SAFETY OF CRYOGENIC LIQUID HYDROGEN BUNKERING OPERATIONS - THE GAPS BETWEEN EXISTING KNOWHOW AND INDUSTRY NEEDS

Jennifer X Wen[1], Antoine Dutertre[2], Lee Phillips[3], Christopher Proust[4], Benjamin Truchot[4], Felicia Tan[5], Gabriele Landucci[6], Dan Allason, Yura Sevcenco[7]

[1]School of Mechanical Engineering Sciences, University of Surrey, UK
[2]TotalEnergies SE, France
Shell International Petroleum Company Limite, UK
[4] Institut National de l'Environnement Industriel et des Risques (INERIS), France
[5]BP Exploration Operating Company Limited
[6]Department of Civil and Industrial Engineering, University of Pisa, IT
[7] DNV Spadeadam Research Centre, UK

ABSTRACT

Hydrogen plays an important role in the global transition towards Net-Zero emission. While pipelines are a viable option to transport large quantities of compressed hydrogen over long distances, it is not always practical in many applications. In such situations, a viable option is to transport and deliver large quantities of hydrogen as cryogenic liquid. The liquefaction process cools hydrogen to cryogenic temperatures below its boiling point of -259.2 ^{0}C. Such extreme low temperature implies specific hazards and risks, which are different from those associated with the relatively well-known compressed gaseous hydrogen. Managing these specific issues brings new challenges for the stakeholders.

Furthermore, the transfer of liquid hydrogen (LH_2) and its technical handling is relatively well known for industrial gas or space applications. Experience with LH_2 in public and populated areas, such as truck and aircraft refuelling stations or port bunkering stations for example, is limited or non-existent. Safety requirements in these applications, which involve or are in proximity of untrained public, are different from rocket/aerospace industry.

The manuscript reviews knowhow already gained by the international hydrogen safety community; and on such basis elucidate the gaps, which are yet to be filled to meet industry needs to design and operate inherently safe LH_2 operations, including the implications for regulations, codes, and standards (RCS). Where relevant, the associated gaps in some underpinning sciences will be mentioned; and the need to contextualise the information and safety practices from NASA[1]/ESA[2]/JAXA[3] to inform risk adoption will be summarised.

Keywords: Liquid hydrogen; loss of containment; potential hazardous consequences; gaps between knowledge and industry needs; RCS

1.0 INTRODUCTION

Liquid hydrogen bunkering facilities typically include storage tanks, hoses, vents, vacuum jacketed liquid transfer lines, control valves, and flexible bunkering hose assembly including loading arms [1], etc. LH_2 is below the freezing temperature of oxygen (-218.8 ^{0}C). It evaporates with a volume expansion of 1:848, posing significant risk as a flammable gas. Loss of containment of LH_2 typically involves pool formation and spreading, flash evaporation [2], cryogenic boiling, condensing, and freezing of surrounding gases, especially oxygen forming liquid oxygen (LO_2). LH_2 jet flames involve complex physicochemical processes like flash evaporation, dispersion and combustion with local extinction and re-ignition [3,4]. In the meantime, LO_2 has different problems in terms of pooling/running. It can also be easily produced off cold pipework, e.g., vapour return lines. The evaporated LO_2 once warmed up

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[1] *The National Aeronautics and Space Administration*
[2] *The European Space Agency*
[3] *The Japan Aerospace Exploration Agency*

by heat exchange with air/soil/flame, would lead to oxygen-enriched combustion or hazardous secondary explosion [5]. Additionally, catastrophic failure of LH_2 storage tanks could result in instantaneous fireball, pool spreading and evaporation, resulting in very large vapour cloud [6], with potential for vapour cloud explosions (VCE). The inner-/inter-phase interactions influence combustion behaviour associated with accidental releases of LH_2. The combustion pressure will also be higher due to lower speed of sound [7,8]. Additionally, fire attack on LH_2 tanks may also result in unwanted tank responses like jet fires [9] and even induce the thermal rupture of LH_2 vessels, with potential boiling liquid expanding vapour explosion (BLEVE), the effects of which are still not well understood 9. For bunkering applications, potential hazards also include LH_2 releases into water, which could potentially result in ignition, VCE in open or semi-confined environment and even rapid phase transition (RPT) [12,13].

The manuscript reviews knowhow already gained by the international hydrogen safety community; and on such basis elucidate the gaps, which are yet to be filled to meet industry needs to design and operate inherently safe LH_2 operations, including the implications for regulations, codes, and standards (RCS). Where relevant, the associated gaps in some underpinning sciences will be mentioned; and the need to contextualise the information and safety practices from NASA/ESA/JAXA to inform risk adoption will also be summarised in the concluding remarks.

2.0 STATE-OF-THE-ART IN EXPERIMENTS

While the international community was developing capability and understanding toward LH_2. Hall et al. [14] conducted large-scale tests to determine the hazards and severity of realistic ignited spill of LH_2 released horizontally. Static electricity, likely caused by ice crystal which form on the release nozzle before the tests was captured in some tests by Hall et al. [14] but not a single test showed spontaneous ignition. The tests of ignited LH_2 jets released at ground level, identified three phenomena: jet-fires in high and low wind conditions, 'burn-back' of ignited clouds and secondary explosions post 'burn-back'. This was thought to be emanating from the solid deposit generated after the initial deflagration of the release cloud due to oxygen (O_2) enrichment [15,16]. However, several attempts were made to reproduce this phenomenon without success. The later was thought to be due to differences in wind conditions.

