

# Liquefied hydrogen (LH<sub>2</sub>)



## Content

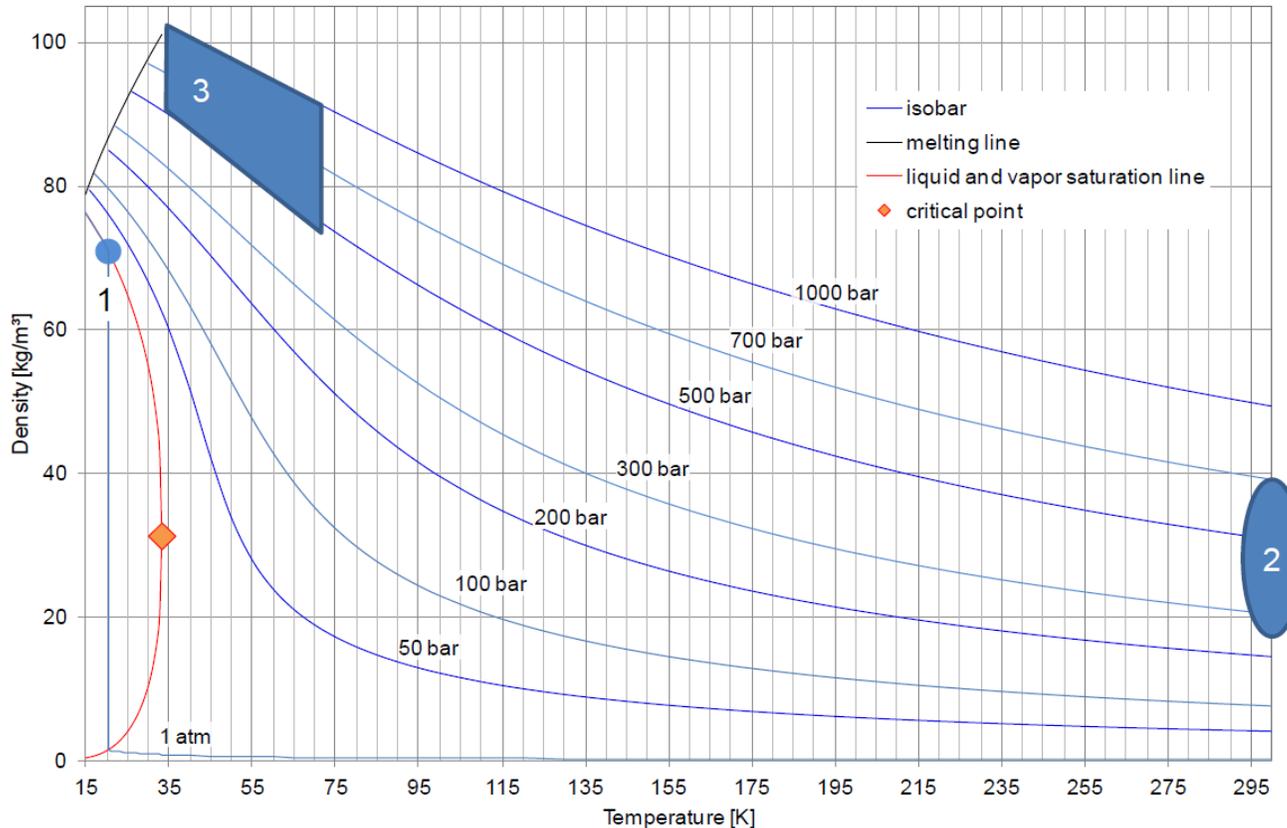
1. Liquid hydrogen properties
2. Liquid hydrogen hazards
3. Cryogenic release
4. Combustion
5. Liquid hydrogen technology
6. Liquid hydrogen hazards and associated risk for Responders
7. Safety measures and engineering solutions

### Objectives of the lecture

1. Understand the properties, in terms of physical and chemical, of LH<sub>2</sub>;
2. Know the hazards of cryogenic hydrogen;
3. Recognise the release and combustion of cryogenic hydrogen and the thermal and pressure hazards;
4. Be familiar with the technologies of LH<sub>2</sub> generation, storage, and transport.
5. Identify the risk and hazard of LH<sub>2</sub> pertinent to responders.

# Liquefied hydrogen (LH<sub>2</sub>)

## Physical characteristics



**1 - liquid @ ~20 K; 2 - pressurised gas @ ~300 K; 3 - cryogenic compressed gas.**

At standard pressure - boiling temperature: 20.3 K

Liquid hydrogen density: 70.8 kg/m<sup>3</sup>

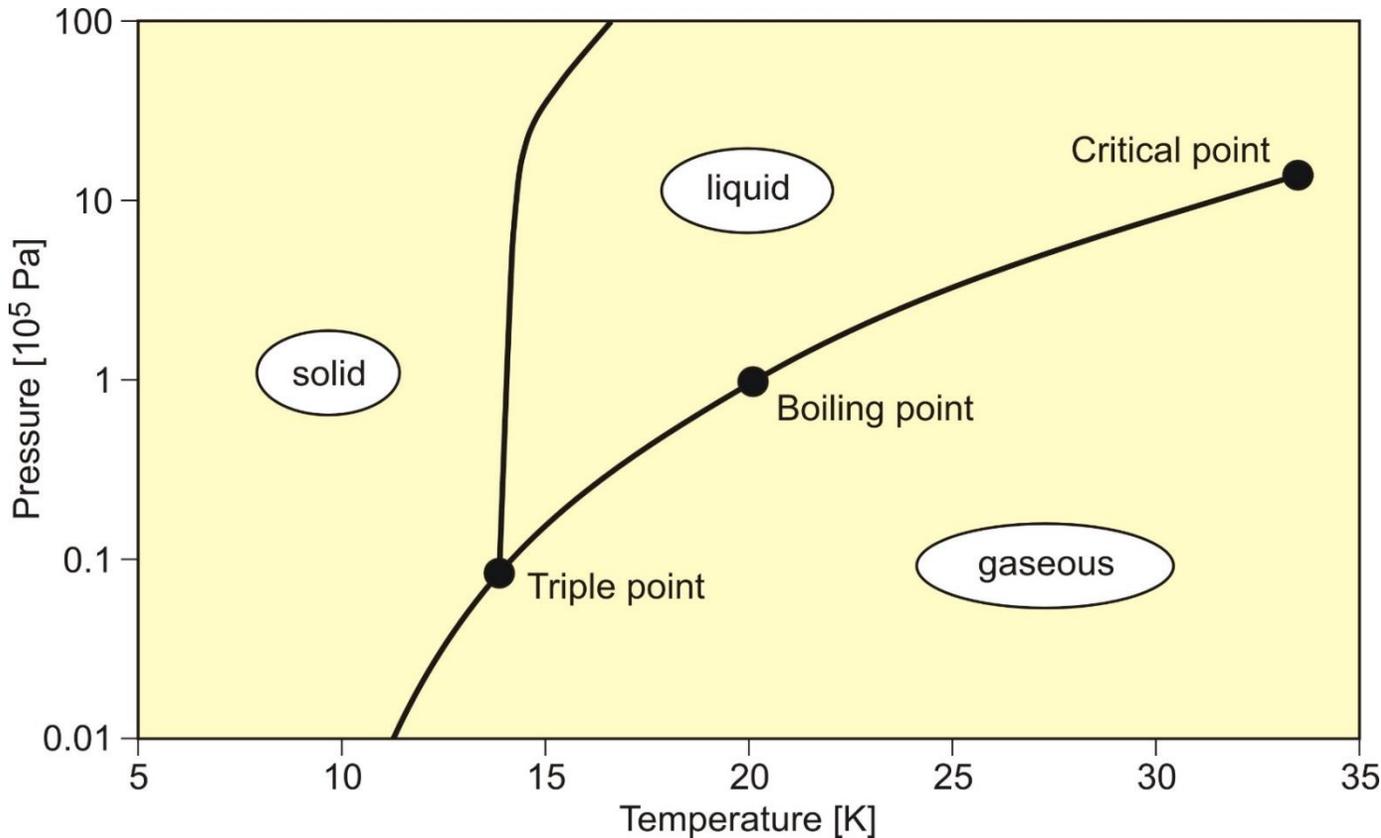
Volume reduction factor: 845 vs. gaseous state

