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Hazard footprint of alternative fuel storage concepts for hydrogen-powered urban buses

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ABSTRACT

Hydrogen mobility is a powerful strategy to fight climate change promoting the decarbonization of the transportation sector. However, the higher flammability of hydrogen in comparison with traditional fuels raises issues concerning the safety of hydrogen-powered vehicles, in particular when urban mobility in crowded areas is concerned. In the present study, a comparative analysis of alternative hydrogen storage concepts for buses is carried out. A specific inherent safety assessment methodology providing a hazard footprint of alternative hydrogen storage technologies was developed. The approach provides a set of ex-ante safety performance indicators and integrates a sensitivity analysis performed by a Monte Carlo method. Integral models for consequence analysis and a set of baseline frequencies are used to provide a preliminary identification of the worst-case credible fire and explosion scenarios and to rank the inherent safety of alternative concepts. Cryo-compressed storage in the supercritical phase resulted as the more hazardous storage concept, while cryogenic storage in the liquid phase at ambient pressure scored the highest safety performance. The results obtained support risk-informed decision-making in the shift towards the promotion of sustainable mobility in urban areas.

1. Introduction

Hydrogen is considered a promising alternative for the replacement of hydrocarbons in the near future. It is foreseen to play a key role in the decarbonization of the hard-to-abate sectors, such as heavy industry, shipping, aviation, and heavy-duty transport, where other mitigation measures are difficult to implement [1]. Due to the strong dependence on hydrocarbon-based fuels, transportation is proven to be the second largest contributor to global greenhouse gas (GHG) emissions [2]. The development of a sustainable transport system relies on decarbonization strategies, based on the introduction of zero or low emissions fuels, such as hydrogen, vehicle electrification, and the switch toward more environmentally friendly transport practices. Buses are the predominant public transport mode and already cover most of the mass transport needs (63% of the share) [3]. However, around 80% of them are still powered by hydrocarbons and only 17% are electric [3]. From the beginning of this century, the interest in buses powered by hydrogen has continuously grown, driven by the high reduction of GHG emissions that may be achieved [3]. The competitiveness of these zero-emission vehicles within the current market (i.e., diesel and natural gas-powered buses) and their fast deployment is hampered by barriers of different nature. One of the main challenges is the onboard storage of the fuel, which requires the application of technologies able to increase the hydrogen density, allowing to transport a sufficient amount of fuel (40 kg of hydrogen is needed for a driving range of 500 km). The US Department of Energy (DOE) has established challenging targets for the gravimetric and volumetric capacity of hydrogen storage technologies (7.5% wt% and 70 g/L respectively) [4]. The concepts more frequently proposed are compressed and liquefied storage. However, they both suffer from limitations. Compressed hydrogen (CH2) tanks (350-700 bar) are usually expensive due to the high design pressure requiring the use of high amounts of costly materials (e.g., metals and composites). In the case of liquefied hydrogen (LH2), the evaporative loss (the so-called boil-off-gas, BOG) caused by the inevitable heat exchanges with the surrounding environment needs to be managed. To prevent the undesired pressurization of the storage vessel, the BOG must be removed, with a possible loss of fuel. Furthermore, liquefaction is a high energy demanding and expensive process [5]. Cryo-compression is an emerging concept that derives from the coupling of the two above-described storage technologies and combines the advantages of both. Cryogenic pressure vessels are designed to withstand high pressure and cryogenic temperatures, storing hydrogen (CcH2) at densities typically higher than

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those of CH2 and LH2, up to 80 kg/m^3 [6].

The technological challenges concerning the fuel storage concept also influence the safety of hydrogen-powered vehicles, due to the hazardous properties of hydrogen. Compared to hydrocarbons, hydrogen has wider flammability and detonability ranges and it is much easier to ignite (its minimum ignition energy of 0.02 mJ is one order of magnitude lower than for hydrocarbons) [7]. Consequently, an accidental leak from the storage system is likely to cause a fire and/or an explosion, resulting in hazardous intensities of thermal radiations or deadly blast waves. The use of hydrogen in the transportation sector is far from consolidated and studies on the safety of hydrogen-powered buses are still limited. Most of the studies available in the literature focus on hydrogen releases in enclosed or poorly ventilated spaces (i.e., tunnels, garages, roofed parkings) which rise specific concerns due to the risk of fire, deflagration, and detonation following the formation of a confined or partially confined flammable gas cloud. Full-scale experimental tests were carried out in garages to assess the effect of the presence of the vehicles on deflagrations and hydrogen dispersion [8,9]. CFD was used to model hydrogen deflagration inside tunnels in homogenous stoichiometric [10] and near stoichiometric [11] hydrogen-air mixtures and to analyze releases from pressure relief devices installed on vehicles [12–14]. Numerical approaches were also applied to assess the effect of release characteristics (e.g., the position of the leak and the flow rate) on the hydrogen cloud dispersion in garages [15–17]. Further studies addressed the optimization of the blowdown from thermal pressure relief devices (TPRDs) for hydrogen-powered heavy-duty vehicles and trains inside tunnels in case of fire [18]. Similar studies were carried out considering hydrogen releases in open spaces. Liu and Christopher [19] analyzed the release of hydrogen following an accidental leak from the storage tank of fuel cell vehicles. Qian et al. [20] carried out a CFD analysis on unintended hydrogen releases in hydrogen refueling stations. Among the safety-related studies on hydrogen vehicles, only a few focused on hydrogen-powered buses. A specific study investigated hydrogen dispersion and explosion following an accidental release from a storage tank (350 bar) on board a CH2 city bus (40 kgH_2 stored in 8 cylinders) in a tunnel by CFD simulation [10]. The results were compared to those obtained from a similar simulation carried out on a CNG city bus (storage pressure of 200 bar and 104 kg of fuel stored in four cylinders). Similarly, high-pressure hydrogen releases (200, 350, and 700 bar) from the PRVs of urban bus storage systems were investigated by Venetsatos et al. [13] and compared to CNG leaks, considering dispersion and combustion. More recently, Kim et al. [14] carried out a specific risk assessment considering fire scenarios arising from hydrogen leaks from TRPDs with the software HyRAM.

Although valuable information can be derived from experimental and numerical studies, the case-specific nature of such studies (e.g with respect to Refs. [10,13,14]) represents an obstacle to the generalization of their outcomes. This aspect is of particular relevance when the comparison among alternative concepts is considered in decision-making. To date, a thorough comparative assessment of the safety issues introduced by the adoption of different storage concepts is not present in the literature. A comparison of the safety performance of alternative hydrogen storage concepts to benchmarks, as the storage concepts adopted for fossil fuels in heavy-duty vehicles (e.g., diesel fuel storage and Liquefied Natural Gas, LNG, storage), is still lacking.

In the present study, the inherent safety of alternative hydrogen storage concepts is assessed. Different hydrogen storage technologies (compression, liquefaction, and cryo-compression) are considered in the analysis. A benchmarking to conventional fuel storage solutions currently adopted for buses, as diesel, Compressed Natural Gas (CNG), and LNG storage tanks is also carried out.

The different Technology Readiness Level (TRL) of the storage concepts analyzed in the present study precludes the possibility of applying a thorough and detailed Quantitative Risk Assessment (QRA) to all the alternative storage solutions considered. Such type of assessment is applicabile only to the more mature technologies, such as diesel and CNG storage tanks, while it is not possible to use it for the assessment of the new and lower TRL hydrogen storage concepts, for which limited design details are presently available for the foreseen future full-scale commercial solutions.

In this perspective, a comparison based on inherent safety principles is a valuable support to decision-makers in the selection of hydrogen storage concepts for the introduction of hydrogen in safety-critical transportation sectors, such as bus mobility in crowded urban areas. Inherent safety principles were first introduced by Kletz [21] to eliminate (or drastically reduce) hazards in the early process design stages of industrial technologies and processes. Their application promotes an informed selection among alternative design concepts, which shall be based on the minimization of inventories, the substitution of hazardous materials, the attenuation of process conditions, the elimination of the effects, and the simplification of processes.

Thus, with the aim of comparing the safety performance of the above-mentioned hydrogen storage technologies, an inherent safety assessment method is applied. Among the numerous approaches available in the literature and reviewed in Section 2, a consequence-based methodology suitable for the comparative assessment of alternative technology concepts with different TRLs originally proposed by Tugnoli et al. [30] was adopted. The original method was extended and modified to allow its application to heavy-duty vehicles and to perform the assessment of key hazardous features specific to hydrogen fuel storage systems. The methodology allows obtaining a specific set of ex-ante inherent safety Key Performance Indicators (KPIs), overcoming the issue posed by the scarce availability of data for hydrogen storage concepts. The hazards and potential damages deriving from fuel leaks due to technical failures and road crashes are addressed.