Panda et al. [17] experimentally investigated jet flames resulting from the ignited releases of cryogenic hydrogen gas ($CryoH_2G$), i.e., hydrogen below 100 K. Higher radiative heat fluxes were found than that under atmospheric conditions due to the lower choked flow velocity. The tests of Friedrich et al. [18,19] for vertically released $CryoH_2G$ identified 3 modes: ignition with flash-back to the release nozzle followed by a stable jet flame; a stable lifted flame and a transient burn with a subsequent blow-off. Hecht et al. [20] reported valuable experimental data of $CryoH_2G$ flames from high-aspect-ratio nozzles.

More recently, a series of full-scale tests involving LH_2 have been conducted in the "Pre-normative research for safe use of liquid hydrogen (PRESLHY)" project funded by the Clean Hydrogen Partnership of the EU [21,22], DNV Spadeadam large-scale experimental campaign [23,24] commissioned by the Norwegian Defence Research Establishment (Forsvarets forskningsinstitutt, FFI) and the NPRA as well as the Safe Hydrogen Fuel Handling and Use for Efficient Implementation (SH_2IFT) project [25-29] funded by the Research Council of Norway, several industry partners and Norwegian counties.

Table 1 provides a summary of relevant tests including the above generic accidental scenarios for LH_2. These tests have covered both unignited and ignited jets; rainout, delayed ignition, ignition over pools with different substrate, combustion in tubes and combustion in congested rig, BLEVE and LH_2 spill onto and under water. Most of these tests used LH_2 while only a small proportion of the PRESLHY tests used $CryoH_2G$, which will be differentiated where relevant. A brief review is provided for each category in the following subsection. Whenever possible, the published papers will be quoted as references but for some tests, no published papers are in the public domain, the specific presentations in the final dissemination conference will be quoted as additional references in addition to [21,22]. Some of these may be presented at this conference by the experimental groups.

Table 1. Summary of available data for LH_2

(H- Horizontal, VD-Vertical downwards, VU-Vertical upwards, HOB-Horizontal with Obstruction)

Scenario	**Direction**	**Nozzle diameter,** mm	**Ignition**	**Measurements**	**References**
CryoH_2G jets (80 K, 5, 50, 100, 200 bar)	H	0.5, 1, 2 and 4 mm	No	Release rates, H_2 concentration distribution and electrostatic field built-up	[29]
CryoH_2G jets (Temperature: 80 K, 290 K; Pressure: 5, 50, 100, 200 bar)	V	1, 2, 4 mm	Yes	Maximum pressure loads, temperature and heat flux radiation	[30]
LH_2 (2-5 bar, 0.0964 kg/s)	H	2, 4	No	Pressure in the vessel, H_2 concentration	[21]
LH_2 rainout tests (1-5 bar, 0.09-0.298)	H, VD, VU, HOB	6, 12, 25.4	No	Mass flow rate, field temperature, H_2 concentration, O_2 depletion	[32]
LH_2 jets (0.8-10 bar, 0.16-0.83 kg/s)/outdoor	H, VD	25.4	Yes (2 of the 7)	Mass flow rate, temperature, H_2 concentration, thermal radiation, pool radius in VD, overpressures	[23,24]
LH_2 jets (0.8-10 bar, 0.16-0.67 kg/s)/indoor	H	12.7, 25.4	Yes (2 out of 7)	Temperature (floor, 1m above nozzle, TCS), H_2 concentration,	[24]
LH_2 jets at ground level	H	25.4	Yes	Flammable extent and flame speed; radiative heat; wind	[14]
LH_2 pool tests (1.32kg)	-	500×500×200	Yes	Temperature, overpressure, video images	[33]
LH_2 explosion in congested rig	H	6, 12, 25.4	Yes	Pressure, temperature & concentration	[34]
Flame acceleration (FA) and deflagration to detonation transition (DDT) in combustion tube	H	54×73×5000	Yes	Flame velocity, cell size, combustion pressure, expansion ratio, flame velocity	[35]
Semi-open duct with obstacles (100 K)	H	400×600×3000	Yes	Flame velocity, temperature, pressure	[36]
BLEVE (25-30 kg)	-	1 m^3	Yes	In-vessel pressure, number and distances of fragments, fireball size and duration, radiative heat fluxes, pressures 22.5 and 26.4 m distance	[25,26]
LH_2 onto and under water	D, H	Basin 10×10×1.5 m	Yes	Blast overpressure, heat fluxes at 70, 90 and 110 m from release point	[27,28]

