

# SAFETY ISSUES OF THE LIQUEFACTION, STORAGE AND TRANSPORTATION OF LIQUID HYDROGEN: STUDIES IN THE IDEALHY PROJECT

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## ABSTRACT

The objectives of the IDEALHY project, which receives funding from the European Union's 7<sup>th</sup> Framework Programme (FP7/2007-2013) for the Fuel Cells and Hydrogen Joint Technology Initiative under grant agreement No. 278177, are to design a novel process that will significantly increase the efficiency of hydrogen liquefaction and be capable of delivering liquid hydrogen at a rate that is an order of magnitude greater than current plants. The liquid hydrogen could then be delivered to refueling stations in road tankers. As part of the project, the safety management of the new large scale process and the transportation of liquid hydrogen by road tanker into urban areas are being considered. Effective safety management requires that the hazards are identified and well understood. This paper describes the scope of the safety work within IDEALHY and presents the output of the work completed so far. Initially, a review of available experimental data on the hazards posed by releases of liquid hydrogen was undertaken, which identified that, generally, there is a dearth of data relevant to liquid hydrogen releases. Subsequently, HAZIDs have been completed for the new liquefaction process, storage of liquid hydrogen and its transportation by road. This included a review of incidents relevant to these activities. The principal causes of the incidents have been analysed. Finally, the remaining safety work for the IDEALHY project is outlined.

## 1.0 BACKGROUND

Hydrogen is seen as an important energy carrier for the future which offers carbon free emissions at the point of use. In particular, hydrogen could be used to power vehicles using hydrogen fuel cell technology and thereby replace the use of petrol and diesel. However, to achieve this goal, vehicle refueling stations would need to be supplied with large quantities of hydrogen on a regular basis. In the absence of a hydrogen pipeline supply network, which would be costly and take considerable time to build, hydrogen could be supplied using road tankers. However, transporting hydrogen by road as a compressed gas is very inefficient, for example, a road tanker carrying high pressure hydrogen might typically carry 300 to 400 kg and be able to refuel up to about 100 cars. A tanker carrying liquefied hydrogen (LH2) can carry a much larger inventory, 2.5 to 3.5 t, and so refuel about 1000 cars [1,2]. Liquid hydrogen can easily be converted to the high pressure hydrogen needed for the vehicles. Shell already operates a liquid hydrogen-supplied refueling station in Berlin, which, with minor modifications, could refuel 400 fuel cell cars per day [2].

In the absence of a gaseous pipeline, supplying LH2 by road tanker is seen as the most effective way forward in the medium term. This will require large quantities of LH2 to be produced, stored and transported to vehicle refueling stations. At present the production of LH2 is generally at small scale (typically 2 to 5 tpd) [3] and is very energy intensive, typically 12 kWh kg<sup>-1</sup>. The IDEALHY project ([www.idealhy.eu](http://www.idealhy.eu)), which receives funding from the European Commission's 7th framework programme (FP7/2007-2013) for the Fuel Cells and Hydrogen Joint Technology Initiative (Contract 278177), has the aim of developing a new hydrogen liquefaction process which will enable LH2 production to be undertaken at increased scale (50 to 200 tpd) and with significantly increased efficiency. The goal is to reduce the specific power consumption to around 6 kWh kg<sup>-1</sup>.

## **2.0 INTRODUCTION**

The production of large quantities of LH2 and the subsequent road transportation and storage at vehicle refueling stations (often in urban areas) present new challenges in terms of ensuring the safety of workers and the public. For example, in relation to the new large scale process for the production of LH2, there are a number of factors which may affect the hazard presented by the process plant, such as larger inventories of stored LH2, higher pressure operation, larger diameter pipework and the use of other hydrocarbons as refrigerants (such as propane). Another specific option which is to be considered by IDEALHY is the possible integration of LH2 production with liquefied natural gas (LNG) storage operations, so that the regasification of LNG can be used as part of the pre-cooling of hydrogen. New designs of equipment will also be required, such as cryogenic valves larger than any available to date, and turbo-compressors operating with lighter gases and higher pressure ratios than current designs. With regard to road transportation, transporting hydrogen as a liquid is significantly more efficient than as a gas in terms of the load carried per vehicle. This reduces the number of tanker deliveries, but since each tanker will have an increased capacity, potentially increases the severity of a 'total loss' accident scenario.

For these reasons, as part of the IDEALHY project, the hazards of the proposed production and supply system are being considered with a view towards understanding the associated risks (and so minimizing them in the design and operation). Three stages of the safety study have been identified. Firstly, existing knowledge is to be reviewed and gaps identified. In particular, the literature review focused on the availability of experimental data (especially from large scale experiments) relating to the hazards posed by releases of LH2. Where possible, parameters, such as the evaporation rate from a liquid spill and the fraction of heat radiated from a fire, which are used in mathematical models of the consequences of releases, have been identified. The second stage was the conduct of two Hazard Identification exercises (HAZIDs). One HAZID concerned the new liquefaction process and storage of LH2, and the other HAZID related to road transportation by tanker and offloading at a refueling station. Both HAZID exercises were conducted with the input of all the partners of the IDEALHY project, building on their expertise of the process involved. This stage also included a review and analysis of incidents involving LH2. Both of these stages have been completed and the results are summarized in Sections 2 and 3 below. At the time of writing, the final stage has not been undertaken. As discussed further in Section 4, the objective is to consider some typical release scenarios identified by the HAZIDs and, where possible, determine the consequences with available mathematical models. However, it is likely that current models may not be suitable or validated for use with LH2. Overall, the aim is to identify information needed for risk and hazard analyses to be undertaken, particularly in relation to the new liquefaction process and the subsequent road transportation of LH2 to refueling stations. Such analyses and subsequent risk mitigation are relevant to the design stage and during operation.