The set of KPIs obtained from the application of the method provides a metric to compare the different storage options analyzed and assess their hazard footprint, thus obtaining an inherent safety ranking of the alternative concepts. This is benchmarked against the ranking derived from the estimation of the Dow Fire and Explosion Index (F&EI) [22], a widely recognized inherent safety index adopted in the evaluation of fire and explosion hazards in chemical process plants [23]. Finally, a sensitivity analysis is integrated into the proposed method, to evaluate the influence of the uncertainty on input parameters on the results, and to validate the robustness of the assessment.

2. State of the art of inherent safety assessment methodologies

Safety plays a vital role throughout the entire life cycle of the process industry, having as its primary objective the prevention and mitigation of major accidents and technological disasters [24]. Four process safety strategies are usually applied to implement safety concepts and safety systems, which can be hierarchically classified as inherent, passive, active, and procedural [25]. The adoption of Inherently Safer Design (ISD) practices is recognized as the most cost-effective strategy to address safety issues in the early process design stages [26,27] with the aim to eliminate or reduce, as far as possible, process hazards [28]. According to ISD, the safest design of a process (or an operation) is identified by ranking different alternatives based on their inherent hazard. This is evaluated by means of inherent safety assessment tools, which are classified into six categories: consequence-based, parameter-based, graphical assessment, risk-based, evaluation based on safety and environmental aspects, and optimization-based methods [29].

Consequence-based approaches assess the inherent safety via the estimation of the consequences of accident scenarios such as fire, explosions, and toxic dispersions that can originate from the process of interest. To this purpose, the first and most used indexes are the Dow Fire and Explosion Index (F&EI) [22] and the Mond Fire, Explosion and Toxicity Index [30]. More recently, new methods that integrate the consequence-based approach with the quantification of indices (e.g., the Integrated Inherent Safety Index, I2SI) [31], simulations of releases [32], or process simulators (e.g., the Toxic Release Consequence

Analysis Tool, TORCAT) [33] have been proposed, and applied by several authors to the analysis of fuel supply chains [32,34,35].

Parameter-based methods are suitable to provide a preliminary inherent safety ranking of different process alternatives in the conceptual design phase. The ranking is built based on a set of selected parameters linked to the hazards identified in the process. Examples of parameter-based indexing methods are the Prototype Inherent Safety Index (PIIS) [36], the Inherent Safety Index (ISI) [37], the iSafe [38], and the Inherent Safety Benefits Index (ISBI) [39]. These approaches are usually coupled with graphical-based methods, that are helpful in the understanding of the cause-effect relationship between the relevant parameters and the hazards and provide an immediate and easily interpretable visual comparison of the safety indices. In risk-based methods, the quantification of the safety performance of process alternatives depends on the risk level, which is determined by both the likelihood of an accident scenario and the severity of its consequences [40]. Lastly, a more comprehensive analysis can be performed by means of multi-objective approaches that deal with the simultaneous optimization of conflicting aspects, such as environmental impact, economy, and safety. Following these methods, the best process design is selected by comparing the accident cost that should be faced in case of the occurrence of an accident, instead of considering the risk acceptance criteria as in the risk-based methods [41].

Several applications of ISD for the assessment of the inherent safety of hydrogen technologies can be found in the literature. For instance, consequence-based approaches were applied to evaluate the safety performance of different hydrogen supply chain routes based on a set of KPIs able to capture specific risk aspects relevant to each process [42–45]. Furthermore, a parameter-based approach was used to carry out an environmental and safety analysis of hydrogen production via biomass gasification [46].

However, a number of shortcomings associated with currently established process safety metrics have become increasingly clear [32,47]. Such limitations may cause several of the established inherent safety metrics somehow inadequate for decision-making among alternative designs, especially during early process development [48]. It is thus important to select appropriate metrics for ISD application, so that inherent safety can be measured systematically as function of choices made during the specific design phases, accounting for a possibly scarce availability of input data in particular during early design. An effective integration of ISD principles requires to adopt a quantitative metric able to support design choices. Consequence-based indexing methods are increasingly being considered for this purpose, in view of their capability of providing objective results by using standard consequence analysis models and similarity to consolidated procedures of the risk assessment practice [48].

In this study, an ISD method is used to assess the inherent safety of the hydrogen storage concepts for urban mobility. The consequence-based KPI approach introduced by Tugnoli et al. [32] was extended and improved to allow its application to heavy-duty vehicles and to perform the assessment of key hazardous features of hydrogen fuel storage systems. The methodology was modified to broaden the scope of the analysis, considering different basis for comparison of the alternative concepts considered, defined according to the most relevant characteristics of the storage concepts (e.g., mass of fuel stored, volume). A key novelty is represented by the definition of an hazard footprint (HF), which condenses the outcomes of the KPI analysis, giving a complete overview of the safety performance of the alternative storage concepts considered, allowing to compare the different alternatives from diverse perspectives (i.e., different basis of comparison) simultaneously. The ISD methodology developed and applied in the present study is illustrated in detail in the following section.

3. Methodology

3.1. Outline of the methodological approach

As discussed in the Introduction section, the application of detailed QRA methods is not suitable for the purpose of the study. Thus, the safety performance of alternative hydrogen storage concepts and the comparison with benchmarks (i.e., diesel, CNG and LNG) is carried out using an inherent safety methodology, derived by extending the consequence-based KPI approach introduced by Tugnoli et al. [32]. The flowchart of the eight-step approach developed is illustrated in Fig. 1.

The starting point of the methodology is the definition of the

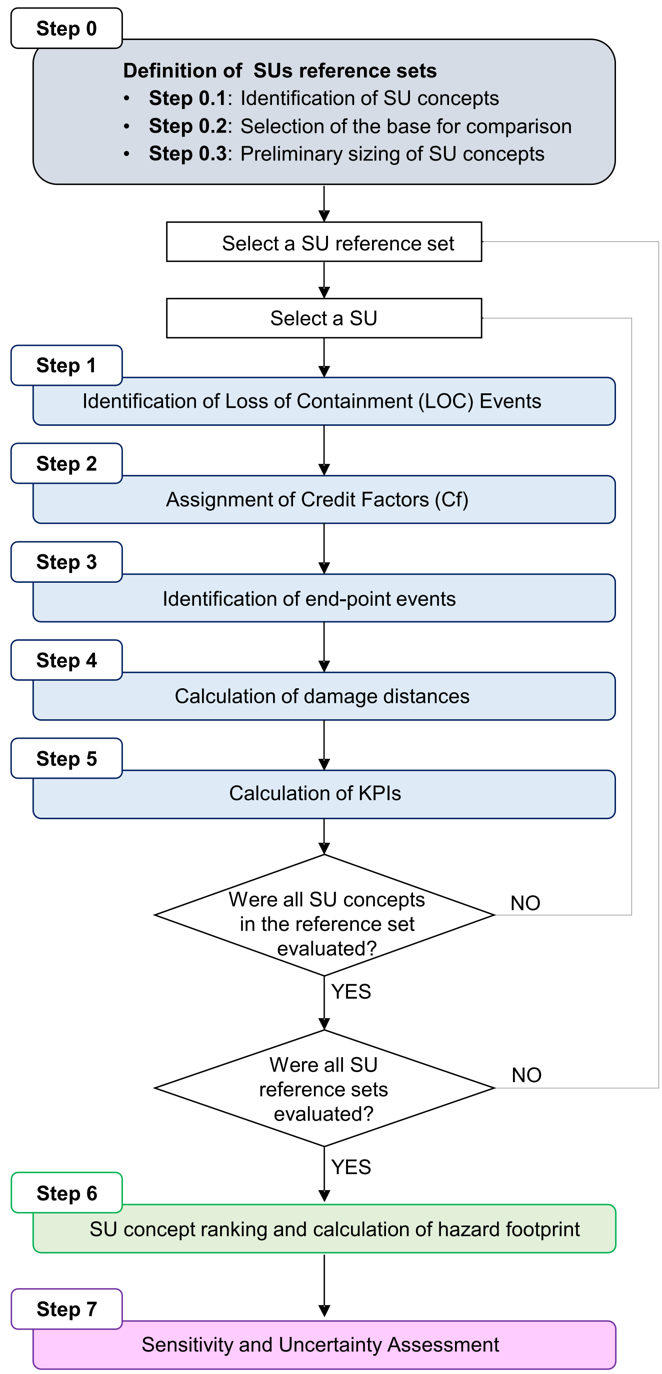

Fig. 1. Flowchart of the methodology developed for the inherent safety assessment of alternative hydrogen storage systems onboard hydrogen-powered buses.

