_2 emissions [1]. In order to align with targets set out by the Paris Agreement, novel fuels must be introduced to shipping. Methanol, hydrogen and ammonia have been identified as promising candidates in this respect. Of these, hydrogen, whether compressed or liquefied, is predominantly discussed for smaller units such as ferries, while methanol and ammonia are more often considered for larger ships, including container vessels [2]. Additionally, liquefied natural gas (LNG) is regarded as a low-carbon fuel and has already been safely utilized in shipping. The liquefaction of hydrogen and LNG requires cryogenic temperatures, whereas ammonia can be liquefied at moderate pressures of approximately 10 bar or by reducing its temperature to -33 °C. Notwithstanding these

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advantages, concerns regarding the safety of ammonia and hydrogen in shipping have been raised on numerous occasions [3, 4].

The objective of this paper is to comparatively analyze the safety of bunkering the three liquefied gases hydrogen, ammonia, and natural gas by employing a quantitative risk assessment. The parameters of concern for the comparison are the frequency with which a hazardous event occurs and the safety distance that needs to be kept to mitigate the hazard, if it would occur. The ignition hazards are not the focus of this paper, as they have been considered in other work (e.g. Depken et al. [5]). This paper will focus on the hazard posed by unburned fuel. In the context of ammonia, the primary concern pertains to its toxicity. As LNG and hydrogen are not toxic, the primary hazard in these scenarios is asphyxiation due to displacement of oxygen.

Depken et al. [5] focused on the ignition hazards of bunkering the fuels LH_2 and LNG. Therefore three hazardous events, pool fire, flash fire and explosion, were investigated. First, they derived the frequencies of these events by means of a event tree. Subsequently, the consequences of these three events were modeled and the safety distance was obtained. It was concluded, that leaks at hydrogen bunkering facilities are more frequent than at LNG plants and that LH_2 requires larger safety distances as well.

A number of publications have already been published on the subject of the risk assessment of ammonia utilization in shipping. Chen et al. [4] analyzed the risk and potential protective measures associated with the utilization of ammonia onboard of a ship. Duong et al. [6] published a review of safety assessments of ammonia bunkering and concluded, that the toxicity of ammonia is more relevant than its flammability. Fan et al. [7] analyzed the dispersion of the three fuels LNG, LH_2 and NH_3 during bunkering and compared the toxicity of ammonia to the flash fire of LNG and LH_2. Ng et al. [8] utilized PHAST software to examine the impact of operational factors and meteorological conditions on the dispersion of ammonia in the Port of Singapore.

2. Methodology

The methodology under discussion is based on the assessment approach developed by Depken et al. [5] and consists of two parts. Initially, a frequency analysis is conducted to obtain the frequencies with which the hazardous events may occur. This is followed by a consequence analysis, the objective of which is to obtain the necessary safety distance. Finally, the use case for this paper is discussed.

2.1 Frequency Analysis

For the frequency analysis, an event tree (according to Depken et al. [5]) is established. The path leading to the toxicity or asphyxiation hazard is amended. This path is highlighted in Figure 1.

The frequencies of the initial leak in this paper are based on the leak frequencies established by the International Association of Oil & Gas Producers (IOGP) [9]. The equipment subject to the frequency analysis can be obtained from Figure 2. This paper only considers the part of the system filled with the liquid fuel, highlighted in Figure 2. The purging and vapor return systems are out of scope of this paper.

The ignition probabilities for the immediate and delayed ignition are based on the UKOOA model developed by the Energy Institute [10]. The model assumed, that the probability of a direct ignition is always 0.001. The overall ignition probability for this case is shown in Table 1, where P_{ign} is the overall ignition probability and Q_L is the leak frequency as described in Equation 1. To obtain the probability of a delayed ignition, the probability of a direct ignition is subtracted from the overall ignition probability. As the model considered 28 different environmental conditions, for this paper the environmental conditions of case 5 "small plant gas LPG" are chosen as fitting the conditions during bunkering best, as it covers not only liquefied petroleum gas (LPG), but all flammable gases. The model assumes, that the probabilities for highly reactive substances, such as hydrogen, need to be doubled, subject to a maximum of 1. According to the model, the ignition probabilities of high flash point substances are multiplied by 0.1. Due to the physical properties of ammonia, this paper applies the same factor for ammonia.