Specific gravity: 0.07

Cryo-range 3: yields even higher densities than the liquid state if at sufficiently high pressures and sufficiently low temperatures

*Density of hydrogen in the low temperature range as a function of pressure*

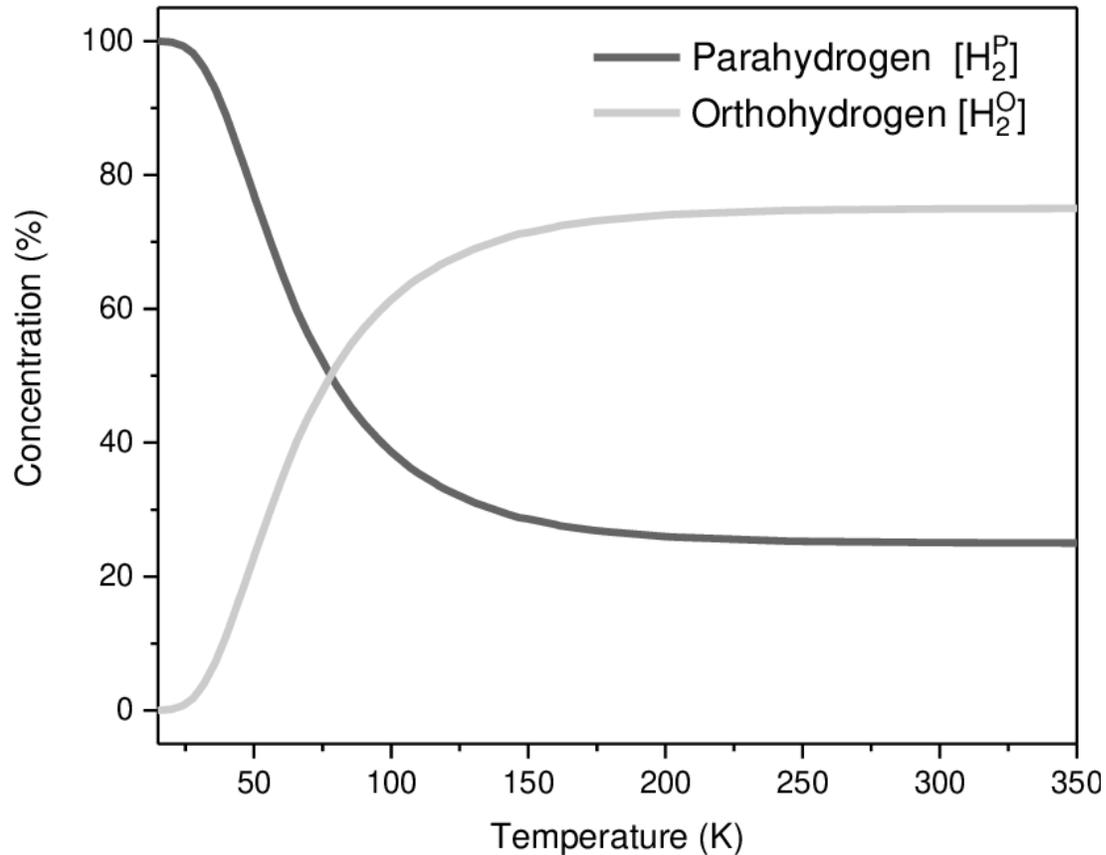
### Physical characteristics



*Phase diagram of hydrogen*

- At the triple point of hydrogen with the temperature of **13.8 K** and a pressure of **7.2 kPa**, all three phases can exist in equilibrium.
- The boiling point increases with pressure to the critical point which is given by  $T_c = 33.15$  K,  $p_c = 1.296$  MPa with a critical density of  $\gamma_c = 31.4$  kg/m<sup>3</sup>. A pressure increase beyond the critical point has no further influence.

## Physical characteristics



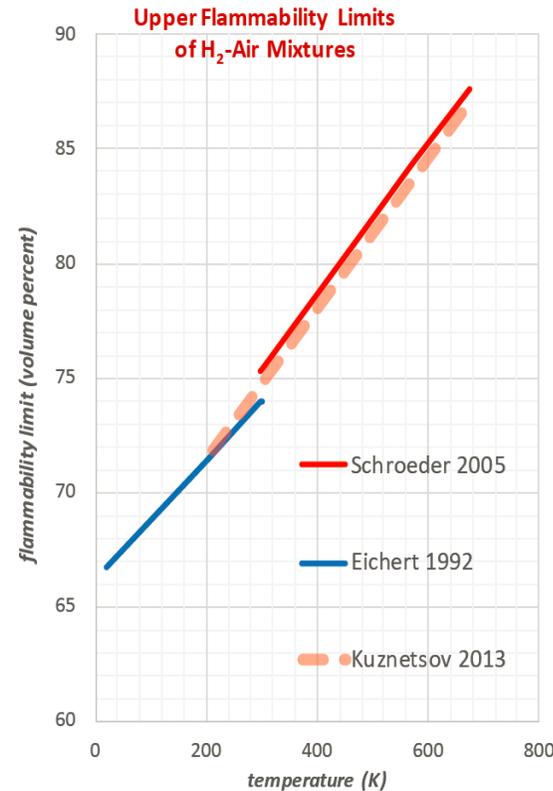
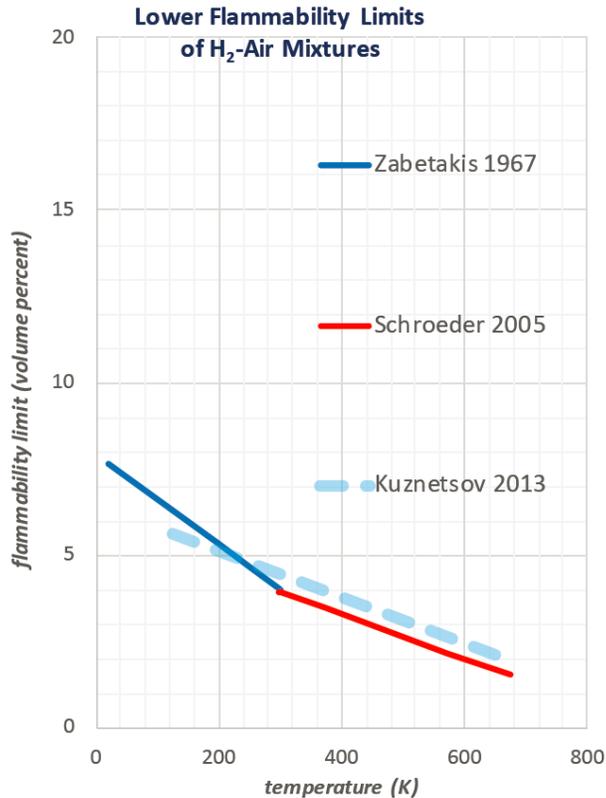
*Equilibrium concentration of ortho- and para-hydrogen vs. T*

Source: Karlsson E., Catalytic ortho- to parahydrogen conversion in liquid hydrogen. (2017).

- Normal hydrogen at room temperature is a mixture of 75% ortho and 25% para hydrogen.
- In the lower temperature range < 80 K, para hydrogen is the more stable form.
- At 20 K, in thermal equilibrium, the concentrations are 99.825% para and 0.175% ortho.
- The rate of conversion between ortho and para states is 0.0114 h<sup>-1</sup> slow in the gas phase.
- The conversion from ortho to para is an exothermal reaction with a conversion energy of 270 kJ/kg at room temperature.
- At temperatures below 77 K, it is almost constant at 523 kJ/kg.
- The liberated heat of ortho-para conversion is larger than the latent heat of vaporization/condensation (446 kJ/kg).