2.1 LH_2 and CryoH_2G Jets with and without ignition

A series of tests were reported by Friedrich et al. for unignited [29] and ignited [30] CryoH_2G jets at cryogenic temperature of ~80 K and release pressure of 5, 50, 100 and 200 bar. The ignited tests considered different ignition locations at 40, 60, 100, 150, 200 cm from nozzle on jet axis. Some unignited LH_2 release tests were also conducted [31]. The nozzle diameters in these tests were 0.5, 1, 2 and 4 mm, which are much smaller than that encountered in bunkering applications. In the ignited CryoH_2G jets tests from a 4 mm diameter nozzle and 200 bar pressure as shown in Figure 1 [30], unburned cold hydrogen jet was ignited with different delay time after jet initiation at different distances from the nozzle. Then, a strong explosion with formation of a spherical shock wave occurred just after ignition. The propensity for the occurrence of such deflagration depends on several factors including release pressure, ignition location and delay time, etc. The captured overpressure from 0.04 to 0.115 MPa corresponds to a visible shock wave velocity from 390 to 480 m/s measured by high-speed imaging. As indicated in the recently added chapter on LH_2 safety in the Handbook of Hydrogen Safety [52]: "Maximum overpressure was found to be up to 3 times higher for the cryogenic releases at 80 K compared to releases at ambient temperature".

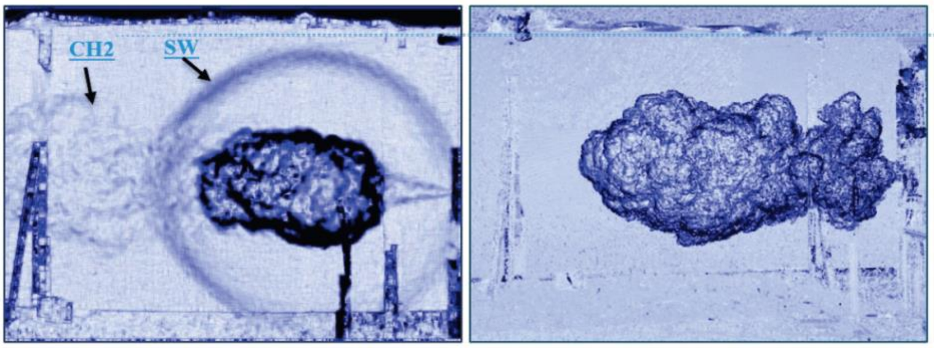

Figure 1. Shock wave formation (left) and a stationary jet fire (right) established under ignition of 4-mm nozzle and 20 MPa pressure hydrogen release: SW –shock wave; CH2 –unignited hydrogen [21].

A series of 25 LH_2 releases from a tanker delivery hose at elevated positions were carried out through 6 mm, 12 mm and 25.4 mm nozzles with an indicated tanker pressure of 1 or 5 barg [32]. No rainout was found during the release phase of the tests, but some LH_2 on the ground was observed immediately after a release with its cause unidentified. This was thought to be due to the significant accumulation of solid material on the instruments which melted and dripped onto the ground. They also quickly vapourised. The experimentalists also observed a few drips from the jet origin at the end of the test, but again these quickly vapourised. It is important to mention that condensed components of air were found to form around the release point and on impingements. In the relatively low release height of 0.5 m, vertically downward releases from a 12 mm nozzle, pools of approximately 1.7 m diameter formed. These pools potentially comprised of LH_2, condensed components of air, or a mixture of the two. It is possible that with different initial conditions or obstruction geometries, rainout and pool formation could still occur.

Allason et al. [23] and Aaneby [24] reported larger-scale tests for bunkering applications. As summarised in Table 1, the release pressures were between 0.8 to 10 bar and nozzle diameter was 25.4 mm. Two of the 7 tests involved ignition. Measurements were conducted for the release outflow conditions, extent of liquid pool and dispersing cloud, atmospheric conditions as well as fire and explosion characteristics for which the resulting thermal radiation was measured at 12 locations and the overpressure in the release near field was measured at six locations for each of the ignited tests. There were also some recordings of normal and high-speed video. Both horizontal and vertically downwards releases gave rise to plumes dispersing downwind close to the ground level. A LH_2 pool of 0.5 to 1.0 m diameter was formed on the ground for vertically downwards releases [23,24]. Ignition resulted in a VCE followed by a fire, but no fast deflagration or detonation occurred anywhere or at any time in either of the two ignited tests. As an example, still images of both the unignited and ignited events for the vertically downward release in Test 05 are shown in Figure 2. Like the HSE[4] tests reported in [32], no evidence of rainout was identified. Leakage tests into a closed room connected to the ventilation mast by Aaneby [24] indicated that it is unlikely that LH_2 releases into Tank Connection Space (TCS) would lead to clogging of the ventilation mast due to solidification of components in the atmosphere.

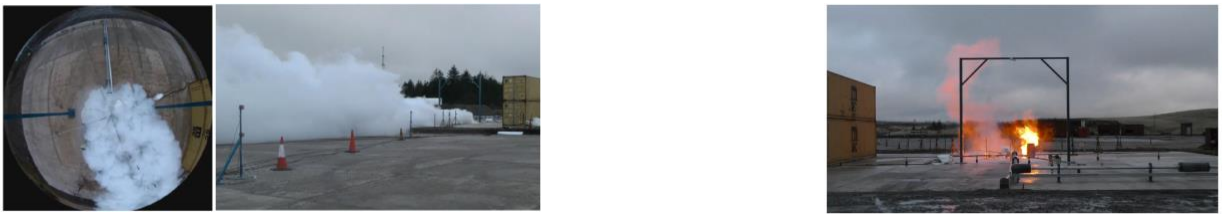

Figure 2. Still images of unignited (left) and ignited (right) tests in the vertically down release viewed from above and from northeast for Test 05 [23].