## **3.0 REVIEW OF EXPERIMENTAL DATA FOR LIQUID HYDROGEN RELEASES**

A detailed literature review of experimental data relating to liquid hydrogen releases was undertaken. The purpose was to gain an understanding of the nature of LH2 releases and where possible identify parameters from experiments which are required for consequence models. An abridged version of this review is provided below.

### **3.1 Releases forming Pools of LH2, Evaporation and Dispersion**

In order to be able to understand and predict the dispersion behaviour of hydrogen following a spill of LH2, it is crucial to understand how the LH2 pool is formed, spreads and evaporates. When a cryogen that is stored at a temperature above its boiling point at atmospheric pressure is released, a certain proportion will flash evaporate. However, a liquid pool may form if the leak rate exceeds the evaporation rate, which itself will vary according to the substrate and usually reduces with time. Verfonden and Dienhart [4] present calculated values of heat flux to a LH2 pool from conduction from

the ground ( $\sim 100 \text{ kW m}^{-2}$ ), atmospheric convection ( $\sim 0.8 \text{ kW m}^{-2}$ ) and solar radiation ( $\sim 1.6 \text{ kW m}^{-2}$ ), from which it can be seen that ground conduction is dominant and that it is reasonable to ignore the other mechanisms. As an approximation, assuming the pool is close to boiling point, the initial (maximum) vapour evolution rate would be about  $0.2 \text{ kg m}^{-2} \text{ s}^{-1}$ . Thereafter, the evaporation rate reduces as the ground cools, in proportion to  $t^{-1/2}$  (where  $t$  is time) [5].

Few systematic experimental tests to determine vapour evolution rate from LH2 pools have been performed and those that have, are at laboratory scale. Zabetakis and Burgess [6] measured evaporation rates from LH2 pools at laboratory scale using a 65mm diameter glass Dewar with the LH2 pool formed on a block of paraffin wax. After an initial period of rapid evaporation, the evaporation rate steadied to about  $0.03$  to  $0.06 \text{ kg m}^{-2} \text{ s}^{-1}$ . More recently, experiments were conducted on 50 and 100 mm diameter pools on concrete and sand substrates [5]. For concrete, an initial heat flux of about  $60 \text{ kW m}^{-2}$  was measured corresponding to a vapour evolution rate of  $\sim 0.13 \text{ kg m}^{-2} \text{ s}^{-1}$ . After this, the vapour evolution rate fell from about  $0.09$  to  $0.04 \text{ kg m}^{-2} \text{ s}^{-1}$  between 20 and 100s. Lower evaporation rates were measured for sand compared to concrete.

Trials by NASA in the 1980s [7] involved 7 spills of  $5.7 \text{ m}^3$  ( $\sim 405 \text{ kg}$ ) of LH2. The spill area was not well instrumented so there is little information on pool spread/size, although in one test where  $5.7 \text{ m}^3$  was spilled over a period of 35 s, the pool radius was between 2 and 3 m.

In general terms, the size and shape of dispersing vapour from a LH2 pool is determined by the density differences between the vapour/air mixture at any location and the atmosphere, the atmospheric conditions and the local topography. Initially, the low temperature results in the vapour/air mixture being heavier than air and spreading close to ground level. Heat transfer from the ground and the entrainment of ambient air will create thermally induced turbulence and increased buoyancy promoting mixing in the vertical direction. LH2 needs only an increase from 20 to 22 K to reach the same density as air. As the buoyancy of the vapour mixture increases it will rise as it progresses downwind. Under stable atmospheric conditions a long plume can be produced in the downwind direction. The worst case is for a large release generated with minimal turbulence on a cold day with strong atmospheric stability, as these conditions will favour an extended plume at low level.

Another factor influencing the dispersion of cold hydrogen is the condensation of moisture from the atmosphere, producing a visible plume. This phase change will liberate heat, reduce the density and so enhance buoyancy. It can be assumed that the mixing of the hydrogen and air is in thermal equilibrium [7, 8], so the temperature of the plume correlates to the concentration. Hence, the dewpoint for the prevailing temperature and humidity will correlate to a particular gas concentration. The visible and flammable plume boundaries coincide for an ambient temperature of around  $-3$  to  $27 \text{ }^\circ\text{C}$  and humidity levels of 50 to 57% [9]. During spills conducted with atmospheric temperatures in the range 12 to  $30 \text{ }^\circ\text{C}$  and humidity levels 18 to 49%, the visible plume corresponded to a concentration of 8 to 9% [7].