# Liquefied hydrogen (LH<sub>2</sub>)

## Chemical properties



Burgess-Wheeler equation for the LFL, which is for hydrogen (at ambient pressure):

$$c_{LFL} = c_{LFL}(300K) - \frac{3.14}{\Delta H_c} (T - 300) = 4.0 - 0.013 (T - 300) (\text{vol}\%)$$

$\Delta H_c$  – net heat of combustion, = 242 kJ/mol  
 $T$  – temperature, K.

For the upper flammability limit (UFL):

$$c_{UFL} = 74.0 + 0.026 (T - 300) (\text{vol}\%)$$

valid for the temperature range  $150 \leq T \leq 300$ , with  $T$  in K.

For open LH<sub>2</sub> pools, it needs to be considered that cold hydrogen gas is less volatile compared to ambient gas.

*Flammability limits in hydrogen-air mixtures, LFL (left) and UFL (right)*

Source: Zabetakis M.G., Safety with cryogenic fluids. Plenum Press, New York (1967).  
 Eichert H., et al. Deutsches Zentrum für Luft- und Raumfahrt (DLR), Stuttgart (1992).  
 Kuznetsov M., Czerniak M., Grune J., Jordan T., Proc. 5th Int Conf Hydrogen Safety (ICH5-5), Brussels (2013), paper 231.

# Liquefied hydrogen (LH<sub>2</sub>)

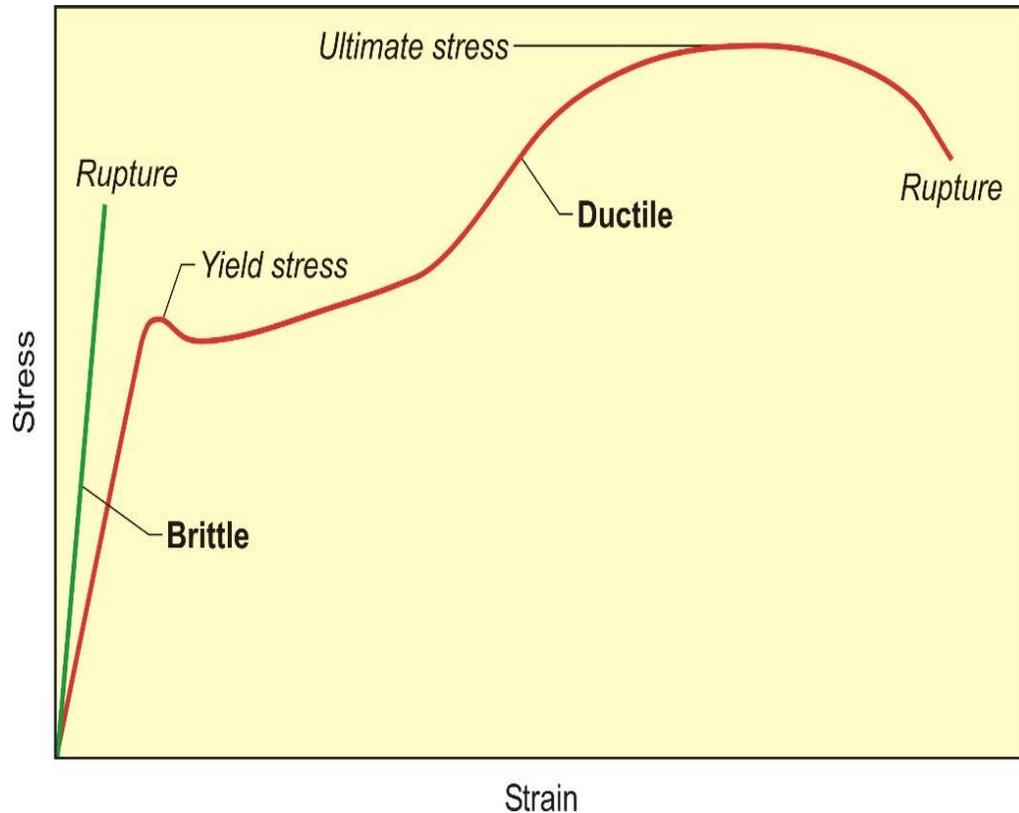
## Liquid hydrogen hazards

Table 1. Description of potential hazardous events

Feared events	Main conditions	Consequences
1 - Burst of the storage at working pressure (P <sub>w</sub> ) (impinging fire/fragment)	100% gaseous H <sub>2</sub> - 10 bar - type I vessel	Overpressure and fragments
2 - Accidental event on storage with liquid H <sub>2</sub> (fire case) at 2P <sub>w</sub>	Burst of LH <sub>2</sub> storage Flash fire	“BLEVE” with thermal effects
3 - Failure on the storage (breach or perforation)	10 bar, rapid liquid H <sub>2</sub> 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 <sub>2</sub> liquid pool, vaporization forming a flammable cloud	Liquid hydrogen jet and potential rainout forming a LH <sub>2</sub> 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 <sub>R</sub> )	100% gaseous - 10 bar, type I	Overpressure and fragments

## Liquefied hydrogen (LH<sub>2</sub>)

### Impact of cryogenic hydrogen on materials



*Ductile and brittle behavior of materials*

Source: Bonhoeffer, K.F., Harteck, P. Experimente über Para- und Orthowasserstoff. Naturwissenschaften 17, 182 (1929).

- Hydrogen is recognized to have a harmful effect on some metals by changing their physical properties.
- With decreasing temperature, the yield stress and ultimate stress increase for most metals.
- A material changes from ductile to brittle behavior as soon as the temperature falls below its so-called “nil-ductility temperature”.
- For some materials at cryogenic temperature, little stress is sufficient to break it very rapidly, resulting in an almost instantaneous failure.
- This effect is a particular problem in cryogenic equipment exposed to periodic changes.
- Low temperatures can also affect materials by thermal contraction causing large thermal stresses.



*LH<sub>2</sub> large-scale release*



*Delayed ignition of LH<sub>2</sub>*

## Liquefied hydrogen (LH<sub>2</sub>)

### Delayed ignition of pressurised LH<sub>2</sub> 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.
- The condensation of atmospheric humidity will also add water to the mixture cloud (making it visible), making it even denser.
- The flammable cloud is significantly larger than the cloud induced by a gaseous hydrogen release.
- If the pressure is low enough or the release diameter is large enough, a rain-out phenomenon (formation of hydrogen droplets falling on the ground and inducing a hydrogen pool) may occur.
- A possible secondary explosion after the initial deflagration of the release cloud due to the oxygen enrichment.

Source: 1. Deliverable 6.1 – Handbook of hydrogen safety: Chapter on LH<sub>2</sub> safety. Pre-normative REsearch for Safe use of Liquid Hydrogen (PRESLHY). 2. J. E. Hall, P. Hooker, D. Willoughby. Int. J. Hydrogen Energy, 2014, 38: 20547-20553.

## Liquefied hydrogen (LH<sub>2</sub>)

### BLEVE and RPT 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.
- An unintended release of liquid hydrogen on water may lead to a sudden and violent vaporization of liquid hydrogen, known as Rapid Phase Transition (RPT).



*BLEVE of LH<sub>2</sub>*



*RPT of LH<sub>2</sub>*

- When BLEVE occurs, some of the liquid hydrogen will flash to vapour resulting in the generation of overpressure, ignition of the released contents produces a large fireball, thermal radiation and blast wave.
- When RPT occurs, the rate of LH<sub>2</sub> vaporization is enhanced, which may lead to severe consequences in case of ignition.



## Liquefied hydrogen (LH<sub>2</sub>)

### 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<sub>2</sub> or cold H<sub>2</sub> releases, it could be possible that solid particles (water and CO<sub>2</sub> freezing) and/or LH<sub>2</sub> droplets and air condensate droplets (friction and break up) may ignite.