2.2 LH_2 spill over different substrates

In the PRESLHY ignited pool tests [21, 33] over different substrates, different degrees of damage were observed for the different substrate materials. As shown in Figure 3, for water as the substrate (upper left) almost no damage was observed; for substrates with a rather low porosity like concrete and sand (upper centre images), only minor damages were observed. However, in the sole tests conducted with the highly porous substrate of gravel, a complete destruction of the facility occurred (upper right image and lower row). This was thought to be due to a combination of the relatively larger amount of LH_2 that was also located in the free space in between the stones of the substrate layer as well as air components that condensed or froze at the cold substrate during the LH_2 evaporation phase in between the two filling procedures.

The above findings provided guidance for industry about these four substrates in LH_2 transfer facilities, but knowledge gaps exist for other substrates which have not been tested as well as about the propensity of such phenomenon in real-life applications. These tests [33] along with the earlier tests of Hall et al. [14] also highlighted the increased severity of VCE involving condensed O_2, for which critical knowledge gaps exist about the occurrence conditions with potential of DDT as observed in 1960s LH_2 spillage tests in open without congestion burning mixtures of LH_2 and solid O_2/N_2 [15,16]. The conditions under which these reactive mixtures could form and the wind countereffect need to be better understood.

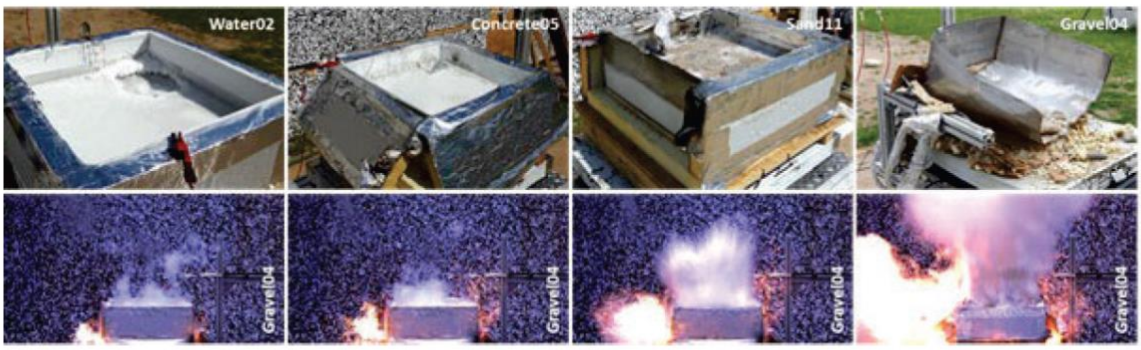

Figure 3 Different degrees of damage to the facility observed in the ignited pool experiments for the different substrates (upper row) and High-Speed video sequence of the final combustion event in experiment Gravel04 (2000 fps, lower row) [21].

2.3 Ignited releases in congested rig

Lyons et al. [34] reported 23 large-scale tests carried out at the HSE Science and Research Centre in

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[4] Health and Safety Executive

Buxton investigating the effect of differing levels of congestion and confinement on the combustion properties of a hydrogen cloud developing from LH_2 release. As shown in Figure 4, the rig included semi-confined/congested regions. Additional congestion was also provided by 99 scaffold poles in some of the tests as illustrated in Figure 4(b). The congestion levels are summarised in Table 2. The releases were from nozzles of 6 to 25.4 mm diameters. Configurable steel structure was placed directly in the path of the release to create the congestion and confinement. The mixing of the jet was also found to play a part; some releases through the largest release orifice diameter showed lower overpressures potentially due to the hydrogen cloud being too rich. Overall, the results indicated that higher levels of volumetric congestion increased the measured overpressures in releases with the same initial conditions; and an increasing hydrogen inventory, either through an increased release pressure or larger nozzle, could result in a larger event upon ignition. The exception was found for trials using the 25.4 mm nozzle, for which the lower overpressures were thought to be due to the hydrogen being too rich to efficiently combust. Details results also indicated that high congestion tests showed large variation in overpressure by an order of magnitude, implying potential for DDT.

(a) (b)

Figure 4. The tests rig used for the ignited tests with congestion and confinement (a) and attitional congestion by scaffold poles (b). [34].