During the NASA trials [7], the vapour spread close to the ground for about 100m then rose at a rate of about  $0.5$  to  $1.0 \text{ m s}^{-1}$ . Momentum and thermally induced turbulence promoted mixing and shortened the dispersion distances compared to that expected for atmospheric turbulence induced mixing. The extent of the flammable plume close to ground level was increased for higher wind speeds. In experiments by Proust et al. using helium [8] the dispersing plume was driven by an upward motion at an angle of about  $30^\circ$  with respect to the horizontal with an upward velocity 1 to  $2 \text{ m s}^{-1}$ , for wind speeds of 3 to  $6 \text{ m s}^{-1}$ . The maximum extent of the plume depended significantly on flowrate and the authors concluded that buoyancy forces played a significant role in plume formation and that the coefficient of turbulent diffusion was at least twice as great as that for atmospheric turbulence alone.

Experiments in Germany [10] studied vapour dispersion near buildings at release rates of typically  $0.6$  to  $0.8 \text{ kg s}^{-1}$ . Complex wind patterns arose resulting in plume back flow near the source, dense behaviour at near range and buoyant behaviour at far range as well as interaction of the building with the release wake.

### 3.2 Prolonged Pressurised Releases , Evaporation and Dispersion

In 2 of 7 experiments conducted by NASA [7, 11], LH2 was released over a prolonged period at a rate of about  $1.7 \text{ kg s}^{-1}$ . The authors found that the extent of the flammable cloud close to the ground was up to 120 m and argued that prolonged spills could result in a greater extent to the lower flammable limit (LFL) compared to an instantaneous spill as there is less momentum induced mixing than arises for larger instantaneous spills. Also, the ground becomes chilled and reduces the heat transfer, which is a major factor in the vaporisation of the LH2. Hence thermally induced mixing is also reduced.

If a cryogen is stored under pressure and hence at a temperature above its normal boiling point, the liquid is superheated and, on release to the atmosphere, flashing will occur. The proportion that flashes depends on the degree of superheat and the vapour fraction which flashes can be estimated using: [12]

$$\frac{\dot{m}_{vf}}{\dot{m}} = \frac{(T_i - T_{bp})C_{pl}}{H_i} \quad (1)$$

where  $\dot{m}_{vf}$  - flowrate of vapour which flashes ( $\text{kg s}^{-1}$ );  $\dot{m}$  - total release rate ( $\text{kg s}^{-1}$ );  $T_i, T_{bp}$  - liquid temperature when stored, normal boiling point respectively;  $C_{pl}$  - specific heat capacity of the liquid;  $H_i$  - latent heat of vaporisation. Assuming storage at an absolute pressure of 3 bar, the storage temperature will be about 24.5 K, giving 4.2 degrees of superheat. The estimated vapour fraction from flashing is 0.1. The expansion and vaporisation also leads to the production of liquid droplets in a spray, which may be carried by the jet and vaporise contributing to the vapour fraction. As an approximation, it is suggested to double the fraction which flashed, giving about 0.2, hence significant rain-out would be expected. More recent experiments [13], (simulating failures of a tanker transfer hose) studied LH2 released from a 26 mm diameter hole at  $60 \text{ litres min}^{-1}$  ( $0.07 \text{ kg s}^{-1}$ ) at a gauge pressure of 1 bar for periods of several minutes. Significant rain-out occurred, consistent with the above assessment) and a pool was formed once the substrate was sufficiently cooled. In addition, solidified air was observed near the release. Substrate temperatures, pool size and gas concentration were measured. A flammable mixture was produced at least 9 m downwind. Friedrich et al [14] studied small pressurized cold (typically 35-45 K) gaseous hydrogen releases at pressures up to 30 bar from 0.5 and 1 mm diameter nozzles giving flowrates of  $0.002\text{-}0.008 \text{ kg s}^{-1}$ . Gas concentration was measured on the release axis.

### 3.3 Ignitability

Hydrogen has wide flammability limits (4 to 75%) and low ignition energy (<0.02 mJ at stoichiometric conditions). Hence possible ignition sources are numerous. ‘Spontaneous ignition’ has also been reported in the context of hydrogen releases. The HYSAFE biennial report [9] provides a comprehensive review of ignition sources of hydrogen and the causes of spontaneous ignition have also been reviewed by Gummer and Hawksworth, [15].

Clearly, ignition sources such as an open flame will in any circumstances ignite a flammable hydrogen/air mixture. Heating above the auto-ignition temperature (585 °C) can also cause ignition. However, hot surface ignition of hydrogen has been observed at 500 °C and down to 347 °C when at reduced pressure [15]. Sparks generated by merely light metal to metal contact (including alloys) have sufficient energy to ignite hydrogen/air mixtures [9]. Ignition by electrostatic sparks generated by 3 different mechanisms have been considered [15]. Firstly, between two isolated conductors, such as could occur due to the electrostatic charging of people standing on an insulated surface during vehicle refueling. Secondly, brush discharges between a charged insulator and a conducting earthed point. Thirdly, corona discharges, particularly from atmospheric electrical activity. This probably accounts for ignitions of hydrogen vents during thunderstorms, sleet, falling snow or cold frosty nights.

Two mechanisms in particular have been postulated for ‘spontaneous ignition’: Joule-Thompson effect and Diffusion Ignition [15]. Calculations have established that the Joule-Thompson effect is incapable

of achieving the auto-ignition temperature [15]. Diffusion ignition is the term used to describe the shock wave produced by the release of high pressure gas into the air, which results in high temperatures at the contact surface, potentially high enough to cause auto-ignition. Experiments reported by Astbury and Hawksworth [16] where hydrogen at 150 bar was released to atmosphere through orifices from 1 to 12 mm diameter resulted in no ignitions. However, experiments by Dryer et al [17] showed, for the first time, that ignition is possible as a result of high pressure hydrogen (~40 bar) released into the atmosphere at normal temperatures (~10 to 30 °C). Rapid pressure release and good mixing are described as being important and that the conditions for ignition are dictated by reflected shock and shock-shock interactions. The downstream geometry or objects in the path of a sudden discharge have an impact on whether shock induced spontaneous ignition will occur.