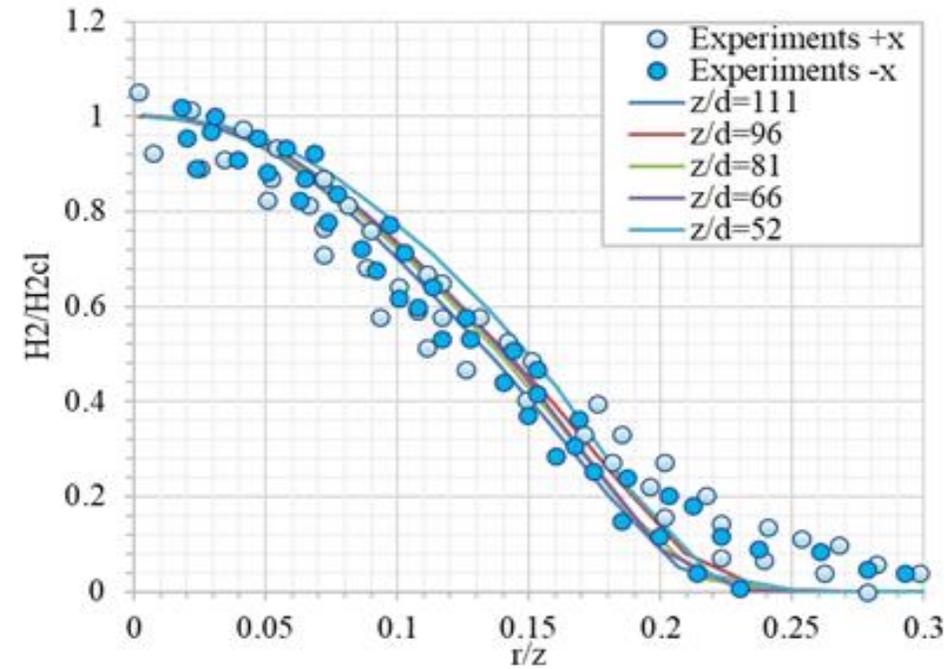
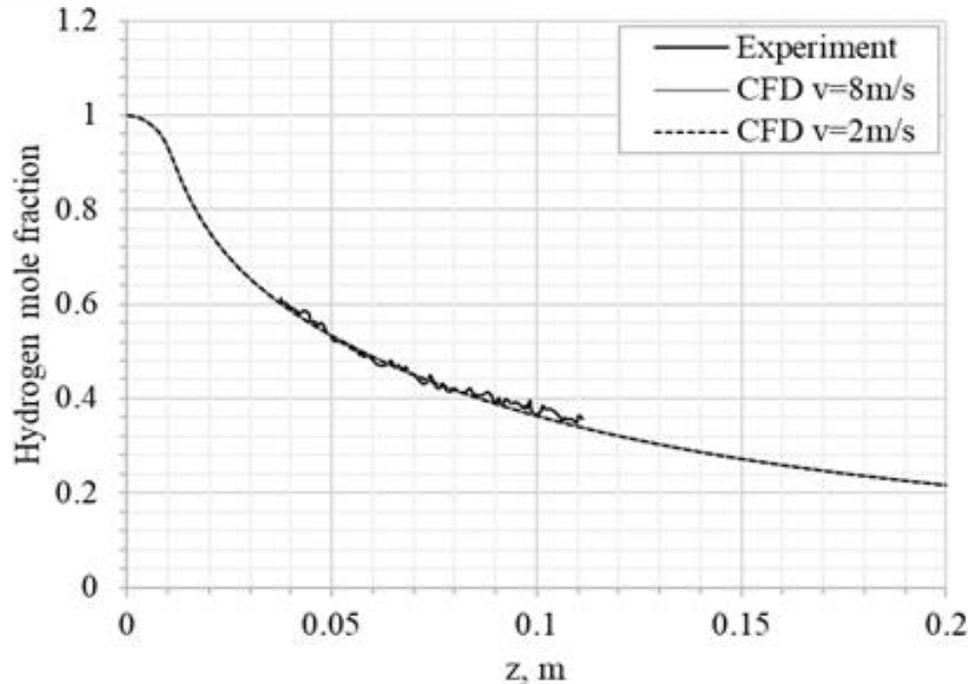
- **Extreme cold hazard**

Cryogenic liquids and their associated cold vapours can produce effects on the skin similar to a thermal burn. Brief exposures can damage delicate tissues such as the eyes. Prolonged exposure of the skin or contact with cold surfaces can cause frostbite.

Unprotected skin can stick to metal that is cooled by cryogenic liquids. The skin can then tear when pulled away. Prolonged breathing of extremely cold air may damage the lungs.

- **Asphyxiation hazard**

The gas produced by evaporation of cryogenic liquids can accumulate in a confined space. Even if the gas is non-toxic, asphyxiation and death can occur. Oxygen deficiency is a serious hazard in enclosed or confined spaces.



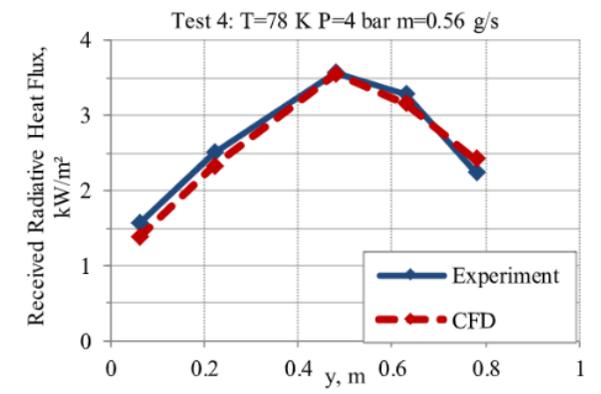
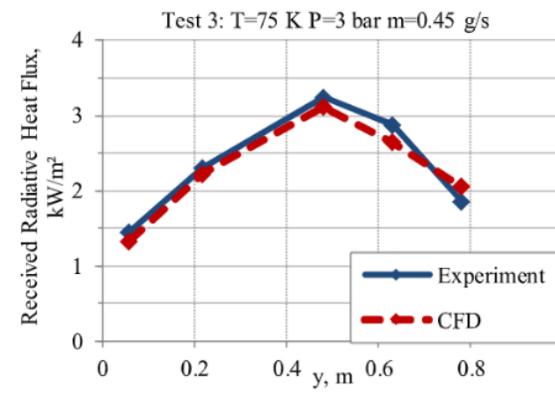
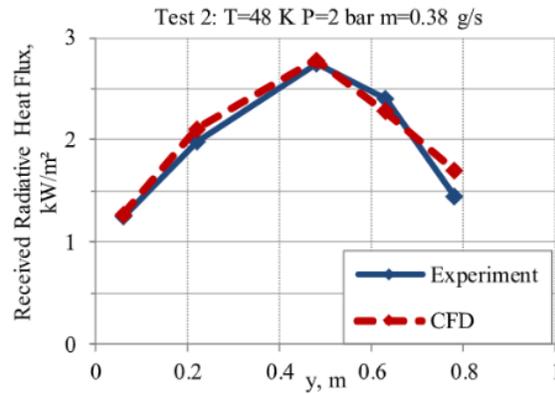
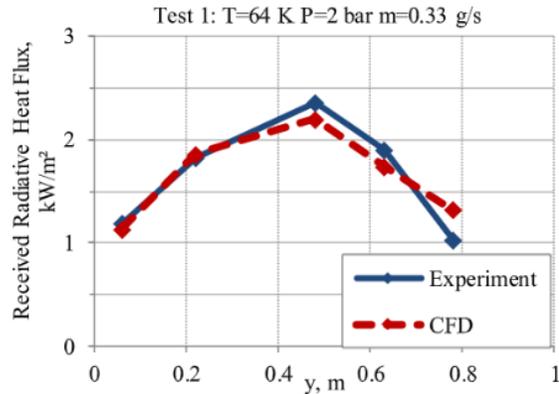
*Hydrogen concentration along the jet axis (left) and normalized radial distance (right): simulation results versus experiments for test with  $T = 61\text{ K}$ ,  $P = 0.2\text{ MPa}$ , and  $d = 1.25\text{ mm}$ .*

The properties of the cryogenic flow at the nozzle can be significantly affected by heat transfer through the wall of a non-insulated pipe connecting the storage system to the nozzle.

