

## Consideration Of The Threat from Hydrogen As We Expand Its Use

### 1.0 Introduction

Hydrogen has been used for many years across a number of industries and its characteristics as a flammable fluid are well known. As the world starts its progression to net zero, hydrogen is seen as a form of energy that is both transportable and flexible and can replace traditional hydrocarbon fuels. Looking forward, there exists plans for uses of liquid and gaseous hydrogen at much wider ranges of volumes and pressures than are typical of current hydrocarbon projects. Assets include production, storage, transmission, transport and distribution and can be across onshore, marine, and offshore locations. Therefore, there is potential for a wide range of fire, explosion and cryogenic spill hazard scenarios from accidental releases of hydrogen.

This paper considers the hazards from hydrogen, for new and developing uses, that are outside the current well understood operating window for hydrogen systems. Extending the following parameters to new operating ranges for hydrogen has potential to present a more severe hazard than current uses:

- Increased and reduced temperature
- Increased pressure
- Increased volumes

This is shown schematically in Figure 1.

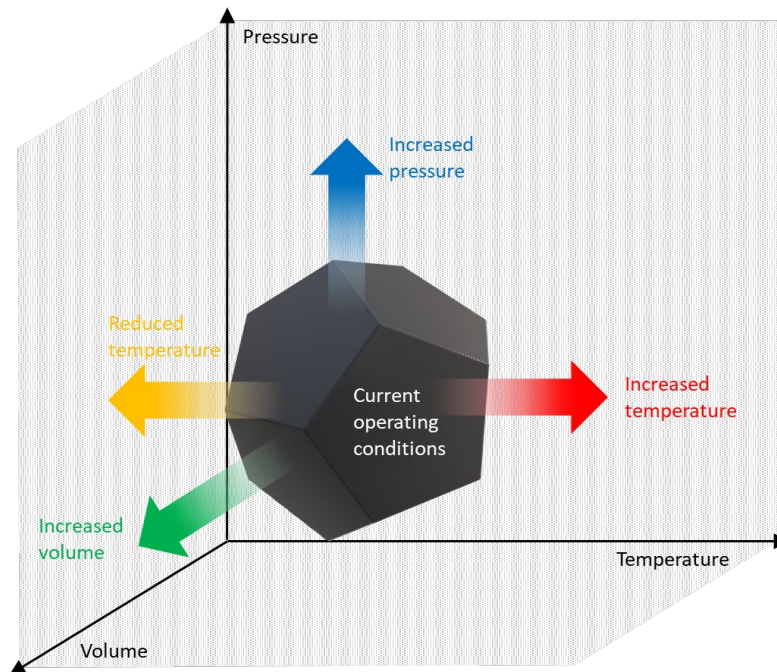


Figure 1: Extending the Traditional Operational Envelope of Hydrogen

## 2.0 Summary of Hydrogen Hazards

The use of hydrogen as a replacement for natural gas or other hydrocarbon fuels presents all of the hazards we associate with natural gas, although the extent of the hazards can be greater for hydrogen. Hydrogen is flammable and has a flammability range in air between 4 % to 75 % by volume which is a much higher range than hydrocarbon fuels, see Table 1. In addition to the large flammable limits, the ignition energy of hydrogen is lower than hydrocarbons which means that the potential for a release of hydrogen to ignite is greater. However, hydrogen is lighter than hydrocarbon fuels and therefore is buoyant in air and will readily disperse. Methane is also lighter than air and therefore buoyant whereas propane and higher hydrocarbon fuels are heavier than air and tend to congregate at ground level. Hydrogen is often stored at high pressure. Releases from high pressure systems promote mixing between the released fluid and the air which can reduce the impact of the buoyancy of the fluid.

The ignition of a release of a flammable fluid early after the release has occurred will result in a fire event; a pool fire for a liquid release and a jet fire for a release of vapour. Hydrogen burns with a hotter flame, higher heat of combustion, than methane and therefore the impact of a fire on equipment or structures can be more severe close to the release. This effect is increased for high pressure releases as the convective heat transfer is related to both the temperature and the velocity of the release.

For a release from a given volume, a release of methane will have a higher mass flow rate than hydrogen, However, multiplying the higher mass flow rate of the methane release by the lower heat of combustion, provides an outflow power that is quite similar to that of hydrogen. A comparison of hydrogen jet fires and methane jet fires is provided in Ref [1].