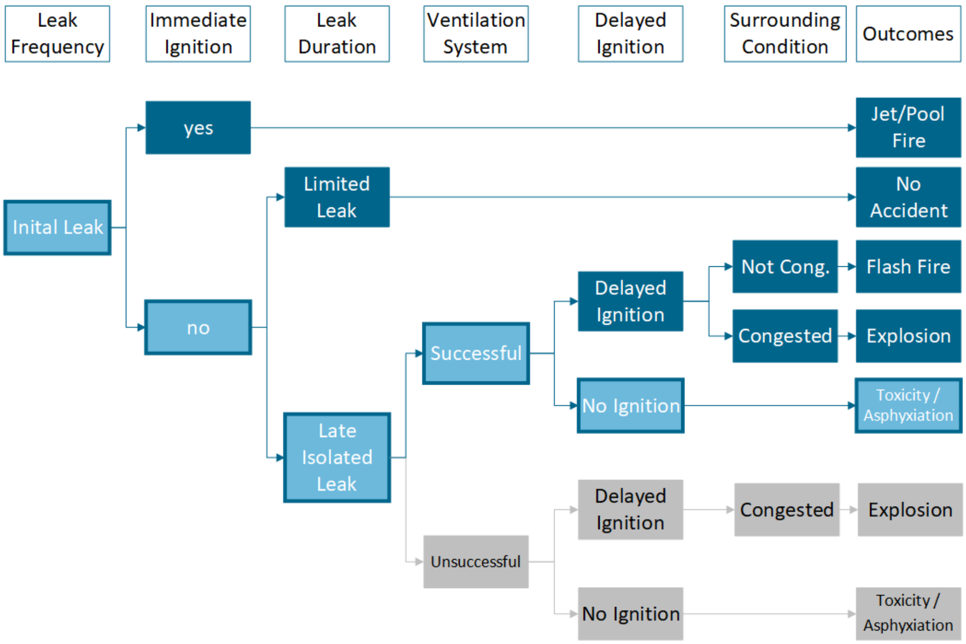


Figure 1 Event tree used to determine the frequency of the hazardous event "Toxicity/Asphyxiation“ highlighted

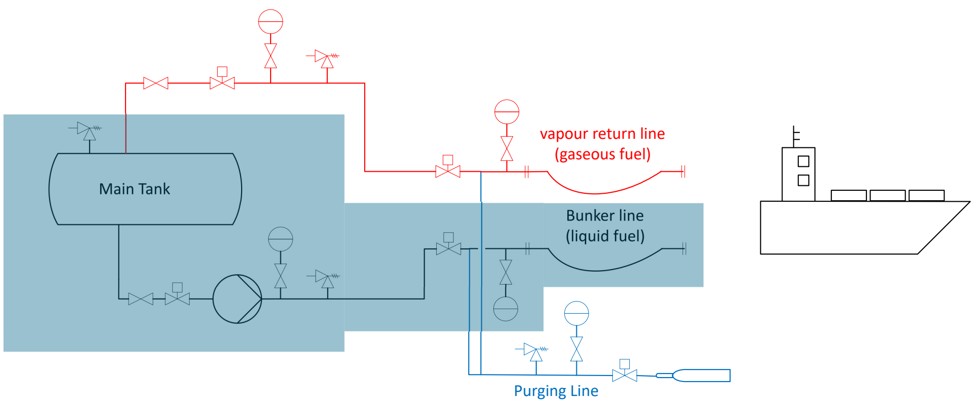


Figure 2 Conceptual design of considered bunker system for LNG, NH3 and LH2 ©CC-BY [5]

