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Report on hydrogen safety aspects of technologies, systems and infrastructures pertinent to responders

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Summary

Through the description of hydrogen energy systems, the deliverable outlines feared events and associated hazardous consequences due to the use of hydrogen. Information relevant for responders intervention - including liquid and gaseous hydrogen behaviour and available safety features for each systems - is inventoried.

D1.1 report presents:
- A reminder on gaseous hydrogen properties, applications and infrastructures;
- A review of hazardous events regarding the liquid hydrogen chain;
- An inventory of hydrogen fuel cell systems and infrastructures involving liquid hydrogen, from production to final use;
- An inventory of existing safety features and mitigation means for liquid hydrogen systems;

At the present time, considering hydrogen energy activities and applications, liquid hydrogen is mainly used for storing higher amounts of hydrogen. Thus the main liquid hydrogen systems are the **liquid trailers** for hydrogen delivery and **liquid hydrogen storages**.

Systems with on-board liquid hydrogen are not largely deployed, but several on-going projects studied future liquid hydrogen-based fuel cell transportation means like ships, trains and planes.

On this basis, a proposal of the main hazardous events to take into account for training materials to be developed in HyResponder project (theoretical and operational), serving Task 1.3 and inputs of D1.3 "Account of scenarios and operational emergency planning and response strategies and tactics" and D2.3 "Educational training materials for responders" deliverables are made. It is noticed that - additionally to hazards inherent to liquid hydrogen - it is essential to include knowledge and means developed in the HyResponse project for gaseous hydrogen.

Collected information will serve the entire project, and more specifically:
- **Deliverable D1.2** aiming at reviewing **existing training materials and activities** for first responders in Europe, and in the World,
- **Deliverable D1.3** describing **scenarios and operational emergency strategies and tactics**, and defining **operational platform** required for responders training, regarding liquid hydrogen potential hazardous events according to hydrogen systems in their environment and conditions of use.

Note that "Regulation, Codes and Standards for first responders" and "Intervention strategies and tactics for responders" are not treated in this document, but will be addressed in WP2-T2.1 within D2.1 aiming at revising "International Curriculum on hydrogen safety training for responders".
A review of RCS for LH_2 was performed in the framework of PRESLHY project and is available in Appendix p 53. Additionally, outcomes from the PRESLHY project were extracted and translated into suitable information and tools for international SDOs, regulatory bodies and industry; Fourteen recommendations were formulated in order to be addressed to RCS organizations, and are available in (D6.3 "Recommendations for RCS", 2021).

Keywords

Liquid hydrogen, gaseous hydrogen, physical phenomena, hydrogen systems, infrastructures for hydrogen mobility, hazardous and feared events, accidental kindling chain, safety features, mitigation

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Glossary

BLEVE	Boiling Liquid Expanding Vapour Explosion
EERG	European Emergency Response Guide
FC	Fuel Cell
FCEV	Fuel Cell Electric Vehicle
LFL	Lower flammability Limit
LH_2	Liquid Hydrogen
LHRS	Liquid Hydrogen Refuelling Station
LNG	Liquid Natural Gas
LOHC	Liquid Organic Hydrogen Carrier
MIE	Minimum Ignition Energy
MLI	Multi-Layer Insulation
PEM	Proton Exchange Membrane
RCS	Regulation, Codes and Standards
RPT	Rapid Phase Transition
P_R	Rupture pressure
P_W	Working pressure
QRA	Quantitative Risk Assessment
SDO	Standard Development Organization
SMR	Steam Methane Reforming
TPRD	Thermally activated Pressure Relief Device
UFL	Upper flammability Limit

Figures and Tables

Figures

Tables

1. Introduction

Over several years, hydrogen fuel cell-based applications have been developed in order to provide alternatives regarding the required ecologic and economic transition.
Hydrogen is a flammable compound, which can be used safely if inherent risks are well known and managed.
In order to avoid catastrophic events lots of collaborative projects were launched aiming at improving technologies, infrastructures and strategies for a safe use of hydrogen.
Despite these active works and studies, "zero-risk" does not exist and it is required to define and disseminate good practices in case of accidental events.
In this framework, first responders and fire fighters have to be early involved and trained to adopt appropriate behaviours.

A first project, so-called HyResponse supported by EC Fuel Cell and Hydrogen Joint Undertaking (June 2013 - September 2016) was led to establish the World's first comprehensive training programme and facilitate safer deployment of FCH systems and infrastructure. This project focused on gaseous hydrogen applications and inherent risks.

The HyResponder project is also supported EC Fuel Cell and Hydrogen Joint Undertaking. The aim of this project is to complete HyResponse project outcomes and to specifically focus on extending the work in HyResponse to reflect advancements in the field, specifically risks and management of liquid hydrogen hazardous events for responders.
In this way, the HyResponder project will develop and implement a sustainable trainer the trainer programme in hydrogen safety for responders throughout Europe, supporting the commercialisation of FCH technologies by informing the participation of responders in the initial permitting process, improving resilience and preparedness through enhanced emergency planning, and ensuring appropriate accident management and recovery.

D1.1 report of HyResponder project focuses on hazards of liquid hydrogen, with a reminder on gaseous hydrogen, outcomes of HyResponse project and recent improvements. This deliverable will be used to help inform the revision and extension of the teaching materials previously prepared.

D1.1 report presents:

- A reminder on gaseous hydrogen properties, applications and infrastructures;
- A review of hazardous events regarding the liquid hydrogen chain;
- An inventory of hydrogen fuel cell systems and infrastructures involving liquid hydrogen, from production to final use;
- An inventory of existing safety features and mitigation means for liquid hydrogen systems;

A proposal of the main hazardous events to take into account for training materials to be developed in HyResponder project (theoretical and operational), serving Task 1.3 and inputs of D1.3 and D2.3 deliverables is made.

Note that "Regulation, Codes and Standards for first responders" and "Intervention strategies and tactics for responders" are not treated in this document, but will be addressed in WP2-T2.1 within D2.1 aiming at revising "International Curriculum on hydrogen safety training for responders".
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2. Hydrogen properties and associated hazardous behaviours

2.1 Hydrogen general properties

In order to better understand hazards and how to manage them, this section presents the main properties of hydrogen and potential accidental kindling chain and consequences regarding gaseous and liquid hydrogen handling.

2.1.1 Gaseous hydrogen properties

First of all, hydrogen at standard temperature and pressure, is a colourless, odourless, tasteless, non-toxic, highly combustible diatomic gas.

In the table below are presented the main hydrogen thermophysical properties.

Table 1. Hydrogen thermophysical properties.

Properties	**Numerical values**
Molecular weight	2 $g.mol^{-1}$
Gaseous density at 273 K	0.0899 $kg.Nm^{-3}$
Diffusion coefficient in air	0.61 $cm^2.s^{-1}$
Compressibility factor	1.0006
Lower Heating Value	119.9 $kJ.g^{-1}$
Higher Heating Value	141.1 $kJ.g^{-1}$
Specific heat (C_p at 273 K)	14199 $J.kg^{-1}.K^{-1}$
Specific heat ratio (at 273 K)	1.4
Minimal ignition energy	20 µJ
Flammability range in air (upward propagation)	4 -75% vol
Detonation range in air	13 - 65% vol
Flame velocity in air	260 $cm.s^{-1}$

Regarding properties given in Table 1, the associated behaviours for hydrogen are the following:

- **Low density**
  - H_2 rises and disperses rapidly (14 times lighter than air)
  - No more H_2 after stopping the release in free space
  - Stratification in the highest locations, close to the enclosure roof in confined spaces
  - High pressure required to store large amount in gaseous state
- **High diffusivity**
  - Concentration will become totally homogeneous in a confined space after stopping release without external disturbance
  - But hydrogen high buoyancy affects its dispersion considerably more than its high diffusivity
- **Low viscosity**
  - Tendency to leak
- **Combustible with a large flammable range and low ignition energy required**
  - High potential for flame or explosion (deflagration)
- **Radiative properties**
  - Flame less radiative than methane and other combustible compounds

If required, for self-education, more details are available in "Educational training" developed in HyResponse project (http://hyresponse.eu/training-mat-1.php), and in "e-learning" module of the HyResponder e-Platform (https://hyresponder.eu/e-platform/e-laboratory/)

2.1.2 Liquid hydrogen properties

Main properties of liquid hydrogen are given in Table 2.

Table 2. Liquid hydrogen thermophysical properties.

Properties	Numerical values
Density (at P_{atm})	70.516 $kg.m^{-3}$
Melting point	-259.14°C
Boiling point	-252.78°C
Latent heat vaporization (at boiling point)	448.69 $kJ.kg^{-1}$

- **Low boiling point**
  - Liquid hydrogen is a cryogenic liquid. Its boiling point – temperature at which the vapour pressure of a liquid equals the pressure surrounding the liquid and the liquid changes into vapour is around -252°C at atmospheric pressure
  - Thus cryogenic liquids are liquefied gases that are kept in their liquid state at very low temperatures
  - For storage, highly insulated vessels are required to maintain low temperature
  - In poorly insulated containers, some cryogenic liquids actually condense the surrounding air, forming a liquid air mixture
- **State at normal temperatures and pressures**
  - All cryogenic liquids are extremely cold and are gases at normal temperatures and pressures

- **High density**
  - Small amounts of liquid can expand into very large volumes of gas (1:848)

- **Vaporization of cryogenic liquids**
  - The vapours and gases released from cryogenic liquids also remain very cold. They often condense the moisture in air, creating a highly visible fog

- **Flammable properties** (Molkov, 2012)
  - Flammable range of cold gas is slightly narrower compared to gaseous hydrogen at higher temperatures. Indeed, lower flammability is increased and upper flammability is decreased for low temperatures
  - Minimum Ignition Energy is slightly higher for cold gases compared to gases at ambient temperatures

Additional information is available in "Educational training" developed in HyResponse project (http://hyresponse.eu/files/Lectures/Hydrogen_properties_relevant_to_safety_slides.pdf).

2.2 Hydrogen main dangers and associated consequences

In this section, dangers related to gaseous and liquid hydrogen are described. Calculation means were developed - or are under-development - in order to assess consequences of feared events. Most of these calculation tools are available on "e-laboratory" platform https://hyresponder.eu/e-platform/e-laboratory/

Additionally, hazard distances or mitigation measures can be defined thanks to these tools.

N.B.: *According to ISO TC197 WG24 - hazard distance is a distance from the (source of) hazard to a determined (by physical or numerical modelling, or by a regulation) physical effect value (normally, thermal or pressure) that may lead to a harm condition (ranging from "no harm" to "max harm") to people, equipment or environment.*

The calculation of hazard distances is usually deterministic. Which means that hazard distances do not consider the probability of a hazardous event occurring. Hence, the direct use of hazard distances may lead to restriction of activities over large areas.

Thus, for practical applications, hazard distances should be used as an input to risk informed safety distances that employ both deterministic and probabilistic components of the QRA methodology.

Note that in WP2, Subtask 2.2.1, appropriate tools for the assessment of hazards and risks, which can be utilised in the support of training activities for responders will be identified and integrated in ePlatform if not already available.

2.2.1 Gaseous hydrogen hazards

The release of hydrogen and either immediate or delated ignition of a hydrogen-air flammable mixture, or the rupture of pressurized vessels are potentially hazardous events.

In the case of gaseous hydrogen accidental release, several points have to take into account in order to assess the appropriate consequences:

- characteristics of the release: pressure, size
- environment: free field or confined space
- potential ignition sources
- in case of ignition, what types: immediate or delayed

In other cases, release is not the feared event, but external aggression (e.g. thermal, mechanical…) on a pressurized vessel - storing hydrogen - can lead to dramatic consequences, like rupture/bursting of the vessel.

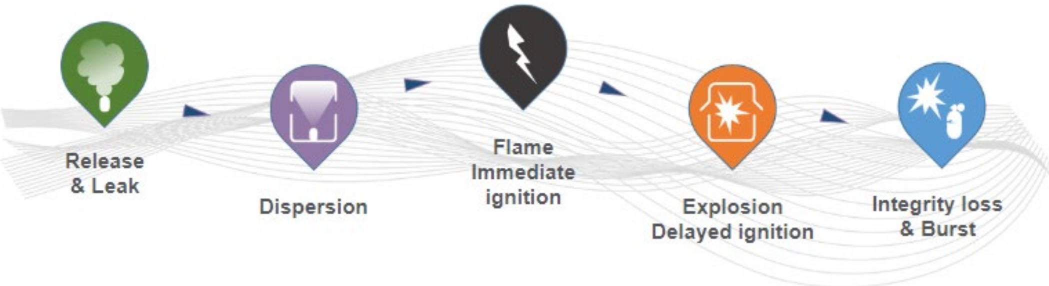


Figure 1. Overview of the accidental kindling chain for gaseous hydrogen.

In this section, hazardous events and associated consequences will be described for gaseous hydrogen.

2.2.1.1 Hydrogen release in free field

In the case of release in a free field, two main scenarios can occur:

- release with immediate ignition
- release with delayed ignition

- **Release with immediate ignition**

For this case, hydrogen releasing is immediately ignited and burns.
A jet fire is produced as long as the hydrogen source is not shut-off.
Consequences of such an event are thermal effects.

(A) (B)
Figure 2. Hydrogen ignited release in free field (200 bar, 3.1-mm diameter).
(A) Flame length, (B) radiative heat fluxes.