Delayed ignition, after a gas cloud comprising a mixture of flammable gas in air has formed, can result in a vapour cloud explosion. A comparison between explosions involving hydrogen and methane is provided in Ref [2]. One thing of note is that hydrogen burns with a faster flame speed than hydrocarbon fluids and therefore is more prone to detonate which results in a large, up to 20 barg, short duration pressure pulse.

The wide flammable range of hydrogen means that there is an increased likelihood of the flammable region of a release encountering an ignition source thus resulting in a fire and explosion event. However, it has been reported that releases of pressurised hydrogen can self ignite due to shock wave formation; the flow velocities in the released jet reaches supersonic levels as it expands through the release orifice forming shock waves due to interaction with the surrounding gas, heating the mixture to temperatures exceeding auto-ignition levels. This would result in a jet fire event.

**Table 1: Comparison of Selected Parameters for Hydrogen, Methane and Propane**

Parameter	Hydrogen	Methane	Propane
Molecular Weight	2	16	44
Flammability Range in Air	4% to 75%	4.4% to 16.4%	2.5% to 9.5%
Stoichiometric Concentration (by volume)	29.5%	9.5%	23.9%
Ignition Energy	20 μJ	290 μJ	250 μJ
Maximum Laminar Flame Speed at RTP	28 m/s	3.8 m/s	4.2 m/s

### 3.0 Potential and Future Uses of Hydrogen

A review of the current uses and potential uses for hydrogen has been undertaken with consideration of the following industries:

- Maritime
- Aerospace
- Nuclear
- Automotive
- Generation of Hydrogen
  - Offshore
  - Onshore
- Storage of Hydrogen
- Transmission and Distribution
- Trains
- Space
- Hydrogen used for Power Generation
- Hydrogen used for heat / cooking
  - Industrial
  - Domestic

The information gathered was focused on the operating conditions of hydrogen, specifically the pressure and temperature and also the volume of hydrogen that could contribute to an accidental release.

The different potential uses and operating conditions/volumes for hydrogen were compared with current hydrocarbon and hydrogen facilities and their operating conditions and areas where the operational parameters for hydrogen are outside the current use were identified.

The initial findings from the review have been tabulated as follows:

Table 1: Generation / Production of Hydrogen

Table 2: Bulk Storage of Hydrogen

Table 3: Transport of Hydrogen

Table 4: Use of Hydrogen

The systems where hydrogen usage is outside the current bounds of hydrocarbon fluids are shaded in yellow. That is, where there is a difference in the 'hazard to assess' for hydrogen systems compared to natural gas/hydrocarbon/hydrogen fluid.

*Table 2: Generation / Production of Hydrogen*

Sector	Main equipment Items	Hydrogen Conditions		
		Pressure (barg)	Temperature (C)	Volume (m3)
Green Hydrogen Production Onshore or Offshore	Electrolysers	30 - 50	80	2
		High pressure 200	80	2
	Associated production equipment / pipework	200	20	60
Blue Hydrogen Production Onshore	Steam methane reformers	30	1900	610
	Associated production equipment / pipework	30	20	100
Hydrogen Production Onshore	Thermal Plasma Process	50	650	2
	Associated production equipment / pipework	50	20	100
Hydrogen Production from Nuclear	Electrolysers	30 - 50	80	2
		High pressure 200	80	2
	High temperature chemical production	20 - 80	500-1000	10
	Chemical production	20	80	10

*Table 3: Bulk Storage of Hydrogen*

Sector	Main Items	Hydrogen Conditions		
		Pressure (bar)	Temperature (C)	Volume (m3)
Hydrogen Storage Offshore	Depleted Gas Reservoirs	800	ambient underground temperature	Very large
		75	ambient	Very large
Hydrogen Storage Onshore	Salt caverns / geological storage	200	ambient underground temperature	Very large
		50	ambient	Very large
Bulk LH2 – Maritime as part of shipping LH2	Storage for transport on bulk carriers and when offloaded	Ambient + possibly a few bar	~-250	Very large
	Pumping prior to gasification	75	~-250	Several m <sup>3</sup>
Bulk LH2 storage - onshore	Spheres or insulated storage systems	Ambient + possibly a few bar	~-250	Very large
Hydrogen Refuelling Stations – Road vehicles	Tanks	LH2 at 0.5	-253	3.2
	Storage cylinders	700 – 900	ambient	10s of m3
	Hoses for re-fuelling	700 – 900	ambient	Limited to hose
Space	Storage sphere	6	~-250	3218

