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Inherent safety of clean fuels for maritime transport

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ABSTRACT

The urgent need to reduce the emission of harmful pollutants in maritime transport promoted the development of several alternative propulsion systems based on clean fuels or carbon-neutral energy vectors. However, the alternative solutions under development pose new concerns from the safety perspective. Thus, an innovative methodology to rank the inherent safety performance of alternative systems at early design stages was developed. A case study representative of long-distance maritime transportation was analysed. The inherent safety performances of Liquefied Natural Gas (LNG), Liquid Hydrogen (LH₂), and Liquid Ammonia (LNH₃) were compared to that of Marine Gas Oil (MGO), assumed as a benchmark representing state-of-the-art technologies. Uncertainty and robustness of the safety ranking obtained were tested via a Monte Carlo analysis. The results show that technologies based on LNG have similar safety performances with respect to the benchmark option. Conversely, LH₂ safety performance is currently limited by the lack of mature technologies for its safe storage whilst the safety of LNH₃-based applications is affected by the toxicity of ammonia.

1. Introduction

The Paris Agreement (United Nations, 2015) proposes to limit the increase in the global average temperature below 2 °C tackling greenhouse gas (GHG) emissions. Maritime transport is responsible for 2.9 % of GHG emitted globally and accounts for approximately 13.5 % of the total EU GHG emissions from transport (European Environment Agency, 2021; International Maritime Organization (IMO), 2021). Shipping represents also a major contributor to air pollution, being responsible for about 15 % of the nitrogen oxides (NO_x) and 8% of the sulfur oxides (SO_x) emitted worldwide by any anthropogenic activities (Beecken et al., 2015; Lee et al., 2020; Maragkogianni et al., 2016). The growing concern for environmental protection has induced the competent international authorities to introduce constraints on the emissions of conventional pollutants, such as SO_x, NO_x and Particulate Matter (PM) (MARPOL, 2006), calling for the reduction of the sulfur content of fuels and the introduction of exhaust gas treatment systems. These requirements, together with the strive to reduce GHG emissions, have triggered the development of alternative clean technologies for maritime propulsion, based on low-carbon fossil fuels (e.g., natural gas), or energy vectors, such as hydrogen and ammonia (Ball and Weeda, 2015; Bicer and Dincer, 2017; Bilgili, 2021).

Nevertheless, the use of carbon-neutral, carbon-compensated, or low-carbon sources should be carefully evaluated under a holistic sustainability perspective to assess its viability at an industrial scale (Kim et al., 2020a). In this framework, it is crucial to address the possible trade-off of impacts among the different sustainability pillars (Munda, 2005), as well as to develop tools for the assessment of specific impacts and expected performances of the proposed clean technologies since their early design. In particular, the physical properties of these compounds pose specific issues concerning their safe storage and handling on board (Khakzad et al., 2017). Indeed, the low density and boiling point of these alternative fuels require the use of cryogenic or compressed storage systems (Durbin and Malardier-Jugroot, 2013). However, in the case of mobility solutions characterized by a large power demand, compressed gases may provide an insufficient amount of fuel considering the limits posed by the volume and weight of the fuel storage system. In the case of natural gas, storage as a cryogenic liquid $(\sim 160 \text{ K})$ at atmospheric pressure is identified as the reference technical solution for maritime transportation (Schinas and Butler, 2016). On the

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contrary, storage as a liquefied gas under pressure (\sim 10 bar) at ambient temperature is widely considered the most convenient solution for ammonia-based propulsion systems (Zincir, 2020). In the case of hydrogen, there is not yet agreement in the literature concerning the reference storage system to be used for long-range mobility applications. Besides liquid cryogenic storage at extremely low temperatures (\sim 20 K) (ABS, 2021), Liquid Organic Hydrogen Carriers (LOHCs) are considered alternatives (Møller et al., 2017; Niermann et al., 2019). However, state-of-the-art technologies, based on high molecular weight organic species, result in an energy density per unit mass considerably lower than that of liquid hydrogen. Furthermore, LOHCs require a larger storage system due to the need for additional tanks to collect the exhaust carrier.

Therefore, the large-scale implementation of innovative propulsion technologies based on clean fuels may be hindered by the need to manage specific risks and safety issues, also considering the uncertainties that may affect the safety performance of large-scale storage systems for mobility applications (Correa-Jullian and Groth, 2022). As an example, the effects of peculiar phenomena occurring at extremely low temperatures on the characterization of the accidental release of cryogenic liquids, such as liquid hydrogen, have been only recently recognized (Salzano et al., 2020). Similarly, the utilization of ammonia for maritime propulsion is expected to introduce new safety challenges compared with conventional oil-based solutions, due to the specific combination of toxic, flammable and corrosive hazardous properties (Fan et al., 2021). Therefore, the assessment and comparison of specific safety issues of clean fuels are paramount to promote the development of safe and sustainable mobility solutions for shipping.

The implementation of the inherent safety concept, as defined by Kletz and Amyotte (2010), has emerged as an effective strategy to screen underlying hazards associated with industrial processes (Landucci et al., 2008; Park et al., 2020; Scarponi et al., 2016; Tugnoli et al., 2012). Established methods to assess inherent safety can be of various types, such as index-based approaches, graphical assessment procedures, risk-based assessment techniques, and multi-objective optimization approaches (Sultana and Haugen, 2022). Among the others, approaches based on the evaluation of indices (i.e., index-based approaches) are widely adopted for a straightforward and time-effective evaluation of the performance of technologies from an inherent safety perspective (Roy et al., 2016; Srinivasan and Natarajan, 2012; Zainal Abidin et al., 2018). The effectiveness in screening the hazard of process options is maximized when inherent safety indices are implemented during early design stages (i.e., conceptual and basic design), where alternative design solutions are more easily implemented (Park et al., 2020). In this regard, the PIIS Index (Edwards and Lawrence, 1993), ISI (Heikkilä, 1999), EHS Index (Koller et al., 1999), GreenPro-I (Khan et al., 2002), Life Cycle Index (Khan et al., 2004), Process Route Index (Leong and Shariff, 2009), Process Stream Index (Shariff et al., 2012) and Risk-based Ranking of Hazardous Thermal Chemical (Busura et al., 2014) are examples that proved to be suitable for application in the conceptual design phase (Park et al., 2020; Roy et al., 2016). However, most of these methods are based on the selection of process-specific empirical factors, limiting their application to the chemical and process industry. More recently, a consequence-based quantification of Key Performance Indicators (KPIs) was developed to evaluate the inherent hazard level associated with the use of fossil fuels (e.g., liquefied natural gas, gas oil) for maritime propulsion (Iannaccone et al., 2019). Nevertheless, ship propulsion systems based on clean fuels (e.g., hydrogen, ammonia) show specific safety criticalities, such as the possible generation of toxic clouds, not specifically addressed by the method of Iannaccone et al. (2019). Thus, in the present study, a systematic method to assess the inherent safety performance of clean maritime propulsion concepts is developed, based on the definition and computation of a specific set of KPIs. A Monte Carlo analysis is introduced to manage uncertainty and assess the robustness of the safety ranking obtained. The method was tested by a case study addressing safety issues associated with the

propulsion system of a large-scale maritime vessel. To this aim, reference technical schemes were defined based on a preliminary design of alternative clean propulsion systems. The results obtained from the inherent safety assessment of the alternative propulsion systems considered were compared with a benchmark, consisting of a state-of-the-art propulsion system based on Internal Combustion Engines (ICEs) fueled with Marine Gas Oil (MGO).