As shown in Figure 2 the jet fire is characterized by its flame length and the associated radiative heat fluxes which have farther effects than the "visible" flame.
Flame length and hazard distances can be calculated - among others – thanks to a dedicated tool available in hydrogen e-laboratory (https://hyresponder.eu/e-platform/e-laboratory/).

- **Release with delayed ignition**

If the ignition of a release is delayed, a flammable cloud will be formed before the ignition.
The ignition of this flammable cloud will induce a deflagration (UVCE: Unconfined Vapour Cloud Explosion) with overpressure effects impacting potential surrounding people and installations.

Figure 3. Consequences on structures of an external deflagration.

According to the characteristics of the release and of the flammable cloud, overpressure effects will be more or less important.

The level of congestion (e.g. presence of obstacles) of the site will be an escalating factor.
Deflagration to detonation transition (DDT) is possible in confined and/or obstructed situations.

2.2.1.2 Hydrogen release in confined spaces

A confined space can be more concretely a container hosting process or hydrogen storages, garages, parking, tunnels.
Hydrogen released in a confined space can result in accumulation of hydrogen in case of release.

Hazards include:

- the formation of a flammable mixture that potentially could burn if ignited with hazardous pressure and thermal effects
- the destruction of the structure, the enclosure or building by the pressure peaking phenomena during unignited or ignited release
- the asphyxiation that can result from displacement of breathable air by the hydrogen (oxygen depletion)

Oxygen depletion case will be not described in this section.

Since the completion of the HyResponse project, there has been ongoing works specifically related to the behaviour of hydrogen in confined spaces examples include but are not limited to the HyTunnel-CS project (https://hytunnel.net/).

2.2.1.2.1 Pressure peaking phenomenon

Pressure peaking is the phenomenon observed for very lighter than air gases, which can result in overpressure exceeding enclosure or building structural strength limit in case of sufficiently high hydrogen release rate.
The enclosure can be strongly damaged up to its total destruction.

In order for pressure peaking to occur, the hydrogen release flow rate should be sufficiently high to result in complete displacement of air from the enclosure, i.e., hydrogen concentration within enclosure must reach 100%.

This phenomenon was theoretically and experimentally treated in HyIndoor project (Fuster et al., 2017) and other studies (Brennan and Molkov, 2013).

Pressure Peaking Phenomenon (PPP) observation is finally a complex combination of the following parameters:

- high release flow rate,
- small enclosure,
- small size of vents.

Pressure peaking phenomenon – unignited or ignited – can be assessed thanks to dedicated tools available on hydrogen e-laboratory (https://hyresponder.eu/e-platform/e-laboratory/)

2.2.1.2.2 Hydrogen build-up

Hydrogen releasing in a confined space will accumulate. According to the ventilation rate in the considered enclosure, concentration level and distribution are different.
Three cases are possible and are briefly described below.

- **No ventilation**

The enclosure is totally closed, hydrogen concentration will depend on release duration, but can reach 100% for long duration releases.

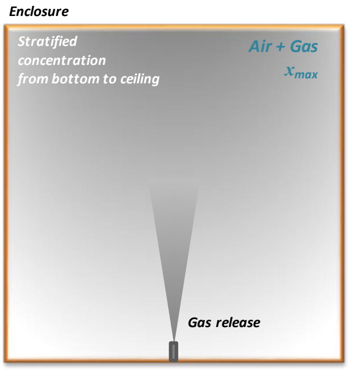
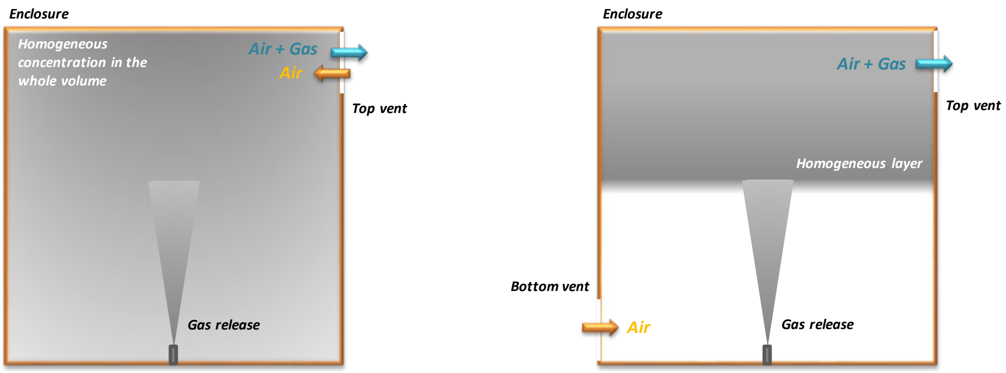


Figure 4. Hydrogen gaseous release inside a closed enclosure.

- **Natural ventilation**

Natural ventilation is driven by the buoyancy effects created by the releasing hydrogen inside an enclosure with ventilation apertures, and limiting hydrogen concentration.



(A) *(B)*

Figure 5. Hydrogen gaseous release inside a natural ventilated enclosure. (A) Mixing regime, (B) displacement regime.

Natural ventilation is a way of hydrogen build-up mitigation in case of accidental release in a confined space.

- **Mechanical ventilation**

Mechanical ventilation is driven by fans or other mechanical devices, limiting hydrogen concentration inside a confined space.

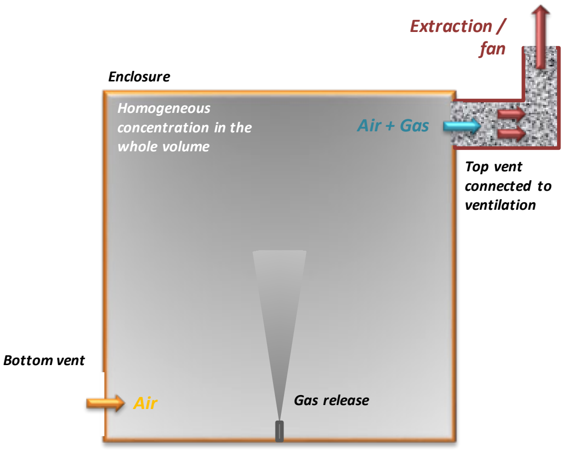


Figure 6. Hydrogen gaseous release inside a mechanically ventilated enclosure.

Mechanical ventilation is a way of hydrogen build-up mitigation in case of accidental release in a confined space. It can be used when natural ventilation is not possible or not sufficient to reach safety targets.

2.2.1.2.3 Vented explosion

If hydrogen flammable range (between 4 and 75%-H_2) is reached in a confined space, an explosion can occur in case of delayed ignition of the flammable mixture.

Figure 7. Consequences on structures of an internal deflagration.

The overpressure generated by the flame acceleration can be limited thanks to dedicated explosion panels, in order to avoid the destruction of the enclosure.

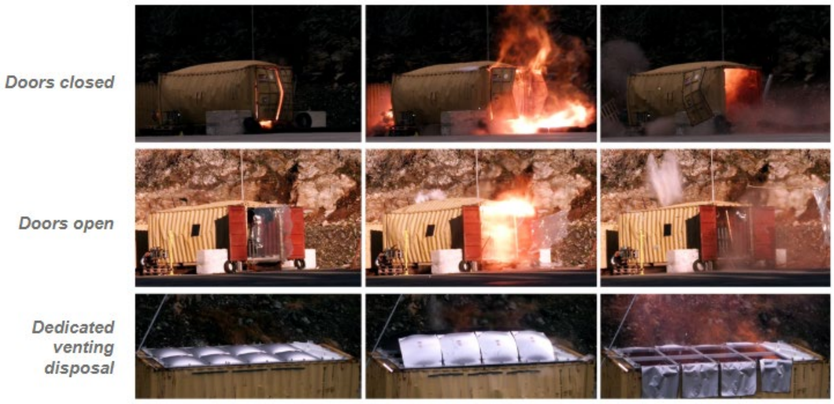


Figure 8. Confined explosion with and without venting disposal. Experiments performed in HySEA project.

Figure 8 illustrates the efficiency of venting panels (see third illustrations line) avoiding destruction of the container and projection of fragments. Thanks to explosion panels set up on the roof of the container, flames are directed upwards, aerial overpressure at ground level is very limited, and container deformation is limited.

Venting panels are by the way an efficient mitigation means allowing limiting the effect of an explosion in a confined space.

2.2.1.3 Burst of a pressurized vessel

Burst of a pressurized vessel is a physical explosion.

For some reasons, resistance of the vessel can be degraded inducing a loss of containment of the stored hydrogen with a rapid expansion, which generates overpressure wave additionally to potential fragments.

Burst can occur at different conditions:

- at normal operating pressure (working pressure), due to:
  - degradation with time of the pressurized volume (e.g. corrosion, fatigue, embrittlement)
  - mechanical impact(s) on the pressurized volume
- at "bursting" pressure (rupture pressure), due to
  - overfilling,
  - inadequate pressure relief,
  - other events, like internal explosion or reaction, fire aggression...

2.2.2 Liquid hydrogen hazards

Due to liquid hydrogen characteristics and requirements of hydrogen energy applications, liquid hydrogen used in confined configurations is out of the scope of HyResponder project. Actually, at this stage, regarding available infrastructures and applications involving liquid hydrogen, in most of the cases dangerous and feared events are free field accidental scenarios. To support this remark and bring additional information, these liquid hydrogen-based applications are concretely described later in this document in section 3.2 p 40.

Additionally, to reinforce this bias, recent experiments performed in PRESLHY project showed that apart massive releases of liquid hydrogen – due to total and instantaneous rupture of a tank for instance – leading to potential liquid hydrogen pool, the main releases – up to piping full bore rupture – thanks to a quick vaporization, tend to behave as cold gaseous hydrogen releases, which is already dealt in confined space in HyResponse project.

A review of the existing literature on physical phenomena associated with liquid hydrogen was performed in PRESLHY project (D2.2 "State of the art analysis", 2018).

On this basis, in order to define the different hazardous scenarios and associated consequences, it has been considered a LH_2 storage. Figure 9 and Table 3 summarizes these events, with initial causes and potential final consequences.

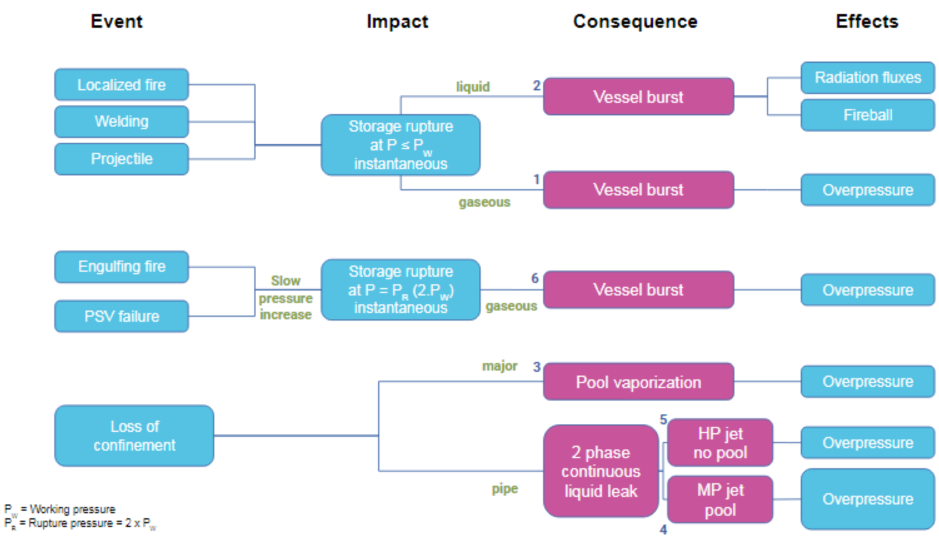


Figure 9. Potential hazardous events around H_2 applications including LH_2 storage.

Table 3. Description of potential hazardous events.

Feared events	Main conditions	Consequences
1 - Burst of the storage at working pressure (P_W) (impinging fire / fragment)	100% gaseous H_2 - 10 bar - type I vessel	Overpressure and fragments
2 - Accidental event on storage with liquid H_2 (fire case) at 2Pw	Burst of LH_2 storage Flash fire	"BLEVE" with thermal effects
3 - Failure on the storage (breech or perforation)	10 bar, rapid liquid H_2 spreading and evaporation on ground	Pool vaporization and cryogenic cloud formation with overpressure effects in case of flammable cloud ignition
4 - Leak on the pipe between storage and pump	10 bar, liquid * diphasic pressurized release * and/or H_2 liquid pool, vaporization forming a flammable cloud	Liquid hydrogen jet and potential rainout forming a LH_2 pool on the ground and overpressure effects due to flammable mixture ignition
5 - Leak on the pipe between pump and atm. vaporizer	1000 bar, liquid * diphasic pressurized release but behaving like a high pressure gaseous jet	Certainly nearly-gaseous high pressure jet behaviour with overpressure effects due to ignition
6 - Burst of the storage at rupture pressure (P_R)	100% gaseous - 10 bar, type I	Overpressure and fragments

Regarding scenarios previously summarized, it can be highlighted that some of them are specific of liquid hydrogen, and other are gaseous feared events already described, or are similar to.
Behaviour of the liquid hydrogen release, and thus associated consequences, will depend on the initial pressure. That is the reason why in the previous Table for each feared event, details are given on the pressure and on the state of hydrogen.

2.2.2.1 Immediate ignition of pressurized LH_2 release

Immediate ignition of a LH_2 high pressure jet seems to be similar to a gaseous hydrogen high pressure jet, with overpressure effects due to ignition.