Source: PRESLHY D3.2, 2021

Friedrich et al. <sup>1</sup> studied ignited hydrogen releases  $p < 3.5$  MPa and  $T = 34$ -65 K.

Radiation level up to **10 kW/m<sup>2</sup>** at **0.75 m** from the jet fire => second-degree burns if exposed for 20 s to the jet fire



UU <sup>2</sup> - CFD model to simulate flame length and radiative heat flux for cryogenic hydrogen jet fires with pressure up to 0.5 MPa (abs) and temperature in the range of 48–82 K.

For all tests, at **0.5 m** from the flame axis people should stand less than **30 s** to not incur in first degree burns.

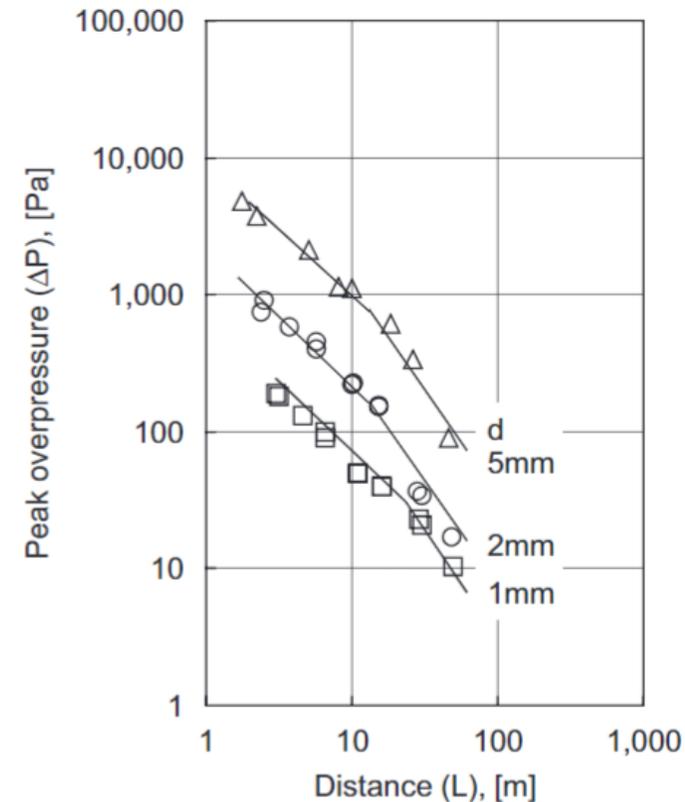
Source: Friedrich A., et al., Ignition and heat radiation of cryogenic hydrogen jets. Int J Hydrogen Energy 37(22) (2012) 17589–17598.

Cirrone D., Makarov D., Molkov V., Thermal radiation from cryogenic hydrogen jet fires. Int J Hydrogen Energy 44(17) (2019) 8874–8885.

Takeo K., et al. <sup>1</sup> studied delayed ignition of releases at ambient temperature and 40 MPa spouting pressure, which generates an overpressure up to **20 kPa** at **4 m** distance with nozzle diameter of 5 mm. The peak overpressure becomes smaller when nozzle diameter reduces.

Friedrich et al. <sup>2</sup> presents experiments on delayed ignition of hydrogen releases with pressure up to **3.5 MPa**, release temperatures in range **34–65 K** and nozzle diameters of **0.5–1.0 mm**.

The maximum ignition distance was found for location corresponding to **7%** by vol hydrogen in air. The maximum flashback distance was found for H<sub>2</sub> = **9%** by vol, which is slightly lower than the distance for ambient temperature releases corresponding to 11%. During the tests, measured sound levels were recorded below **120 dB(A)**.

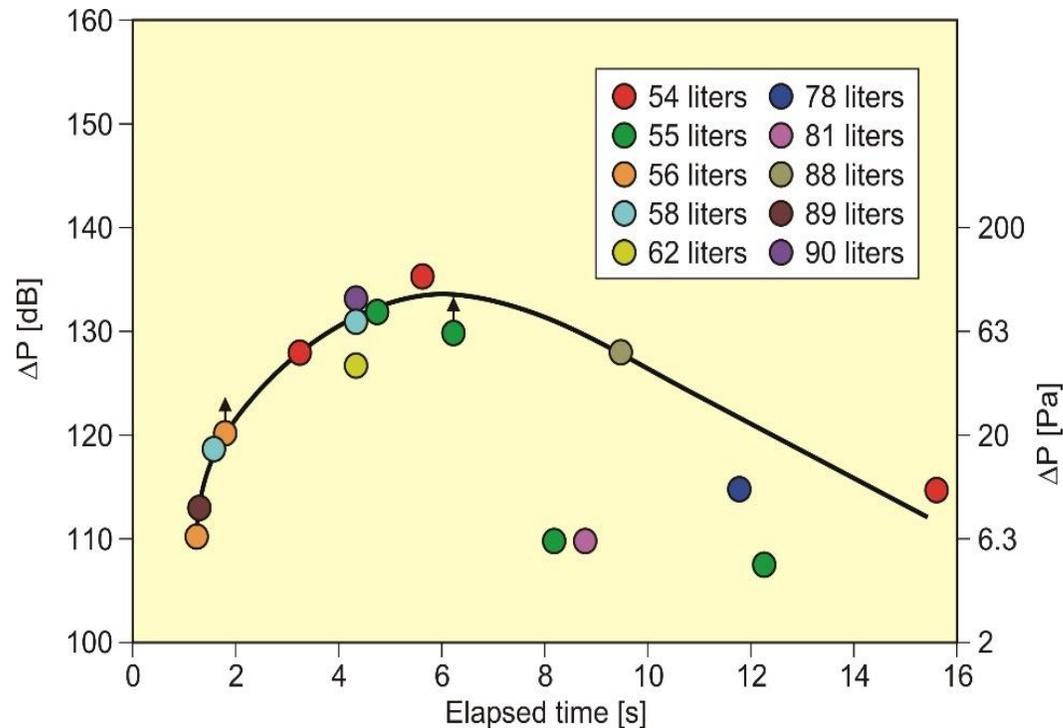


Source: Takeo K., et al., Dispersion and explosion field tests for 40 MPa pressurized hydrogen. Int J Hydrogen Energy 32 (2007) 2144–2153.

Friedrich, A. et al. Ignition and heat radiation of cryogenic hydrogen jets. Int J Hydrogen Energy. 31 (2012) 17589-17598.

## Liquid pool burning

- Liquid hydrogen pool fires are dynamic and non-homogeneous with a highly intermittent pulsing structure of the flame.
- The cyclic changing of flame height is mainly due to the turbulent mixing of air, which affects the flame temperature.
- The burning-in phase of LH<sub>2</sub> is extremely short, because the ground keeps the liquid's temperature at the boiling point.