Table 2. Summary of the congestion levels [34]

	Bottom half area	Top half area blockage ration (m^2/m^3)	Bottom half volume blockage (%)	Top half volume blockage ratio (&)
Low congestion	0.80	1.00	1.54	1.93
High congestion	1.53	1.33	4.20	4.60

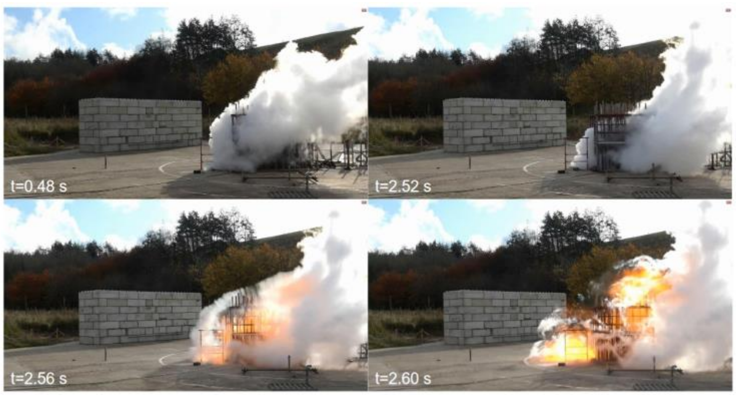


Figure 5. Stills images showing sudden gust immediately prior to ignition in Trial 23 [34].

Ambient conditions, in particular the wind speed and direction, were also found to have a significant impact in the resulting explosion for similar initial conditions. Figure 7 compares the measured over pressures from Trails 21-23, which were repeat tests with initial conditions of 1 barg tanker pressure, 12 mm nozzle and front ignitions using the high level of congestion rig shown in Figure 5(b). Trials 21 and 22 showed consistent behaviour, but Trial 23 showed a qualitatively different behaviour to other the two preceding tests even though these were carried out immediately before, in similar conditions, showing almost a tenfold increase in overpressure. The severe explosion that caused damage to the building housing the video and IR cameras. Details results illustrated the effect on cloud shape of a sudden strengthening of the opposing wind immediately prior to ignition in Test 23 [53].

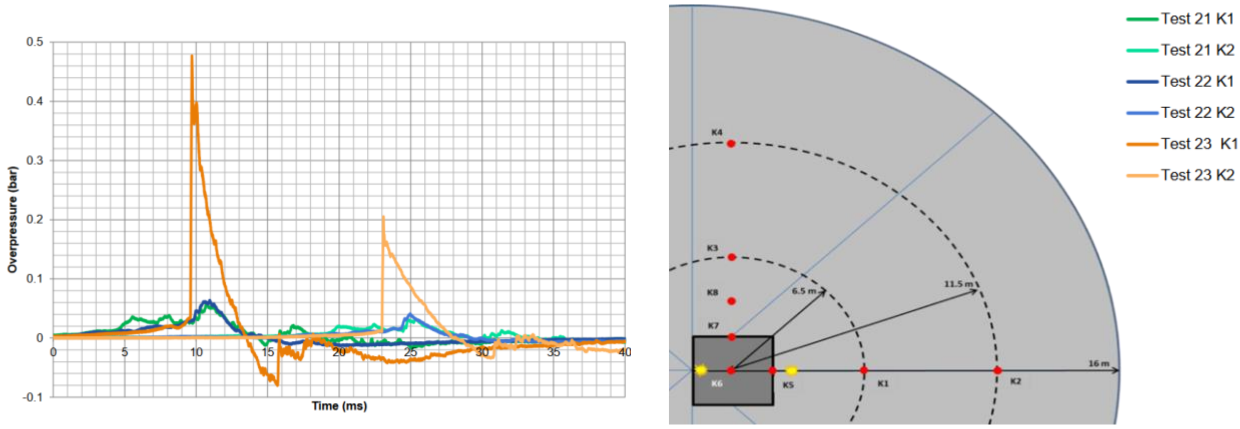


Figure 6. Overpressure comparison for the repeated trials 21 to 23 [34].

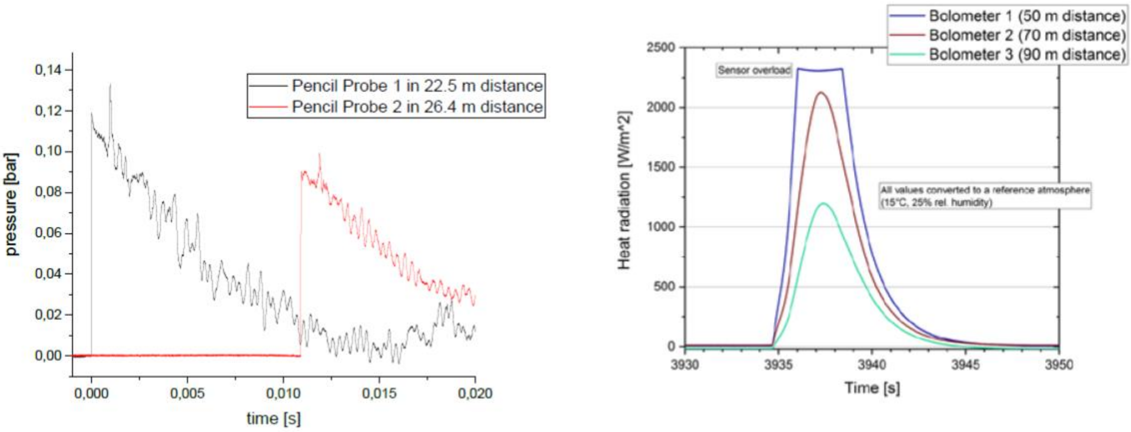
2.4 CryoH_2G flame acceleration in a shock tube

The series of tests of Kuznetsov et al. [35] in a shock tube at cryogenic temperatures (80 – 130 K) identified critical conditions for flame acceleration (FA) to the speed of sound and to the onset of detonation. The run-up distance to detonation at cryogenic temperatures was found to be two times shorter and the maximum combustion pressure at cryogenic temperatures was 2-3 times higher than that for ambient conditions due to the lower speed of sound. Further tests in a semi-confined obstructed channel by Friedrich et al. [36] provided insight into the combustion process of cryogenic inhomogeneous H_2-air layers in the semi-confined geometry and provided data for model validation.