hydrogen storage unit (SU) concepts object of the analysis (Step 0), which includes the identification of the SU concepts (Step 0.1), the selection of a base for comparison (Step 0.2), and the preliminary sizing of the SU (Step 0.3). These initial steps are described in detail in Section 3.2 and represent an original approach to the definition of the scope of the analysis concerning consequence-based inherent safety studies available in the literature (Tugnoli et al. [32,43], Landucci et al. [44,45], Scarponi et al. [49], Iannaccone et al. [34]), in which the assessment of process alternatives is usually carried out considering a single base for comparison (e.g., fixing a reference production rate for the product of interest). The analysis proceeds by identifying a set of Loss of Containment (LOC) events (Step 1) for each SU concept and assigning a credit factor (C_f) (Step 2) to each of the LOCs (see Section 3.3). Then, the end-point events that can arise from the LOCs selected in Step 1 are identified through an event tree analysis (Step 3). Step 4 consists of calculating the damage distances, defined as the maximum distances at which the effect of each end-point event equals a specific threshold value. Damage distance values are used in Step 5 to calculate two KPIs as described in detail in Section 3.4. These provide a metric to quantify the hazard deriving from releases due to technical failure of the hydrogen containment system or road accidents. The procedure for the calculation of the KPIs is discussed in detail in Section 3.5. KPI values are used in Step 6 to define inherent safety-based rankings of the SU concepts and to obtain their HF (see Section 3.5). The concept of HF is introduced to condense in a single metric the outcomes of the assessment carried out considering all the different reference sets of alternative SU concepts defined in Step 0. Finally, the robustness of the results is assessed through sensitivity analysis (Step 7), addressing the effects of the variation in the values of the credit factors and of the mass inventory of the different SUs (see Section 3.6).

3.2. Definition of the reference set of alternative SU concepts (step 0)

The aim of the methodology is the assessment and comparison of the inherent safety of alternative concepts for hydrogen storage specifically defined for hydrogen-powered buses. Thus, the starting point is the identification and definition of the alternative hydrogen storage concepts included in the assessment (Step 0.1). A more significant comparison is obtained if the mature technologies applied in current practice are included as benchmarks in the assessment, in order to understand the advantages and/or potential criticalities of alternative hydrogen storage technologies. In particular, fossil-fuel-based storage concepts used in diesel and natural gas-powered buses shall be considered as benchmarks.

In the following step of the methodology (Step 0.2), the basis for the comparative assessment needs to be defined. In order to carry out the comparison from different points of view and provide a thorough assessment of the hazard footprint characterizing the different storage concepts considered in the analysis, three different reference sets of SUs were defined:

- Reference set RM: all SUs store the same mass of fuel;
- Reference set RV: all SUs store the same volume of fuel;
- Reference set RC: the most common commercial configuration is selected for each SU.

Each of the three reference sets provides a specific perspective. Set RM compares a hypothetical configuration in which the same amount of energy is available to the bus, irrespectively of the volume of the SU needed to store it. Set RV provides a design perspective, where the same volume is considered for the onboard installation of SUs based on different storage concepts. Set RC provides a comparison based on the current state-of-the-art. For each reference set, a preliminary sizing of the SU is performed (Step 0.3) selecting a reference mass for set RM, a reference volume for set RV, and specific SU features reported in the technical literature for set RC.

3.3. Identification of LOCs, credit factors, and end-point events (steps 1 to 3)

The set of potential LOCs considered in the methodology (Step 1) is selected considering the list provided in the TNO "Purple Book" for pressurized road tankers [50]. Table 1 shows the LOCs selected for the release scenarios considered. In the case of LH2 and LNG SUs, the filling degree of the vessel is always lower than 100% to prevent the fast pressurization of the tank in case of BOG formation [51]. Thus, two phases are present for the fuel (liquid and vapor) and the LOCs resulting in continuous releases (LOC 2 and 3) were assumed to originate both above and below the liquid-vapor interface.

Step 2 of the methodology requires assigning a credit factor, C_f, to each LOC identified in the previous step. Two alternative sources were considered in the present study for the C_f values: the TNO "Purple Book" [50], reporting generic baseline failure frequencies for pressurized road tankers, and a report from Sandia National Laboratories (SNL) [52], including failure frequencies specific for hydrogen components.

3.4. Calculation of damage distances (step 4)

Damage distances are defined in the present study as the maximum distances at which the effect of each end-point event (i.e., radiation for fires, hydrogen concentration in the air for the flash fire, and overpressure for the Vapor Cloud Explosion, VCE) equals a specific threshold value. The threshold values for the calculation of damage distances for each end-point event are reported in Table 2. These values represent the intensity of the effect of the end-point event that corresponds to a 1 % probability of death of a person exposed to the event (Tugnoli et al. [32]).

Damage distances are calculated using adequate models and tools. Since the aim of the methodology is the calculation of a hazard footprint and not a detailed risk assessment, integral models are adequate to provide an estimate of expected damage distances with a limited computational cost. The PHAST 8.4 software by DNV was used in the present study for the calculation of the damage distances. This software tool was applied by several authors in hydrogen safety studies to assess the consequences of fires and explosions [53–55]. Clearly enough, different models and tools may be used for the calculation, provided that a coherent set of models and a single software tool is used in the assessment.

In the calculation of the damage distances, a critical role is played by the accuracy by which the physicochemical properties of hydrogen are

Table 1
Reference values of credit factors reported by TNO "Purple Book" and Sandia National Laboratories (SNL).

LOC	LOC description	TNO C_f values	SNL C_f values[d]	End-point events
LOC 1	Instantaneous release of the complete inventory	$5x10^{-7}$	$2.7x10^{-7}$	- VCE - flash fire - pool fire - fireball
LOC 2	Continuous release from a 10 mm hole in one of the tank connection pipes	0.002628[a]	$8.2x10^{-6}$[b,c]	- VCE - flash fire - pool fire - jet-fire
LOC 3	Continuous release from the full-bore rupture of a 25 mm diameter tank connection pipe	0.002628[a]	$5.3x10^{-6}$[b]	- VCE - flash fire - pool fire - jet-fire

[a] in the TNO "Purple Book" the leak frequency is expressed as $3x10^{-7}$ h^{-1}; this value is obtained assuming a conservative operating time for the bus (24 h/d for 365 d/y).
[b] values calculated assuming a pipe length of 10 m
[c] obtained by linear interpolation from available data.
[d] specific to hydrogen applications.

Table 2
Threshold values for the effects of the end-point events [32].

End-point event	Parameter for the calculation of damage	Threshold value
Vapor Cloud Explosion (VCE)	Overpressure	14 kPa
Fireball, Jet fire, Pool fire	Radiation	7 kW/m^2
Flash fire	Concentration	½ LFL

represented. In the PHAST 8.4 software, they are implemented as temperature-dependent functions derived from the DIPPR 801 database (by the Design Institute for Physical Properties – DIPPR® [56]), recognized by the American Institute of Chemical Engineers as the world's premier source of critically evaluated thermo-physical properties. The set of equations implemented in the software and used in the present analysis to calculate the relevant properties of hydrogen is summarized in Table 3.

In order to obtain representative damage distances, the simulations were performed introducing two conservative assumptions: a low wind speed of 1.5 m/s and stable atmospheric conditions (Pasquill's class F). Damage distances were calculated at 1 m height from the ground level. Two positions were considered for the release: respectively 1 and 3 m above the ground. The first is representative of a release following a crash that causes the overturn of the bus, while the second simulates a release from a tank in its typical position, on the top of the bus. Conservatively, the release position for LOCs 2 and 3 was considered directly on the storage tank, neglecting the possibility that the failure may take place from a low diameter connection pipes resulting in a lower release rate.