In the following, Section 2 presents the methodology developed. Section 3 describes the case study introduced to exemplify the application of the methodology. Section 4 reports the results obtained in the case study. Section 5 provides a discussion of the methodology and results, also reporting some lessons learned from the case study. Section 6 draws some conclusions concerning the methodology and its potential use.

2. Methodology

A methodology suitable for the comparison of the inherent safety performance of different ship propulsion technologies is developed. A schematic representation of the workflow required to apply the methodology is reported in Fig. 1. As shown in the figure, the methodology may be divided into 8 sequential steps, that address three different activities: collection of input data, inherent safety assessment, and comparative analysis of results.

The proposed methodology starts from the collection of technical data from the available literature (Step 1), such as nominal power capacity, fuel demand, and operating conditions of the propulsion systems. These data are strongly related to the class of ship as well as to the type of propulsion system analysed, since geometrical and technical constraints related to the vessel class may exclude low-density storage systems if a large fuel demand is required. Indeed, a preliminary screening on suitable propulsion systems (e.g., internal combustion engines or fuel cells) needs to be carried out for each alternative fuel considered. A reference process scheme is then generated per each alternative propulsion system under analysis, based on the conceptual design of the fuel storage and preparation system. Eventually, energy and material balances are applied to provide the preliminary estimation of fuel inventories processed by the units constituting the propulsion systems (Step 2). The main outcome of the activity referred to as the collection of input data (Steps 1 and 2 in Fig. 1) is thus the development of a reference quantified process flow diagram, including the definition of the main features of the equipment items to be considered in the following steps of the methodology. Concerning the case study introduced in the following, Section 3.2 provides an example of the level of detail of the reference process schemes that are obtained in Step 2 of the methodology.

The inherent safety performance of each propulsion system identified in the previous stages is evaluated through Steps 3–6. Existing methodologies based on the evaluation of the safety fingerprint in early design stages through a set of KPIs (Scarponi et al., 2016; Tugnoli et al., 2009, 2007) are integrated and modified to obtain a systematic approach. The consequences of each scenario are evaluated separately, allowing the assessment and comparison of the contribution of specific hazardous properties (e.g., toxicity and flammability) to the overall safety fingerprint of the investigated systems. The distinction in ship operation modes performed in Step 1 (i.e., maneuvering, at berth, navigation, etc.) allows for the identification of the most stringent conditions, providing input data for the evaluation of the set of inherent safety KPIs which represents the main outcome of the inherent safety assessment activity.

Lastly, a ranking of the safety performances of the alternative propulsion technologies considered is established based on the values computed for the KPIs. The robustness of the outcome of the comparative assessment is verified by a sensitivity analysis carried out by a probabilistic approach aimed at modeling the propagation of the various sources of uncertainty on the values calculated for the inherent safety

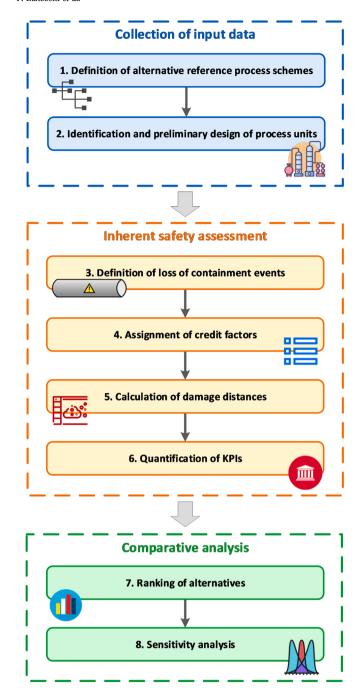


Fig. 1. Flow chart of the methodology developed for the inherent safety assessment of alternative ship propulsion technologies.

indices.

In the following, the specific steps of the procedure are described in detail in a general form.

2.1. Collection of input data

The selection of the ship type to be evaluated and the subsequent collection of its main characteristics are carried out at this stage. More specifically, the ship to be investigated can be selected among various types (e.g., passenger ships and cargo vessels). Technical data intended to provide a minimum level of detail on the ship operation and propulsion system are retrieved: nominal power capacity, fuel demand as well as the duration and power demand of the ship activity. The power demand can be expressed in terms of real-time distribution or averaged

over a period of time for a set of operational modes. Standard operational modes that are typically assumed are navigation, maneuvering and at berth. In case the procedure is applied to an early design stage, real-time distributions may not be available, thus averaged values for power demand can be conveniently implemented.

A matrix of possible combinations among alternative fuels (e.g., hydrogen, ammonia, and natural gas) and propulsion systems (e.g., fuel cell and internal combustion engine) suitable for the selected ship needs to be obtained. The selected power system affects the operational conditions and, subsequently, the auxiliary systems. Thus, based on this input, data on operating conditions (i.e., temperature and pressure), exhaust conditions, and fuel conversion efficiency should be gathered.

Based on the data collected, a reference process scheme specifying the main unit operations involved in fuel storage and preparation is obtained for each alternative propulsion system considered. A preliminary design of each piece of equipment (Step 2) completes the phase of data collection, providing an estimation of the inventories of fuel stored and processed in each reference scheme.

2.2. Inherent safety assessment

In Step 3 of the methodology (see Fig. 1), a set of specific Loss Of Containment events (LOCs) is assigned to each equipment item, based on the reference process scheme defined in Step 2. More specifically, five LOCs were considered (Table 1) as suggested in the literature (Uijt de Haag and Ale, 2005).

A specific criterion considering the average residence time (τ) of the handled fluid was adopted to attribute the relevant LOCs to each equipment item (Scarponi et al., 2016):

$$\tau = \frac{PUFI}{\underset{i}{max} \left(\dot{V}_{i}\right)} \tag{1}$$

where PUFI and \dot{V}_i are, respectively, the volumetric fuel inventory and the volumetric flow rate of the i-th material stream entering or leaving the process unit. More specifically, R1, R2, and R3 are considered for any equipment having τ higher than 180 s, whereas R4 and R5 are assigned in case τ is lower than 180 s

A credit factor is then attributed to each LOC (Step 4 in Fig. 1). Credit factors are baseline values for expected LOC frequency, based on generic data reported in the literature derived from the statistical elaboration of quantitative data on past failure occurrences available for the equipment item of interest. The values of the credit factors may be obtained from specific publications and handbooks (American Petroleum Institute, 2000; Uijt de Haag and Ale, 2005). Examples of values selected for the credit factors of process equipment considered in the case study introduced in the following are reported in Section 3.3.