Recent work has shown that the similarity law can be applied for cryogenic releases, and jet flame correlations developed for gaseous releases are also applicable (Cirrone, Makarov and Molkov, 2019).

Corresponding tools are available at https://hyresponder.eu/e-platform/e-laboratory/ .

Figure 10. Example with an immediate ignition of LNG release.

2.2.2.2 Delayed ignition of pressurized LH_2 release

The higher density of the saturated hydrogen vapour at low temperatures may cause the hydrogen cloud to flow horizontally or downwards after immediate release of liquid hydrogen (should be accounted for during intervention at an accident scene). Usually the condensation of atmospheric humidity will also add water to the mixture cloud (making it visible), making it even denser.

Figure 11. LH_2 large-scale release and delayed ignition (5 bar - 12 mm; PRESLHY project - HSE).

Due to liquid high density and vaporization at ambient temperature, the flammable cloud is significantly larger than the cloud induced by a gaseous hydrogen release. Therefore, consequences in case of ignition of this flammable cloud are more important in terms of intensity and distance of effects.

If the pressure is low enough or release diameter large enough, in some conditions additionally to the hydrogen jet, a rain-out phenomenon (formation of hydrogen droplets falling on the ground and inducing a hydrogen pool) could be observed. In these cases, it is difficult to know which phenomenon - between jet or pool - will induce the most important consequence in case of ignition, or what will be the consequence of the combination of these two physical phenomena.

Experiments will be performed in on-going projects (e.g. PRESLHY project).

2.2.2.3 Cryogenic hydrogen pool vaporization

A hydrogen liquid spillage can induce a pool. Liquid hydrogen will vaporize and form a flammable cloud with a significant volume.
Wind conditions have a significant impact on the propagation and the dispersion of the cloud.
In 2020 small-scale pool experiments were performed by KIT, showing no spontaneous ignition of hydrogen liquid pool.
However forced ignition (spark) above the pool highlighted the importance of the ground characteristics on the deflagration effects.
Sand and concrete induce the same behaviour, but gravels escalated consequences.

Additionally first simulations with the presence of a retention pit – aiming at limiting the spreading of the liquid – show a significant impact of this configuration on vaporization rate.
In presence of retention pit, vaporization rate of LH2 would be significantly reduced, resulting in a smaller and long lasting dispersed cloud.
The dispersed cloud from a release scenario without retention pit would tend to propagate higher from the ground and die out quickly. Results have to be confirmed with additional calculations and comparisons with other future experiments.

2.2.2.4 Unconfined Vapour Cloud Explosion (UVCE)

In case of LH_2 spillage on an industrial site, a cold and reactive H_2/air cloud could be formed. In case of ignition, the flame could interact with the obstacles (vaporizer, pipe rack, vegetation) possibly leading to flame acceleration and even to a deflagration to detonation transition in the worst case scenario.

2.2.2.5 BLEVE phenomenon

A BLEVE (Boiling Liquid Expanding Vapor Explosion) 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_2 which, although stored cryogenically, is also at modest pressure. Although LH_2 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.

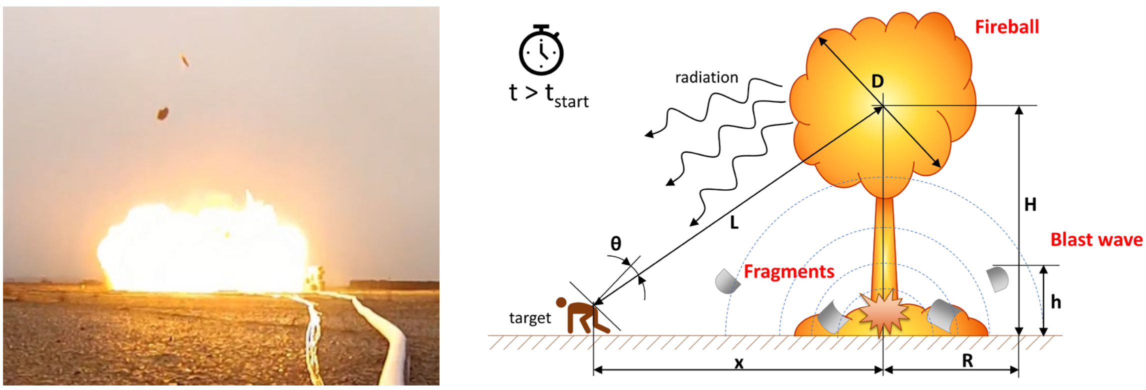


Figure 12. BLEVE main consequences (Photo: BLEVE on LNG tank).

BLEVE should be experimentally studied by BAM in SH2IFT project. Initially scheduled for Q2 2020, due to Covid-19, trials are postponed to fall 2020.
As soon as available, results will be taken into account into HyResponder project.

2.2.2.6 RPT phenomenon

Rapid Phase Transition (RPT) is a known phenomenon for the LNG in particular. When the liquid at cryogenic temperature comes into contact with water, it quickly heats up causing a violent vaporization which can lead to a so-called “cold” or “physical” explosion, i.e. flameless.

Theoretically, there are three types of Rapid Phase Transition events (RPT):
- spontaneous,
- delayed,
- and triggered.

Figure 13. LNG RPT phenomenon.

Regarding the specific conditions required for these phenomena, occurrence probability with pure liquid hydrogen is very low.

HSE

Nevertheless, trials should be performed by BAM in SH2IFT project in September 2020 (trials – initially scheduled for Q2 2020 – postponed due to Covid-19) in order to confirm, or not, theoretical preliminary assessments. These trials will consist in 20-mm diameter release of LH_2 (0.5 to 2 $kg.s^{-1}$), over and under water, in a L10 x l10 x H1 m basin filled with water. Sprays of water onto LH_2 are expected as well.
As soon as available, results will be taken into account in HyResponder project.

2.2.2.7 Purely cryogenic hazards

- **Material embrittlement**

Cryogenic temperatures on materials can reduce strength of structures up to irreversible failures.

- **Solidification of air components**

In case of LH_2 or cold H_2 releases, it could be possible that solid particles (water and CO_2 freezing) and/or LH_2 droplets and air condensate droplets (friction and break up) may ignite.

- **Extreme cold hazard**

Cryogenic liquids and their associated cold vapours and gases can produce effects on the skin similar to a thermal burn. Brief exposures that would not affect skin on the face or hands can damage delicate tissues such as the eyes. Prolonged exposure of the skin or contact with cold surfaces can cause frostbite. The skin appears waxy yellow. There is no initial pain, but there is intense pain when frozen tissue thaws.

Unprotected skin can stick to metal that is cooled by cryogenic liquids. The skin can then tear when pulled away. Even non-metallic materials are dangerous to touch at low temperatures. Prolonged breathing of extremely cold air may damage the lungs.

- **Asphyxiation hazard**

When cryogenic liquids form a gas, the gas is very cold and usually heavier than air. This cold, heavy gas does not disperse very well and can accumulate near the floor. Even if the gas is non-toxic, it displaces air. When there is not enough air or oxygen, asphyxiation and death can occur. Oxygen deficiency is a serious hazard in enclosed or confined spaces.

Small amounts of liquid can evaporate into very large volumes of gas. For example, one litre of liquid hydrogen vaporizes to 848 litres of hydrogen gas when warmed to room temperature.

3. Safety aspects of hydrogen systems and infrastructures

The aim of this chapter is to describe and analyse hydrogen systems, fuel cell applications and associated infrastructures, in order to well understand the working, the potential issues, the hazards due to hydrogen use… and to know what are the available safety features in order to ensure safe use or exploitation of these applications in different environments. Applications were considered from the production of hydrogen to its final use.

A similar work was performed in HyResponse project (D2.1 "Description of selected FCH systems and infrastructure, relevant safety features and concepts", 2015), with a specific focus on gaseous hydrogen systems.

Since the completion of HyResponse project, improvements were brought for some gaseous hydrogen systems, some developments are on-going and liquid hydrogen is considered more and more. They are presented in the following sections, highlighting available safety features or other relevant information for responders intervention under conditions as safe as possible.

Regulation, Codes and standards are not treated in this document, but remain available through the dedicated course developed in HyResponse project (D7.2 "Regulations, codes and standards for first responders", 2016) and will be updated thanks to Task 2.1 in WP2 of HyResponder project.

3.1 Gaseous hydrogen technologies

3.1.1 Gaseous hydrogen production process and infrastructures

It exists several ways to produce hydrogen. The figure below makes a review of these processes.

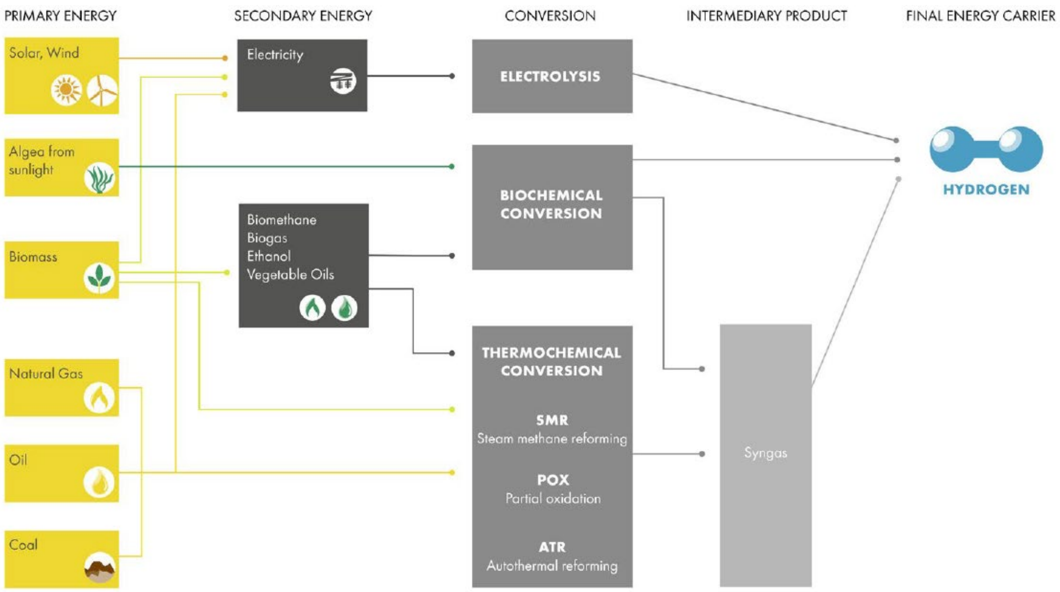


Figure 14. Production of hydrogen.

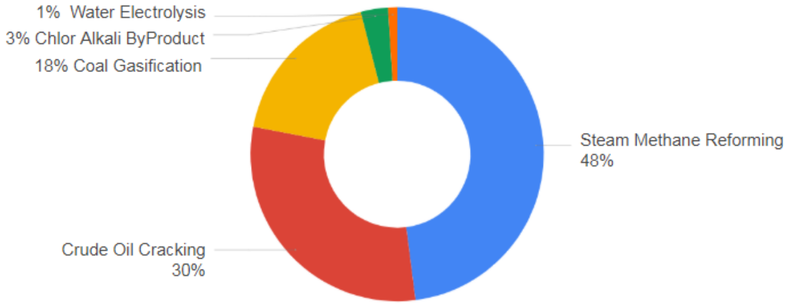


Figure 15. Production of hydrogen.

The main ways of hydrogen production are taking into account environmental issues are:

steam methane reforming with CCS (Carbon Capture and Storage),
biomethane and biomass reforming,
and water electrolysis.

3.1.1.1 Steam methane reforming

- **Description**

The SMR process uses steam and a catalyst to make hydrogen from a light hydrocarbon such as methane or propane. The process basically strips the hydrogen from the hydrocarbon and from the water necessary to convert all of the resulting carbon and oxygen to CO_2.

Figure 16. Air Liquide steam methane reforming plant.

The two main steps of the conversion are as follows:

$CH_4 + H_2O \rightarrow 3\ H_2 + CO$ - Steam Methane Reforming

- Endothermic reaction: $\Delta Ho = + 206\ kJ.mol^{-1}$
- Catalytic reaction: Ni / Al_2O_3
- 20 - 30 bara, 900 – 1000°C, few minutes

$CO + H_2O \rightarrow CO_2 + H_2$ - Water Gas Shift

- Slightly exothermic reaction
- Catalytic reaction: CuO ; Fe_2O_3 ; Cr_2O_3
- 20 - 30 bara, 400°C (High Temperature) / 200°C (Low Temperature)

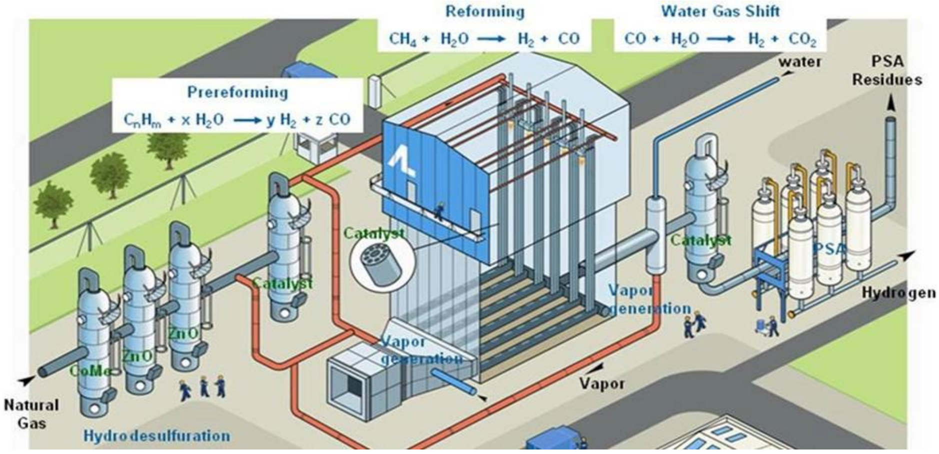


Figure 17. Sketch of a steam methane reforming plant.