3.5. Calculation of KPIs and hazard footprint

Based on the values of the damage distances, two KPIs are calculated in Step 5 of the methodology:

$$UHI_i = \sum_j C_{f,i,j} \bullet h_{i,j}^2 \quad \text{Eq. (1)}$$

$$UPI_i = \max_j \left(h_{i,j}^2 \right) \quad \text{Eq. (2)}$$

Where the subscript i indicates the *i-th* SU considered, the subscript j refers to the LOC, $h_{i,j}$ is the maximum damage distance calculated for the LOC j assigned to the *i-th* SU, SU_i, considering all credible end-point events. The Unit Inherent Hazard Index (UHI) combines damage distances with the values of the credit factors. Credit factors are baseline failure frequency values used to quantify the credibility of the LOC events associated with each piece of equipment when caused by technical failures of components [32]. While it is reasonable to assume that the occurrence frequency of technical failures for a storage tank (and related pipework) is comparable in a process plant and onboard a vehicle, road crashes represent an additional cause of leaks for vehicles. Thus, the UHI provides a metric for the risk associated with technical failures. When considering failure due to road collisions, a high uncertainty affects the statistical data available in the literature quantifying the conditional probability of occurrence of a specific LOC given a road crash involving a specific and innovative SU concept for hydrogen. Thus, the Unit Potential Hazard Index (UPI) is introduced in the analysis, which expresses the maximum potential damage of a given SU concept regardless of the cause of the release scenario.

Table 3
Input parameters used in the PHAST 8.4 software for the calculation of damage distances for the different storage concepts. Details on the equations and the relevant parameters are reported in the software user guide [57].

Physical property	Equation
Density (Liquid)	DIPPR 105
Density (Vapor)	DIPPR 104
Specific heat capacity	DIPPR 114
Specific heat capacity of ideal gas	DIPPR 107
Vapor pressure	DIPPR 101

The calculation of the KPIs is carried out for all three reference sets defined in Step 0 of the methodology. While these indicators allow the definition of inherent safety-based rankings of the SU concepts that are specific to each reference set, the HF is introduced to provide an overall metric that summarizes the outcomes of the analysis. The calculation procedure of HF is illustrated by means of Fig. 2, which provides an example in which two generic SU concepts, namely SU_1 and SU_2, are compared. The spider plot in the figure is obtained by normalizing the UPI and UHI with respect to the maximum value of the index among all the SUs considered for each reference set. For a given SU, the HF is calculated as the ratio between the surface area of the hexagon corresponding to the SU (i.e. the shaded areas HF_1 and HF_2 in Fig. 2) and the surface area of a regular hexagon having a unitary edge. Comparing the HFs, it is possible to define an overall ranking of the SU concepts considered in the analysis. Clearly enough, a wider HF corresponds to a more hazardous technology.

3.6. Sensitivity and uncertainty assessment (step 7)

Most of the steps described above require the adoption of simplifying assumptions and the selection of values (e.g., the storage capacity considered as the reference for a given SU or the credit factor assigned to each LOC) that may, to different extents, present some degree of uncertainty or of variability that may impact on the final ranking. Thus, the robustness of the hazard ranking obtained by the KPIs and HF ranking is assessed in Step 7 by a sensitivity analysis. First, following the approach proposed by Scarponi et al. [49], the influence of the modification of the C_f values on the UHI-based ranking is investigated. Then, the effect of variation of the mass inventory of each SU on both the UHI- and UPI-based rankings is analyzed by a specific approach. Section 4.2 describes in detail the procedure for the sensitivity analysis of the case study and summarizes the inputs and assumptions considered.

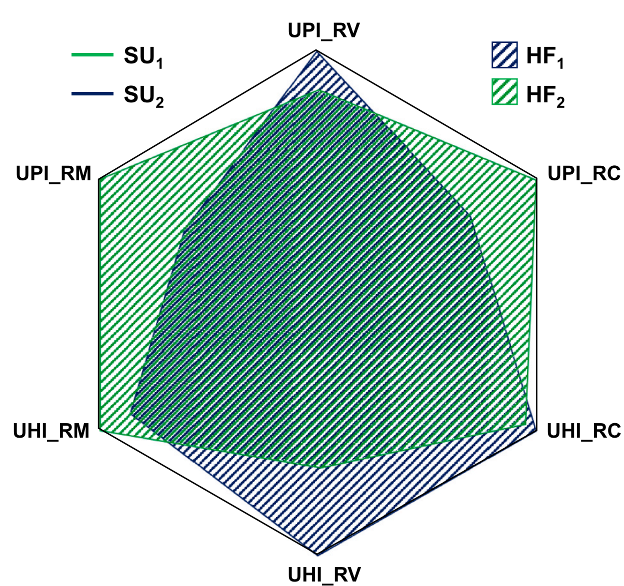

Fig. 2. Example of the calculation of the HF for two hypothetical SUs.

4. Case study

4.1. Definition of SU reference sets (step 0)

In the case study carried out in the following, a total of six hydrogen SU concepts (SUs 1 to 6 in Table 4) are identified. The storage technologies described in Section 1 (i.e., compression, cryogenic liquefaction, and cryo-compression) are considered in the present assessment since they are the most common solution currently in use or proposed for future use to store hydrogen on board urban hydrogen-powered buses. As shown in Table 4, these concepts are different in terms of the storage phase, operating pressure (P_o), and temperature (T_o): two concepts selected are based on CH2, one on LH2 and three on CcH2. Three fossil fuel SU concepts were selected as benchmarks: a diesel SU, a CNG SU, and an LNG SU (SUs 7 to 9 in Table 4). Table 4 summarizes the features of the 9 SU concepts considered in the present analysis. When available, data from solutions proposed for commercial applications were selected.

The reference hydrogen mass inventory (7.79 kg) and tank volume (322 L) for reference sets RM and RV (Section 3.2) are selected as the maximum values in the mass and volume range for the C350 tank, which, among the options considered, is the most widespread storage concept currently applied for buses. The SU features selected for the RC set are representative of the most common commercial tanks available on the market for each storage SU concept considered in the study. In all the reference sets, cryogenic liquid fluids (LH2 and LNG) are assumed to be stored as saturated liquids at the boiling point.

4.2. Input data and assumptions for the sensitivity analysis (step 7)

In the sensitivity analysis, the influence of the variation of C_f values and of mass inventory on the UPI- and UHI-based rankings is investigated. Following the approach proposed by Scarponi et al. [49], a sensitivity analysis is performed (Step 7) to assess the robustness of the ranking. First, C_f values are varied assuming a uniform distribution within the range defined by increasing/decreasing the TNO values (see Table 1) by an order of magnitude. A total of 10^6 simulations were carried out by randomly changing the C_f values in the above-mentioned interval. It is worth remarking that, in each simulation, the value of the C_f assigned to a given LOC is the same for all the SUs for which the LOC is relevant.

The sensitivity of the results to the mass inventory was also investigated. Differently from the C_f, the dependence of the indicators on the mass inventory is implicit and is reflected by the variation of the damage distances. Unfortunately, no explicit expression exists that correlates the latter parameter to the mass inventory: damage distances need to be calculated by a specific run of the consequence assessment software for each LOC. Since this approach is hardly applicable, the damage distances considered in the sensitivity analysis were obtained from PHAST simulations considering four different values of mass inventory: the value indicated in the RC set, its half, its double, and the mean between the two latter values (see Table 5). Then, a regression is performed to obtain a linear function correlating the mass inventory and the damage distances for each LOC and each SU. Finally, the sensitivity analysis is carried out considering 10^6 simulations, in which the value of the mass contained in each SU is randomly selected between m_{min} and m_{max} (see Table 5). A uniform distribution is assumed in this interval. It is worth remarking that this approach, although based on simplifying assumptions, is more physically sound with respect to inherent safety assessment studies available in the literature (e.g. Refs. [49,66]), which usually consider the direct variation of the damage distances.

5. Results

A detailed overview of the damage distances at the base of the KPIs calculation is shown in Fig. 3 for the RM and RC sets. Since the results obtained for the RV set are very similar to those obtained for the RM set, they are not reported for the sake of brevity.

Fig. 3a and b report the representative damage distances caused by the end-point events generated by the catastrophic rupture of the SU (LOC 1). In the case of the RM set (Fig. 3a), the fireball that follows the instantaneous release of cryogenic liquids (LH2 and LNG) is the most critical outcome, resulting in damage distances higher than 20 m. In the case of LH2, similar distances are calculated for the VCE and the flash fire. The catastrophic failure of compressed and cryo-compressed

Table 5
Relevant mass values for the sensitivity analysis.

Vessel	Mass of hydrogen (kg_{H2})			
	m_{min}	m_{RC}	m_{mean}	m_{max}
C350	2.48	4.96	6.20	9.92
C700	3.70	7.40	9.25	14.8
LH2	20	40	50	80
Cc350	4.53	9.05	11.31	18.10
Cc500	5.27	10.53	13.16	21.06
Cc700	6.11	12.21	15.26	24.42

Table 4
Commercial vessels for onboard hydrogen storage on buses.