Credit factors are introduced to assess the credibility of LOCs attributed to the process units considered in the analysis. Such parameters should thus be intended as metrics summarizing the expected safety score of process equipment rather than the actual frequencies of equipment failure. When assigning the credit factors, it is important to remark that the design pressure should also be considered. This is of particular importance in the case of storage tanks, where important differences are present in the typical shell thickness and in the

 Table 1

 Definition of loss of containment events considered in the present study.

Loss Of Containment (LOC)	Symbol
Small leak, continuous release from a 10 mm equivalent diameter hole	R1
Catastrophic rupture, release of the entire inventory in 600 s	R2
Catastrophic rupture, instantaneous release of the entire inventory and release from the full-bore feed pipe	R3
Pipe leak, continuous release from a hole having 10 % of pipe diameter	R4
Pipe rupture, continuous release from the full-bore pipe	R5

equipment layout.

In Step 5 (see Fig. 1), a damage distance, $d_{i,j,k}$, is calculated for each k-th scenario following the j-th LOC considered for the i-th process unit. The damage distances are intended as the maximum distance from the release source at which a physical effect of a given scenario equals a threshold value. Threshold values for fatalities and injuries are reported by several literature sources and handbooks (e.g., see Mannan, 2012 and references cited therein). Table 2 reports the threshold values for fatalities considered in the present study to define the damage distances (Tugnoli et al., 2009, 2007).

Different approaches can be adopted to estimate the time and spatial distribution of physical vectors potentially causing damages (e.g., computational fluid dynamics or integral models). Significant variations in computational requirements, level of details of input and output parameters can be associated with different numerical approaches. Considering the lack of details on geometrical features and three-dimensional layout during the early design steps, the implementation of integral models is recommended in this case due to the low computational costs. For each LOC, the value of the damage distance is assumed as the maximum damage distance obtained considering all the alternative outcomes (pool or jet fire, toxic dispersion, etc.) identified by the event tree technique.

In Step 6 (see Fig. 1), two sets of inherent safety KPIs are calculated from the damage distances and the credit factors obtained in the previous steps of the methodology. The first set of KPIs addresses the performance of the single process units present in each reference scheme, while the second set provides an overall assessment of the expected inherent safety performance of the entire system considered.

The first set is composed of four KPIs to be calculated for each process unit: the Unit Potential hazard Index (UPIi), the Unit inherent Hazard Index (UHI_i), the Unit Flammability inherent Hazard Index (UFHI_i) and the Unit Toxicity inherent Hazard Index (UTHI_i). Table 3 summarizes the definition of each of the unit-based KPIs considered. As shown in the table, the Unit Potential hazard Index (UPI_i) is calculated as the square of the maximum value of damage distance obtained considering all the damage distance values, hi,i, calculated for each LOCi associated to the ith unit of concern. Such indicator may therefore be considered as a measure of the area that could potentially be impacted by the worst-case scenario originating from the considered process unit. The Unit inherent Hazard Index (UHI_i) is calculated as the sum of the products of the credit factor, C_{f,i,i}, and the square of the damage distance, h_{i,i}, assessed for each LOC_i originating from the i-th unit. This indicator is introduced to consider also the likelihood of the LOC events considered for the unit of concern, based on the available operational experience. As shown in Table 3, the Unit Flammability inherent Hazard Index (UFHI_i) and the Unit Toxicity inherent Hazard Index (UTHI_i) are calculated with the same procedure used for the Unit inherent Hazard Index, but considering only the damage distances related to fires/explosions (fi,i) in the case of UFHI_i and related to toxic dispersions (t_{i.i}) in the case of UTHI_i. The latter two KPIs are introduced to provide a more detailed figure of the hazard profile posed by the process unit of concern, delivering a separate assessment of the inherent hazard caused by fires with respect to that caused by toxic dispersions.

The second set of KPIs consists in four metrics that are calculated for

Table 2Typical threshold values for the consequence analysis.

Accident scenario	Threshold value (Effect on humans)
Flash Fire	½ LFL ^a , %vol.
Jet Fire	7 kW/m^2
Pool Fire	7 kW/m^2
Fireball	7 kW/m^2
Vapor Cloud Explosion	0.14 bar
Toxic Cloud	IDLH ^b , ppm

^a LFL, Lower Flammability Limit;

Table 3

Key Performance Indicators (KPIs) employed for the inherent safety assessment of alternative ship propulsion technologies ($h_{i,j}$: maximum damage distance assessed for the LOC_j of the i-th unit, $C_{f,i,j}$: credit factor assessed for the LOC_j of the i-th unit, $f_{i,j}$: maximum damage distance due to fires and explosions assessed for the LOC_j of the i-th unit, $t_{i,j}$: maximum damage distance due to toxic clouds assessed for the LOC_j of the i-th unit).

Key Performance Indicator (KPI)	Formula	
Set 1: Unit-based KPIs Unit Potential hazard Index (m ²)	$UPI_i = max_j \Big(h_{i,j}^2 \Big)$	(2)
Unit inherent Hazard Index (m²/y)	$UHI_i = \sum_j C_{f,i,j} \bullet h_{i,j}^2$	(3)
Unit Flammability inherent Hazard Index (m^2/y)	$UFHI_i = \sum_j C_{f,i,j} \bullet f_{i,j}^2$	(4)
Unit Toxic inherent Hazard Index (m²/y)	$UTHI_i = \sum_j C_{f,i,j} \bullet t_{i,j}^2$	(5)
Set 2: System-based KPIs		
Overall Potential hazard Index (m ²)	$PI = \textstyle \sum_i UPI_i$	(6)
Overall inherent Hazard Index (m ² /y)	$HI = \sum_{i} UHI_{i}$	(7)
Overall Flammability inherent Hazard Index (m ² /y)	$FHI = \sum_{i} UFHI_{i}$	(8)
Overall Toxic inherent Hazard Index (m ² /y)	$THI = \sum_{i}^{n} UTHI_{i}$	(9)

the entire system assessed, considering all the units included in the reference scheme of interest: the overall Potential hazard Index (PI), the overall inherent Hazard Index (HI), the overall Flammability Hazard Index (FHI) and the overall Toxicity Hazard Index (THI). As shown in Table 3, all these KPIs are obtained by summing the values of the corresponding unit-based KPIs considering all the units included in the reference process scheme considered.

2.3. Comparative analysis

Based on the two sets of KPIs obtained, a comparative analysis resulting in a performance ranking is carried out (Step 7 in Fig. 1). Normalization may be applied to improve the comparison among the KPI values. In the case study carried out in the following, internal normalization was applied, dividing each KPI value by the maximum value obtained among the analysed schemes, although alternative approaches may be considered (Norris, 2001).