Table 1 ignition probabilities according to Energy Institute model

Case No.	Case Description	Release Rate Range (kg/s)	Equation
5	Small Plant	0.1 - 1	$P_{ign} = 0.00250 \cdot Q_L^{0.357}$
	Gas LPG	1 - 3	$P_{ign} = 0.00250 \cdot Q_L^{1.568}$
		3 - 498	$P_{ign} = 0.00624 \cdot Q_L^{0.735}$
		> 498	$P_{ign} = 0.600$

It is assumed that in 90 % of cases, the duration of the leak is limited. It is further assumed that ventilation is always successful, as bunkering takes place on the open deck and natural ventilation is present. The surrounding area is assumed to be congested in 20 % of cases and uncongested in 80 % of cases.

2.2 Consequence Analysis

In order to obtain the required safety distance for the toxicity/asphyxiation case, a Gaussian dispersion model is employed. Liu et al. [11] compares Gaussian dispersion models with a CFD analysis for ammonia releases and shows a good correlation in the far field. Nevertheless, close to the release there were larger deviations observed. So far, such a comparison has not been conducted for LNG or hydrogen.

The threshold for ammonia is obtained from the commonly used acute exposure guideline levels (AEGL). The AEGL defines three levels where the third is defined by a concentration causing "life-threating health effects or death" [7]. This paper defines the AEGL3 for 10 minutes (2,700 ppm) as the threshold. For LNG and hydrogen, the threshold is the concentration at which oxygen is displaced below a level that might be deadly, namely an oxygen concentration of 12 vol.-%. This level is reached at concentration of natural gas or hydrogen of 42.9 vol.-%.

The first step in the consequence analysis is to calculate the release rate of fuel with Equation 1 [12]. This leak rate is also necessary for the ignition probabilities in Table 1.

$$Q_L = C_D \cdot A \cdot \sqrt{2 \cdot \rho_L [(P_0 - P_a) + \rho_L g h]} \tag{1}$$

The Gaussian dispersion model employed here is a simplified version, only considering the downwind direction (x-direction) as illustrated in Equation 2 [13].

$$C(x, 0, 0) = \frac{Q_L}{\pi u_w \sigma_y \sigma_z} \tag{2}$$

The parameters σ_y and σ_z are dependent on the wind stability class. In this case the most stable class F has been chosen as a worst-case scenario. The wind speed is selected to be 5 $^{m}/_{s}$ as representative for Northern Germany. Usually both parameters are obtained from graphs; Equations 3 and 4 are approximations of these graphs [14] as a function of the distance from the release point R_d in m.

$$\sigma_y = 0.04 \cdot R_d \cdot (1 + 0.0001 \cdot R_d)^{-0.5} \tag{3}$$

$$\sigma_z = 0.016 \cdot R_d \cdot (1 + 0.0003 \cdot R_d)^{-1} \tag{4}$$

2.3 Use case

The use case under consideration is a 140 m long cruise ship. It is hypothezised that the cruise ship possesses an engine power of 11.2 MW, and operates on voyages of 7 days. With a fuel margin of 1.2 and an energy efficiency of 0.5, a necessary stored energy per journey of 4,516 MWh is derived, which results in 135 t or 1,910 m^3 of LH_2, 874 t or 1,460 m^3 of NH_3 and 345 t or 758 m^3 of LNG.