- **Safety features**

This technology is well established so there are no specific concerns.

3.1.1.2 Electrolysis

- **Description**

Water electrolysis comprises the splitting of water molecules into their constituent parts (H_2 and O_2) by passage of an electrical current.

Figure 18. Principle of electrolysis process.

Main figures are given in the following sketch of the process.

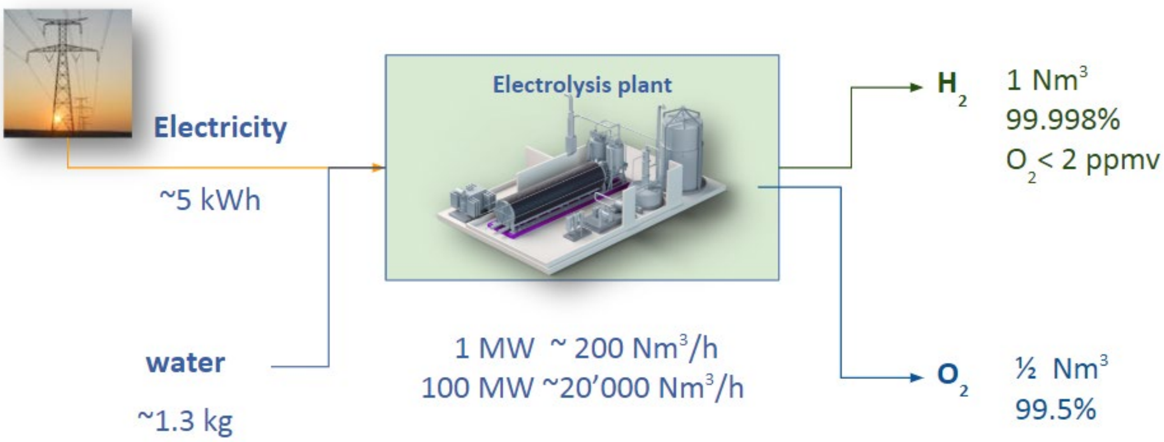


Figure 19. Electrolysis system.

There are several electrolysis existing technologies with different maturity levels (TRL):

Proton Exchange Membrane – TRL 8
Alkaline electrolyzer – TRL 9
Solid Oxide Electrolyzer – TRL 6

But the main electrolyzer technologies are alkaline, which contain liquid electrolytes (potassium or sodium hydroxide), and solid polymer electrolyte electrolysers (PEM).

	Proton Exchange Membrane	Alkaline Electrolysis	Solid Oxide Electrolysis
Cathode	$2H^+ + 2e^- \rightarrow H_2$	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	$H_2O + 2e^- \rightarrow H_2 + O^{2-}$
Anode	$H_2O \rightarrow ½O_2 + 2H^+ + 2e^-$	$2HO^- \rightarrow ½O_2 + H_2O + 2e^-$	$O^{2-} \rightarrow ½O_2 + 2e^-$
	$H_2O \rightarrow ½O_2 + H_2$	$H_2O \rightarrow ½O_2 + H_2$	$H_2O \rightarrow ½O_2 + H_2$

Figure 20. Main reactions according to electrolysis technologies.

The main differences between these technologies are

1. The separator: diaphragm or membrane
2. The electrolyte: liquid, solid, acid or basic

Besides the electrolyser unit, an on-site station generating hydrogen by electrolysis requires water purification systems and a hydrogen purification and drier unit to treat the hydrogen produced.

Many electrolysers generate hydrogen at relatively low pressure, e.g. 10 to 25 bar, so further compression is required to elevate the pressure to storage pressures.

Figure 21. Sketch of Hydrogenics electrolyzer skid.

- **Safety features**

Table 4. Safety features for electrolyzer.

What	Where	For what
Process monitoring (pressure, temperature)	General	Detect leak and dysfunction
ATEX certified equipment	In the skid which is a confined space where leaks can occur	Avoid ignition sources
H_2 detection	Inside the skid	Activate warning, and shut-off valves if required in case of accidental leakage
Flame (UV/IR) detector	Outside the skid	Activate warning, and shut-off valves if required in case of accidental ignited release

3.1.2 Gaseous hydrogen storage & delivery

3.1.2.1 Cylinders for gaseous hydrogen storage

- ***Available cylinders***

It exists different types of hydrogen storage cylinders presented in Figure 22.

Specificities mainly depend on the internal maximal pressure of storage.
Classical cylinders, so-called type-I, are in metal and can stored gaseous hydrogen at a maximal working pressure of 200 bar. In order to slightly increase storage pressure reinforcement of these cylinders is possible and applied on type-II cylinders.
Type-I and type-II cylinders have a satisfying fire resistance.

In order to significantly increase the storage pressure – up to 700-1000 bar – composite cylinders were developed. They are composed of an internal liner in aluminium or steel for type-III, in "plastic" for type-IV, and wrapped with fibres for mechanical resistance.

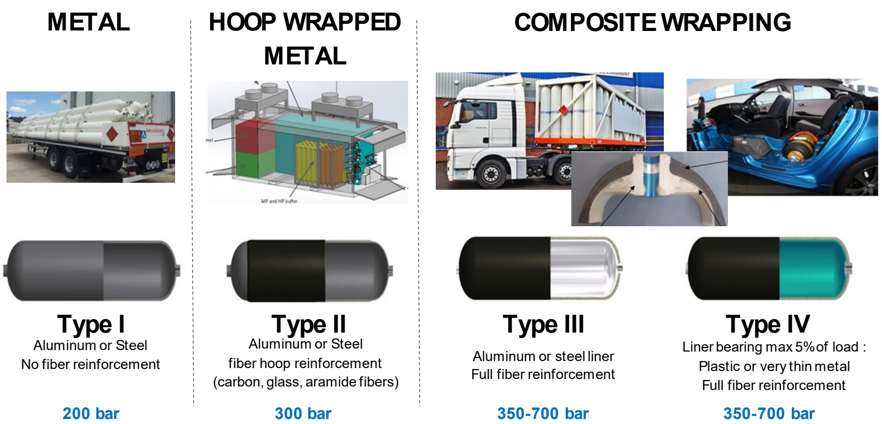


Figure 22. Pressure vessel types. Ready-to-use cylinders.

Principal risk with composite cylinders is fire and thermal aggressions. Thus in most of the applications using composite cylinders a Thermally activated Pressure Relief Device (TPRD) is connected to an outlet line allowing to release hydrogen before drastic increasing of the pressure due to the temperature and avoiding cylinder mechanical rupture (burst).

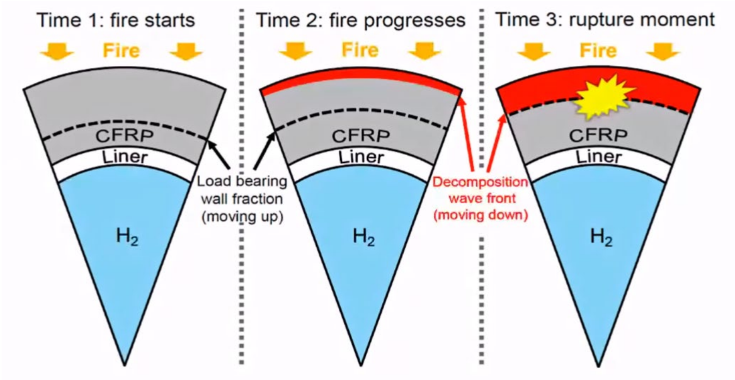


Figure 23. Composite tank rupture mechanism.

The main types of TPRD are

- glass bulb, that will break at the targeted temperature
- And eutectic material, that will melt at the targeted temperature

Additional safety features – check valve and shut-off valve – are installed on on-board composite cylinders as shown in Figure 24.

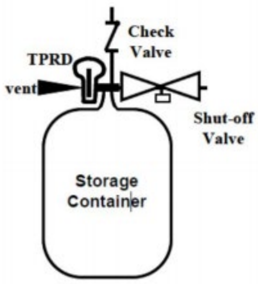


Figure 24. Safety features on on-board hydrogen high pressure composite cylinders.

- ***Under-development cylinders***

Research is on-going on several types of tank for hydrogen energy applications.

TPRD-less composite tanks are studied through few years and will be tested in full-scale conditions in HyTunnel-CS FCH JU project. Four 19-L prototypes - having successfully passed GTR#13 fire test - are shown in Figure 25 (Molkov et al.,2020).

Figure 25. TPRD-less tank prototypes and fire test bench.

Technology is based on leak-no-burst concept. The liner melting in fire initiates microleaks of hydrogen through the whole tank wall (if liner and wall are not bounded) or part of the wall where the liner is melted (if bounded).

First results on TPRD-less composite cylinders are the following:

- the explosion-free in a fire safety technology eliminates tank rupture in localised and engulfing fire of any intensity
- the technology does not produce dangerous jet fires during the release, but instead microleaks provide not- or barely seen flames

Thus this kind of cylinder could be considered as inherently safe regarding fire aggression and burst risk. Additional trials are still required before final conclusions and approvals.

Other research works are performed on composite cylinders in order to avoid common issues with "complex" protocols of filling and emptying type-IV cylinders like collapse of the liner. In this way a composite cylinder, so-called type-V, without internal liner (also leak-before-break inherently) for hydrogen high pressure storage is under-development (see Figure 26).

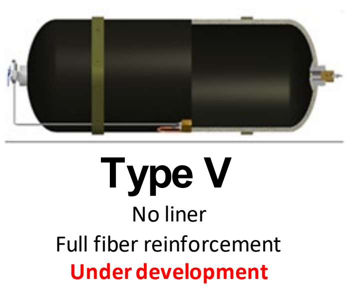


Figure 26. Under-development type-V cylinder.

3.1.2.2 Trailers

- ***Description***

Main existing trailers for gaseous hydrogen transportation are 200-bar tube trailers with long horizontal metallic tubes.
Capacity of this kind of trailer is around 300-500 kg-H_2.

Figure 27. Air Liquide 200-bar H_2 tube trailer.

Regarding the needs of hydrogen energy applications, new trailers using composite cylinders can transport hydrogen at higher pressure (up to 500-bar). Thus the capacity of hydrogen transportation can reach 1 t.

Figure 28. Air Liquide high capacity trailer (500 bar+).

- ***Safety features***

Table 5. Safety features for gaseous hydrogen trailer.

What	Where	For what
Isolation valves	Cylinders	According to ADR, during transportation all storage are isolated by a valve
TPRD	Specifically on trailers with type-IV cylinders Located on the roof of the trailer, and upward directed	Avoid the pressurization and the burst of the cylinder in case of fire NB: not mandatory but set-up on some high capacity trailers with type-IV cylinders
Leak tightness test	Trailer storage	Avoid major leaks after trailer refuelling

3.1.2.3 Pipelines

- ***Description***

Pipelines are used in order to transport gaseous compounds in large amounts.

According to the properties of the carried gas and the requirements of the customers the pressure in the pipelines can vary.

For hydrogen transportation, the pressure inside pipelines can reach 100 bar.

Figure 29 shows Air Liquide pipeline network and production plants for hydrogen, syngas and other gases in USA and northern Europe.

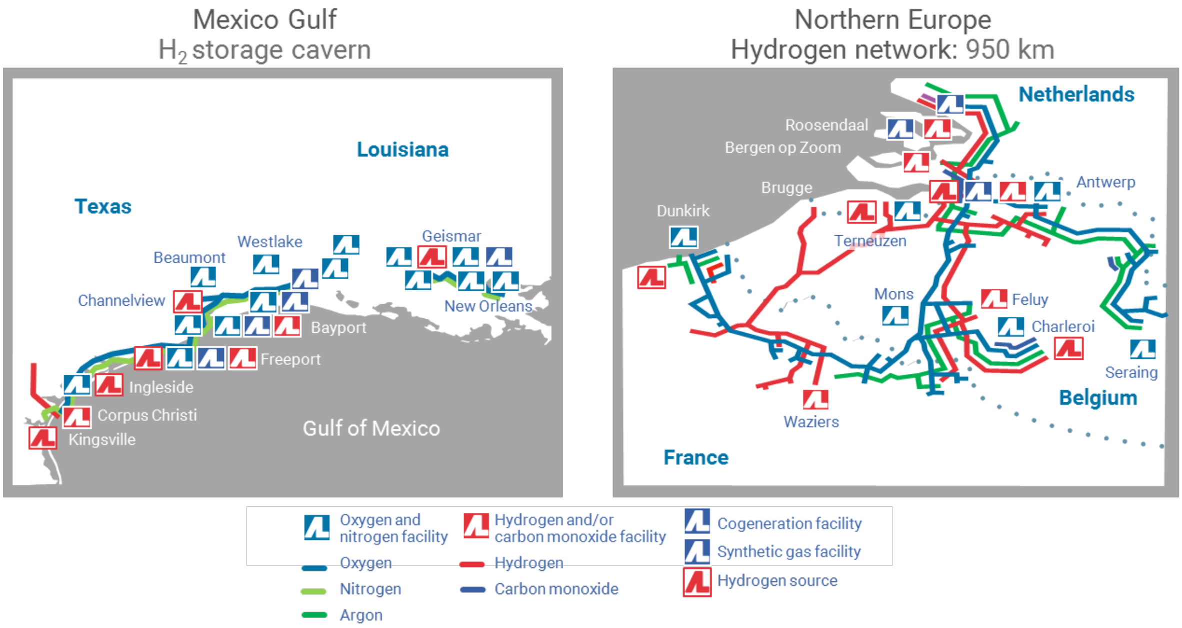


Figure 29. Air Liquide hydrogen sources and network.