Sensitivity and uncertainty analyses are then applied to assess the robustness of the results and the inherent safety-based ranking obtained (Step 8 in Fig. 1). Indeed, uncertainty in the assessment of damage distances and in the available credit factors affects the Overall Potential and Inherent Hazard indices resulting from the implementation of the presented method. In the current study, a Monte Carlo method is applied to assess the cumulative probability of modifications in the ranking of alternatives due to variations of the uncertain parameters mentioned above. A confidence interval of \pm 10 % was assumed for the damage distances computed by integral consequence analysis models, whilst variations of the credit factors up to one order of magnitude were considered, according to the typical uncertainty ranges reported in the literature (Crivellari and Cozzani, 2020; Dal Pozzo et al., 2017; Scarponi et al., 2016). All damage distances attributable to the same scenario are set to be equally varied since they derive from the application of the same consequence analysis model. Similarly, the variation imposed on each credit factor is a function of the type of process equipment and LOC considered. Damage distances and credit factors are randomly sampled within the defined ranges and used as input parameters to apply the Monte Carlo technique. A uniform probability distribution function is considered to assess the values of each input parameter within the defined confidence interval since it yields more conservative results in the absence of case-specific data to set up more rigorous distribution functions (e.g. a beta distribution) (Scarponi et al., 2016). The uncertainty analysis is carried out using 106 runs, which are proved to be sufficient to guarantee a robust convergence without employing excessive computation resources. The results are ultimately used to display the robustness of the values obtained for the safety indices presented with respect to the input parameters adopted.

^b IDLH, Immediately Dangerous to Life and Health concentration.

3. Case study

To test the developed methodology, a case study considering a passenger vessel as the reference ship category was analysed. More specifically, the Hyperion-class cruise vessel described in The Maritime Executive (2016) was considered to obtain the input data required in the analysis (Step 1 in Fig. 1).

3.1. General features of the shipping category used for the case study

The selected vessel has an overall nominal power capacity of 36 MW and operates for 10 days during each voyage. Additional characteristics and geometrical features are reported elsewhere (The Maritime Executive, 2016). Table 4 shows the time percentage and average power demand of the ship in each operation mode (i.e., maneuvering, at berth, and navigation), as reported in the literature (Iannaccone et al., 2020).

3.2. Alternative fuels and propulsion systems considered

Propulsion systems based on hydrogen, ammonia and natural gas were identified as alternatives to be analysed. Fuel cells have been proven to be the most effective way to convert the energy carried either by hydrogen or ammonia (McKinlay et al., 2021). Proton Exchange Membrane Fuel Cells (PEMFC) and Solid Oxide Fuel Cells (SOFC) are indicated as the most promising solutions (van Biert et al., 2016). The former is characterized by mild operative conditions (i.e., moderate pressure and temperatures below 400 K), whereas the latter usually operates at higher temperatures (Kim et al., 2020b). The increased temperature favors the cracking of reactants, which is desirable in the case of ammonia since it leads to hydrogen formation. Hence, PEMFC and SOFC are considered for hydrogen and ammonia applications, respectively. Conversely, the current trend for the utilization of liquefied natural gas (LNG) for energy supply suggests the on-board gasification and the combustion of natural gas in single or dual-fuel engines (Cheenkachorn et al., 2013; Wei and Geng, 2016). Thus, an LNG-based Lean Burn Spark Ignition (LNG-LBSI) is considered in the analysis. Eventually, a conventional propulsion scheme based on MGO is considered as the benchmark.

For the sake of simplicity, the investigated fuels are modeled as pure hydrogen, pure ammonia, pure methane and pure n-nonane, respectively. Considering the energy and mass density of the investigated species at typical storage conditions (Rao et al., 2014), cryogenic liquid storage was considered for both $\rm H_2$ and LNG, while liquefied compressed storage was considered for NH₃ (ABS, 2021, 2020; Iannaccone et al., 2020, 2019).

The overall amount of fuel to be stored was estimated for each reference scheme considering 10 days of continuous operation and the data reported in Table 4 for ship time activity and power requirement. The total amount of fuel was assumed to be split into tanks of equal volume, specifically $1200 \, \text{m}^3$ for H_2 , LNG and LNH $_3$ and $400 \, \text{m}^3$ for MGO (Fan et al., 2021; Iannaccone et al., 2020). The resulting number of storage vessels was equal to 3 for H_2 and LNG, 4 for LNH $_3$, and 5 for MGO. Table 5 summarizes the operating conditions, flow rates of the processed material streams and inventories estimated for the relevant equipment in each reference scheme. The calculation of the inventory of the fuel was based on the overall energy required (E_{req}) over the time of ship activity (t_{act}), which can be calculated as follows:

Table 4Breakdowns of the ship time activity and power requirement by type of vessel activity.

Activity	Activity time (%)	Power consumption [MW]
Maneuvering	3	17.1
At berth	44	10.8
Navigation	53	19.8

$$E_{req} = \int_{0}^{t_{act}} Pdt$$
 (10)

where P is the required power at a given time of activity of the considered ship. The overall mass inventory of stored fuel, M, is therefore computed as:

$$M = \frac{E_{\text{req}}}{\eta \bullet \Delta H_c} \tag{11}$$

where η and ΔH_c are the conversion efficiency and heat of combustion of the fuel, respectively. The volume to be provided by the storage tanks may additionally be computed at this point by knowing the density of the fuel and obtaining the maximum filling coefficient by technical standards.

The reference process schemes considered in the case study are shown in Fig. 2 and are described in detail in section S1 of the Supplementary material.

3.3. Inherent safety KPIs calculation

In the case study, average residence times resulted larger than 180 s for all the storage tanks, exclusively. Therefore, LOCs were associated with each equipment item following the posed criterion (see Eq. 1). Tanks handling cryogenic liquids at atmospheric pressure were assumed to present geometric features similar to those of pressurized storage vessels due to the required thickness of the shell. However, it should be noted that the contact with hydrogen at extremely low temperatures may also promote the embrittlement of the shell material, thus potentially increasing the likelihood of corresponding failure modes (Li et al., 2022). Hence, credit factors associated with atmospheric storage vessels were conservatively assumed for this type of equipment, as shown in Table 6.

Since the case study addresses the assessment of alternative propulsion technologies in the early design step, conventional integral models (van den Bosch and Weterings, 1997) were selected to carry out the consequence analysis of the outcomes of each LOC. More specifically, the consequence analysis models included in the Phast v.8.4 (DNV GL, 2021) software were applied to calculate the damage distances in Step 5 of the methodology, according to the procedure described in Section 2.2. Clearly enough, other software tools and other models for consequence assessment may be selected to carry out this step. To minimize the uncertainty introduced by integral consequence analysis models in the near field regions, the effective value considered for each damage distance was set to the maximum between the estimate given by the software and 5 m.