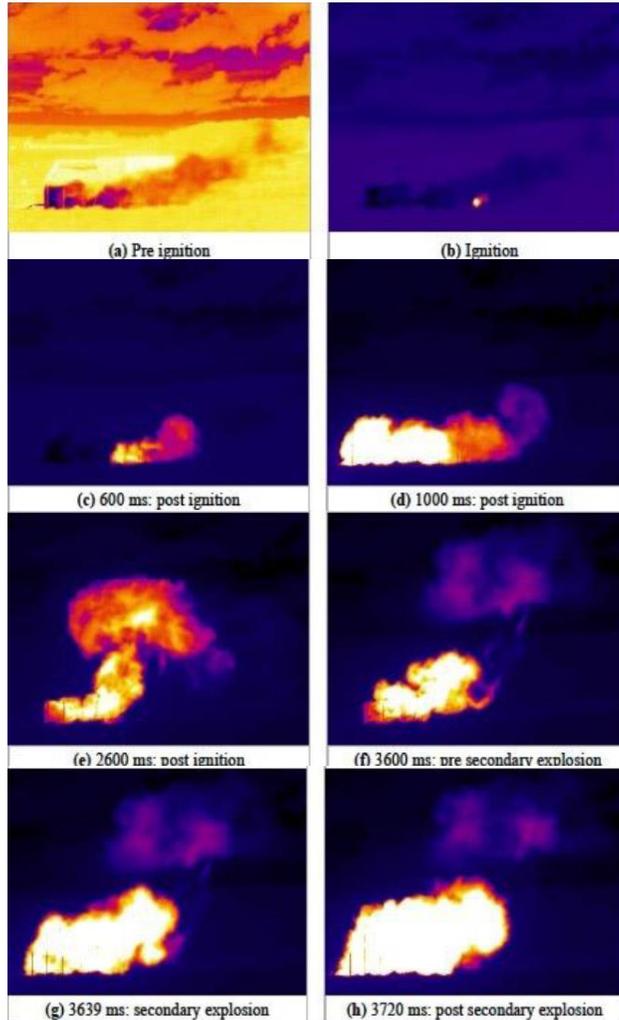


- For the LH<sub>2</sub> spill and ignition tests, with quantities of 54-90 L released onto a steel plate or loose gravel, the overpressures were measured at ~50 m.
- The blast pressures produced were relatively small and were depending on the time delay for ignition.
- They were found to increase with delay time, until after more than 5–6 s of delay, they were decreasing again as soon as the H<sub>2</sub> concentration in the rising and diffusing vapor clouds became smaller.

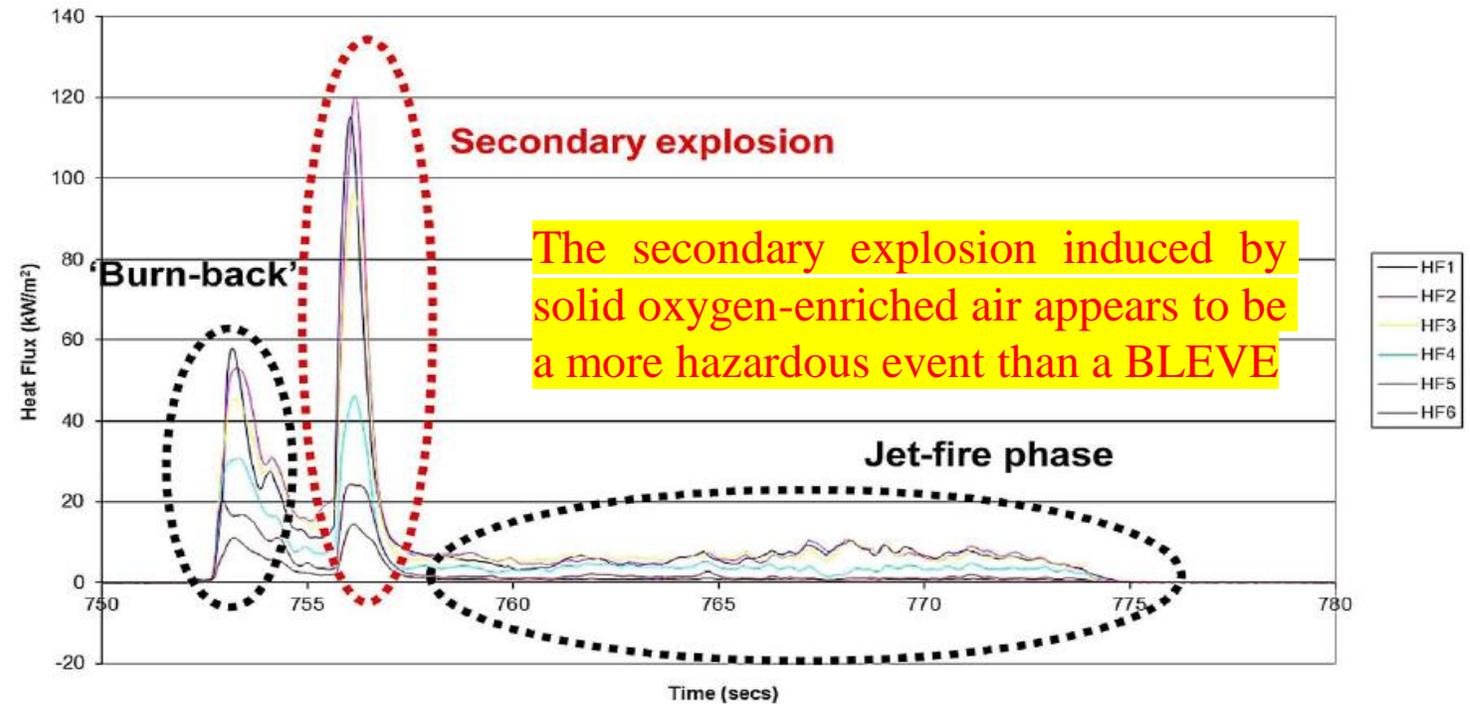
Source: Zabetakis M.G., Safety with cryogenic fluids. Plenum Press, New York (1967).

# Liquefied hydrogen (LH<sub>2</sub>)

## Ignition of a continuous liquid hydrogen releases



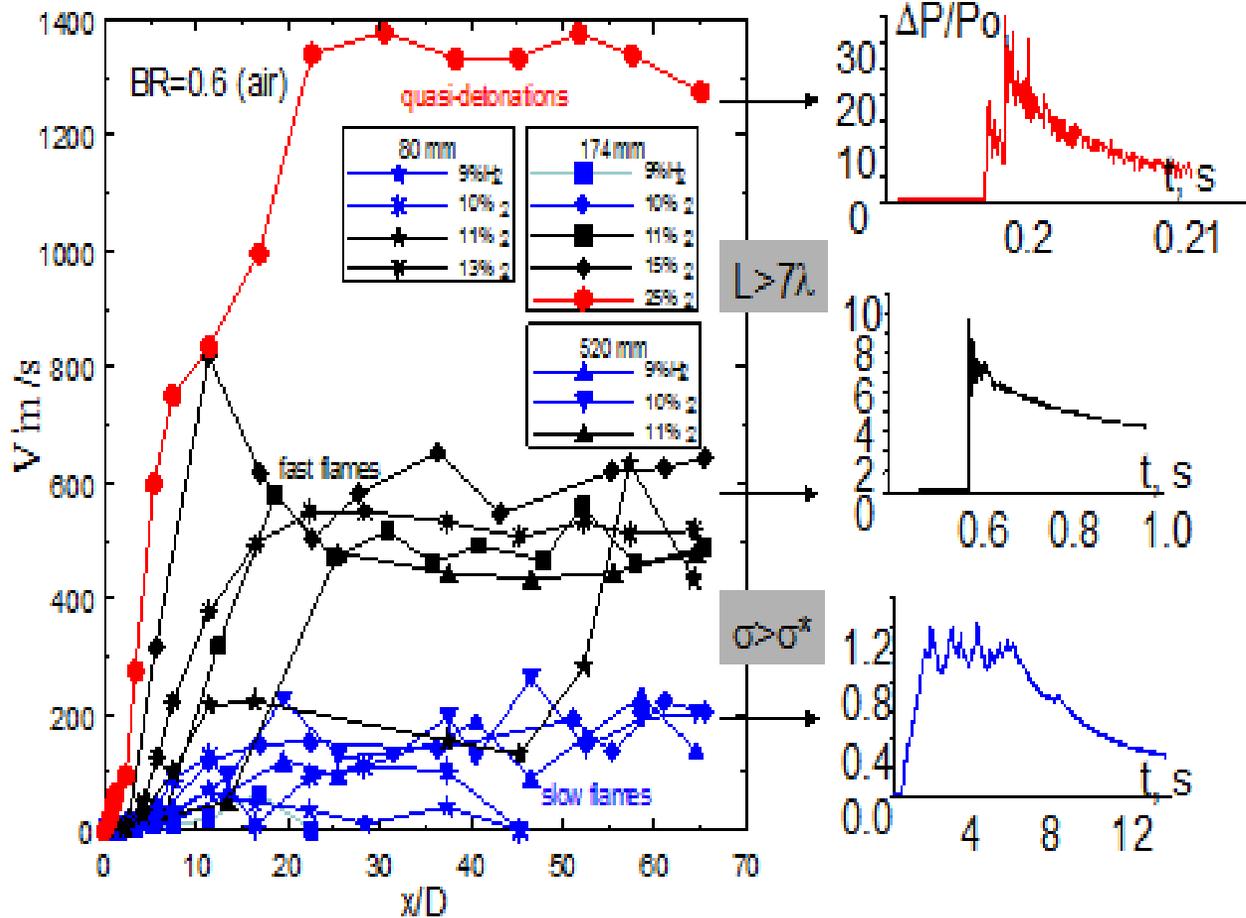
(a) Pre ignition; (b) ignition; (c) 600 ms post ignition; (d) 1000 ms post ignition; (e) 2600 ms post ignition; (f) 3600 ms pre secondary explosion; (g) 3639 ms secondary explosion; (h) 3720 ms post secondary explosion.