2.5 BLEVE

Experiments of LH_2 BLEVE were firstly conducted by Pehr [37] in a small tank for automobiles containing 1.8 to 5.4 kg of LH_2. More recent tests were reported by Klug et al. [25] and Wingerden [26] for 3 vessels with perlite or multi-layer insulation (MLI) insulation being heated by propane burners from underneath. The two vessels with perlite insulation did not rupture. The vessel with MLI insulation catastrophically ruptured causing a fireball, blast wave and fragments. All together 53 fragments were found but only 28 were generated by the vessel itself, 11 parts of these from the additional instrumentation. Larger parts of the vessel were found at distances between 6 m and 167 m from the original position of the vessel. The burst of the vessel resulted in sharp shockwave and in the formation of a fireball with an irregular shape of about 24,2 m x 31.2 m. Blast waves show at least two peaks occurring shortly one after another as can be seen in Figure 7. At 22.5 m from the tank a maximum pressure of 133 mbar was measured and at 26.4 m 99 mbar. The radiative heat flux of 2.1 kW/m² was measured at 70 m from the vessel, which were less than equivalent BLEVE of LPG or LNG tanks.

It should be noted that the test conditions were not representative of transferring operations, where the fire hazards would be H_2 jet fires (localised or engulfing) rather than hydrocarbon pool fires. The instrumentation was insufficient to quantify the behaviour of the insulation layer and effects of its variation.



a) *b)*

Figure 7. Overpressure and thermal radiation after the failure of an MLI-insulated vessel positioned horizontally filled with LH_2 (a) Blast waves measured at distances of 22.5 m and 26.4 m; (b) heat radiation from the burst of the MLI-insulated vessel [25,26].

2.6 Release of LH_2 onto and under water

RPT tests were reported by Klug et al. [27] and Wingerden [28] with LH_2 around 10 bar, which is above the pressure associated with bunkering related LOC. The evaporation mechanism was found to differ from that previously observed for (liquified natural gas) LNG [28]. Traditional RPT was not observed in any of the 75 tests. Many of the releases resulted in VCE with ignition source unidentified. Only far field camera recordings were done. Using the IR-cameras allowed to locate the ignition in "free-air" with a clear distance from the instrumentation bridge and any instrumentation as shown in Figure 8.

It should, however, be noted that these tests were not representative of transfer operations in terms of height above/underneath fresh water with regards to early RPT, i.e., direct mixing with water, for which height can indeed promote penetration depth and intense mixing while for more traditional delayed RPT, height is unlikely to be influential. Semi-confined explosions associated with potential releases between ship hull and harbour was not investigated in these tests.

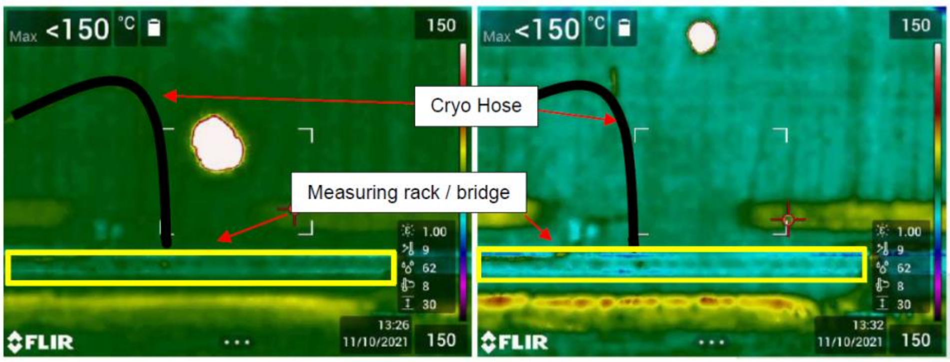


Figure 8. Moment of initial flame propagation in H_2-air clouds ("white spots") generated by releases of LH_2 onto and under water. The ignition location appears to be somewhere in the cloud at a distance from any physical object. The locations of the release point (cryo hose) and measuring rack/bridge have been indicated [27,28].

3.0 STATE-OF-THE-ART IN CFD MODELS

Published CFD models with validation for cryogenic H_2 gas mainly involve unignited [2,38] and ignited jets [4,39]. Few CFD simulations involving LH_2 are available in the open literature covering only pool spread [8,40]. Wen and Xu [41] developed a CFD model for VCE from large-scale LH_2 spill, jet dispersion and fires in two short feasibility study projects. These were mainly exploratory studies without validation. As an example, Figure 9 illustrates the pressure evolution in the middle after the ignition for the case with a 10 m barrier wall. The ignition process produces a strong blast wave emitting from the ignition point. It was found that the strength of this blast wave is affected by the size and temperature increasing rate of the ignition source. This initial blast wave is reflected from both the ground and barrier wall and propagates outwards, quickly dying out at 60 ms after the ignition. Meanwhile another blast wave caused by the fast deflagration is initiated and catching up with the first blast wave. The second blast wave passes the barrier wall and is reflected from the ground behind the barrier wall, creating a local high-pressure region.