An average wind speed equal to 2 m/s and a Pasquill atmospheric stability class F were assumed as reference environmental conditions.

4. Results

Fig. 3 reports the unit and overall inherent safety indices calculated for each of the reference schemes considered in the present study. Details on the LOCs considered, the credit factors attributed, the damage distances calculated and the inherent safety KPIs values calculated for all the critical equipment items in the propulsion systems under analysis are reported in the Supplementary material.

As shown in Fig. 3a, storage tanks turn out to be the units scoring the highest hazard potential, regardless of the reference scheme considered. This is due to the hold-up of hazardous materials, always higher than other equipment items. As a matter of fact, the value of the overall potential hazard index of each scheme is mostly determined by the contribution of the fuel storage tanks.

When computing the unit inherent hazard indices, credit factors apply to the identified reference failure modes. The inclusion of such parameters in the analysis allows to assess the influence of the expected

Table 5Operating conditions for the alternative ship propulsion systems.

Scheme 71. Trydrogen-ruch	ed proton exchange meml	Dialie Ittel Cell (H2-PEIVI	FC)						
Process unit	Storage tank	Pump		Vaporizer	Heat	er BOG he	ater	BOG compressor	
(D01-D03) (G0		(G01)			(E02) (E03			(P01)	
Nominal capacity (m ³)	1200	-		-	-	-		-	
Inventory (t)	79.72	-		-	-			-	
Flow rate (kg/s)	-	0.21		0.21	0.21	7.1×1	7.1×10^{-2}		
Pressure (MPa)	0.10	0.35		0.35	0.35	0.35 0.10		0.35	
Temperature (K)	20.61	20.75		25.39	343.	15 222.53		343.15	
Fuel state	Liquid	Liquid		Vapor	Vapo	or Vapor		Vapor	
Scheme B: Ammonia-fuel	ed Solid Oxide Fuel Cell (I	NH ₃ -SOFC)							
Process unit	Storage tank			Vaporizer		Heater			
	(D01-D04)			(E01)		(E02)			
Nominal capacity (m ³)	1200			-		-			
Inventory (t)	620.18			-		-			
Flow rate (kg/s)	-			2.87		2.87			
Pressure (MPa)	0.86			0.86		0.86			
Temperature (K)	293.15			293.15		874.16			
Fuel state	Liquid			Vapor Vapor					
Scheme C: Liquefied Natu	ıral Gas-based Lean Burn S	Spark Ignition (LNG-LBS	SI)						
Process unit									
Process unit	Storage tank	Pressure build-up un	nit Vaporize	r		Fuel ga	s heater	BOG heater	
Process unit	Storage tank (D01-D03)	Pressure build-up un (E01-E03)	nit Vaporize (E04)	r		Fuel ga (E05)	s heater	BOG heater (E06)	
Nominal capacity (m ³)	•		-	r			s heater		
Nominal capacity (m ³)	(D01-D03)		-	r			s heater	(E06) - -	
Nominal capacity (m ³) Inventory (t)	(D01-D03) 1200		-	r			s heater		
Nominal capacity (m ³) Inventory (t) Flow rate (kg/s)	(D01-D03) 1200	(E01-E03)	(E04) - -	r		(E05) - -	s heater	(E06) - -	
Nominal capacity (m ³) Inventory (t) Flow rate (kg/s) Pressure (MPa)	(D01-D03) 1200 495	(E01-E03) 0.20	(E04) - - 1.62	r		(E05) - - 1.62	s heater	(E06) 6.96 × 10 ⁻³	
Nominal capacity (m³) Inventory (t) Flow rate (kg/s) Pressure (MPa) Temperature (K)	(D01-D03) 1200 495 - 0.60	(E01-E03) 0.20 0.60	(E04) 1.62 0.60	r		(E05) - - 1.62 0.60	s heater	(E06) 6.96 × 10 ⁻³ 0.60	
Nominal capacity (m³) Inventory (t) Flow rate (kg/s) Pressure (MPa) Temperature (K) Fuel state	(D01-D03) 1200 495 - 0.60 140	(E01-E03) 0.20 0.60 143 Vapor	(E04) 1.62 0.60 150	r		(E05) - - 1.62 0.60 293	s heater	(E06) - - 6.96 × 10 ⁻³ 0.60 293	
Nominal capacity (m³) Inventory (t) Flow rate (kg/s) Pressure (MPa) Temperature (K) Fuel state Scheme D: Conventional	(D01-D03) 1200 495 - 0.60 140 Liquid	(E01-E03) 0.20 0.60 143 Vapor ne Gas Oil (MGO)	(E04) 1.62 0.60 150	Feed pump (G02)	Heater (E01)	(E05) - - 1.62 0.60 293	s heater Heater (E02)	(E06) - - 6.96 × 10 ⁻³ 0.60 293	
Nominal capacity (m³) Inventory (t) Flow rate (kg/s) Pressure (MPa) Temperature (K) Fuel state Scheme D: Conventional Process unit	(D01-D03) 1200 495 - 0.60 140 Liquid technology based on Mari	(E01-E03) - 0.20 0.60 143 Vapor ne Gas Oil (MGO) Transfer pump (G01)	(E04) 1.62 0.60 150 Vapor	Feed pump		(E05) 1.62 0.60 293 Vapor Service tank	Heater	(E06) 6.96 × 10 ⁻³ 0.60 293 Vapor	
Nominal capacity (m³) Inventory (t) Flow rate (kg/s) Pressure (MPa) Temperature (K) Fuel state Scheme D: Conventional Process unit Nominal capacity (m³)	(D01-D03) 1200 495 - 0.60 140 Liquid technology based on Marie Storage tank (D01-D05)	(E01-E03)	(E04) 1.62 0.60 150 Vapor Settling tank (D06-D07)	Feed pump (G02)		(E05) 1.62 0.60 293 Vapor Service tank (D08-D09)	Heater	(E06) 6.96 × 10 ⁻³ 0.60 293 Vapor	
Nominal capacity (m³) Inventory (t) Flow rate (kg/s) Pressure (MPa) Temperature (K) Fuel state Scheme D: Conventional Process unit Nominal capacity (m³) Inventory (t)	(D01-D03) 1200 495 - 0.60 140 Liquid technology based on Marie Storage tank (D01-D05)	(E01-E03)	(E04) - 1.62 0.60 150 Vapor Settling tank (D06-D07) 25	Feed pump (G02)		(E05) 1.62 0.60 293 Vapor Service tank (D08-D09) 25	Heater	(E06) 6.96 × 10 ⁻³ 0.60 293 Vapor	
Nominal capacity (m³) Inventory (t) Flow rate (kg/s) Pressure (MPa) Temperature (K) Fuel state Scheme D: Conventional Process unit Nominal capacity (m³) Inventory (t) Flow rate (kg/s)	(D01-D03) 1200 495 - 0.60 140 Liquid technology based on Marie Storage tank (D01-D05) 400 293.4	(E01-E03) - 0.20 0.60 143 Vapor ne Gas Oil (MGO) Transfer pump (G01) - 1.78	(E04) - 1.62 0.60 150 Vapor Settling tank (D06-D07) 25	Feed pump (G02)	(E01) - -	(E05) 1.62 0.60 293 Vapor Service tank (D08-D09) 25	Heater (E02)	(E06) 6.96 × 10 ⁻³ 0.60 293 Vapor Booster pun (G03)	
Nominal capacity (m³) Inventory (t) Flow rate (kg/s) Pressure (MPa) Temperature (K) Fuel state	(D01-D03) 1200 495 - 0.60 140 Liquid technology based on Marin Storage tank (D01-D05) 400 293.4	(E01-E03) - 0.20 0.60 143 Vapor ne Gas Oil (MGO) Transfer pump (G01) - 1.78 0.35	(E04) - 1.62 0.60 150 Vapor Settling tank (D06-D07) 25 20.0	Feed pump (G02) - - 1.78	(E01) - - 1.78	(E05) 1.62 0.60 293 Vapor Service tank (D08-D09) 25 20.0 -	Heater (E02) - - 1.78	(E06) 6.96 × 10 ⁻³ 0.60 293 Vapor Booster pum (G03) 1.78	