Source: Deliverable 6.1 – Handbook of hydrogen safety: Chapter on LH<sub>2</sub> safety. Pre-normative PRESLHY.

# Liquefied hydrogen (LH<sub>2</sub>)

## Deflagration of cold H<sub>2</sub>-air mixtures



### Three combustion regimes:

Expansion rate  $\sigma < \text{critical expansion rate } \sigma^*$ , subsonic combustion regime may occur. The characteristic pressure loads are in the range 0.1–0.2 MPa for an initial pressure of 0.1 MPa.

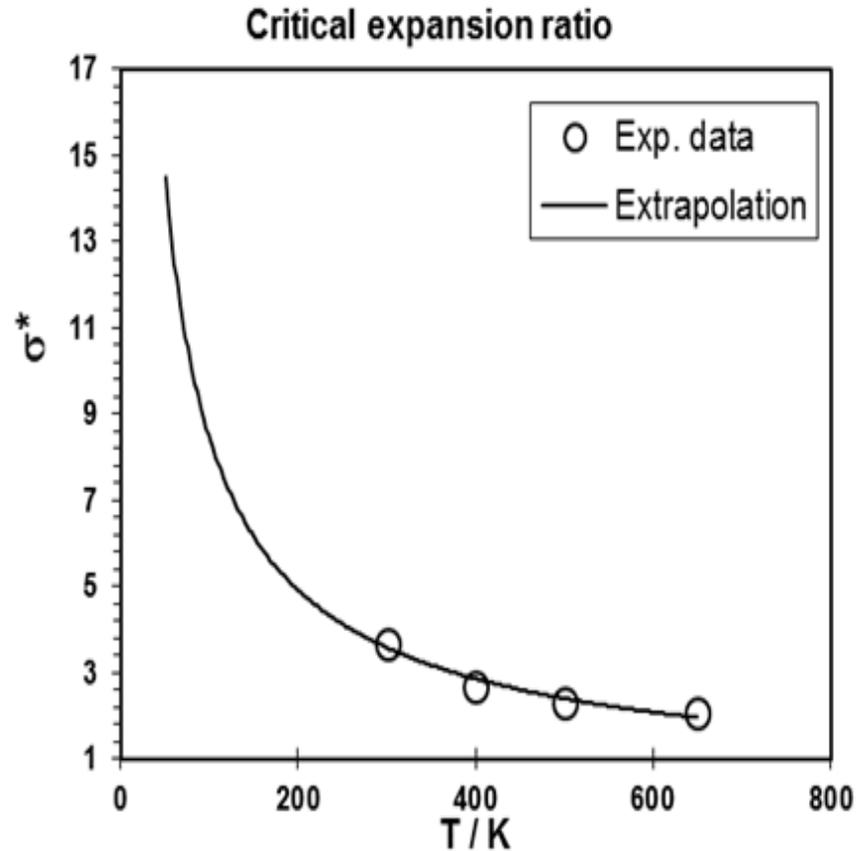
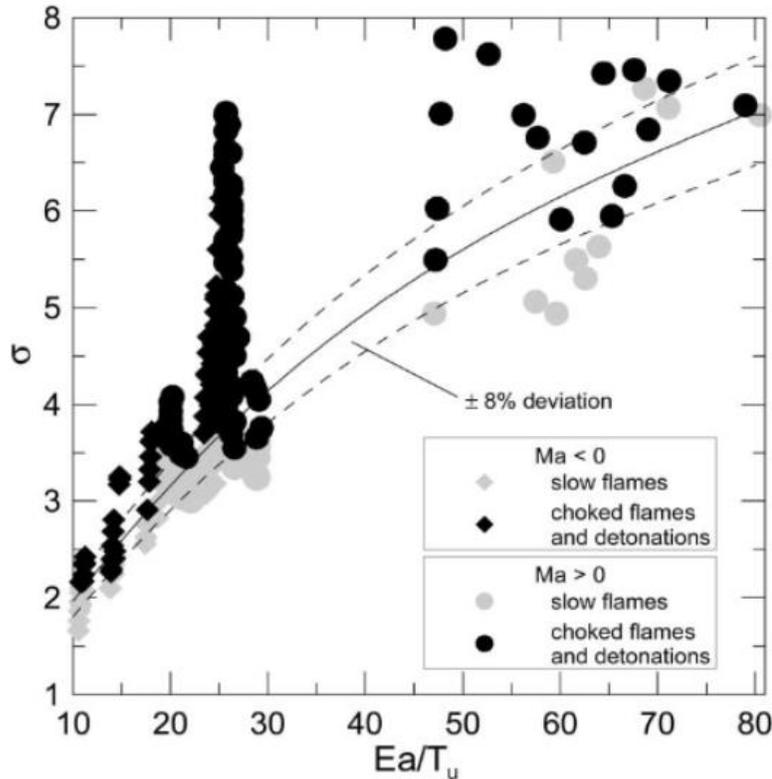
Mixtures with  $\sigma > \sigma^*$  can effectively accelerate and detonate if condition  $L > 7\lambda$  is verified, where  $L$  is the characteristic size of combustible domain and  $\lambda$  is the detonation cell size. In these cases, the characteristic pressure loads can vary from 0.6-0.8 MPa for sonic flames, to 2–4 MPa for detonation.

Source: Dorofeev S.B., Kuznetsov M.S., Alekseev V.I., Efimenko A.A., Breitung W., J Loss Prevention in the Process Industries 14(6) (2001) 583–589.  
 Dorofeev S.B., Sidorov V.P., Kuznetsov M.S., Matsukov I.D., Alekseev V.I., Effect of scale on the onset of detonations. Shock Waves 10 (2000) 137–149.

Combustion regimes for different hydrogen-air mixtures ( $P = 0.1 \text{ MPa}$ ,  $T = 293\text{K}$ )

# Liquefied hydrogen (LH<sub>2</sub>)

## Deflagration of cold H<sub>2</sub>-air mixtures



The critical expansion ratio  $\sigma^*$  decreases with initial temperature ( $T$ ) increase and overall activation energy ( $E_a$ ) decrease.

T, K	C <sub>H2</sub> , %mol	$\sigma^*$
300	11	3.75
200	10.34	4.92
150	10.09	6.14
100	9.58	8.49
78	9.13	10.67
50	8.60	13.89

Critical expansion rate  $\sigma^*$  as a function of initial temperature  $T$  and activation energy  $E_a$

Source: Dorofeev S.B., Kuznetsov M.S., Alekseev V.I., Efimenko A.A., Breitung W., J Loss Prevention in the Process Industries 14(6) (2001) 583–589.

## Liquefied hydrogen (LH<sub>2</sub>)

### Liquid hydrogen production process

- Liquefaction of H<sub>2</sub> is a highly energy intensive process, which suffers from low energy efficiencies.
- The minimum work required for the liquefaction of hydrogen (at ortho-para equilibrium) is 3.92 kWh of electricity/kg of H<sub>2</sub> or 0.12 kWh /kWh of H<sub>2</sub>.
- Typical values for the whole process, however, are in the range of 8 - 14 kWh/kg for relatively large liquefaction units.
- Large scale installations are typically implemented with a Claude process with LN<sub>2</sub> pre-cooling providing acceptable efficiencies.
- The complete process comprises an initial purification unit, additional external coolers with helium or mixed refrigerants as operating medium.
- The expansion is split in up to 6 stages and several ortho-para converters are integrated.
- All cold parts are mounted in a cold box, which is thermally insulated for instance with perlite.