Due to the very low temperature of liquid hydrogen, condensation of air occurs and, in particular, solid oxygen can be formed. The resultant solid oxygen in an excess of liquid hydrogen is shock sensitive and can be detonated by impact with an explosive yield greater than that for equivalent weights of TNT [9]. In the context of hydrogen liquefaction processes, the presence of solid oxygen in valves is a hazard as closure of the valve may provide the necessary shock for an explosion to result. Also, a spill of liquid hydrogen forming a pool, may result in solid oxygen forming. Any subsequent re-gasification of oxygen will result in an oxygen-enriched flammable mixture with reduced ignition energy and enhanced rate of combustion, increasing the likelihood of detonation [1].

### 3.4 Pool Fires

Following a spill of LH2, vapours will readily evolve due to the warm surface below the pool. Once ignited, the back radiation from the fire to the pool surface will enhance vaporisation of the liquid, until a steady state level is reached. The combustion rate of the fire is directly related to the vapour evolution rate, that is, the mass burning rate equals the vapour evolution rate and is usually expressed in  $\text{kg m}^{-2} \text{s}^{-1}$ . The mass burning rate increases with size of pool to an upper level once the pool exceeds a certain size, which itself is fuel dependent. The mass burning rate is an important parameter for the modelling of pool fires and assessing the hazard as this gives the rate that energy is released by combustion, a proportion of which is released as radiation to the surroundings, and referred to as the 'fraction of heat radiated'.

There is a dearth of information on the behaviour of liquid hydrogen pool fires, with only one source of experimental data being identified [6]. The pool sizes were small (up to 0.33m diameter) and extrapolation to large fires may be questionable. Furthermore, they were conducted in Dewars, eliminating heat transfer from the substrate. As expected, the mass burning rate increased with pool size with the maximum measured rate being  $0.015 \text{ kg m}^{-2} \text{ s}^{-1}$ , but theoretical analysis suggested that the maximum rate (for a large fire) would be  $0.018 \text{ kg m}^{-2} \text{ s}^{-1}$  (with a noted error of up to 50%). For LNG, the mass burning rate is of the order of  $0.1 \text{ kg m}^{-2} \text{ s}^{-1}$ . In later work by the same authors [18], focused on LNG, an empirical relationship for mass burning rate was derived in terms of the net calorific value and latent heat of vaporisation. For LH2, this gave a maximum mass burning rate of  $0.024 \text{ kg m}^{-2} \text{ s}^{-1}$ , consistent with the earlier experimental work. This value seems low compared with the evaporation rate already discussed in Section 3.1 above (up to  $0.1 \text{ kg m}^{-2} \text{ s}^{-1}$ ) and is probably due to the lack of heat transfer from the substrate. Consequently, the mass burning rate for LH2 spills onto a realistic substrates such as concrete could be substantially higher. In a realistic situation, the evaporation rate as a result of heat transfer from the substrate together with the evaporation rate as a result of the radiative feedback from the flame will affect the size of the flame and hence, in turn, affect the radiative feedback from the flame, so the pseudo-steady mass burning rate cannot be obtained by summing the evaporation rate when unignited and the mass burning rate from fires in a Dewar.

Regarding the fraction of heat radiated for LH2 pool fires, Zabetakis and Burgess [6] comment that they were expecting the LH2 pool fires to be similar to methanol, since both produce flames that are nearly non-luminous. However, the fraction of heat radiated was determined to be 0.25, making LH2 pool fires more akin to hydrocarbon fires (compared to about 0.15 for methanol). However, there was

no detail provided on how the fraction of heat radiated was determined. Finally, it is possible that atmospheric absorption (due to water vapour) of the radiation from hydrogen fires may be greater than that experienced for hydrocarbon fires, which may reduce the incident radiation received from a hydrogen fire [6].

### 3.5 Jet Fires

Jet fires may arise following the pressurised release of a gas or volatile liquid from a hole in a vessel or pipework. Such fires are characteristically long and thin. At high pressures, the momentum causes the initial fire direction to be in the direction of the release, regardless of the buoyancy of the fuel involved. Flashing liquid jet fires, such as those from pressurised releases of propane or LH2, may have less momentum, depending on the drive pressure and be more affected by buoyancy. Small hydrogen jet fires are non-luminous in daylight, although generally visible as a yellow/orange flame in lower light conditions. Larger fires are more visible. The key parameters that need to be determined in order to assess the thermal hazard are: release rate, flame length and fraction of heat radiated.