#	SU ID	Type of storage	Ranges for most common commercial tanks		Operating conditions		Reference SUs sets				Data source
			Mass of fuel (kg)	Storage volume (L)	Temperature (K)	Pressure (bar)	RM (mass of fuel = 7.79 kg)	RV (SU volume = 322 L)	RC		
							SU volume (L)	Mass of fuel (kg)	Fuel mass (kg)	SU volume (L)	
1	C350	Compressed gas	0.1-7.79	4-322	293	350	322	7.79	4.96	205	[58,59]
2	C700		0.7-10.5	19-270	293	700	190	13.5	7.4	205	[58,59]
3	LH2	Cryogenic liquid	40	300	23.1	Psat	110[a,b]	19.4[b]	40[b]	300	[60]
4	Cc350	Cryo-compressed gas	9.05	131	66	350	113	22.25	9.05	131	[61]
5	Cc500		10.53	141	72	500	104	24.05	10.53	141	[61]
6	Cc700		12.21	152	78	700	97	25.86	12.21	152	[61]
7	Diesel	Liquid	280.5-765	330-900	293	1	9.2	273.3	280.5	330	[62]
8	CNG	Compressed gas	31.82-160.82	148-748	293	250	36.2	69.23	67.73	315	[63]
9	LNG	Cryogenic liquid	120.5-157	315-410	145.41	Psat	17.3[b]	123.17[b]	73[c]	410	[64,65]

[a] Tank for on-board hydrogen storage for heavy trucks due to lack of data for bus storage tanks.
[b] Liquid fill level of 85 % as suggested by Ref. [51], the rest of the tank volume is occupied by the vapor in equilibrium with the liquid.
[c] Liquid fill level of 40%.

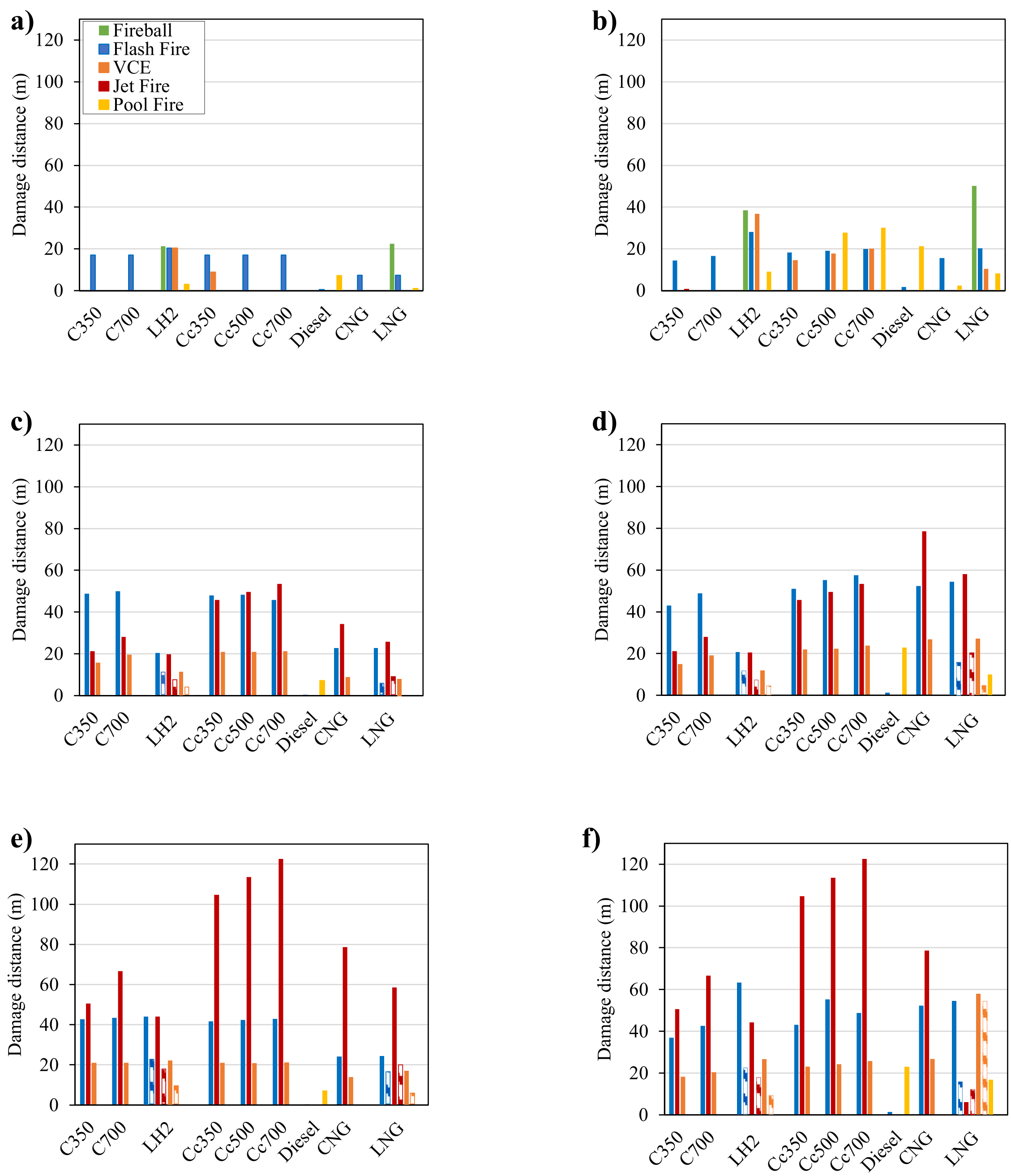

Fig. 3. Reference damage distances calculated for the end-point events following LOCs 1, 2, and 3, considering the RM SUs (panels a, c, and e respectively) and the RC SUs (panels b, d, and f respectively). Dashed bars (panels c, d, e, f) represent damage distances in case of the release of the vapor phase from LH2 and LNG cryogenic tanks.

hydrogen SUs results in flash fires with damage distances of around 17 m, while the adverse effect of flash fire from the CNG SU is limited to 7 m. In the case of the RC set (Fig. 3b), the fireball is again the worst event, with a damage distance of 38 m for LH2 and 50 m for LNG. In addition to the flash fire, the release from cryo-compressed tanks results in a VCE and a pool fire, the latter being the most hazardous.

When LOC 2 is considered (Fig. 3c and d), damage distances calculated for fuels in the liquid state are the lowest, and, in the case of cryogenic fuels, the release of the vapor phase is less critical than that of the liquid phase. In RM SUs, compressed and cryo-compressed hydrogen SUs result in similar flash fire damage distances (around 48 m), while jet fire damage distances for cryo-compressed systems are almost double those of compressed storage concepts when the same pressure level is considered. The results obtained for the RC SUs are qualitatively similar, with the exception that natural gas releases score significantly higher damage distances than those calculated for the RM set, with values up to 77 m in case of jet fire from the CNG tank.

With respect to the full-bore rupture of the pipe (LOC 3), the jet fire is the end-point event resulting in the highest damage distances for all the reference sets (Fig. 3e and f). Jet fires result particularly critical for cryo-compressed hydrogen, with damage distances increasing with pressure. The maximum value of damage distances (122 m) is obtained for Cc700. The flash fire is the most relevant end-point for the LH2 SU, with a damage distance of 63 m, obtained in the case of liquid release, while in the case of LNG, the highest damage distance (58 m) was obtained for the VCE.

In summary, the effects of the catastrophic rupture result in intense but localized events, while the full-bore rupture of connecting pipes can be deemed as the most critical LOC. The variation of the release height from 1 m to 3 m does not produce any relevant difference in the results shown in Fig. 3.

The values of the KPIs obtained for the three reference sets of SUs are shown in Fig. 4. Overall the two indicators (UPI and UHI) present similar trends for all the reference sets, with few exceptions. On the one hand, cryo-compressed hydrogen SUs clearly show a higher hazard, scoring the highest values of both UPI and UHI (Fig. 4a and b respectively), that increase when increasing the operating pressure of the storage. The values of the KPIs for the Cc350 (the less hazardous among the cryo-compression-based storage concepts) are almost double that of SUs C350, not based on cryo-compression. On the other hand, SUs of liquid fuels show better inherent safety performance, with diesel fuel SU showing the highest safety performance. Among pressurized SUs operating at atmospheric temperature, the UPI and UHI values of compressed hydrogen (C700 and C350) SUs are slightly lower than those of CNG, even if the storage pressure is higher than that of CNG.