equipment safety performance on the final safety ranking of the units. It is evident from Fig. 3b that the UHI metric turns out to produce a different pattern in the inherent safety profiles of the equipment items. Indeed, heat exchangers become the most hazardous equipment when considering Scheme B and Scheme D. This trend can be attributed to the high credibility of the LOCs (i.e., R4 and R5) considered for this type of process unit. It is also worth remarking that the UPI values associated with storage tanks in schemes involving cryogenic fuels are quite similar. Conversely, the UHI value obtained for Scheme A (cryogenic hydrogen storage) is significantly higher than that related to Scheme C (cryogenic storage of LNG). The differences among these KPIs are particularly high given the assumptions posed for the LH2 tanks. Indeed, the specific storage conditions, materials, and layout may have a significant impact on failure mechanisms (Li et al., 2022) and thus on the credit factors to be used.

Auxiliary equipment with a high recorded failure rate (e.g., pumps, compressors, heat exchangers) may significantly undermine the overall inherent safety performance of a given propulsion system. This is particularly evident when considering the HI and UHIs of Scheme D. Indeed, the presence of multiple heat exchangers and pumps in the MGO-based propulsion concept leads to a lower safety performance in terms of HI than Scheme C (LNG-LBSI), even if the PI of Scheme D is more than one order of magnitude lower than that of Scheme C.

Fig. 4 shows the relative contribution of accident scenarios to the overall inherent safety KPIs of the reference propulsion systems examined. It is worth noting that the PI related to each reference propulsion scheme is determined by a single scenario. However, the most hazardous

scenario is different.

When cryogenic fuels are considered, in the case of Scheme A (H2-PEMFC) the PI is mostly affected by Flash Fire (FF), while in the case of Scheme C (LNG-LBSI) the PI is mostly influenced by Vapor Cloud Explosion (VCE). This discrepancy can be attributed to the difference in the flammability range of the fuels, which affects the damage distances of FF, as well as in the difference in the mass density resulting in a lower overall amount of energy available for VCE in the case of hydrogen. These aspects are particularly remarkable if the maximum reactivity, typically evaluated as the fundamental laminar burning velocity at the storage conditions, is compared for these fuels. Indeed, according to the typical classification (Baker et al., 1983) and data from the current literature (Pio and Salzano, 2018), hydrogen and natural gas should be considered respectively as high and low reactive species. Due to the low reactivity of methane, the occurrence of a VCE, once LNG is released, is likely to occur only for specific compositions and elevated congestion levels (Gavelli et al., 2011). In this perspective, the effects of VCE on the risk picture of Scheme C are very low, especially during a navigation phase where the level of congestion outside the ship may be limited.

In the case of Scheme B (NH₃-SOFC), a negligible contribution from scenarios different from a Toxic Cloud (TC) can be observed for both PI and HI. When neglecting toxicity, the PI is ruled by Fireball (FB), due to the high lower flammability limit of ammonia. Conversely, Jet Fire (JF) has a large share in the case of HI, since this scenario can derive from LOCs more credible than those from which FB originates. Eventually, Pool Fire (PF) turns out to be relevant only for Scheme D (MGO).

Fig. 5 reports a radar plot summarizing the main outcomes of the

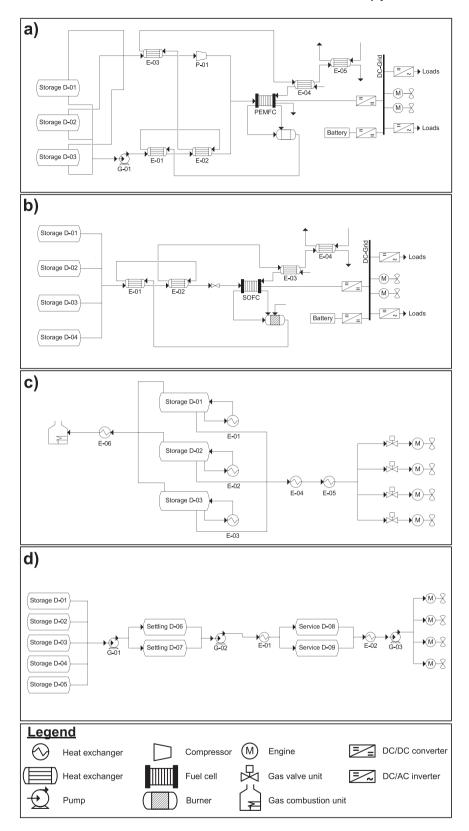


Fig. 2. Reference process schemes for the alternative ship propulsion systems considered: a) Hydrogen-fueled Proton Exchange Membrane Fuel Cell (H₂-PEMFC); b) Ammonia-fueled Solid Oxide Fuel Cell (NH₃-SOFC); c) Liquefied Natural Gas-based Lean Burn Spark Ignition (LNG-LBSI); d) Conventional technology based on Marine Gas Oil (MGO).

Table 6
Loss of Containment events (LOCs) and corresponding credit factors (1/y) associated with the typologies of process equipment relevant to the present study (n.a., not applicable; n.c., not considered).