For gaseous jet fires, the rate of combustion is equal to the release rate, which can be readily calculated. A number of experimental studies of gaseous hydrogen jet fires have been undertaken and correlations for the flame length derived, some of which are summarized below in Table 1. The vast majority of studies are at small scale. In many cases, the flame length,  $L$  (m), is calculated as a function of the power of the release,  $Q$  (W), determined by the mass flowrate times the net calorific value, although some authors adopt a more complex approach, correlating a non-dimensionalised flame length with an expression involving the flame Froude number ( $Fr$ ). API 521 [19] suggests  $L=0.013Q^{0.41}$  for a power range of  $10^8$  to  $10^{10}$  W and Lowesmith et al [20] uses the correlation  $L=0.0167Q^{0.3728}$  which was developed from an extensive body of data for natural gas but shown to be applicable to other hydrocarbons and large scale hydrogen fires for a power range  $5 \times 10^6$  to  $2 \times 10^{11}$  W.

Table 1. Summary of Experimental Studies of Gaseous Hydrogen Jet Fires

Ref	Dia (mm)	Pressure (bar)	Flow (kgs-1)	Energy (MW)	Flame length (m)	F
[21]	0.1-4	Up to 400	$10^{-3}$ - $10^{-1}$	0.12-12	< 1m for 0.4mm dia. 5m for 2mm dia at 350bar. $L=0.00106 Q^{0.53}$	0.0078-0.03
[22]	1-3	Up to 900	0.04-0.17	4.8-10	Up to 6.5m for 3mm dia.	0.05-0.15
[23]	4-10	Up to 100		1-25	~7m for 7mm dia. 5m for 4mm dia. $L=0.0016 Q^{0.5}$	0.04-0.1
[24]	1.91	0.021	0.083	10	Correlated with $Fr$	0.05-0.1
[24]	5	431	0.359	40	Up to 10.5m. Correlated with $Fr$	0.05-0.08
[25]	7.94	140-160	0.057	6.9	Up to 5m. Correlated with $Fr$	0.04-0.08
[26]	21 52.5	60 60	1 7.4	120 900	17.4 48.5	0.15* 0.22*
[6]	5-406					0.09-0.17
[14]	0.5	30	0.002	0.24		0.06

\* on multi-point source basis

The fraction of heat,  $F$ , radiated is usually derived from measurements of the incident radiation from a fire. The simplest approach, which is commonly used, is the point source method, whereby the flame is represented by a single point located half-way along the flame length, using:

$$I = \frac{FQ\tau}{4\pi d^2} \quad (2)$$

where  $I$  - incident radiation ( $W m^{-2}$ ) measured  $d$  (m) from the point source;  $\tau$  - atmospheric transmissivity;  $Q$  - power of the release (W);  $F$  - fraction of heat radiated. Due to the large aspect ratio

of jet fires, this method can be inaccurate and a multi-point source approach can significantly improve the method [27]. Other workers have calculated the fraction of heat radiated using [28]:

$$F = 0.085 \log_{10}(t_f a_f T_{ad}^4) - 1.16 \quad (3)$$

where  $t_f$  - flame residence time (s);  $a_f$  - Planck mean absorption coefficient ( $m^{-1}$ );  $T_{ad}$  - adiabatic flame temperature (K). Lowesmith et al [30] suggests that F is a constant for large scale jet fires, dependent only on fuel type. However, other workers have shown that F increases with fire size, as does the Molina et al. correlation. This certainly seems to be the case for small scale fires as can be seen in Table 1. What is notable is that, for larger gaseous hydrogen releases, the fraction of heat radiated can be comparable to natural gas fires which is in contrast to the perception that hydrogen flames have a low radiation hazard due to their low luminosity.

Concerning liquid hydrogen jet fires, Kikukawa et al [29] cite some jet fires at relatively low pressure from 1 and 14 mm diameter holes resulting in flames 1.7 and 10 m long respectively. It is not made clear if the released hydrogen was liquid or gas, nor is the release rate given. More recently, Hooker et al [13] studied ignited releases of LH2 from a 26 mm diameter hole at a gauge pressure of 1 bar, resulting in a flowrate of  $0.07 kg s^{-1}$ . Measurements of thermal radiation were made. A theoretical assessment, of an unignited release (Section 3.2) suggests that for the expected storage pressure, only about 20% of the liquid will flash overall, so significant liquid drop-out might be expected, although radiation from the fire may significantly reduce or eliminate this effect. At this release pressure, the jet fire will be relatively low momentum and buoyancy of the flame will play a part in determining the flame trajectory. The flame length may also be shorter if not all the fuel released is involved in the jet fire. It is reasonable to expect that the fraction of heat radiated for LH2 jet fires will be the same as for gaseous jet fires.

### 3.6 Gas Accumulation and Explosion Hazards

**Gas accumulation:** Due to the low density and high diffusivity of hydrogen, the likelihood of a release of gaseous hydrogen in an open or well-ventilated region forming a flammable mixture in the vicinity of the release is reduced [1]. Within an enclosure, low momentum releases will tend to form a layer of uniform concentration above the release height, as demonstrated by Cariteau et al [30] using helium, in an enclosure typical of a private domestic garage. However, factors such as the size and aspect ratio of the enclosure, ventilation flows and, in particular, release momentum can modify this behaviour and lead to accumulations throughout the entire enclosure, as demonstrated by Tanaka et al [31] in tests within a replica of a high pressure storage room. In other tests, [31], high momentum releases into an open area with a boundary wall 10.5m downstream produced cylindrical flammable regions extending 3.5 and 6.5m downstream for 0.8 and 1.6mm diameter nozzles. For an 8mm diameter nozzle, the cylindrical region extended to the wall and spread along the wall.