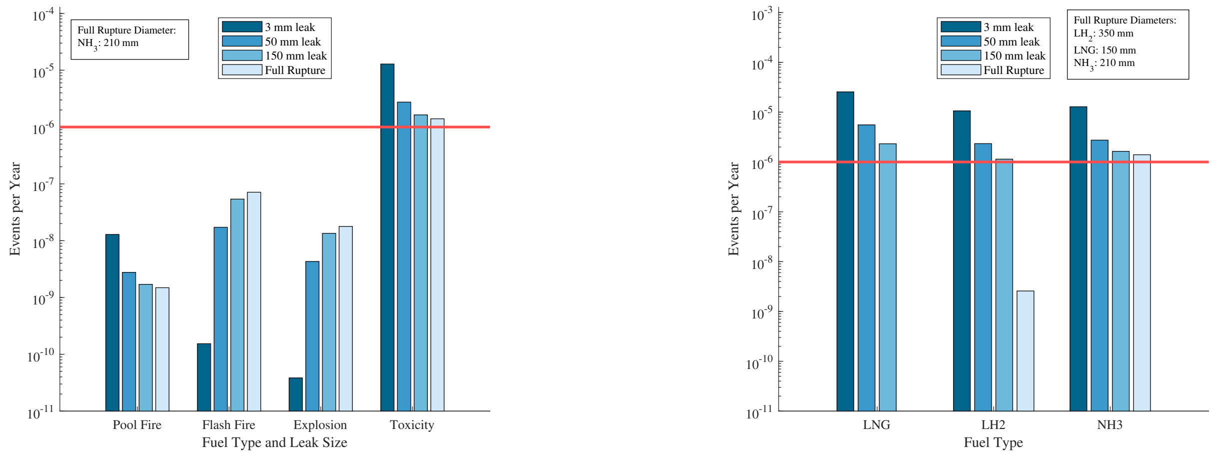
It is estimated that the bunker station has the capacity to accommodate 280 ships per year. It is assumed that all ships have the same size and energy requirements as the cruise ship defined above. While other vessel types and sizes may be present, the cruise ship is used as a representative example.

3. Results and Discussion

The methodology described in the previous chapter is employed to calculate and compare the frequencies of hazardous events and the required safety distance between the three fuels.

3.1 *Frequency Analysis*

As delineated in section 2.1, a frequency analysis is conducted. This analysis yields two results. Initially, the frequencies of all possible hazardous events from the event tree in Figure 1 are compared for ammonia as a fuel. LNG and LH_2 have been thoroughly analyzed in the context of the pool fire, flash fire and explosion case by Depken et al. [5]. Subsequently, the frequencies of the toxicity/asphyxiation case are compared between all three fuels.



(a) frequencies of all hazardous events for Ammonia

(b) frequencies of the toxicity / asphyxiation event for all fuels

Figure 3 results of frequency analysis

Figure 3a presents the frequencies of the hazardous events pool fire, flash fire, explosion and toxicity for ammonia as a fuel. Thus, the frequency of toxicity cases is at least one order of magnitude higher than that of the other cases. It is also the sole instance that exceeds 10^{-6}, as indicated by the horizontal line. For the general population, an individual risk per annum (IRPA) of 10^{-6} is generally considered acceptable. However, for employees in high-risk professions, an even higher IRPA may be deemed appropriate [15, 16]. Consequently, this paper will concentrate on the toxicity/asphyxiation case.

The toxicity/asphyxiation case is further analyzed in Figure 3b, where all fuels are compared for this case. As illustrated in Figure 3b, it is evident that all fuels and leak sizes, with the exception of the LH_2 full rupture case, exceed the IPRA of 10^{-6}. It is noteworthy that all cases and leak sizes, with the exception of the LH_2 full rupture case, are of comparable order of magnitude, thereby rendering them analogous. However, the frequencies of LNG are observed to be the greatest for all leak diameters and they are approximately twice as high as that of LH_2. The ammonia frequencies are larger than those of LH_2 but smaller than those of LNG.

3.2 *Consequence Analysis*

Subsequent to the establishment of the Gaussian dispersion model in chapter 2.2, a comparison of the safety distances for the three fuels can be conducted. According to Figure 4a, the concentration of the fuel is depicted as a function of distance from the release point in downwind direction. This Figure serves as an example for a 150 mm continuous leak. The other leak diameters demonstrate a comparable trend. As illustrated in Figure 4a, ammonia and LNG exhibit comparable concentrations. However, hydrogen, due to its lower density, has higher concentrations. Given the disparate acceptable concentrations of LNG and ammonia, the requisite safety distance differs.