As illustrated in Figure 29, these pipelines are installed relatively close to the production plants.

On pipeline network, according to the distance between the production plant and the customer, pressurization stations can be required in order to maintain the targeted pressure in the pipeline.

- ***Safety features***

Table 6. Safety features for high pressure hydrogen pipelines.

What	Where	For what
Pressure monitoring	Pipeline	Detect major leaks on network
Periodic inspection	Pipeline	Detect coating defects and avoid major leaks
Cathodic protection	Pipeline	Avoid pipeline corrosion

3.1.2.4 Liquid Organic Hydrogen Carrier

- ***Description***

This technology consists in handling hydrogen in chemically bound form as liquid organic hydrogen carrier (LOHC). LOHC systems are composed of pairs of hydrogen-lean (LOHC-) and hydrogen-rich (LOHC+) organic compounds that store hydrogen by repeated catalytic hydrogenation and dehydrogenation cycles.

In contrast to hydrogen storage by hydrogenation of gases, such as CO_2 or N_2, hydrogen release from LOHC systems produces pure hydrogen after condensation of the high-boiling carrier compounds.

The different step of LOHC concept are the following:

1. Hydrogen generation
   Production by methane steam reforming, electrolysis…
2. Hydrogenation
   Chemical bonding of hydrogen molecules to liquid carrier via catalytic reaction → LOHC+
   Exothermal process with 9 kWh per kg hydrogen useable heat at 200°C+
   High temperature heat is produced, which can be used on-site
3. Liquid organic carrier
   Transportation to H_2 end-use site
   57 kg H_2 uptake per m^3 LOHC (corresponding to 630 Nm^3 H_2 per m^3 LOHC)
4. Dehydrogenation
   Release of hydrogen molecules from liquid carrier medium via catalytic reaction → LOHC-
   Endothermic process with 12 kWh per kg H_2 required at 300°C
   Hydrogen release process requires heat, which can be supplied by high-temperature waste-heat, natural gas, electricity or hydrogen
5. Hydrogen use

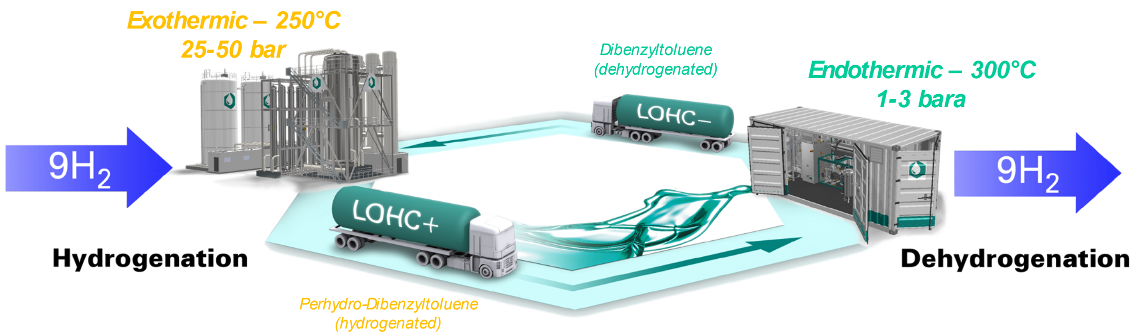


Figure 30. LOHC Hydrogenious concept.

Advantages of LOHC are:

- No molecular hydrogen stored
- Non-toxic and not classified as dangerous good
- Hardly flammable and non-explosible
- No evaporation of stored hydrogen (multi-month storage possible without any losses)
- Liquid state in broad temperature range between -39 to 390°C and ambient pressure
- Low pressure process
- Transportable in conventional fuel infrastructure

Main drawbacks are:

- Management of chemical hazards
- Energy management: potential loss of heat during hydrogenation step (heat production), and need of heat for dehydrogenation step (heat demand)…
- Limited hydrogen carrying capacity
- Require important compression step of hydrogen for final use in refuelling station for instance because of the low hydrogen pressure after dehydrogenation step
- Loss of optimization in the transportation phase due to the organic liquid transported in the same time (not only hydrogen)
- Time consuming with loading/unloading procedures

LOHC feasibility is studied in HySTOC (Hydrogen Supply and Transportation using Liquid Organic Hydrogen Carriers) FCH JU funded project (duration: 2018-2021).

Figure 31. LOHC-supplied HRS HySTOC FCH JU funded project.

- ***Safety features***

Main dangers with chemicals is exposure of personnel and environment to Dibenzyltoluene and its hydrogenated forms and dissociation products. Benzene has been identified as most toxic compound in liquid organic hydrogen carrier. Benzene is only present in traces as by product of the LOHC process, nevertheless it is added to workplace safety instructions and protective equipment based on its MSDS (Material Safety Data Sheet) when operating with Dibenzyltoluene. Potential leaks are prevented by double skinned tanks and spill pools. Adsorbent materials will be available in case of leakage. Regular monitoring of leaks will be implemented as well.

Table 7. Safety features for LOHC concept.

What	Where	For what
Use of technical tight equipment	NA	test of tightness
Collection tray	installed at the bottom of each container	Avoid chemical spreading
Level indicator	In the collection tray	Shut down in case of chemical leakage
Double walled tanks	Tanks	Limit risk of chemical leakage
Overfill protection	Tanks	Limit risk of chemical spreading by overfilling

3.1.2.5 Gaseous refuelling station infrastructures

The main function of the refuelling station is to fill the tanks of vehicles (forklift truck, bus, car) powered by fuel cells with gaseous hydrogen.

Figure 32. Hydrogen refuelling station of Les Loges-en-Josas (France, near Paris).

The gaseous hydrogen, contained initially in a semi-trailer at a pressure of 200 bar, is compressed in a high pressure storage (1000 bar in most of the cases). During the filling, the tank is filled by a balancing of the pressure. The pressure in vehicle tank is between 350 bar for bus and 700 bar for car.

To fill as fast as possible a car, hydrogen could be pre-cooled before filling.

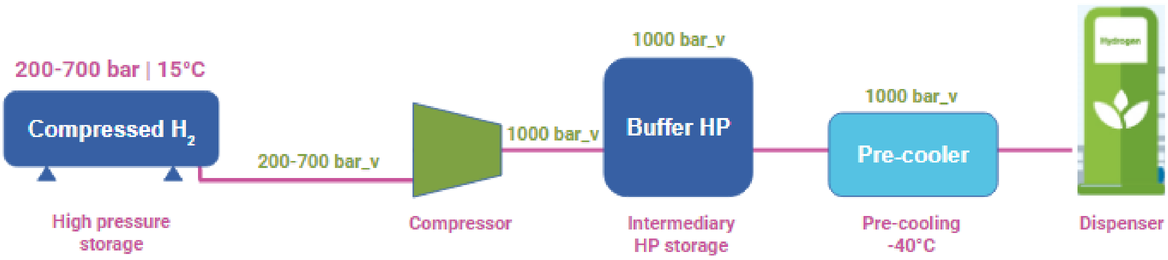


Figure 33. Simplified sketch of a gaseous hydrogen refuelling station.

In France, a safety distance of 8 m between public domain and gaseous hydrogen source is required.

- ***Safety features***

Table 8. Safety features for gaseous HRS.

What	**Where**	**For what**
Qualified and validated hose and fittings	Process and dispenser	Avoid accidental leakages
Periodic replacement of the hose	Dispenser	Avoid accidental leakages
H_2 detection	Inside the process container Inside the dispenser	Activate warning, and shut-off valves if required in case of accidental leakage
Flame (UV/IR) detector	In the process container Outside, close to the dispenser	Activate warning, and shut-off valves if required in case of accidental ignited release
Automatic shut-off valve	Several between H_2 storage and dispenser	Limit H_2 inventory in case of accidental release
Process pressure monitoring	General	Detect abnormal pressure drop due to leak or piping rupture

Naturally ventilated confined spaces	Process container Dispenser	Avoid to reach flammable limits of H_2-air mixture in case of accidental release
Forced ventilation	Process container for some models	Avoid to reach flammable limits of H_2-air mixture in case of accidental release if natural ventilation not possible or not efficient enough
ATEX certified equipment	In confined spaces where leaks can occur (i.e. skids and dispenser)	Avoid ignition sources
Hose grounded	Dispenser	Prevent sparks caused by static electricity during refuelling
Automatic leak test before filling	General	Avoid accidental leakages
Flow restrictors	General	Limit flowrate in case of release or piping rupture
Automatic closing time	General	Close H_2 feeding valves in case of hose rupture or leak
Hose break-away device	Dispenser	Avoid major leak by closing feeding flexible in case of tearing by forgetting to disconnect the vehicle
Shock protection (bollard)	Dispenser	Protect the dispenser from major mechanical aggression by vehicle accidental stamping and avoid catastrophic leak
Emergency punch stop	Few meters from the dispenser	Close H_2 feeding valves in case of emergency
Conductive (grounded) concrete slab	Dispenser	Prevent sparks caused by static electricity during refuelling

3.1.3 Gaseous hydrogen existing systems for mobility

While the various fuel cell electric vehicles – cars, buses, trains, trucks… – are likely to differ in the details of the systems and hardware/software implementations, the following major systems are common to most fuel cell electric vehicles equipped with gaseous hydrogen storage:

- Hydrogen fuelling system,
- Hydrogen storage system (350 or 700 bar),
- Hydrogen fuel delivery system,
- Fuel cell system,
- Electric propulsion and power management system.

In the following sections, details are given on main existing fuel cell electric vehicles and associated safety features.

3.1.3.1 Hydrogen fuel cell electric vehicle

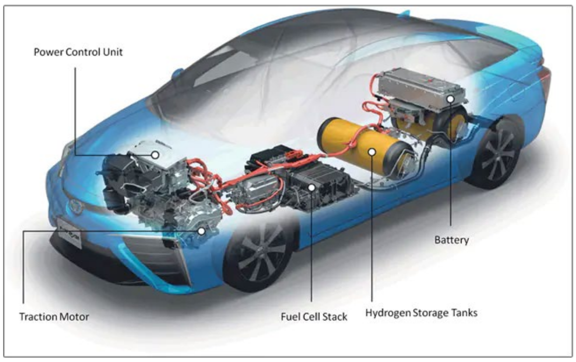


Figure 34. Simplified sketch of a FCEV.

In addition to car homologation (e.g. several normalized full-scale tests: crash, fire…) and a design compliant with many codes and standards, many mitigation barriers are present based on risk analysis.

Table 9. Safety features for FCEV.

What	Where	For what
TPRD	Connected to 700-bar H_2 composite cylinders Located at the bottom of the car, and downward directed	Avoid the pressurization and the burst of the cylinder in case of fire
Thermal insulation	Around the gas storage	Delay warming of gas storage
H_2 detection	Close to the H_2 storage tanks In the car cockpit	Activate warning, and shutdown valves
Automatic shut-off valve	Between H_2 storage tanks and fuel cell	Limit H_2 inventory in case of accidental release
Very short high pressure line	Between H_2 storage tanks and fuel cell	Limit H_2 inventory in case of accidental release
Low medium pressure (10 bar or less)	Between H_2 storage tanks and fuel cell	Limit H_2 inventory in case of accidental release
Excess flow valve	on the low pressure piping	Limit flowrate in case of release or piping rupture
Shock detector	In the car	Close H_2 feeding valve
Shock absorbing shielding	around the gas storage	Protect from mechanical aggression for avoiding potential leaks
Earthing connection	Car refuelling nozzle	Prevent sparks caused by static electricity during refuelling

3.1.3.2 Hydrogen fuel cell bus

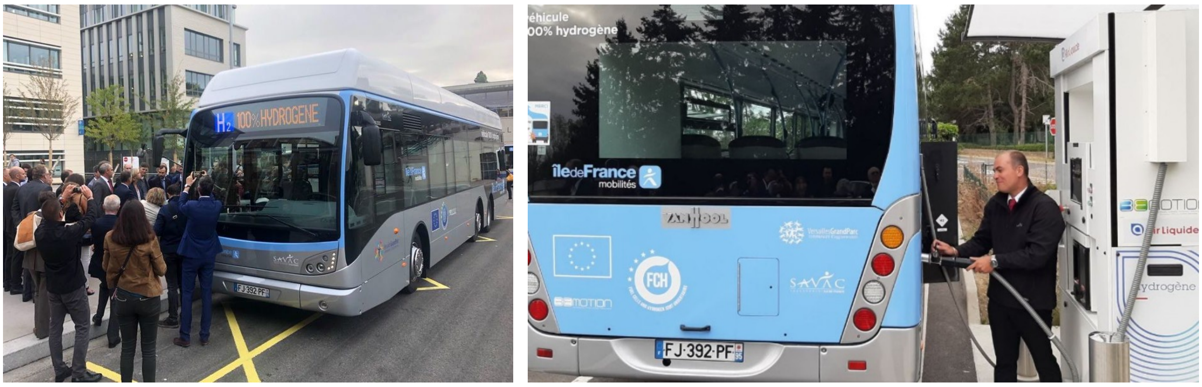


Figure 35. Hydrogen fuel cell bus and refuelling (France).