As discussed in Section 3.1, in relation to vapours from LH2 spills, the initial cold gas is heavier than air and hence can result in accumulation close to the ground even in an open area and dispersion can be hampered by buildings or obstructions.

**Explosions:** Without any confinement or congestion within a gas/air mixture, the overpressures generated are generally low. For hydrogen, in the absence of confinement or congestion, deflagration is expected to produce an overpressure of about 100 mbar [9]. By contrast, in the presence of significant congestion, hydrogen flames are capable of accelerating sufficiently that a Deflagration to Detonation Transition (DDT) occurs, with very high overpressures, typically 20bar. Hydrogen is readily detonated in tubes or channels, particularly containing obstacles. Of more relevance, are the potential overpressures for more realistic open geometries that are likely to be experienced for process plant, storage facilities, transportation facilities and hydrogen refuelling stations. Some examples of relevant experimental studies are given here, although none relate specifically to accumulations arising from LH2 spillage.



Merilo and Groethe [32] conducted explosion experiments in an unconfined, uncongested region retained by a plastic tent, 2.24m square and 1.05m tall. With a H<sub>2</sub> concentration of 29.8%, overpressures of 20 mbar were measured. In a larger 300 m<sup>3</sup> geodesic dome, without congestion (and also with limited congestion), Groethe et al. [33] performed explosions tests with H<sub>2</sub> concentrations from 15 to 30% and measured up to 150 mbar at 15 m and no increase in overpressure was experienced for the low level of congestion used.

Vented explosions with an 18% H<sub>2</sub> concentration in an empty chamber 4.6 x 4.6 x 3m with a single vent area 2.7 or 5.4m<sup>2</sup>, produced overpressures of 300 and 125mbar respectively [34]. In a larger enclosure (8.25 x 3 x 2.7m) with one open end, Tanaka et al [31] measured ~130 mbar at 5m outside the vent for a 30% H<sub>2</sub> concentration occupying 1/3<sup>rd</sup> of the enclosure volume. In a 78.5m long, 1/5<sup>th</sup> scale tunnel [33] experiments with and without obstacles studied the effect of hydrogen concentration. At 9.5%, the overpressure was too low to register on the sensors, at 20% it was about 350 mbar and at 30% mixture over 1.5bar was measured. In a full scale replica of a refueling station, explosions in a storage room containing banks of cylinders achieved over 1bar for a 26% H<sub>2</sub> concentration, but much lower at 15% [31]. Schneider [35] studied explosions in a 10m long 'lane' bounded by walls 3m apart and 3m high. Quiescent mixtures with H<sub>2</sub> concentrations between 37 and 41% were ignited and achieved overpressures up to 150mbar with flame speeds of 170 m s<sup>-1</sup>. Turbulence was also added using a fan and with a turbulence intensity of 1.6m s<sup>-1</sup> resulted in a DDT producing over 21 bar. In other tests, with initial confinement, DDT also occurred for H<sub>2</sub> concentrations over 20.8%.

Cracknell et al [36] reported unconfined vapour cloud explosion in a region of pipework congestion with maximum dimension 1.2m. No DDT occurred even when additional turbulence was added in the form of a 25 bar jet release. However, in a similar but larger rig measuring 3 x 3 x 2m high, DDT occurred at the corners of the congested region [37]. Experiments in typical refueling station geometries have shown that higher overpressures can result if a high pressure jet release generates the accumulation even if the inventory is smaller, and the shortest delay before ignition generated the highest overpressure [38, 39, 31]. A similar result was observed for jets in an open area [40].

### **3.7 BLEVE (Boiling Liquid Expanding Vapour Explosion), Fireballs**

A BLEVE is an event associated with the catastrophic failure of a pressure vessel containing a liquid which is stored at a temperature above its saturation temperature at atmospheric pressure. On failure, some of the liquid will flash to vapour resulting in the generation of overpressure, ignition of the released contents produces a large fireball which can determine the hazard range. This hazard is thus relevant to LH<sub>2</sub> which, although stored cryogenically, is also at modest pressure. Although LH<sub>2</sub> vessels are designed to relieve safely in the event of loss of the insulating vacuum, failure/blockage of this system could lead to a BLEVE, or fire attack could raise pressures and lead to a BLEVE with a fireball due to inadequate venting of pressure. Experimental data on BLEVEs is available for butane, propane and fireballs involving natural gas, but no information has been identified for LH<sub>2</sub>. In many cases, the dimensions of the fireball are correlated with the mass of fuel involved in the fireball.

## **4.0 HAZIDS AND REVIEW OF INCIDENTS**

Two HAZID (Hazard Identification) exercises were completed by means of 'brainstorming' sessions with the project partners, to identify potential accident scenarios. One HAZID focused on the new liquefaction process and storage of LH<sub>2</sub>. The other considered the road transportation of LH<sub>2</sub> by tanker and the loading and offloading operations. The high pressure gaseous storage at refueling stations and dispensing of high pressure hydrogen to vehicles is outside the scope of the IDEALHY project, and has been studied elsewhere [31,38,39]. After the brainstorming session, the suggested scenarios were reviewed and the principal cause(s) and expected consequences, including the estimated magnitude, were identified (that is, dispersion, liquid spill, fire, explosion etc). For example: Leak from a valve seal due to equipment failure leads to small leak which disperses (possible small fire).