*Table 4: Transport of Hydrogen*

Sector	Main equipment Items	Hydrogen Conditions		
		Pressure (bar)	Temperature (C)	Volume (m <sup>3</sup> )
Maritime / Trains	Bunkering facilities – gas phase	300-700	Hotter than ambient	Very small volume

Maritime / Trains / Aerospace	Bunkering facilities – liquid phase	Ambient + possibly a few bar	~-250	Several 10s of thousand m3
Road transport	Road Tanker	228	Ambient	15
	Road tanker	LH2 at 0.7	-253	35
Natural Gas Network Conversion to Hydrogen	Transmission Pipelines	85	Ambient	Very large
	Distribution Network	7	Ambient	Very large
Conversion from storage to transport	Process plant for taking from storage to transport system	85	Ambient	100

Table 5: Use of Hydrogen

Sector	Main equipment Items	Hydrogen Conditions		
		Pressure (bar)	Temperature (C)	Volume (m3)
Maritime	GCH2 Bulk storage	300-700	ambient	Cylinders ~2m <sup>3</sup> but a few may be manifolded together at any one time
	GCH2 fuel systems	Pressure dropped in stages to ~5bar	ambient	Small, once isolated releases over in 10s of seconds
	LH2 coastal ferry – Storage	Ambient + possibly a few bar	~-250	Depends on bunkering frequency but ~100m <sup>3</sup> to replace conventional fuels
	LH2 Long Range Vessel - Storage	Ambient + possibly a few bar	~-250	15,000 to 20,000 m <sup>3</sup> based on energy stored in conventionally fueled vessels
	LH2 fuel systems	~5 bar	Cold up to ambient	Typically relatively small, situation is developing but isolated releases last < 5 mins
Transport - Buses	Storage cylinders	495	ambient	0.17
	Storage cylinders	Few bar	~-250	0.7
Transport - Cars	Storage cylinders	700	ambient	0.5
	Storage cylinders	Few bar	~-250	0.1
	Cylinder	950	Ambient	0.25
	Cylinder	250	Ambient	1.5
	Multi-cylinder pack	175	Ambient	0.5
Transport – HGVs	Storage cylinders	350	ambient	2
	Multi-cylinder pack	356	Ambient	1.65
Power Generation	Gas Turbines	30 – 60 barg	ambient	4

Sector	Main equipment Items	Hydrogen Conditions		
		Pressure (bar)	Temperature (C)	Volume (m3)
Replacement of Natural Gas	Domestic appliances – cookers, heating, etc	25mBar	ambient	very large
	Industrial appliances – cookers, heating, etc	7	ambient	very large
Trains	Gas storage cylinders	700 - 900	ambient	Cylinders (typically 2 m <sup>3</sup> ) manifolded together
	LH2 fuel systems	Ambient + possibly a few bar	-253	200
Aviation	LH2 storge	Ambient + possibly a few bar	-253	50
	LH2 storge	Ambient + possibly a few bar	-253	80

#### 4.0 Potential Impact When Moving From Current Operating Conditions

The following tables provide information on the potential increase in hazard as the operating conditions for hydrogen move away from the current operational envelope.

*Table 5: Variation in Pressure*

Parameter	Potential Impact
Increase in Pressure	Explosion: greater turbulence in a release – greater explosion overpressure
	Fire: greater momentum of the release – increased convective heat transfer
	Other: greater momentum of the release – hazard in own right plus potential for erosion
	Dispersion: greater air entrainment - better mixing potential promotes dispersion
	Fire: compression of the jet downstream of the release – more likely to self ignite

*Table 6: Variation in Temperature*

Parameter	Potential Impact
Increase in Temperature	Fire: hotter initial flame – increased convective heat transfer
	Other: hot gaseous release – hazard in own right plus potential for erosion
	Fire: hotter gas closer to autoignition temperature – more likely to self ignite
Decrease in Temperature	Explosion: liquid H2 condensing oxygen from the air
	Other: liquid H2 causing cryogenic damage to coatings
	Dispersion: cold H2 less buoyant therefore slower to disperse
	Fire: cold jet gives thermal gradient on impacted item

*Table 7: Variation in Volume*

Parameter	Potential Impact
Increase in Volume	General: Longer duration release increases potential for hazard