Main characteristics of the fuel cell buses is that hydrogen tanks and fuel cell are set up on the roof of the bus. The pressure of storage in the tanks is 350 bar.

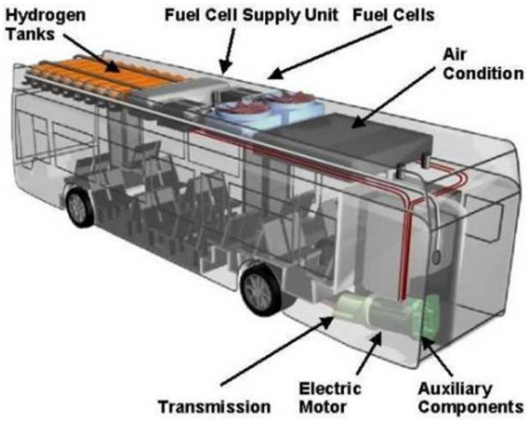


Figure 36. Simplified sketch of a FC bus.

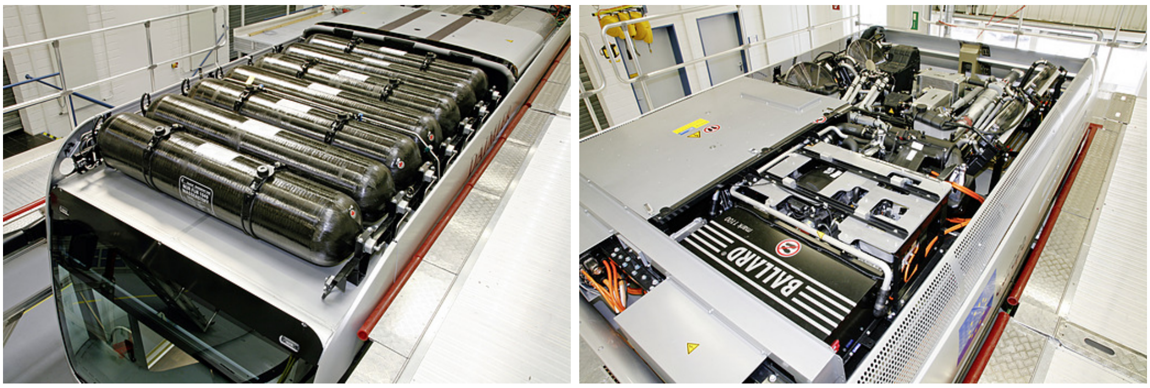


Figure 37. FC bus. Left: H2 storage, right: fuel cell system.

Table 10. Safety features for FC buses.

What	Where	For what
TPRD	Connected to 350-bar H_2 composite cylinders Located on the roof of the bus, and upward directed	Avoid the pressurization and the burst of the cylinder in case of fire
H_2 detection for some models	Close to the H_2 storage tanks Close to the fuel cell	Activate warning, and shutdown valves
Shutdown valves	Between H_2 storage tanks and fuel cell	Limit H_2 inventory in case of accidental release
Earthing connection	Bus refuelling nozzle	prevent sparks caused by static electricity

3.1.3.3 Hydrogen fuel cell truck

Comparatively to buses, hydrogen tanks and fuel cell are located in the bottom part of the trucks (see Figure 38). In order to provide an autonomy of more than 600 km, the hydrogen pressure in the storage tanks is 700 bar.

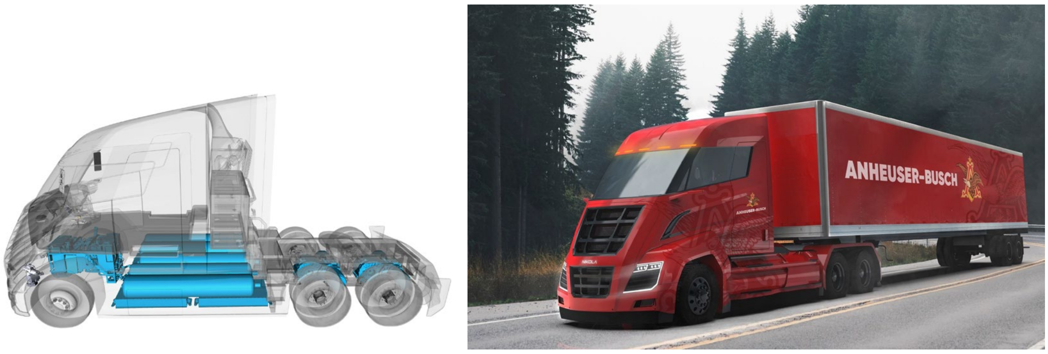


Figure 38. Hydrogen fuel cell truck (photo credit: Nikola).

Table 11. Safety features for FC trucks.

What	Where	For what
TPRD	Connected to 700-bar H_2 composite cylinders	Avoid the pressurization and the burst of the cylinder in case of fire
H_2 detection for some models	Close to the H_2 storage tanks Close to the fuel cell	Activate warning, and shutdown valves
Shutdown valves	Between H_2 storage tanks and fuel cell	Limit H_2 inventory in case of accidental release
Earthing connection	Truck refuelling nozzle	prevent sparks caused by static electricity

3.1.3.4 Hydrogen fuel cell train

As shown in Figure 40, hydrogen storage and fuel cell are on the roof of the train. Pressure in the storage tanks is 350 bar. An evolution of the pressure of storage for fuel cell trains could be 700 bar.

Figure 39. ALSTOM CORADIA iLINT FC train (Germany).

Electricity for the traction and on-board equipment is generated by a fuel cell, stored in battery and recovered during braking.

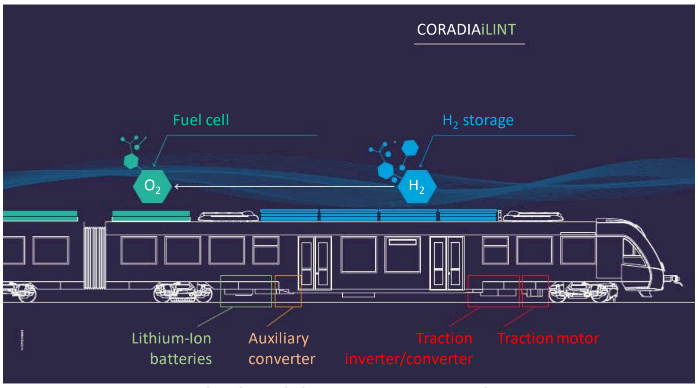


Figure 40. ALSTOM CORADIA iLINT FC train concept.

Table 12. Safety features for FC trains.

What	Where	For what
TPRD	Connected to 350-bar (or 700-bar) H_2 composite cylinders Located on the roof of the train, and upward directed	Avoid the pressurization and the burst of the cylinder in case of fire
H_2 detection for some models	Close to the H_2 storage tanks Close to the fuel cell	Activate warning, and shutdown valves
Pressure monitoring	On medium and high pressure lines between fuel cell and storage tanks	Detect hydrogen leaks
Shutdown valves	Between H_2 storage tanks and fuel cell	Limit H_2 inventory in case of accidental release
Earthing connection	Bus refuelling nozzle	prevent sparks caused by static electricity

3.1.3.5 Other mobility applications

Some studies and projects were performed on planes and boats using gaseous hydrogen but these applications appear not relevant for gaseous hydrogen and are now more oriented concepts based on liquid hydrogen.
Thus they are presented in next chapter, dedicated to liquid hydrogen.

3.1.4 Focus on detection devices for gaseous hydrogen releases

Several types of devices are available to detect gaseous leak, or flame in case of release ignition.
In Table 13 and Table 14, are presented examples of equipment, respectively portable and fixed.

Table 13. Portable hydrogen release detection devices.

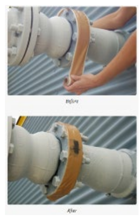
Explosimeter (gas)	Combustible detector (gas)	Acoustic detector (gas) Without screen	Acoustic detector (gas) With localisation of leak by screen	Chemochromic* tapes or other chemochromic media (gas)	Soap/”1000 bulles” (gas)	Thermal imaging camera (flame)
						

Table 14. Fixed hydrogen release detection devices.

Explosimeter (gas)	Acoustic detector (gas)	UV/IR (flame)	Multi-IR (flame)
			

3.2 Liquid hydrogen technologies

3.2.1 Liquid hydrogen production process and infrastructures

One of the challenges in building a hydrogen economy is the establishment of an efficient production and supply infrastructure. Large scale distribution favours the relatively dense liquid phase LH_2, but liquefaction still suffers from low energy efficiencies. Historically, LH_2 was mainly used as a rocket fuel, where the low efficiency in the production did not matter. A major program of hydrogen liquefaction was started in the USA within space programs leading to the design and construction of large-scale liquefaction plants.

The liquefaction of H_2 is a highly energy intensive process. The minimum work required for the liquefaction of hydrogen (at ortho-para equilibrium) is 3.92 kWh of electricity /kg of H_2 or 0.12 kWh /kWh of H_2. Typical values for the whole process, however, are in the range of 8 - 14 kWh/kg for relatively large liquefaction units. Reducing the energy consumption of liquefiers is an active subject of development for the LH_2 industry (see IDEALHy FCH JU project for instance).
Most plants (11) are located in North America. In Europe, plants (3) in France, Netherlands, and Germany are operated with a total capacity of 19 $t.day^{-1}$. The largest plant size is currently 68 t/d (New Orleans, USA). The latest (2017) start-up liquefier (10 $t.day^{-1}$) is owned by Airgas (now Air Liquide) in Calvert City.

Figure 41. Air Liquide LH_2 filling stations (left: Little Town, USA; right: Becancour, Canada).

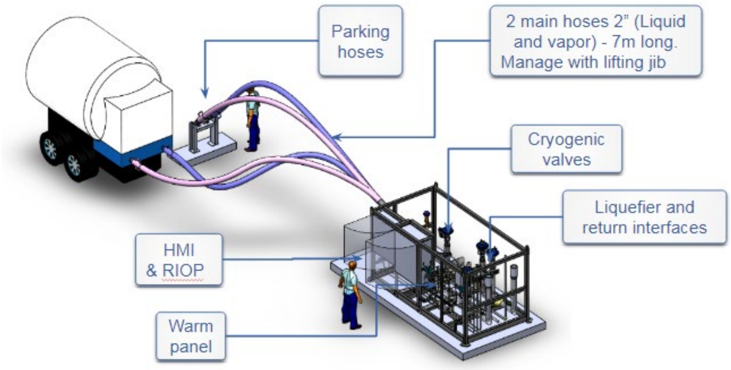


Figure 42. Generic loading bay ergonomy for LH_2 trailer filling.

For transferring LH_2 from a storage to another (for instance from a large storage to a truck or from a trailer to a storage at use site), there are two methods:

- pressure build up (natural pressure build up or voluntary vaporization of LH_2 via a small external heat exchanger). Hence, the pressure in the "mother storage" becomes more than the pressure in the "daughter storage" and LH_2 transfer is easy. The main drawbacks of this method are a long operating time and an increase of the pressure of the "mother" storage leading sometime to the need of a pressure venting;
- pumping in the "mother storage" using an appropriate transfer centrifugal cryogenic pump. The main drawbacks of this method are the cost of the pump and the need of frequent maintenance of the pump mostly due to cavitation (low available NPSH - Net Positive Suction Head: difference between liquid pressure and saturation vapour pressure of the considered compound - due to low density of LH_2).

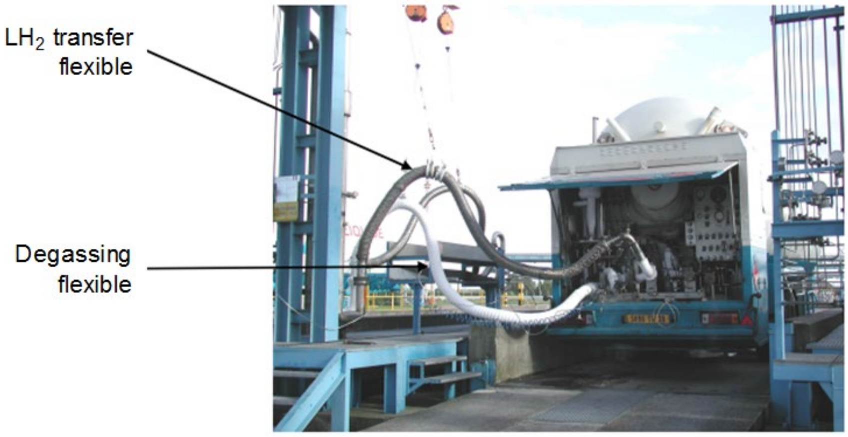


Figure 43. LH_2 trailer during transfer.

3.2.2 Liquid hydrogen storage & delivery

3.2.2.1 Liquid hydrogen delivery

Cryogenic liquid hydrogen trailers can carry up to 5000 kg of hydrogen and operate up to 12 bar.

Boil-off is the consequence of LH_2 warming up along a delivery sequence (during storage but also and especially during transfer).