In addition to lack of validation, the turbulent flame speed correlations required in all CFD simulations of cryogenic jet fires and VCE are still based on those for ambient conditions, the resulting error in prediction is unknown and affects all existing CFD/engineering models. The tests of Kuznetsov et al. [35] indicated that such extrapolation may be erroneous due to faster flame development in cryogenic conditions.

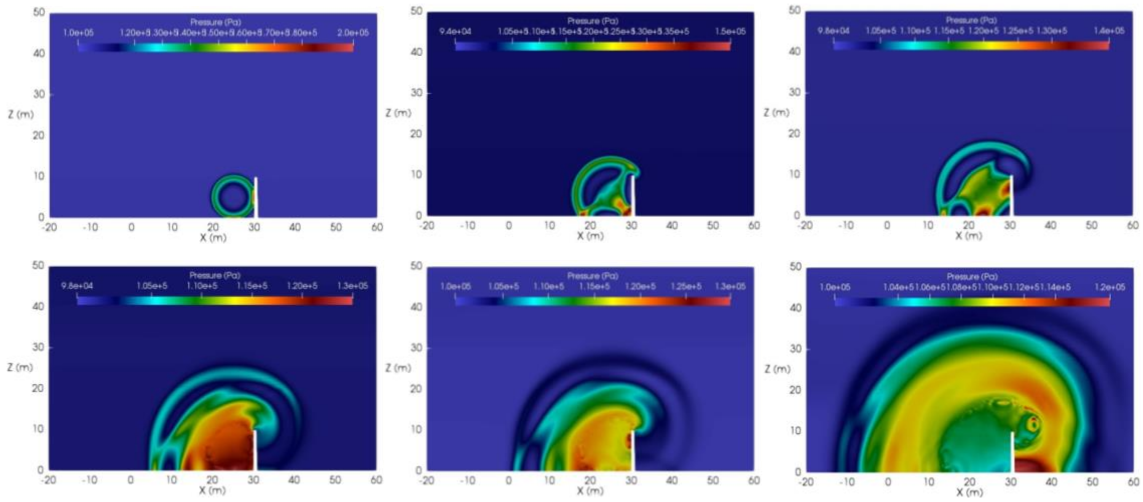


Figure 9. Predicted contours of pressure in the middle plane for the case of IR10 at a time sequence of 10 ms, 20 ms, 30 ms, 50 ms, 60 ms, 100 ms after the ignition.

Concerning the prediction of pressure build up in cryogenic tanks exposed to external heat sources, such as thermal flux resulting from lack of insulation or external fire, limited studies are available in the literature. Landucci and co-workers [56] evaluated the effect of pressure build up in i) LNG vertical tanks in case of defective insulation and ii) LNG horizontal tanks engulfed in fire. The developed model can predict detailed temperature contours during the heat up; but the model has yet to be extended to LH_2 tanks and non-uniform thermal impact, e.g., from a localized hydrogen jet fire. Neither is the model able to handle the prediction of vessel discharge following the opening of a pressure relief device.

CFD simulations of BLEVE consequences were attempted simulated by Ustolin et al. [11] by predicting pressure waves following tank rupture without incorporating the fireball captured in the tests of both Pehr [37] and Wingerden [25,26], omitting a primary consequence of LH_2 BLEVE which significantly affects the explosion yield.

4.0 STATE-OF-THE-ART IN ENGINEERING MODELS AND TOOLS

The list compiled in PRESLHY [42] included HyPOND for the extent of cryogenic pools and laminar burning velocity and expansion ratios for cryogenic H_2 -air mixtures developed by partner INERIS; the final state when mixing LH_2 and moisture in the air, flow in a discharge line, electrostatic field-up generated during H_2 releases, FA and DDT, fireball size, flame length, hazard distance and thermal load from jet fires developed by other PRESLHY partners. While the list includes some engineering models developed for gaseous H_2 at ambient conditions, e.g., concentration decay in momentum jets, the suggestion that such model can be used for LH_2 jets with reasonable accuracy is not fully backed by evidence.

Focus of available models is rather on fireball and blast effects. There are methods for projectiles but either purely empirically based or considering more deterministic ballistic type approach. A comprehensive review was conducted in SH_2IFT project [10], identifying the ones giving conservative results with uncertainty surrounding the contribution of combustion to explosion yield.

An attempt to simulate the consequences of the catastrophic rupture of LH_2 tanks using engineering models was carried out by Ustolin et al. [11] by predicting pressure waves following tank rupture without incorporating the fireball captured in the tests of both Pehr [37] and Wingerden [25,26], omitting a primary consequence of LH_2 BLEVE which significantly affects the explosion yield.