## 4.1 Increase in Pressure

### 4.1.1 Explosion Events

Due to the density of hydrogen, to store the same energy as a hydrocarbon fuel where there is limited space available, the pressure of the hydrogen must be increased. The main identified uses where hydrogen would be stored at high pressure are associated with the transport sector such as road transport and rail transport. A release of high pressure hydrogen will induce turbulence in the air and, if ignited, turbulent flow can result in an increased explosion overpressure with potential to lead to detonation. The overpressure generated is also influenced by the confinement and the congestion of the area of the release. A high pressure release, generating turbulence close to the release, also promotes mixing with the air which can support the dispersion of the hydrogen in the air. With the large flammability limits of hydrogen, 4% to 75 % by volume in air, it may be difficult to disperse a release of hydrogen in a confined area below these limits. A passenger car has a volume of around 3,000 litres, to reach a concentration of 29.5% hydrogen by volume, which is the stoichiometric concentration, would require a release of 885 litres of hydrogen, at STP, assuming it is a closed system, which is less than the volume of hydrogen stored in a typical cylinder in a car. Similarly for a bus with an internal volume of 70,000 litres, it would require a release of 20,500 litres (20 m<sup>3</sup>) hydrogen at STP to reach a stoichiometric concentration in air. The volume of hydrogen in a high pressure cylinder is typically 10,000 litres and therefore would not reach a stoichiometric concentration, although it could reach a concentration of gas in air of around 14% which is within the flammable range for hydrogen. A high pressure release will have a high initial flow rate and momentum which will reduce the effectiveness of natural ventilation in the early stages of the release. The use of ATEX rated equipment is therefore an important consideration when designing systems which may be subject to a release of flammable gases, however, intrinsically safe equipment is not practical in passenger vehicles. Segregation of the fuel from other areas such as locating the fuel source externally would remove the potential for a build-up of a flammable volume.

The transport of hydrogen in cylinder banks, for example see Figure 1, provides congestion close to the source of a potential leak. Congestion promotes the mixing of gas in air, and, if ignited, the mixing ahead of the flame front can result in the generation of large overpressures and even detonation.



Figure 2: Image of Hydrogen Cylinders Transported by Road

It is possible to model hydrogen explosion events using commercially available software such as FLACS. These models use defined congestion and congestion specific to the scenario being modelled. When developing explosion



exceedance curves, such as to support the design of a process area or protection measures for a building, it is usual to consider quiescent gas clouds of different volumes and consider different ignition locations. While this will provide a statistical probability of exceeding a specific pressure, it does not provide information on the worst-case event. Hydrogen has greater potential to transition to detonation than methane due to having a higher flame speed [2], which can have devastating effects on local equipment, people and properties. It is therefore important to understand the worst-case event and the potential for hydrogen to detonate. Modelling a transient release, including the turbulence induced by the release itself is possible although computationally more challenging. However, armed with the knowledge of the worst-case event allows mitigations to be built into the design such as the use of segregation / separation, forced ventilation, blast walls, etc.

#### **4.1.2 Fire Events**

A release from a high pressure system will result in a high momentum gas jet close to the release point which can give rise to greater erosion to systems or coatings close to the release. If the release is ignited the momentum of the release can give rise to a high rate of convective heat transfer and thus increase the heat loading on items impacted. The flame temperature of hydrogen can be up to 1900 K [1] which results in a higher convective heat load than conventional hydrocarbon fuels. The impact this higher heat load and associated higher velocity will have on fire protective coatings is not currently known.

The ability to model hydrogen fire events is available in a number of commercial software packages including both phenomenological models and more complex CFD solvers. It is possible to use CFD tools to calculate the heat load on an obstacle in terms of both the convective and the radiative components. This allows a comparison between natural gas and propane jet releases and hydrogen releases with the importance of the methane and propane releases being that fire protective systems are tested using reduced scale propane jet fires which were designed based on the heat load from full scale natural gas jet fires. Understanding the heat load, and in particular the convective and radiative components, can provide information on the response of the obstacle and the potential for it to fail. Structural engineers can undertake finite element fire collapse assessments and use this information to develop an optimised, cost effective fire protection scheme.

Hydrogen has an autoignition temperature of around 770 K and a relatively low ignition energy of around 20  $\mu\text{J}$ . Based on these parameters ostensibly a release of hydrogen will not ignite without the influence of external factors. However, it has been reported that releases of pressurised hydrogen can self ignite due to shock wave formation, see Section 2.0. As the pressure of the stored hydrogen is increased, a release is more likely to result in this self-ignition. Other mechanisms that could result in ignition of a high pressure release of hydrogen include electrostatic discharge. Pure hydrogen is not likely to become electrostatically charged however impurities in the flowing gas such as rust particles can result in electrostatic charging. Ignition due to electrostatic discharge is more likely for insulated storage systems, such as composite cylinders as providing a robust earth is more difficult.