The safety distances for all leak sizes and fuels are compared in Figure 4b. Ammonia exhibits a safety distance that is approximately one order of magnitude larger than those of LNG and hydrogen. It has been demonstrated that hydrogen necessitates larger safety distances than LNG. The safety distance for

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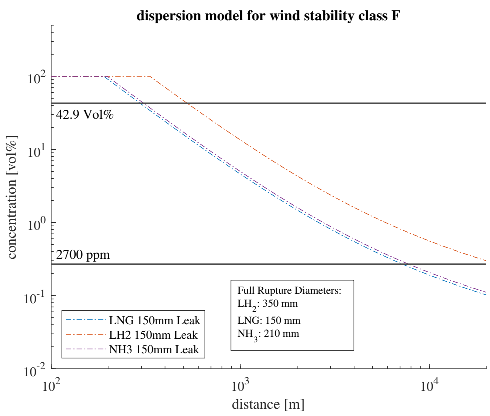
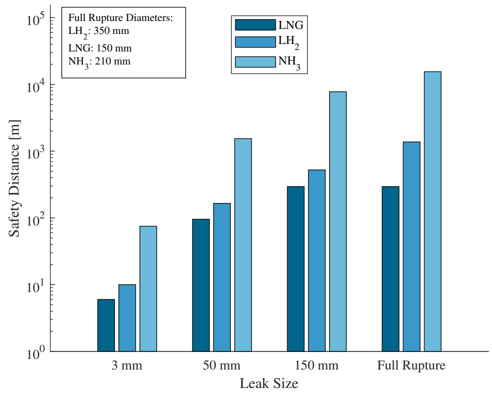


(a) Dispersion model for the 150 mm leak of all three fuels. The horizontal lines indicate the thresholds of 2,700 ppm and 42.9 Vol% respectively



(b) Necessary safety distances for the three fuels and 3 mm, 50 mm, 150 mm and full rupture leaks

Figure 4 Results of consequence analysis

all fuels increase with increasing leak size, owing to the greater release rate that results. The sole safety mechanism in this analysis is a watchkeeper on the deck. Further safety mechanisms, that would be installed in a real application would further reduce the frequencies and possibly also the safety distances as the amount of leak fuel is limited. But as the fuels and not the safety mechanisms are compared, the safety mechanisms are out of scope of this comparison.

4. Conclusion

The methodology developed by Depken et al. [5] is amended to include a toxicity/asphyxiation case as well. With this extended methodology it is shown that ammonia releases leading to a toxicity hazard have a frequency in the same order of magnitude as the asphyxiation cases of LNG and LH_2. Although all fuels are of the same order of magnitude, in this specific case, LNG leaks occur with the highest frequency, followed by ammonia and hydrogen. The safety distance on the other hand is by one order of magnitude larger for ammonia, than for LNG and LH_2. The demonstrated methodology can be adapted to other applications than bunkering, by adapting the event tree (Figure 1) and the system under consideration (Figure 2.

List of Symbols

ρ_L liquid density, in kg/m^3
σ_y dispersion constant as functions of the distance and the wind stability class, in m
σ_z dispersion constant as functions of the distance and the wind stability class, in m
A hole area, in m^2
$C(x, 0, 0)$ Concentration at some point in space in kg/m^3
C_D discharge coefficient (= 0.61)
g acceleration of gravity (= 9.81 m/s^2)
h height of liquid surface above hole m
P_0 initial absolute pressure of liquid, in N/m^2
P_a atmospheric pressure (= 10^5 N/m^2)
P_{ign} ignition probability
Q_L initial liquid release rate, in kg/s
u_w wind speed in m/s (here 5 m/s)

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