A comprehensive review of engineering models for BLEVE simulations was conducted in SH_2IFT project [10], focusing on the mechanical energy evaluation and fireball heat radiation calculation. The models for mechanical energy evaluation were applied for the simplified assessment of BLEVE overpressure and fragments projection evaluation, identifying the approaches that provide conservative predictions. More detailed approaches for fragments projection following BLEVE events of pressurised tanks were developed in previous works based on probabilistic models but not yet applied for the analysis of LH_2 BLEVEs.

In the context of RPT, thermodynamical analysis of the physical processes following a film-boiling collapse by Odsæter, et al. [12] suggested triggering of an LH_2 RPT event from LH_2 spill on water is very unlikely, and the consequences of a hypothetical LH_2 RPT are small compared to LNG RPT. These analyses were not thoroughly benchmarked against experimental data. Further benchmarking tests are necessary before these correlations or existing industry consequence models can be recommended for practical applications. In addition, the investigation in [12] was restricted to delayed RPT i.e. with a layer of LH_2 over water. Early RPT involving LH_2 sinking and evaporating through water was not addressed.

5. RISK ANALYSIS

Considerable studies have been conducted for quantified risk analysis (QRA) of gas hydrogen transfer facilities [43,44] using established QRA methodologies and tools, CFD and engineering models/tools. It is useful to add the development of procedures for the aerospace industry – NASA, ESA and JAXA. For example, NASA did a lot of work in the 50's and 60's developing the constituent parts of a QRA [54], with important details such as the increased flammability for LH_2 to 94% when mixed with LO_2. Liquefaction of the surrounding air was observed in LH_2 release tests, making this significant. JAXA has invested in remote ship to land transfer system specifically designed to negate this and avoid LO_2 being formed [55]. These developments were purely sector driven and independent of the recent global trend.

QRA for LH_2 transfer applications received considerably less attention in the open literature. The lack of reliability data for bulk LH_2 storage systems located on site at fuelling stations limits the use of QRAs and hinders the ability to develop the necessary RCS that enable worldwide deployment of LH_2 transfer technologies [45]. Growth and co-workers [46] identified gaps of scenario and reliability data for LH_2-related components to inform QRA using Failure Mode and Effect Analysis (FMEA) as well as traditional QRA tools such as Event Sequence Diagrams (ESD) and Fault Tree Analysis (FTA). The exploratory CFD analysis of Hansen [47] indicated the need for higher safety standards for LH_2 fuelled vessels than that of LNG. The current zoning definition in NFPA 2 for electrical classification, for example, considers the extent of LH_2 in zone 2 to be between 1-7.6 m *vs* gas hydrogen 0.9-4.6 m. Such prescription is not supported by QRA and may indeed result in costly over conservative design.

Among the 4 tools identified by Growth and co-workers [48] that collect H_2 system safety data, H2Tools (https://h2tools.org/) and HIAD 2.0 [48] are most widely used. The former also contains Best Practice Recommendation for the handling of cryogenic LH_2. HYRAM is a QRA tool used by some of the international H_2 community [49,50], for which engineering models and reliability data for LH_2 systems are still to be implemented. In should be noted that these tools collect information about the incidents, information relevant for reliability and risk analysis or of relevance to general safety, they do not contain statistics that enable derivation of failure rate or leak frequencies.

Kim et al. [51] considered the interactions between LH_2 tanks and recommended that the neighbouring facilities need to be considered and the design judgement should be made from the holistic view over the entire LH_2 supply chain with appropriate operation scenarios.

6. CONCLUDING REMARKS

The manuscript has reviewed knowledge gained by the international hydrogen safety community that is relevant to LH_2 bunkering and in the public domain. Despite the progress made, improved understanding needs to be developed to meet industry needs to design and operate inherently safe LH_2 operations as well as inform RCS. These include:

- While tests have investigated LH_2 spill over some substrates, there are still some substrates which need to be considered for bunkering facilities that were not addressed in these tests.
- Critical safety related knowledge gaps still exist about the formation of condensed H_2-O_2-N_2 mixture with potential for DDT, especially the propensity for such scenario in real applications.
- No tests have been conducted to investigate the effects of the impact of both unignited and ignited LH_2 jets on materials/equipment.
- The effect of localised or engulfing H_2 jet fires on LH_2 tanks has not been investigated. Quantitative data is missing concerning the effect of different insulation materials as well as the same materials but different grade and packing density on the propensity to BLEVE.
- The mechanical and thermal consequence of BLEVE in practical scenarios have not been analysed as well as the phenomena occurring during the heat up of LH_2 tanks exposed to fire.
- Previous LH_2 spill over water tests were not representative of bunkering applications, e.g., for shore to ship loading where RPT is a likely scenario and the associated VCE in semi-confined environment has not been addressed.
- A viable approach is lacking in the current lack of LH_2 failure data to estimate failure frequency in QRA.
- An effective framework is missing to collect and update frequency data repository to facilitate QRA.
- Currently, there is no standard for any LH_2 transfer operations. Barrier walls are required by NFPA2 for LH_2 bulk storage systems. While barrier walls can limit spread of unintended releases, mitigate fire thermal dose and explosion pressure, they also inhibit cloud dispersion and increase explosion severity. Their pros and cons need to be analysed for specific operational environment.

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