Loss Of Containment (LOC)	Pressurized storage vessel	Cryogenic/Atmospheric storage vessel	Shell and tube heat exchanger	Compressor	Pump
R1: small leak, continuous release from a $10~\mathrm{mm}$ equivalent diameter hole	1×10^{-5}	1×10^{-4}	n.c.	n.a.	n.a.
R2: catastrophic rupture, release of the entire inventory in 600 s	$5 imes 10^{-7}$	$5 imes 10^{-6}$	n.c.	n.a.	n.a.
R3: catastrophic rupture, instantaneous release of the entire inventory and release from the full-bore feed pipe	5×10^{-7}	5×10^{-6}	n.c.	n.a.	n.a.
R4: pipe leak, continuous release from a hole having 10% of pipe diameter	n.c.	n.c.	$1 imes 10^{-3}$	1×10^{-3}	5×10^{-4}
R5: pipe rupture, continuous release from the full-bore pipe	n.c.	n.c.	5×10^{-5}	1×10^{-4}	1×10^{-4}

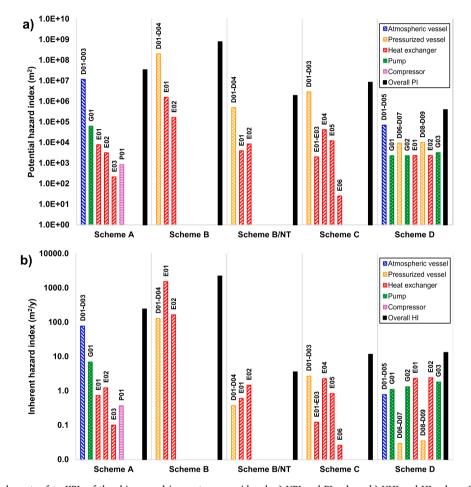


Fig. 3. Unit and overall inherent safety KPIs of the ship propulsion systems considered: a) UPI and PI values; b) UHI and HI values. Scheme B/NT excludes the damage distances of the toxic dispersions in Scheme B, only considering fire and explosion hazards.

analysis of the case study. The radar plot includes the normalized values of the PI, HI, THI and FHI indices, as well as the maximum UHI and UPI values recorded in each scheme. Internal normalization was applied, dividing each KPI value by the maximum value recorded for the KPI of interest among the four alternative systems considered. Thus, the figure provides a detailed fingerprint of the hazards related to the four systems compared. Clearly enough, a lower area in the radar plot corresponds to a higher expected safety performance of the propulsion system.

Thus, as shown in Fig. 5, Scheme B (NH_3 -SOFC) presents the worst inherent safety performance, featuring the highest values of all the KPIs considered, except for the overall Flammability Hazard Index (FHI) where a higher value is calculated for Scheme A.

It is clear from Fig. 5 that the conventional fuel propulsion system (Scheme D, based on MGO) scores the lowest potential hazard finger-print, thus the highest safety score, while Scheme C (LNG-LBSI) scores

slightly higher values of the KPI. However, it should be remarked that, while Scheme D features lower scores of the $\mathrm{UPI}_{\mathrm{max}}$ and PI with respect to Scheme C, the introduction of credit factors modifies the picture. In particular, the radar plot in Fig. 5 highlights that the ranking between Scheme C (LNG-LBSI) and Scheme D (MGO) is inverted when considering HI, with Scheme D featuring a higher value of this index with respect to Scheme C, as shown also in Fig. 3, where the non-normalized values of HI are reported. This is caused by the high number of auxiliary equipment, such as intermediate heaters and processing pumps, required in the MGO propulsion system, increasing the value of the overall inherent hazard posed by this propulsion system.

Comparing the values of the Potential and inherent Hazard Indices (HI and PI) for cryogenic solutions (Scheme A and Scheme C), it is possible to infer that the safety performance of Scheme A (H₂-PEMFC) is currently limited by a poor understanding and control of the interactions

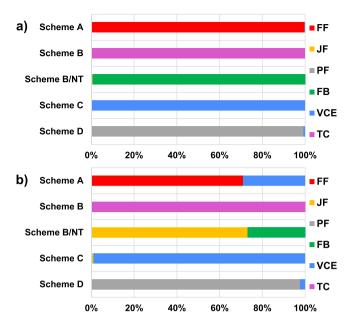


Fig. 4. Relative contribution of different scenarios to the inherent safety KPIs for the reference ship propulsion systems considered: a) potential hazard index, PI; b) inherent hazard index, HI (FF, Flash Fire; JF, Jet Fire; PF, Pool Fire; FB, Fireball; VCE, Vapor Cloud Explosion; TC, Toxic Cloud). The values reported for Scheme B/NT were calculated from those of Scheme B excluding the contribution of toxic dispersion scenarios.

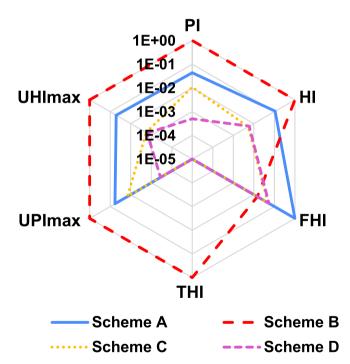


Fig. 5. Comparative assessment of the inherent safety performance of the four reference ship propulsion schemes considered.

between hydrogen and vessel materials at low temperatures, that imposes the selection of high values for the credit factors of LOC events in this scheme. Hence, further advances in the development and establishment of materials suitable for long-term use of cryogenic applications may greatly enhance the safety fingerprint of the concept (Qiu et al., 2021).

Fig. 6 reports the results of the sensitivity and uncertainty analysis performed on the overall potential and inherent hazard indices of the $\frac{1}{2}$

alternative propulsion schemes considered. The methodology described in Section 2.3 (Step 8 in Fig. 1) was applied. Since the PI and HI indices provide key information to rank the inherent safety performance of alternatives, it is paramount to assess the extent to which uncertainty in the evaluation of credit factors and damage distances may affect the calculation of such KPIs and thus the ranking among propulsion systems. The outcome of the Monte Carlo technique is presented in Fig. 6 plotting the cumulative probability curves of the differences among the overall KPIs of the alternative clean fuel-based systems (Scheme A, Scheme B and Scheme C) with respect to the benchmark option based on MGO (Scheme D), considered as the baseline.

According to the ranges assumed for the uncertainty of the damage distances and credit factors (see Section 2.3), variations in the ranking among alternatives are extremely unlikely when adopting a metric based on PI (Fig. 6a). Similar results are obtained also when the sensitivity analysis with respect to damage distances is applied to the HI values of alternatives, as shown in Fig. 6b. Indeed, also in this case, there is not any intersection among the curves and none of the cumulative probability functions assumes a zero value. This implies that there is no modification in the reported ranking when considering only the model uncertainty associated with damage distances. Such observation suggests that the comparison of propulsion systems only according to their hazard potential is weakly affected by the uncertainties associated with the conventional consequence assessment models.