In addition to these HAZID exercises, a review was undertaken of incidents involving LH2, particularly related to liquefaction, storage and transportation. The sources of information were principally a review of hydrogen incidents (gaseous as well as liquid) by NASA [41] and a US database [42]. Some incidents appeared in both sources. Although the European database (HIAD), originating from the HYSAFE project, was reviewed, it was not possible to use any incidents from this source due to the lack of information on the causes and consequences. Overall, seven causes of incidents were identified and most incidents were as a result of one cause, occasionally two. The causes were:

- Design/Construction failure (including inadequate hazard assessment, usually due to insufficient understanding at the time)
- Equipment failure (note this excludes failure arising from incorrect equipment/materials as this would be considered a design/construction failure)
- Incorrect operation/procedural deficiency/inadequate maintenance
- Impact or RTA (Road Traffic Accident)
- Contamination
- Natural causes/Terrorism (includes storms, floods, extreme weather)
- Escalation

#### **4.1 Road Transportation Incidents**

Of the 18 incidents identified, 5 (28%) occurred in transit and 13 (72%) during loading/offloading. The causes of the incidents were classified as follows: Design/Construction failure/inadequate Hazard Assessment 0 (0%); Equipment failure 6 (33%); Incorrect operation/procedural deficiency/poor maintenance 8 (44%); Impact or RTA 3 (17%); Contamination 0 (0%); Natural causes/Terrorism 1 (5%); Escalation 0 (0%).

All the incidents attributed to Incorrect operation/Procedural deficiency arose during offloading operations. For example, due to over-pressurising the head space, or operating valves incorrectly or too quickly. Deviating from procedures relating to transfer hoses was also noted and using an impromptu procedure accounted for one incident. The consequences of these incidents were varied leading to gas venting, sometimes liquid release, fire, gas entering a building, and explosion. Equipment failure included unexpected burst disc failure, loss of vacuum or a loose flange connection. Of the 5 cases during transit, 2 related to Road Traffic Accidents (RTA) and the other 3 concerned venting due to burst disc failure and/or loss of vacuum. In one of the RTAs, the tanker overturned and landed in a ditch. Subsequently, the safety discs functioned and the liquid load was dumped. In the event of blockage of the relief, this incident could have resulted in more serious consequences.

Overall, the consequences which arose were: No release 2 (11%); Accumulation/Dispersion 12 (67%); Fire 4 (22%); Explosion 1 (5%); BLEVE 0 (0%). (Note: multiple consequences can arise). Injury to personnel occurred in 3 (17%) cases, 2 of which were cold burns. This rate of injury is greater than that noted for incidents concerning storage and liquefaction (see below) and probably reflects the required proximity of personnel during tanker operations. Property/equipment damage occurred in 7 (39%) of cases.

#### **4.2 Liquefaction and Storage Incidents**

Of the 39 incidents identified, the locations of the incidents were: Liquefier/Purifier 2 (5%); Vent system and pipework 11 (28%); Storage vessels including fittings, valves and reliefs 14 (36%); Valves/Components/Fittings 6 (15%); Pumps/Compressors/Vaporisers 6 (15%); Transfer lines/pipelines 5 (13%).

Incidents concerning storage vessels had a tendency to be either minor in nature, that is, a small leak from a fitting or valve packing or a major incident. It was also noted that out of 6 major incidents involving storage vessels, 3 occurred during decommissioning/commissioning (warm-up/cool-down). A further two less serious incidents also occurred when the vessel was not in service. There were several incidents relating to venting systems where unexpected ignition had occurred resulting in fire or explosion in vent system pipework or in the vicinity of the vent stack outlet.

The causes of the incidents were classified as: Design/Construction failure/Inadequate Hazard Assessment 12 (31%); Equipment failure 8 (21%); Incorrect operation/procedural deficiency/poor maintenance 18 (46%); Impact or RTA 0 (0%); Contamination 1 (3%); Natural causes/Terrorism 5 (13%); Escalation 2 (5%). (Note: multiple causes in some cases).

The incidents attributed to poor design included 4 where the wrong material had been used. Two cases related to storage systems which were over-sized and, after a prolonged period of storage, this led to failure of a burst disc and a leak from a gland nut. Two other cases were interesting in that it was inadequate hazard assessment (perhaps due to insufficient knowledge at the time) which led to an unforeseen explosion in the vicinity of a vent stack. It had been assumed that the hydrogen would disperse quickly, but due to prolonged venting of cold gas in calm conditions an accumulation formed around the vent stack which then ignited. Incorrect operation, procedural deficiency or poor maintenance was the most common cause, as it was for the transportation incidents. Of these 18 incidents, 7 were attributed to inadequate purging, leading to the formation of a flammable mixture. In terms of equipment failure, this typically related to leaking seals, valve packings or O rings.

Two incidents were attributed to an escalation event. In both cases, an improper method of fire fighting was used. In one case, firefighters were attending a fire on a vessel relief vent. Although the vessel had been part drained, some LH2 remained in the tank. The firefighters directed water at the fire on the relief and water entered the vent and froze, blocking it. The residual LH2 warmed up, vaporised and due to the blocked relief, a BLEVE occurred. In the second case, again, a fire was present on a vessel relief. Firefighters attempted to protect an adjacent vessel by spraying it with liquid nitrogen, but the cold temperatures caused cracking of the outer skin of the vessel and loss of the vacuum. This caused a rapid increase in temperature and pressure. Subsequent failure of the rupture disc on this second vessel resulted in an additional fire, as the contents of this vessel boiled off. Although it did not occur in this case, the potential for a BLEVE is obvious.