The UHI and UPI values of cryogenic liquids (LH2 and LNG) strongly depend on the reference system. On the one hand, when considering the RM reference set, LH2 results in lower UHI and UPI values than LNG. On the other hand, when the comparison is carried out considering the RC set, an inversion in the hazard ranking is observed.

The effect of the C_f values selected on the UHI-based ranking of hydrogen SU concepts is shown in Fig. 5 for the RC set (the results

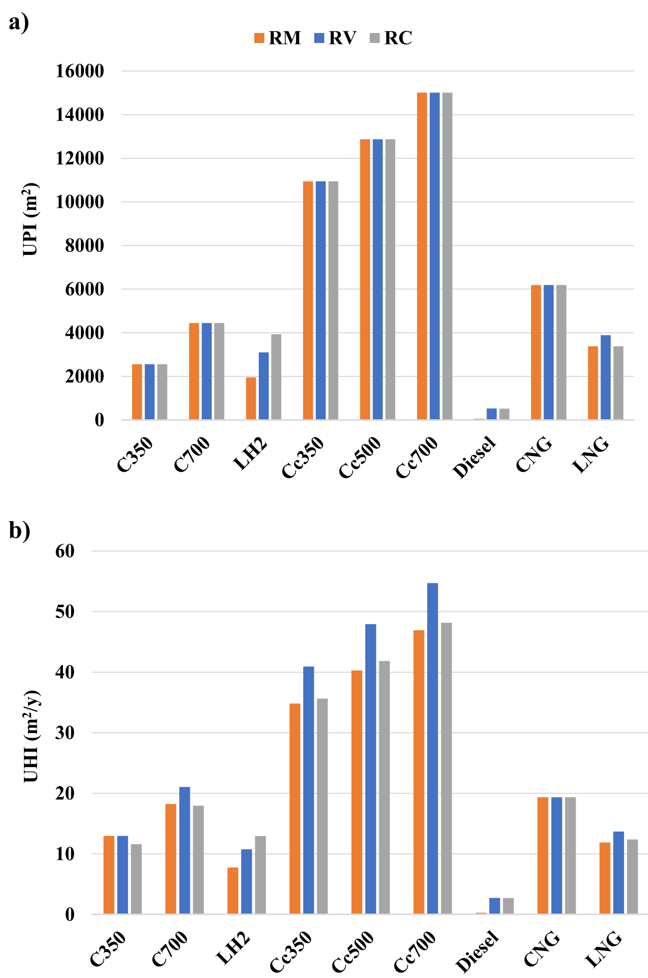

Fig. 4. Values of UPI (a) and UHI (b) calculated for the three SU reference sets listed in Table 3. UHI values reported are calculated using the TNO C_f values.

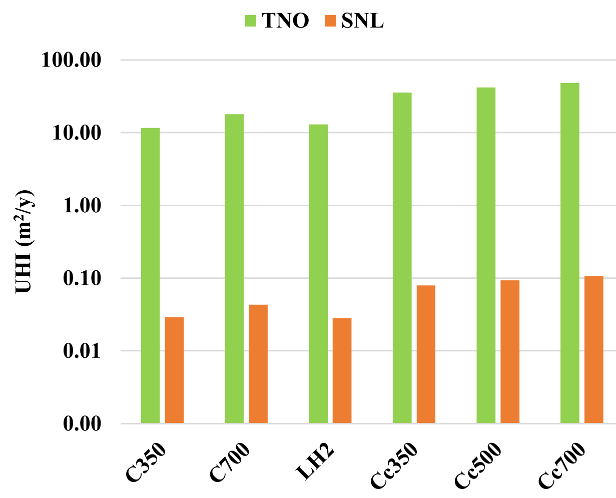

Fig. 5. UHI indicator relative to hydrogen commercial SUs (RC set) using C_f s from TNO "Purple Book" and Sandia National Laboratories (SNL) databases. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

obtained for the RM and RV sets are qualitatively very similar and are not shown for the sake of brevity). In the figure, the values of the UHI are calculated considering both the TNO and SNL datasets C_f s values. According to Eq. (2), the much lower value of the C_f proposed by the SNLs as compared with TNO results in a strong decrease of the UHI values for all the SUs. However, the ranking of the SUs is unchanged. Thus, the use of different data sources for the C_f values, when coherently applied to the entire analysis is expected to have an important effect on the overall KPI values, while the possible effect on the relative ranking of the system may be limited.

The HF calculated for the hydrogen storage concepts considered in the present study is shown in Fig. 6, together with that of the selected benchmarks. As shown in Fig. 6a, the hazard footprint of cryo-compressed storage technologies is the largest and increases when increasing the operating pressure. As already highlighted, diesel fuel always represents the safest solution, scoring by far the smallest hazard footprint, mostly due to its stability in the liquid phase at ambient temperature and its low vapor pressure. When considering hydrogen storage concepts, Fig. 6a evidences that LH2 emerges as the inherently safest SU concept, scoring a smaller hazard footprint than the other SUs. The HF of LH2 results are comparable to that of LNG, which is a socially accepted technology currently used to power urban buses.

With the aim of benchmarking the HF results against a consolidated approach to inherent safety assessment, the hazard of the alternative storage concepts considered was evaluated by the Dow Fire and Explosion Index, which is a conventional and widely recognized method with significant basis in the principles of inherent safety [67]. The method was applied according to the procedure provided in the Dow's Fire and Explosion Index Hazard and Classification Guide [22]. Table 6 reports the values of the non-mitigated F&EI calculated for all the three reference sets of hydrogen storage concepts considered (RM, RV, and RC). The table also reports the normalized values of the index, calculated as in the case of the HF by an internal normalization approach.

Despite the F&EI calculation procedure introduces a specific factor that accounts for the influence of the mass of fuel, the same value of the FE&I was obtained for each SU regardless of the reference set considered (RM, RV and RC). Thus, a single value of the F&EI is reported in Table 6. Actually, this outcome is due to the limited sensitivity of the F&EI to the inventory of hazardous substances: the differences in the amount of hydrogen stored in the alternative reference sets considered is not sufficient to influence the FE&I. For instance, in the case of the SU C350,