## **4.2 Increase in Temperature**

High temperature hydrogen is possible from the production of hydrogen either as a by-product of nuclear energy production or from steam reformation.

### **4.2.1 Fire Events**

An increase in the temperature of a fluid being released means that the fluid is pre-heated and, if ignited, can result in high convective heat transfer. This can result in an increased heat load to any impacted object. The total heat dose, related to heat load and time, is an important factor in the response of structures or equipment to a fire event.

For pressurised vessels impacted by a fire, the heating of the fluid inside the vessel causes it to expand increasing the stress on the vessel walls. The increased stress combined with the weakening of the vessel due to it getting hotter can result in the catastrophic failure of the vessel, which for a liquid filled vessel is a BLEVE event. While pressure safety valves are not generally designed to protect against a fire event, they can offer limited protection by reducing the pressure in the vessel. For a preheated fluid the rate of heat transfer, and therefore pressure rise, may be increased which can reduce the effectiveness of protection systems. The response of a vessel to heat load can be calculated using specialist software as can the heat transfer into the vessel from the fire event.

Mitigation measures include passive fire protection and water deluge. Neither of these systems have been rigorously tested against high temperature and high pressure hydrogen events although modelling techniques are available to provide information of the ability of these systems to provide protection.

### 4.3 Decrease in Temperature

The storage of hydrogen as a cryogenic liquid provides a higher energy density storage means than gaseous hydrogen. To store hydrogen as a liquid requires temperatures of around -254 C at ambient pressure increasing to -240 C at 12 barg. Hydrogen becomes a supercritical fluid at pressures above around 14 barg and temperatures above -240 C.

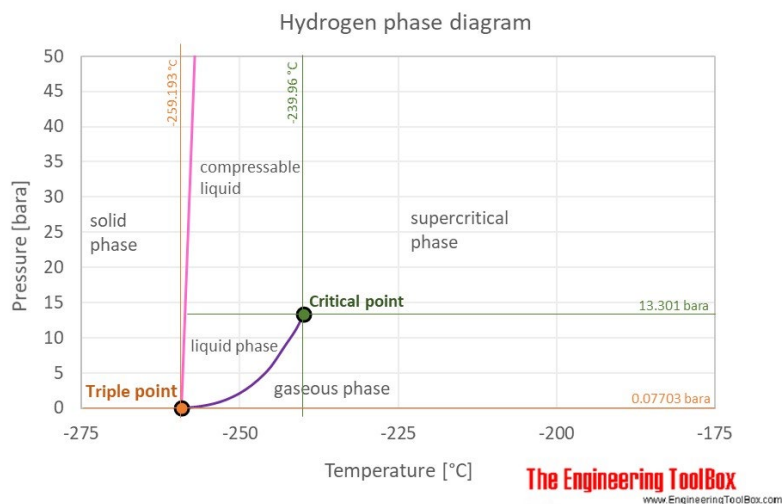


Figure 3: Phase Diagram of Hydrogen

#### 4.3.1 Explosion Events

An explosion event from a release of liquid hydrogen can be related to ignition of the hydrogen vapours, combustion with liquid oxygen condensed from the air, or if spilled on water a rapid phase transition.

Hydrogen released as a cold liquid will vapourise and can form a flammable hydrogen air mixture. The cold temperature of the hydrogen will mean that it is less buoyant than a gaseous hydrogen release, although it is likely to warm up as it mixes with air.

A release of liquid hydrogen is colder than liquid oxygen and can cause oxygen to condense out of the atmosphere. Liquid oxygen is also a very powerful oxidising agent and organic materials will burn rapidly and energetically in liquid oxygen. Liquid oxygen and liquid hydrogen when mixed together form Hydrolox which is used as a rocket fuel.

Hydrolox can generate a lot of energy and is considered one of the most efficient rocket propellant combinations. Therefore, a spill of liquid hydrogen has potential to result in a large hazard event and controls and mitigations should be identified and put in place to prevent or manage a potential release.