Hydrogen boil-off can occur during transport despite the super-insulated design of these tankers, potentially on the order of 0.5% per day. Hydrogen boil-off up to roughly 5% also occurs when unloading the liquid hydrogen on delivery.
The LH_2 trailers are insulated using a vacuum super insulation. This insulation is also used for transfer piping systems (Vacuum MLI Insulated Piping).
The Vacuum Super Insulation is a system of thermal insulation which includes:

- A double-shell insulation space (inter-space) where static or dynamic (for large storage) high vacuum is limiting heat transfer by conduction and convection.
- A blanket of alternate layers of highly reflecting shields (Aluminium for instance) and insulating spacers (Lydall for instance) to prevent heat transfer by radiation as well as conduction between shields.
- An adsorbent (molecular sieve) placed in the vacuum space in order to achieve an adequate level of vacuum at low temperature by adsorption of residual gases and moisture.

Figure 44. Air Liquide LH_2 trailer.

In more details, connection for filling and distribution are at the rear of the trailer as shown on sketch below.

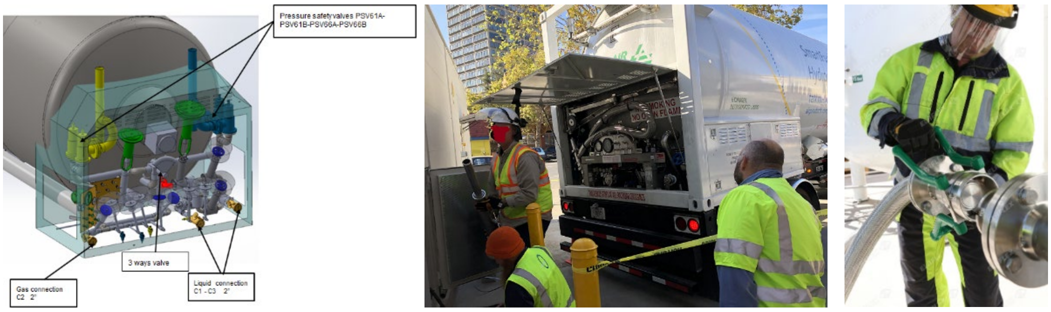


Figure 45. Connection and command system on LH_2 trailer and flexible.

High capacity trailers are under-development, so called Jumbo trailers.

Table 15. Safety features for liquid hydrogen trailers.

What	Where	For what
Two safety valves with at least one pneumatics	Tank	According to ADR, during transportation all storage are isolated by a valve
Road safety valve	Tank	Evacuate overpressure
Rupture disc	Tank	Avoid burst of the storage in case of pressure increase
PRD	Tank	Limit the risk of boil-off

3.2.2.2 Liquid hydrogen storage

Liquid hydrogen storages are already existing for professional for long time ago. But up to now there is no liquid hydrogen storage in public domain.
These storages can be in vertical or horizontal position.
Cryogenic fixed storage have a volume from 10 m^3 to 300 m^3 with an internal pressure around 12 bar.

Figure 46. Horizontal and vertical liquid hydrogen storages.

In order to manage storage at -253°C, for large storage (> 100 m^3 water volume) double-walled vacuum insulated pressure tanks are used (see Figure 47). Such vessels consist of an inner pressure vessel, an external protective jacket and compressed perlite under vacuum in the space between the inner vessel and the outer jacket. Perlite is an inorganic amorphous volcanic glass that represents a good tradeoff between cost and insulation properties.

For smaller storages (< 100 m^3), single-walled pressure tank with multi-layer insulation coating are used.

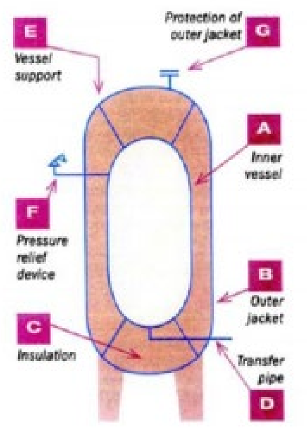


Figure 47. Sketch of a double jacket LH_2 tank.

In most of the cases, LH_2 storages are aerial.

Nevertheless, it exists few cases of underground LH_2 storages, buried or vault as illustrated and defined in Figure 48.

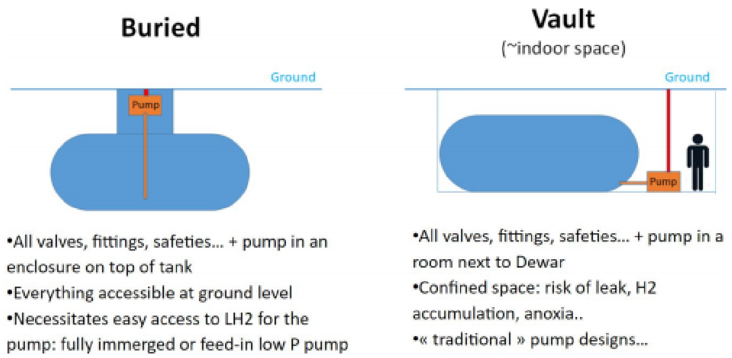


Figure 48. The two main possible designs for underground LH_2 storages.

"Buried" design has safety advantage, but necessitates an immersed LH_2 pump (low or high pressure), that is a technology not very well mastered… "Vault" design keeps the earth/fill away from direct contact with the system using a wall. It does not have any technical barriers, but has limitations in terms of safety (leaks, anoxia), and possibly higher civil work cost.

Table 16. List of known underground liquid hydrogen storages.

Year	Location	Design	Station operator
2004	Washington DC	Vertical, in a sleeve	Shell
2005	London	Vault	BP
2007	Munich	Vault	Total
2010	Berlin	Vault	NA

Table 17. Safety features for liquid hydrogen storages.

What	Where	For what
Pressure and temperature monitoring	Tank	Detect insulation default
Level monitoring	Tank	Avoid overfilling
Rupture disc	Tank	Avoid burst of the storage in case of pressure increase
PRD	Tank	Limit the risk of boil-off

3.2.2.3 Liquid hydrogen refuelling station

Basically, a LH_2-based refuelling station consists in:

- a LH_2 tank (around 20 m^3 - 1000 kg-H_2) with a maximal operating pressure of 10.3 bara
- an insulated process line from the bottom of the storage to the LH_2 pump, driving LH_2 from the storage tank to a vaporizer; this device allows to pump LH_2 up to 1000 bar
- a heater (named VAP: hot oil, electric in order to heat up hydrogen at 1000 bar)
- 1000 bar gaseous buffers (few m^3); these buffers are generally bundles of type I or II (i.e. metallic cylinders or long metallic tube)

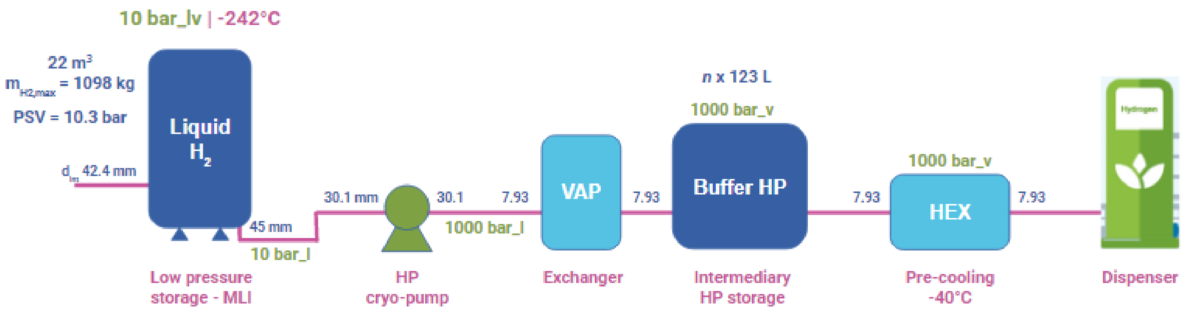


Figure 49. Simplified sketch of a liquid hydrogen refuelling station.

All the other parts (e.g. dispenser, filling hose…) of the refuelling station are similar to classical gaseous refuelling station (see comparison in Figure 50).

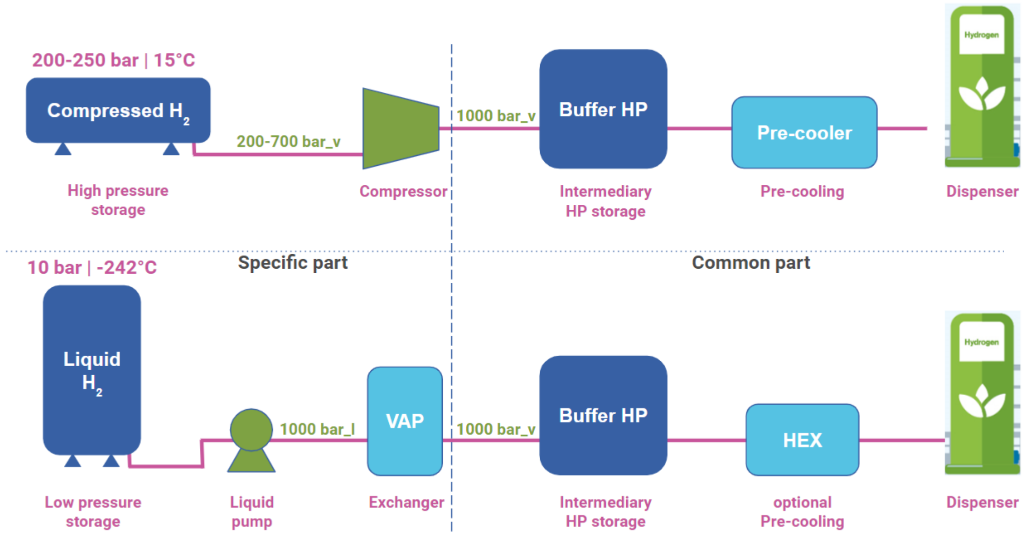


Figure 50. Simplified comparison between gaseous and liquid hydrogen refuelling stations. Top: gaseous HRS, bottom liquid HRS.

The LH_2 tank is delivered by a LH_2 truck. This LH_2 truck is composed of a 40 m^3 horizontal tank operating between 1 and 12 bar (inventory: 4 t-H_2).

The connection between the storage and the truck is done by a flexible transfer line. The transfer is performed without a pump. A small vaporizer is present on the trailer to produce a pressure build-up in the truck tank and allow the transfer of liquid hydrogen in the stationary vertical storage.

More concretely below the Linde Liquid hydrogen refuelling station installed at Oakland (US).

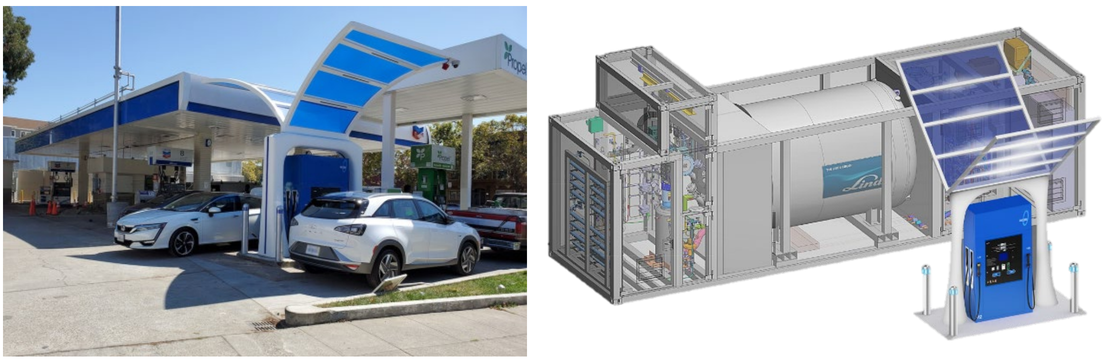


Figure 51. Linde LHRS in Oakland.

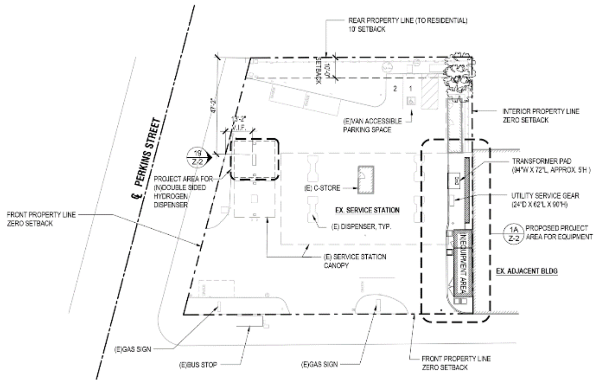
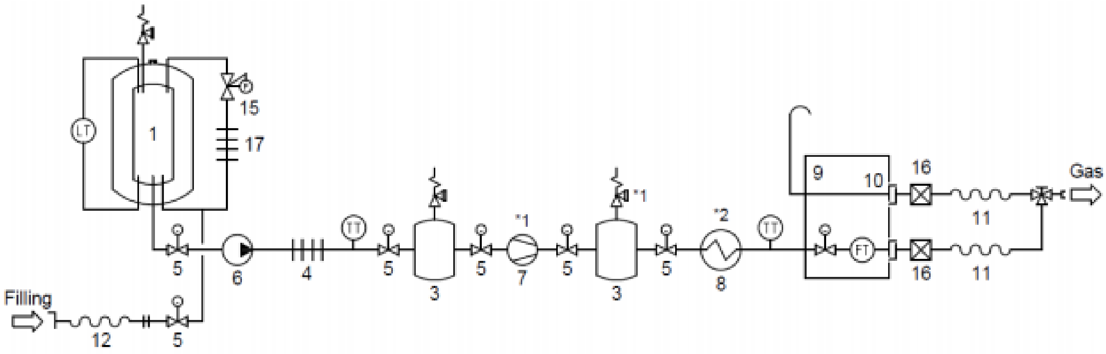


Figure 52. Linde LHRS layout.