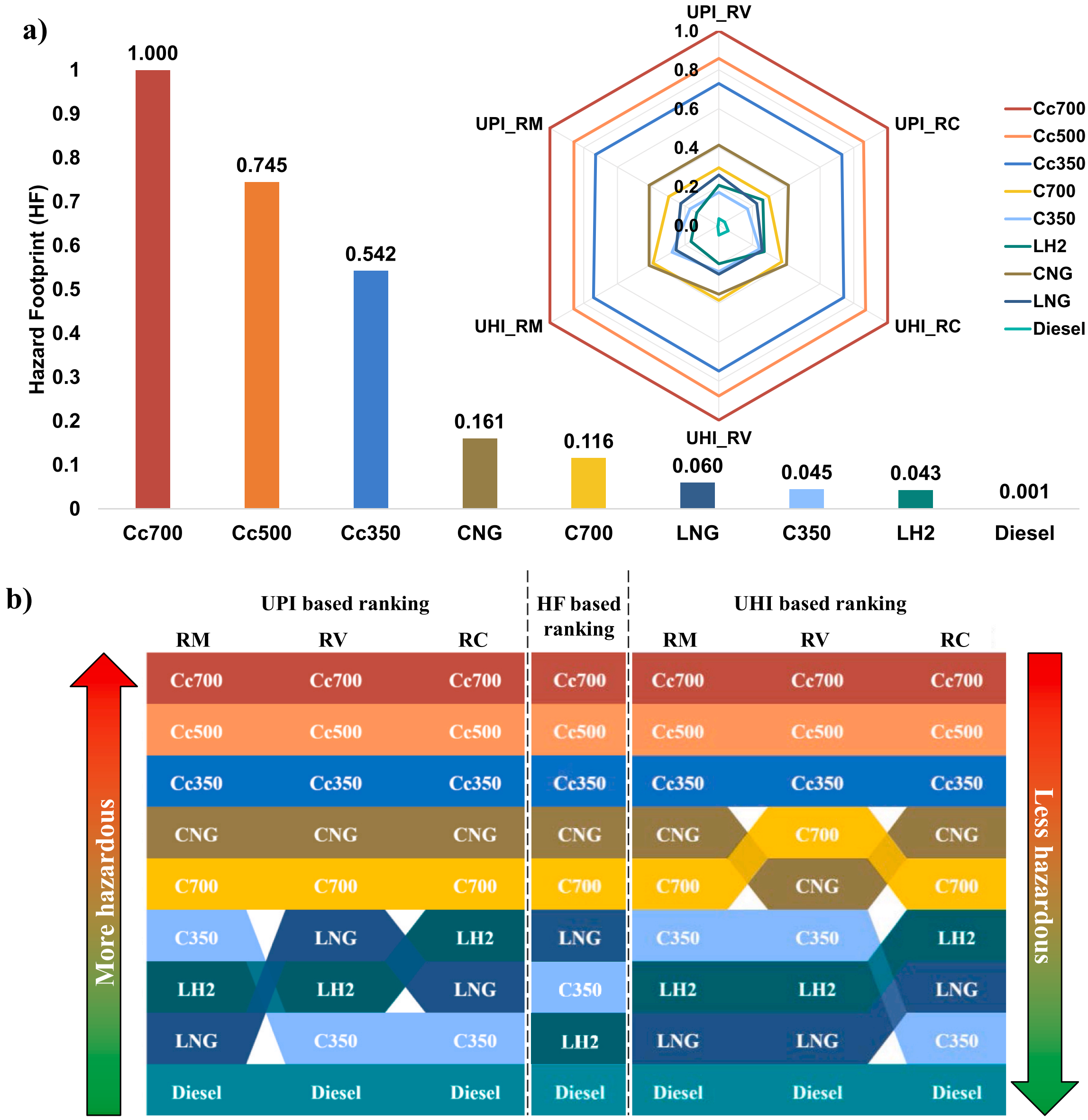

Fig. 6. (a) Hazard footprint of the hydrogen SU concepts and benchmarks considered in the analysis; (b) breakdown of ranking based on UPI and UHI for each SU reference set.

Table 6
Non-mitigated value of the F&EI calculated for the SU concepts considered. Normalized values are calculated with respect to the highest value.

SU	F&EI	Normalized F&EI
C350	52.50	0.704
C700	65.10	0.873
LH2	38.70	0.519
Cc350	60.90	0.817
Cc500	60.90	0.817
Cc700	74.55	1.000
Diesel	13.00	0.174
CNG	52.50	0.704
LNG	46.49	0.624

the variation of the hydrogen mass between the reference sets (RM: 7.79 kg; RV: 4.96 kg, see Table 4) is of only 2.83 kg.

Also storage temperature seems to play a minor role in determining the hazard ranking according to the F&EI. Cryogenic liquid fuels (LNG and LH2) are identified as the less hazardous technologies after diesel fuel.

Differently, the values of the F&EI in Table 6 are clearly influenced by the pressure of the hydrogen storage. Actually, the F&EI values decrease with the decrease of the storage pressure. This emerges also from Fig. 7, showing the comparison between the HF and the F&EI-based rankings: the concepts operating at lower pressure are those classified as less hazardous (see Fig. 7).

Clearly enough, as shown in Fig. 7, the F&EI is moslty influenced by a limited number of hazard factors, as pressure, while the influence of others is almost negligible. The method is clearly less sensitive to the inventory ho hazardous substances and to other hazardous factors as storage temperature. Moreover, the HF methodology provided in the present study, being based on a specific assessment of potential consequences of the hydrogen releases from the different storage concepts, proved to have a higher sensivitiy. The HF obtained is actually able to capture the influence of even limited variation in the inventory released, and in the storage operating conditions, which in turn affect the potential release rates. This highlights the advantages introduced by the

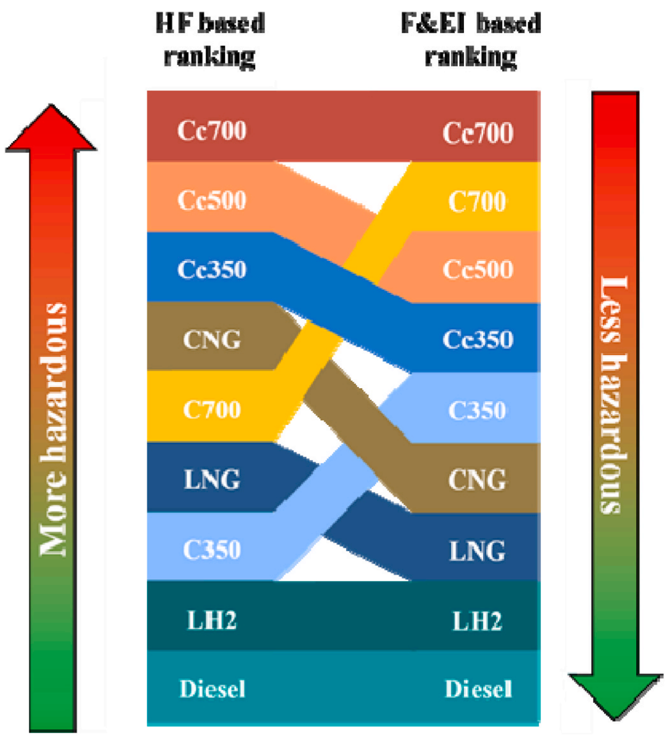

Fig. 7. Comparison between the rankings of the SUs obtained considering the hazard footprint (HF) and the Dow Fire and Explosion Index (F&EI).

proposed methodology, which allows to perform a more detailed analysis by capturing specific features relevant to the inherent safety of alternative storage technologies.

The robustness of the UPI and UHI-based rankings of hydrogen SUs was assessed by a sensitivity analysis, carried out by the methodology discussed in section 3.6, using the data introduced in section 4.2. First, the effect of C_f variation, which only affects the UHI values, is analyzed. The ranking presented in Fig. 4b for the reference set RC is confirmed in 35.6% of the 10^6 Monte Carlo simulations carried out. In the remaining 64.4% of the cases, the only change observed is a swap between the C350 and LH2 SUs in the last positions (lowest UHI). Thus, the UHI ranking, addressing the expected safety performance with respect to technical failures seems robust, with the liquefied hydrogen and the lowest pressure compressed hydrogen storage concepts showing a higher inherent safety performance.

The second step of the sensitivity analysis focuses on the effect of mass inventory variation, which affects the values of both KPIs. As far as the UHI is concerned, Fig. 8 shows the cumulative probability of the differences in the UHI of SUs alternatives in consecutive positions in the ranking presented in Fig. 4. The analysis shows that this ranking is confirmed with a probability of 72.7 % and that only one variation has a relevant probability to occur: 27.3 % probability that the UHI of C350 may score a higher value than that of LH2. The only non-zero probability of modification of the UPI rankings considering the variations of the mass inventory within the ranges indicated in Table 5 concerns the inversion of the ranking of Cc500 and Cc700 and is equal to 0.01%. Thus, the results of the sensitivity analysis support the robustness of the UPI ranking obtained, shown in Fig. 4a.

6. Discussion

The methodology developed in the present study allowed the definition of an inherent safety ranking among the possible alternatives for hydrogen storage concepts onboard hydrogen-powered buses. Critical aspects are identified and, at the same time, a comparison with benchmarks consisting of the conventional fossil fuel storage solutions currently adopted for buses is provided.

It must be remarked that the consequence assessment of release scenarios used to calculate the KPI values is carried out with conventional tools based on integral models in the PHAST 8.4 software by DNV, which are adequate for an inherent safety screening. Nevertheless, alternative models may be used to apply the methodology. In particular, more detailed models and tools such as CFD-based software should be considered for the characterization of specific accident scenarios [10, 20], that can integrate the outcome of the present study providing system-specific and site-specific results, useful in the basic and detailed design steps.

The outcome of the analysis identifies cryo-compressed storage conditions as the most critical from a safety standpoint. The combination of low temperature and high pressure, which has a positive impact on the energy density per unit volume, determines a significant increase in HF. On the other hand, cryogenic storage at a pressure close to atmospheric shows a much higher inherent safety performance. The same applies to storage concepts exploiting compression alone, provided that maximum storage pressure values are in the lower range among those considered for heavy vehicles fuelled with hydrogen (350 bar). From all the above, it appears that the "attenuation of process conditions" inherent safety principle [21] is the most relevant in the identification of the inherently safest solutions. The comparison with traditional fuels shows that LH2 is safer than LNG if the same mass is assumed as the basis for the analysis. However, when the most common tank sizes available on the market are considered (which are bigger than those considered for LNG), similar values of the potential (UPI) and hazard (UHI) KPIs were obtained for both fuels as well as for compressed hydrogen at 350 bar.

Overall, the HF suggests that LH2 is the safest SU concept. On the contrary, CNG (250 bar) and compressed hydrogen at 700 bar both present worse inherent safety performance than storage under cryogenic conditions, with the latter showing the largest HF among all the SU concepts based on compressed gas storage at atmospheric pressure analyzed. Not surprisingly, diesel fuel storage results as the safest solution by far, regardless of the base assumed for the comparison, due to its low vapor pressure, high flash-point, and stability in the liquid phase.