A rapid phase transition (RPT) can occur when liquid hydrogen is spilled onto water, and it is initiated by a breakdown of the gas film separating the two liquids. An RPT can occur for LNG as well as liquid hydrogen. The mechanism for an RPT is:

1. **Film boiling.** If the water temperature is higher than the Leidenfrost temperature of the cryogen, a stable insulating vapor film will form between the cryogen and the water. This is known as film boiling, and the lack of direct contact between the two fluids reduces heat transfer. In this stage, the cryogen stays in quasi-equilibrium, and the energy transferred from the water goes to evaporating the cryogen.
2. **Breakdown of the gas film separating the liquids.** At some point, there is a sudden and localised collapse of the vapor film. This can be caused by wave motion or an external source.
3. **Rapid superheating.** The direct contact between the water and the cryogen induces a large and rapid increase in the heat flux. The cryogenic liquid is superheated and the temperature can continue to increase until a maximum temperature is reached known as the superheat limit.
4. **Homogeneous nucleation.** When the liquid gets close to the superheat limit spontaneous nucleation occurs throughout the volume and large amounts of liquid are vaporised in a very short timeframe.
5. **Explosive expansion.** Liquid is typically 1–2 orders of magnitude denser than vapor in mechanical equilibrium. The rapid formation of vapor leads to a large local increase in pressure that is followed by an explosive expansion. This is observed as a loud and potentially destructive vapor explosion. An RPT is a phase change not combustion.

Some theoretical results suggest that a RPT from a liquid hydrogen spill will be smaller and less severe than one for a spill of LNG [3], although there is limited information available. If shipping liquid hydrogen it would be prudent to consider the hazard from an accidental spill resulting in an RPT.

#### **4.3.2 Fire Events**

A release of liquid hydrogen can result in a pool fire, or if pressurised a spray or liquid jet fire. The hazard from the fire event itself is described elsewhere in the document. The cold liquid released, and the fire event contribute to form a large thermal gradient. The thermal gradient can result in additional stresses to coatings or equipment items which can result in a reduction in their operating lifetime or failure. For the case of a coating on an equipment or structural item, there is a level of complexity as the coating and substrate will expand / contract differently which can result in delamination between the two. This is also the case for unignited cryogenic spills although the thermal gradient is reduced. In both cases the different response of the materials can lead to delamination. While in the ignited case the systems will be tested and certified before being reinstated, for the unignited event this may not be the case.

#### **4.4 Increase in Volume**

Hydrogen is often stored in relatively small high pressure volumes. A release of hydrogen is therefore of short duration although at high pressure, see Section 4.1. For fire events the duration of the release is important as the total heat dose from the fire is an important parameter in the response of structure and equipment. Increasing the volume of hydrogen storage can provide a longer duration event. In the event that there is immediate ignition, the

fire event will have a longer duration. If there is no immediate ignition the formation of a large gas cloud could, if it reaches an ignition source, result in a vapour cloud explosion. The potential for the formation of a large gas cloud, as opposed to the hydrogen release dispersing, is dependent on the release conditions, the atmospheric conditions and the confinement and congestion of the area. This can be assessed using CFD modelling which can provide an understanding of the impact the different parameters have on the dispersion of a gas cloud and therefore can provide means to prevent the formation of a flammable cloud.

## 5.0 Summary

As the use of hydrogen becomes more widespread as both a medium for energy storage and as a fuel in its own right, the operational conditions of hydrogen will increase with hydrogen stored in greater volumes at both greater temperatures and pressures and as a liquid. While the hazard from hydrogen is well known, increasing the operating conditions can result in increasing the hazard envelope such as:

- Increasing the volumes can result in longer duration events.
- Increase in pressure can result in an increase in the velocity of a release which can:
  - Increase turbulence increasing the explosion overpressure
  - Increase the convective heat component
  - Promote mixing with air forming a flammable mixture
- Increase in temperature can result in:
  - Hotter flame temperatures and higher convective heat loads
  - Increased potential for self-ignition
- Releases of liquid hydrogen can:
  - Generate hydrogen vapour and form an explosive mixture
  - For a fire event result in large thermal gradients between areas of cold liquid and hot flame
  - Result in an RPT if spilled on water

A detailed understanding of the potential hazards is important to ensure that the controls and mitigations in place are both suitable and adequate to afford protection.

## 6.0 References

- [1] Review of the Current Understanding of Hydrogen Jet Fires and the Potential Effect on PFP Performance, D. M. Johnson, R. Crewe, DNV, J. A Evans, G. Boaler, Thornton Tomasetti, Hazards31, Symposium Series No. 168, 2021
- [2] Introduction to Hydrogen Explosion Events and Comparison with Methane, J. Evans, Thornton Tomasetti
- [3] Liquid Hydrogen Spills on Water—Risk and Consequences of Rapid Phase Transition, *Energies* 2021, 14, 4789.