On the contrary, the evaluation of the uncertainty associated with credit factors may produce changes in the final ranking. In particular, the difference $\rm HI_C-\rm HI_D$ becomes zero when cumulative probability equals 92 % if only credit factors are modified (Fig. 6c) and when cumulative probability equals 91 % if the uncertainty associated with damage distances and credit factors is considered simultaneously (Fig. 6d). In other words, there is a cumulative probability of respectively 8 % and 9 % that the MGO-based system (Scheme D) may results inherently safer than the LNG-fueled lean burn spark ignition option (Scheme C), thus altering the HI-based ranking. Thus, very limited differences are present in the HI values of the two propulsion systems, well within the range of the uncertainty associated with the consequence analysis models and the credit factors.

The results of the sensitivity analysis (see Fig. 6a) confirms the lower safety performance in terms of PI of Scheme C (LNG-LBSI) with respect to Scheme D (MGO). Hence, the risk control measures and inherently safer design in LNG-based systems are indicated as critical strategies to equal the state-of-the-art benchmark technologies such as MGO-based propulsion systems.

5. Discussion and lessons learned

The results obtained provide important insights for the practical understanding of the investigated systems. Figs. 3, 5 and 6 report specific sets of KPIs providing a systematic tool to rank the overall inherent hazard and to identify the criticality of the different units in the propulsion systems. The introduction of specific indicators targeting different types of dangerous phenomena for humans also allows identifying the more critical accident scenarios.

In particular, tanks for on-board fuel storage result the most critical units in determining the overall Potential hazard Index (PI), due to the wide area that could be affected by accident scenarios originating from such units.

When introducing credit factors in the analysis, heat exchangers emerge as critical items due to the tendency to leak recorded in the current experience for such units (Uijt de Haag and Ale, 2005). More in general, the safety performance of the propulsion systems may be significantly compromised by the presence of a high number of secondary equipment (e.g., pumps, compressors and heat exchangers) intrinsically prone to loss of containment, as demonstrated in the case of the MGO-based option.

Results from the comparative inherent safety assessment of

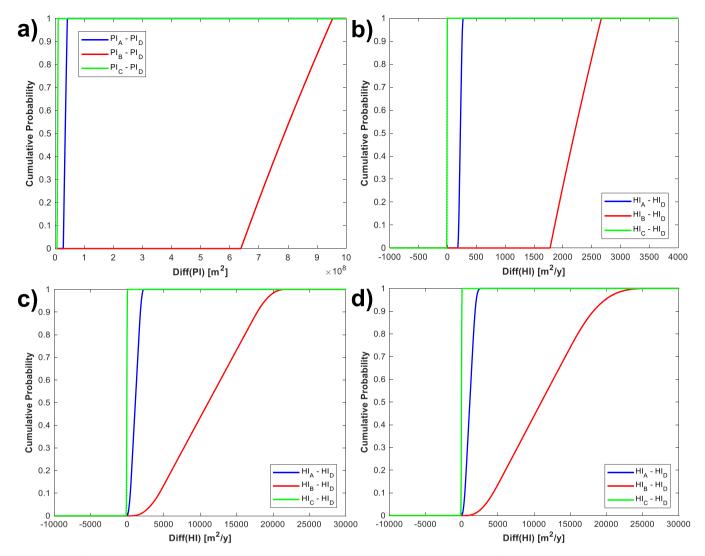


Fig. 6. Results of the sensitivity analysis for the overall inherent safety KPIs in terms of the cumulative probability of the difference among the overall KPIs calculated for each clean fuel-based reference scheme (Schemes A to C) and the MGO benchmark (Scheme D). Cumulative probability calculated for: a) the PI index only considering variations in the damage distances; b) the HI index only considering variations in the damage distances; c) the HI index considering variations in the credit factors; d) the HI index considering both variations in the damage distances and in the credit factors. Damage distances and credit factors varied within the ranges of 90 %— 110 % and 10 %— 1000 %, respectively.

alternatives when considering credit factors indicate that LNG-based solutions have a safety fingerprint similar to that of conventional systems based on MGO, most likely leading to an enhanced safety performance provided that appropriate safety barriers and safety systems are applied. This may be attributed to the simpler design of lean burn spark ignition technologies relying on LNG, which turns out not to be penalized by the presence of multiple low-safety performance equipment items.

Conversely, the adoption of NH_3 -based solutions produces an increase of up to three orders of magnitude of the calculated KPIs with respect to the benchmark (Scheme D, MGO). This variation is mostly related to ammonia toxicity, which yields significantly higher damage distances in case of accidental releases of NH_3 . The high inherent hazard associated with ammonia suggests that in the further development of such systems the complexity and cost of risk control measures may significantly impact the sustainability of such technologies.

The hydrogen-based propulsion scheme investigated (Scheme A, H₂-PEMFC) scores a larger HI value than the LNG-based scheme (Scheme C, LNG-LBSI), although the values of the PI are comparable for the two schemes. This implies that the selection of suitable technologies characterized by lower credit factors for the loss of containment events

considered may lead to a relevant improvement in the performances of hydrogen-based solutions. Therefore, further investigation on specific safety barriers and safety systems, as well as on the behavior of solid materials used for equipment items operating at extremely low temperatures is recommended, especially for those handling cryogenic liquid H_2 , to strengthen the evaluation of the safety score of such critical units.

It should also be remarked that the results obtained in the present study may be useful to integrate safety issues in a broader sustainability assessment, considering also the economic and environmental performance of the alternative propulsion schemes, as successfully demonstrated by previous studies targeting chemical production processes (Crivellari et al., 2021; Tugnoli et al., 2008, 2011) and marine fuel supply chains (Jannaccone et al., 2020).

Eventually, it should be pointed out that the method developed, which is conceived as a tool supporting decision-making during early design stages, is intended to integrate and not at all to replace detailed quantitative risk assessment approaches, that should be implemented during detailed design steps. Indeed, the KPIs defined may be considered effective metrics allowing for a preliminary screening of inherent hazards. The KPIs are also useful to identify the most safety-critical elements

that can be addressed in the following design stages, where more detailed data are available, allowing the application of conventional methods for risk assessment and management.

6. Conclusions

A comparative analysis of the inherent safety performances of alternative technological concepts proposed for clean marine propulsion applications was carried out. In particular, propulsion concepts based on liquid hydrogen, liquid ammonia, and liquefied natural gas were investigated and compared with a state-of-the-art technology based on marine gas oil.

The results of a case study show that technologies based on LNG have safety performances similar to the MGO benchmark. Conversely, $\rm LH_2$ safety performance is currently limited by the lack of mature technologies for its safe storage whilst the safety of LNH $_3$ -based applications is affected by the toxicity of ammonia.

The results proved the effectiveness of the approach in providing a preliminary ranking of the inherent hazard of alternative propulsion concepts, and in identifying safety-critical units, both considering the potential hazard and the recorded safety performance and leak proneness.

Overall, the method proposed, based on limited data usually available in an early design stage, is a tool that may provide crucial support to orient further developments of safe and sustainable propulsion concepts, focusing on the specific safety issues posed by innovative solutions and technologies proposed for maritime propulsion.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.psep.2023.05.018.

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