In summary, a safety-improved design and operation of storage concepts for hydrogen-powered urban buses may be achieved exploiting the following key lessons obtained from the analysis carried out in the present study:

- Concepts operating at lower pressure are inherently safer and shall be preferred.
- The full-bore rupture (LOC 3) of connection pipes is the LOC associated with the worst consequences, especially when considering jet fire scenario. Design solutions aimed at preserving connections and pipe integrity in case of impact are paramount.
- Small leaks with an equivalent diameter of 10 mm (LOC 2), which are compatible with technical failures of pipes (e.g. the failure of a connection or a gasket) may also lead to severe damage. An appropriate maintenance plan shall be in place to minimize the occurrence frequency of these leaks.
- Flash fire is the second most relevant scenario, with damage distances limited to a few tens of meters (see Fig. 3). Awareness about the need for immediate evacuation may drastically reduce the possibility of fatalities.

From the methodological standpoint, the approach presented constitutes an important extension of the inherent safety performance assessment methods developed for chemical and process plants. The introduction of a dedicated step for the definition of the scope of the analysis, with the identification of multiple reference sets of technological solutions and the inclusion of benchmark concepts allows a wider and more comprehensive assessment, preventing the outcomes from being biased due to the selection of a single base for comparison. As for

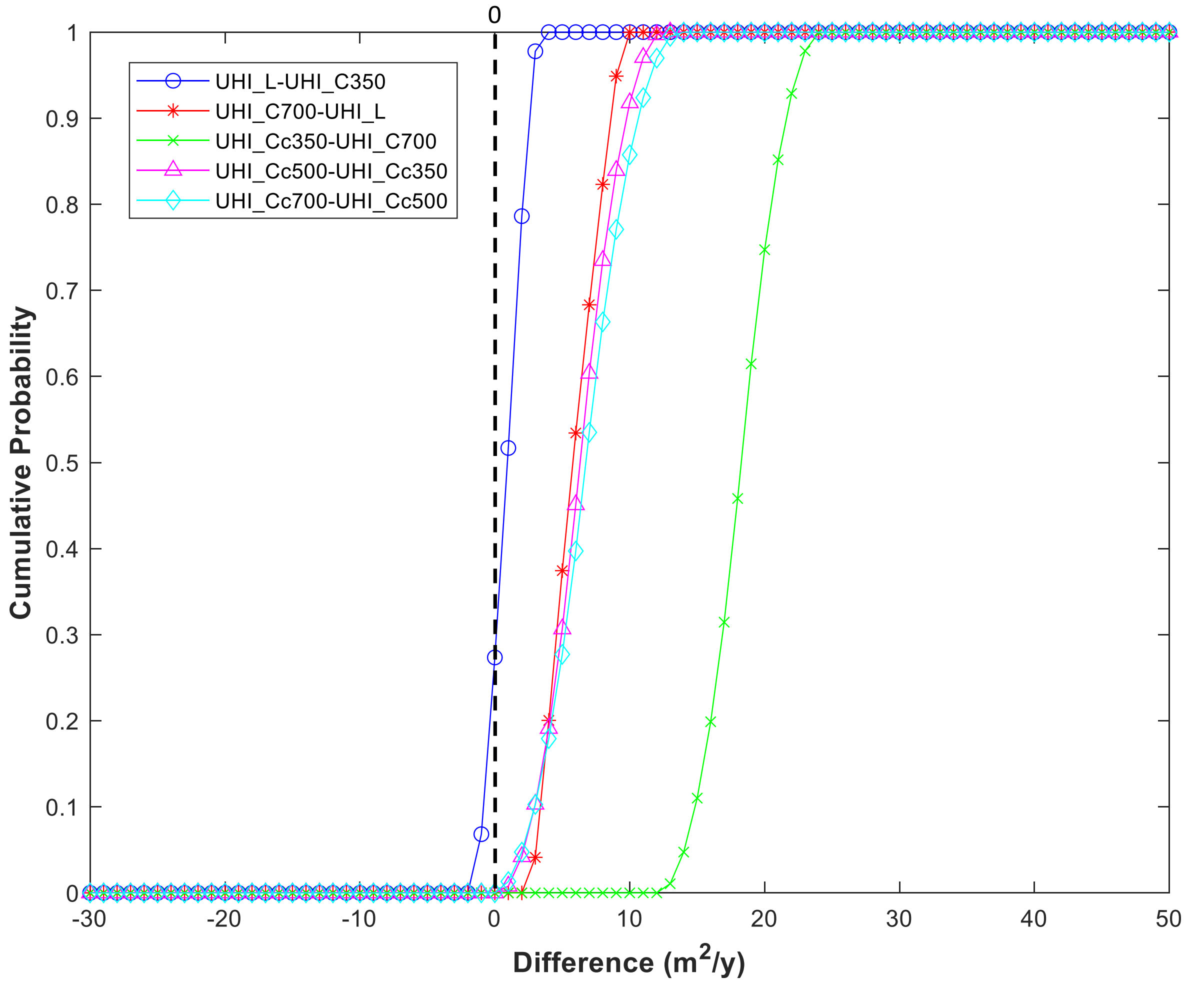

Fig. 8. Variation of the UHI indicator of the hydrogen SU concepts with the reference mass inventories.

the indicators adopted in the analysis, the UHI and UPI allow capturing risk features that are specific to each fuel storage system, considering the hazard of release scenarios caused by both technical failures and road crashes. On the other hand, the introduction of the HF concept provides an effective strategy to summarize the overall outcome of the assessment.

The benchmarking with the results obtained on the basis of the F&EI index highlights the advantages of the use of the proposed methodology, which is able to capture specifically critical technological features (e.g., amount of fuel, high pressure, and low temperature).

Overall, the comparative analysis of alternative hydrogen storage concepts performed in this study provides relevant information to support risk-informed decision-making and promotes the shift towards sustainable mobility in urban areas. The estimation of the hazard footprint of the alternative hydrogen storage concepts for buses allows identifying the safer technologies and the most critical accident scenarios, fostering the development of effective safety measures and enhancing the public acceptance of hydrogen use in public transport. The outcomes of the assessment may thus be used to assist decision-makers in the selection of safer alternatives for hydrogen-powered vehicles and be integrated as a risk metric in sustainability assessments of technologies for the decarbonization of the transportation sector.

In perspective, the proposed approach may also be integrated into the holistic evaluation of novel green fuel technologies for heavy-duty vehicles, providing a detailed screening of safety issues to be integrated with the analysis of environmental and economic aspects, as those proposed in Refs. [68,69].

7. Conclusions

The large-scale diffusion of hydrogen-powered vehicles to reduce the ecological footprint of the transportation sector requires a consensus of decision-makers and the general public concerning the widespread of hydrogen storage units onboard urban buses. This will only be possible if the hazards introduced by the adoption of hydrogen are understood, and the risk deriving from hydrogen technology are properly managed. The present study provides a screening of the hazards and potential damage distances for several alternative technology concepts proposed for hydrogen storage onboard hydrogen-powered buses.

The comparison of hydrogen storage concepts with conventional fuels shows that diesel fuel has by far the smallest hazard footprint. However, the greenhouse gases emitted in its combustion exclude it from playing any role in the decarbonization of the transportation sector. Efforts should therefore address the control and reduction of risks associated with zero carbon emission (green) hydrogen storage technologies fuels. Among all the hydrogen SU concepts analyzed, cryo-compressed hydrogen resulted as that having the widest hazard footprint. By contrast, atmospheric cryogenic storage resulted the most promising from a safety standpoint. From this perspective, the present study provides useful information concerning the critical issues of the different storage solutions, identifying the most credible and severe fire and explosion scenarios for each concept. Several recommendations can be drawn on the basis of the lessons learned analyzing the outcomes of the present assessment: e.g., low-pressure storage conditions shall be preferred; design solutions aimed at preserving connection pipes integrity in case of impact shall be developed; an appropriate maintenance plan shall be in place to minimize the risk of leakage; operators and passengers shall be informed about the risks connected to hydrogen-fuelled buses and the necessity of immediate evacuation in case of accidents. Thus, the methodology developed is a useful tool to support risk-informed decision-making and to orient further research in the development of hydrogen storage concepts and in the improvement of safety standards. Overall, the methodology and results obtained in the present study are valuable to support the shift toward more sustainable and safe mobility.

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.

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