In 4 incidents cold weather and/or still conditions contributed to the cause of an incident and in one case lightning was believed to have ignited a vent stack.

Overall, the consequences which arose from the incidents were: No release 5 (13%); Accumulation or Dispersion 14 (36%); Fire 9 (23%); Explosion 13 (33%); BLEVE 1 (3%). Injury occurred in 3 (8%) of incidents and non-trivial damage in 23 (59%) of cases.

## **5.0 CONSEQUENCE AND RISK CONSIDERATIONS**

The third and final stage of the safety studies within IDEALHY is to consider the hazard and risks presented by the new large scale liquefaction process and transportation of LH2 to refueling stations, and the need for mitigation measures. It is envisaged that the output of the HAZID exercises and the review of incidents will enable a range of release scenarios to be identified, from small leaks to catastrophic failures. Where possible, the consequences of these releases will be assessed using existing engineering models, of the kind typically used for risk assessment work in the oil and gas industry, in order to determine the maximum hazard ranges where fatalities would be expected. Parameters identified in the literature review of LH2 experimental studies are likely to be useful when applying the models to LH2 releases, although the range of such data appears to be limited. In addition, the validity of the models to the behaviour of LH2 may be questionable. Determination of risk is likely to be restricted by the availability of quantitative failure frequencies and ignition probabilities, so a more qualitative approach will be adopted. Some factors of particular relevance to

liquefaction, storage and transportation are summarised below, and these will be explored further during the completion of the safety study of IDEALHY. The above approach is similar to that followed by Moonis et al [43], although their study did not include the liquefaction process. Extremely large hazard ranges (tens of kilometres) were identified in that study for some release scenarios, which is certainly a matter for concern.

**Liquefaction Process:** The new liquefaction process [44] is intended to produce at least 50 tonnes per day, making it an order of magnitude larger than current processes. This will result in larger diameter pipework with higher throughput. Novel equipment will need to be developed, such as larger cryogenic valves and efficient turbo-compressors capable of operating with the expected He/Ne coolant. Pre-compression up to 80 bar is also envisaged, increasing the release rate of any leakage upstream of the liquefier. A mixed refrigerant (MR) of hydrocarbons, (such as methane, ethane, propane and butane) is also being considered and the hazards of these fuels must also be taken into account. In addition, the IDEALHY project is assessing the benefits of locating a hydrogen liquefaction plant close to an LNG storage facility, where practicable, in order to improve the efficiency of the process by using the vaporization of LNG as a pre-coolant, possibly replacing the MR.

**Storage:** The increased scale of the liquefaction process and widespread use of hydrogen vehicles is likely to lead to increased storage capacity at the liquefier and at refueling stations. Of particular concern at the latter is their location in urban areas in close proximity to people, where the conventional separation distances applicable for industrial sites would be impractical [1].

**Transportation:** In terms of consequences, the much increased inventory of a LH2 road tanker, compared to a gaseous tanker, is likely to increase the consequences of catastrophic failure, but the lower pressure associated with LH2 tankers may reduce the consequences of smaller, more credible release scenarios. In terms of risk, there are two opposing factors: the larger inventory of each tanker but the reduced number of tankers required compared to gaseous transport (by a factor of ~10).

The use of mitigation measures will also be addressed. Mitigation could be preventative, that is, measures taken to reduce the likelihood of an accidental release in the first place, or they could be ameliorative, that is, to make the consequences of a release less harmful. For example, it is evident from the analysis of the causes of incidents, discussed in Section 4, that good design and the establishment of robust procedures will be key preventative mitigation measures. Good design would also include the provision of adequate instrumentation and systems to detect the onset of problems, such as temperature changes, loss of pressure or over-pressurising, at an early stage. By such means, small releases can be prevented from becoming more serious events. Ameliorative measures may also extend to the use of fire-fighting systems or walls although care needs to be taken to ensure that mitigation of one hazard does not increase the severity of another – for example, the use of confining walls may reduce a fire hazard beyond the wall but its presence may increase the likelihood of gas accumulation and the severity of an explosion.

## 6.0 CONCLUSIONS

The safety work of the IDEALHY project is aiming to assess the impact on safety (hazard consequences and risk) of a new large scale liquefaction process and the widespread transportation of LH2 to refueling stations, in order to facilitate the development of a hydrogen economy in the medium term. A literature review of experimental studies of the hazards posed by LH2 releases found that there was a dearth of experimental data, especially at large scale. Limited information was available on the evaporation from LH2 spills and the subsequent dispersion. Only one small scale study of LH2 pool fires was identified and one study of flashing liquid jet fires. Gas accumulation and explosion hazards were perhaps the most studied, including experimental studies at full scale in refueling station geometries and unconfined explosions in congested regions. However, no studies were identified that were specifically related to gas accumulation and explosions arising from a spill of LH2 in a confined

or congested region. HAZID exercises have been conducted for the liquefaction, storage and transportation by road of LH2 and relevant incidents have been identified. Further analysis classified the underlying cause of incidents and categorised the consequences.

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