Generic process safety features are illustrated and summarized in Figure 53 below.



1. liquid hydrogen storage unit	8. chiller	15. pressure regulator
2. gaseous hydrogen storage unit	9. dispenser	16. breakaway coupling
3. intermediate gas storage	10. safety valve	17. pressure build-up evaporator
4. evaporator	11. delivery hose	
5. emergency shutdown system	12. off-loading hose	LT level sensor
6. pump	13. fill	FT flow sensor
7. compressor	14. purifier	TT temperature sensor

Figure 53. Process flow of a LH_2-based refuelling station.

In France, a safety distance of 20 m between public domain and liquid hydrogen source is required.

Safety features on liquid refuelling stations are almost the same as for a gaseous refuelling station (see Table 8 p 34).

The additional safety means are on liquid hydrogen storage as described in section 3.2.2.2 p 43.

Table 18 makes a brief overview of available information regarding regulation for liquid hydrogen refuelling stations.

Table 18. Overview of regulation for liquid hydrogen refuelling stations.

Country	**Status**	**Distance to property lines**
USA	Permit given by Fire Marshals NFPA55 "recommended"	Lot lines ⇒ 15 m Buildings ⇒ 23 m
France	Storage > 1 t (Europe 5 t) ⇒ authorization given by Prefecture	LH_2 ⇒ 20 m Dispenser (60-120 $g.s^{-1}$) ⇒ 10 m
Germany	No specific regulation for LH_2 if < 5 t (Low Seveso)	LH_2 ⇒ 5 m Dispenser ⇒ 2 m
Japan	Specific LH_2 regulation	LH_2 ⇒ 10 m Dispenser ⇒ 8 m
China	Strictly restricted to military use up to 2018	Under-development

Considering the regulation, it clearly appears a lack of harmonization between the countries both on processes and measures (e.g. authorization required, just recommendations or no specifications; not the same safety distances when defined etc).

3.2.2.4 Liquid hydrogen pipeline

No pipeline large network existing for liquid hydrogen.

3.2.3 Liquid hydrogen systems for mobility

As described in this section, except for spatial applications, liquid hydrogen is, up to now, commonly used for off-board storage and transportation up to delivery to end-user sites.

There is few existing mobile applications using directly liquid hydrogen in an on-board storage.

On-board liquid hydrogen appears not relevant for fuel cell cars. Autonomy given by 700-bar composite cylinders - and maybe more in coming years - is sufficient.

However recently more and more projects are launched for public transportation. Examples are given below:

- LH_2-based ships: SH2IFT project, MARHySAFE project
- LH_2-based planes: HEAVEN project, ENABLEH2 project
- LH_2-based trains: under consideration
- LH_2-based trucks: submitted project on LH_2 on-board storage tank

Figure 54. Norled LH_2-based ship.
75 m^3 LH_2 tank at 5 bar.

Identification of hazardous events and mitigation measures through a qualitative approach was led for LH2-based ship in MARHySAFE project in April 2020. Related report is not yet public.

4. Liquid hydrogen hazards and associated risks, concretely for first responders

Regarding safety properties of liquid hydrogen and behaviour after release, it appears that - in order to well manage the risk of the existing applications and potential future applications - it is necessary to take into account knowledge developed for gaseous hydrogen hazard as well.

At present time, considering hydrogen energy activities and applications, liquid hydrogen is mainly used for storing higher amounts of hydrogen. Thus the main liquid hydrogen systems are the **liquid trailers** for hydrogen delivery and **liquid hydrogen storages**.

Systems with on-board liquid hydrogen are not largely deployed, but several on-going projects studied future liquid hydrogen-based fuel cell transportation means like ships, trains and planes.

Most important phenomena for responders in order to cover hazards associated to the described systems in this report are:

- For physical phenomena

- **Liquid hydrogen pool and spreading**
  What kind of behavior, from liquid to vapour, cold embrittlement of equipment
- **Effects of cryogenics**
  Very low temperature, cold burn, solidification of air components, interaction of liquid hydrogen and water (due to water curtains, water sprays, water fire hose… to contain a fire, a hazardous cloud…)
- **Cryogenic cloud**
  - in normal conditions (during normal venting for instance)
  - in accidental conditions

  Limited visibility for intervention, anoxia risk, safety features frozen, containment of the cloud
- **Ignited high pressure release**
  Flame length, radiative heat fluxes, invisible flame
- **Deflagration due to flammable cloud ignition**
  Feel overpressure, energy, intensity

- **Differences between ignition modes**
  Delayed versus immediate ignition

- **Pressure hazards**
  Burst of pressurized vessel, fragments/missiles danger

- For concrete scenarios

- **Liquid storage in fire**
  How to intervene, what are the good practices to protect the tank against burst…

- **Road accident and overturning of a liquid hydrogen trailer**
  How to intervene, how to detect if there is a danger (e.g. release or not), is it possible to stop a liquid spreading, what are the good practices to protect trailer against burst in case of fire…

- **Release on a connection between the liquid hydrogen trailer and the storage**
  How to intervene, what are the good practices to limit cloud propagation, is it possible to stop the release in safe conditions…

- **Release**
  How to detect a release, what are the available devices, how to use them…

- **More generally**
  What are the safety features on LH_2 systems – for what – where

It is now necessary to analyse these hazardous events and consequences in order to define how they can be transmitted by the most relevant and efficient way(s).

When possible and of interest, nearly-full scale events will be simulated thanks to the operational platform that will be built at ENSOSP (France) in the framework of HyResponder project. Existing operational modules developed in HyResponse project could be adapted in order to complete the future platform.

Figure 55. HyResponse Jet fire operational module (ENSOSP, France).

For some cases, for safety reasons for instance, it will be not possible to physically simulate them. Thus the situation will be treated through other training materials like:

- theoretical learning,
- videos,
- techno-library (safety devices and equipment handled by trainees),
- numerical simulations (see picture below) to be developed by CRISE in WP2

Figure 56. HyResponse virtual reality: fuel cell car scenario.

5. Conclusions

In this review of existing and future hydrogen systems and infrastructures, knowledge and details important for safe intervention of responders regarding liquid hydrogen use and inherent hazards were highlighted and will be used to build relevant training materials.

To summarize, since the completion of HyResponse project:

- No significant improvements on gaseous hydrogen systems and infrastructures
- But
    - Rationalization of hazard distances and mitigation means thanks to a better knowledge of feared events, associated consequences and their management
    - More and **more applications** for mobility in **public domain** and **diversification** *increase of the number of vehicles, different types, in different environments (e.g. tunnels, underground parking, private garages…)*
    - **New cylinders** under-approval *(e.g. TPRD-less composite cylinders…)*
    - **Available tools** for hazard assessment *(e.g. hydrogen e-laboratory)*
- Liquid hydrogen - commonly used for industrial needs - appears for **public applications** *(e.g. LHRS of Oakland)*
- Additionally to flammable and burst risks, **cryogenic conditions** and risks
- At present time, **few LH_2 on-board applications** for mobility, **but** on-going projects and pilots for this use

On this basis, collected information will serve for:

- **Deliverable D1.2** aiming at reviewing **existing training activities** for first responders in Europe, and in the World,
- **Deliverable D1.3** describing **scenarios and operational emergency strategies and tactics**, and defining **operational platform** required for responders training, regarding liquid hydrogen potential hazardous events according to hydrogen systems in their environment and conditions of use.

It must be noted that – at present – some hazardous events and associated consequences remain not totally clear. Outcomes and answers coming from other on-going projects were expected to be integrated in this report. But, due to Covid-19 pandemic, lots of experimental campaigns were postponed. Thus results and interpretation of these scheduled trials on liquid hydrogen release and deflagration cannot be considered. However as soon as they will be available, they will be analyzed and taken into account in HyResponder project if relevant with a satisfying accuracy.

It could be noted that HyResponder consortium will endeavour to reflect any results of other projects – not already dealt in this document – through links on the HyResponder website and through the revised educational materials and the EERG (European Emergency Response Guide), which are due in December 2022, at the end of the project.

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HyResponse – D2.1 report: Description of selected FCH systems and infrastructure, relevant safety features and concepts, 2015

HyResponse – Educational materials: hydrogen safety basics for First Responders (http://www.hyresponse.eu/training-mat-1.php)

HyResponse – D7.2 report: RCS recommendations for international standardisation bodies, 2016 & Lecture – Regulations, codes and standards for first responders (http://hyresponse.eu/files/Lectures/RegulationCodesStandards_slides.pdf), may 2016

Molkov, V. Fundamentals of Hydrogen Safety Engineering I, www.bookboon.com, 2012, ISBN 978-87-403-0226-4.

Molkov, V. Fundamentals of Hydrogen Safety Engineering II, www.bookboon.com, 2012, ISBN 978-87-403-0279-0.

Molkov V, Makarov D, Kashkarov S. Performance of TPRD-less tank in a fire, 2020 May 4-5, HyTunnel-CS project Workshop

PRESLHY – D2.2 report: State of the art analysis, 2018

PRESLHY – D6.3 report: Recommendations for RCS, 2021

Project websites

ENABLEH2 – ENABLing cryogenic Hydrogen based CO_2 free air transport (https://www.enableh2.eu/)

HEAVEN – Cryogenic Hydrogen Tech Aircraft (https://heaven-fch-project.eu/)

Hydrogen e-laboratory (https://fch2edu.eu/home/e-laboratory).

HyTunnel-CS project - Pre-normative research for safety of hydrogen driven vehicles and transport through tunnels and similar confined spaces. Grant agreement No 826193 (https://hytunnel.net/)

Net-Tools project (https://www.h2fc-net.eu/)

PRESLHY project - Prenormative REsearch for Safe use of Liquid HYdrogen. Grant agreement No 779613 (https://preslhy.eu/)

SH2IFT project - Safe Hydrogen Fuel Handling and Use for Efficient Implementation (https://www.sintef.no/projectweb/sh2ift/)

Appendix: Regulations, codes and standards

Review performed in the framework of PRESLHY FCH JU funded project (www.preslhy.eu/regulations-codes-and-standards).

International Standards (LH_2 specific)

- ISO 13984:1999(en), Liquid hydrogen — Land vehicle fuelling system interface, https://www.iso.org/obp/ui/#iso:std:iso:13984:ed-1:v1:en
- ISO 13985:2006(en), Liquid hydrogen — Land vehicle fuel tanks, https://www.iso.org/standard/39892.html

International Standards (generic cryo)

- ISO 20421-1:2019 Cryogenic vessels — Large transportable vacuum-insulated vessels — Part 1: Design, fabrication, inspection and testing
  ISO 20421-2, Cryogenic vessels — Large transportable vacuum-insulated vessels — Part 2: Operational requirements
- ISO 21010, Cryogenic vessels – Gas/material compatibility
- ISO 21011, Cryogenic vessels – Valves for cryogenic service
- ISO 21013-1,2,3, Cryogenic vessels – Pressure-relief accessories for cryogenic service – Part 1: Reclosable pressure-relief valves. Part 2: Non-reclosable pressure-relief devices, Part 3: Sizing and capacity determination
- ISO 21028-1, Cryogenic vessels – Toughness requirements for materials at cryogenic temperature – Part 1: Temperatures below -80°C
- ISO 21029-1:2018 Cryogenic vessels — Transportable vacuum insulated vessels of not more than 1 000 litres volume — Part 1: Design, fabrication, inspection and tests
- ISO 24490, Cryogenic vessels -Pumps for cryogenic service

National Standards

- US; 29 CFR 1910.103 – Hydrogen Paragraph (c), https://www.law.cornell.edu/cfr/text/29/1910.103#c
- NFPA 50B – Standard for Liquefied Hydrogen Systems at Consumer Sites Scope, https://www.nfpa.org/codes-and-standards/all-codes-and-standards/list-of-codes-and-standards/detail?code=50B
- NFPA 2: Hydrogen Technologies Code 2016 PDF, https://catalog.nfpa.org/NFPA-2-Hydrogen-Technologies-Code-P1144.aspx

Codes

- Doc. 06/19 Safety in Storage, Handling and Distribution of Liquid Hydrogen, https://h2tools.org/sites/default/files/bp-docs/Doc6_02SafetyLiquidHydrogen.pdf (replaces IGC Doc 06/02/E EIGA)
- **IGC Doc 7/03** Metering of cryogenic liquids
- **IGC Doc 24/02** Vacuum insulated cryogenic storage tank systems pressure protection devices
- **IGC Doc 41/89/E** Guidelines for transport of vacuum insulated tank containers by sea EIGA
- **IGC Doc 43/01/E** Hazards associated with the use of activated charcoal cryogenic gas purifiers
- **IGC Doc 59/98/E** Prevention of excessive pressure in cryogenic tanks during filling
- **IGC Doc 77/01/E** Protection of cryogenic transportable tanks against excessive pressure during filling
- **IGC Doc 93/03/E** Safety features of portable cryogenic liquid containers for industrial and medical gases
- **IGC Doc 103/03/E** Transporting gas cylinders or cryogenic receptacles in "enclosed vehicles"
- **IGC Doc 114/03/E** Operation of static cryogenic vessels

Guidelines

Linde – Off-Loading Procedures for Liquid Hydrogen Pressure Trailers, https://nsc.linde.com/public/Lh2%20Del%20TRO-19-21.pdf