## Liquefied hydrogen (LH<sub>2</sub>)

### Liquid hydrogen production infrastructures

- Worldwide nearly 30 large scale liquefiers in operation with production capacities from 1 to ~35 t/d of LH<sub>2</sub> in a unit.
- Most and with the largest capacities are installed in the USA.



*Air Liquide LH<sub>2</sub> filling stations (left: Little Town, USA; right: Becancour, Canada).*

## Liquefied hydrogen (LH<sub>2</sub>)

### Liquid hydrogen storage

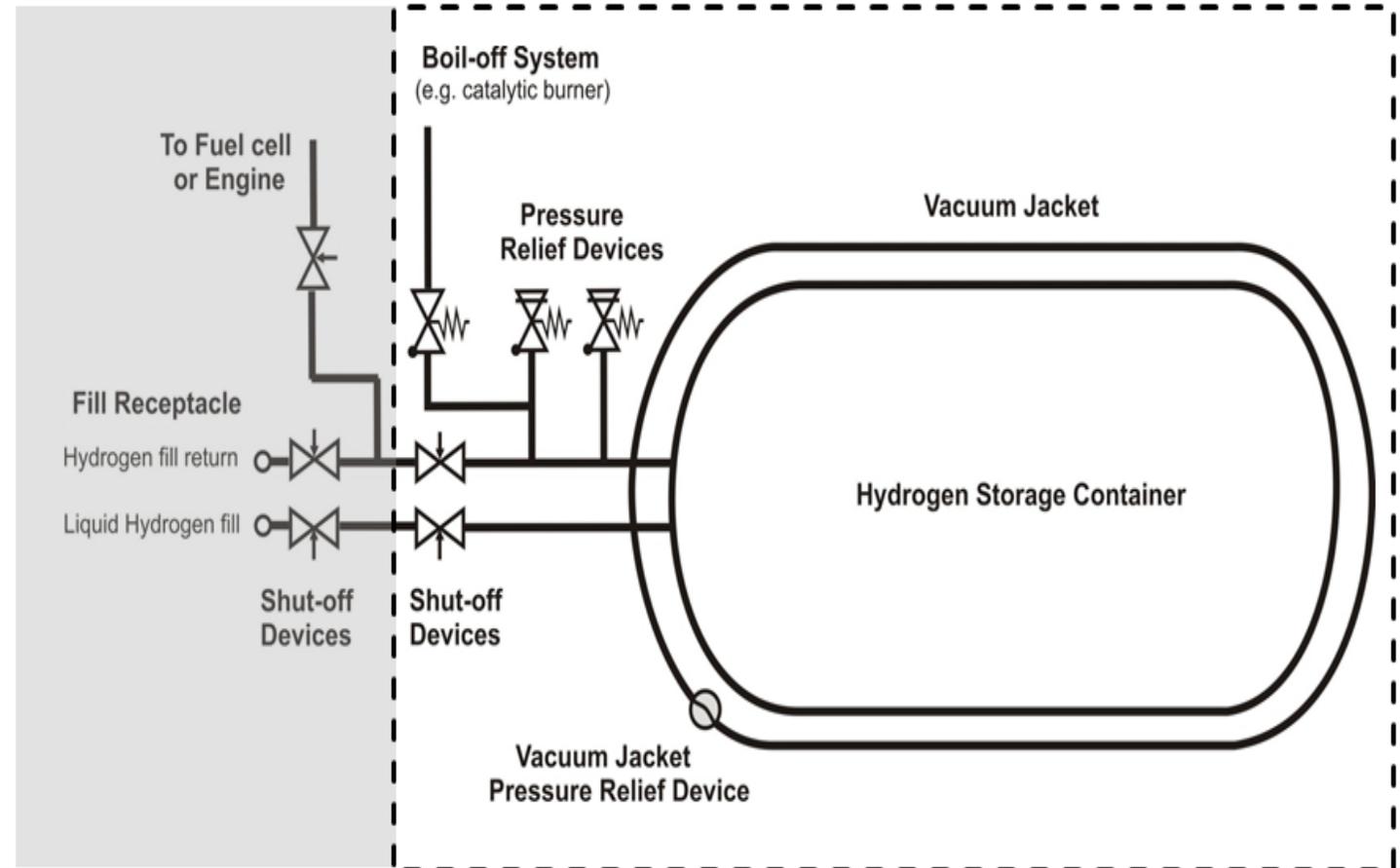
- Volumetric capacity of LH<sub>2</sub> is **0.070 kg/L** as opposed to **0.030 kg/L** for GH<sub>2</sub> tanks at 70 MPa.
- Around 30% of the energy contained in hydrogen is required for liquefaction.
- LH<sub>2</sub> stored at low (cryogenic) temperatures and at pressures of around 0.6 MPa.
- The costs of materials suitable for LH<sub>2</sub> storage tanks are significantly higher than those for GH<sub>2</sub>.
- LH<sub>2</sub> storage tank is a Dewar, double-walled, vacuum-insulated vessel made of lightweight steel alloys.
- Boil-off (evaporation of LH<sub>2</sub> due to environmental warm up) is a major challenge, which can be caused by:
  - *The exothermic ortho- para-hydrogen conversion.*
  - *Residual thermal leaks.*
  - *Sloshing.*
  - *Flashing.*

## Liquefied hydrogen (LH<sub>2</sub>)

### Liquid hydrogen storage

The main components of on-board LH<sub>2</sub> tank should include:

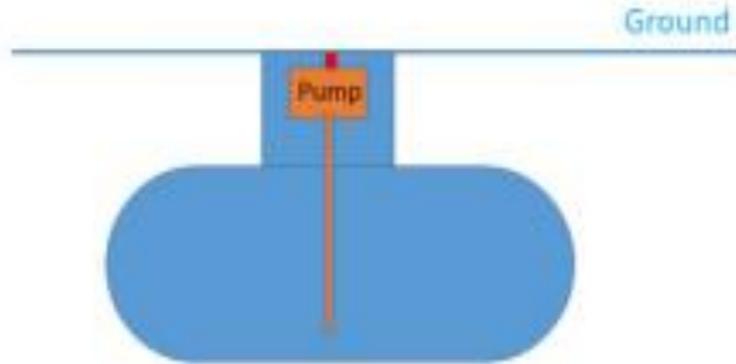
- LH<sub>2</sub> storage container
- Shut-off devices
- A boil-off system
- TPRDs
- The interconnecting piping (if any) and fittings between the above-mentioned components.



## Liquefied hydrogen (LH<sub>2</sub>)

### Liquid hydrogen storage - Underground

#### Buried



- All valves, fittings, safeties... + pump in an enclosure on top of tank
- Everything accessible at ground level
- Necessitates easy access to LH<sub>2</sub> for the pump: fully immersed or feed-in low P pump

#### Vault (~indoor space)



- All valves, fittings, safeties... + pump in a room next to Dewar
- Confined space: risk of leak, H<sub>2</sub> accumulation, anoxia..
- « traditional » pump designs...

## Liquefied hydrogen (LH<sub>2</sub>)

### Cryostat for stationary applications



*LH<sub>2</sub> storage vessel with 3800 m<sup>3</sup> capacity at KSC in Florida*

World's largest, 3800 m<sup>3</sup> (3218 m<sup>3</sup> of LH<sub>2</sub>) double-wall vacuum perlite (1.3 m of thickness) insulated spherical (in/ex diameter = 18.75/21.34 m) storage vessel. The tank is operated at a pressure of 0.62 MPa and has a boil-off rate of 0.025%/d.



*LH<sub>2</sub> stores at the Waziers liquefaction plant in French*

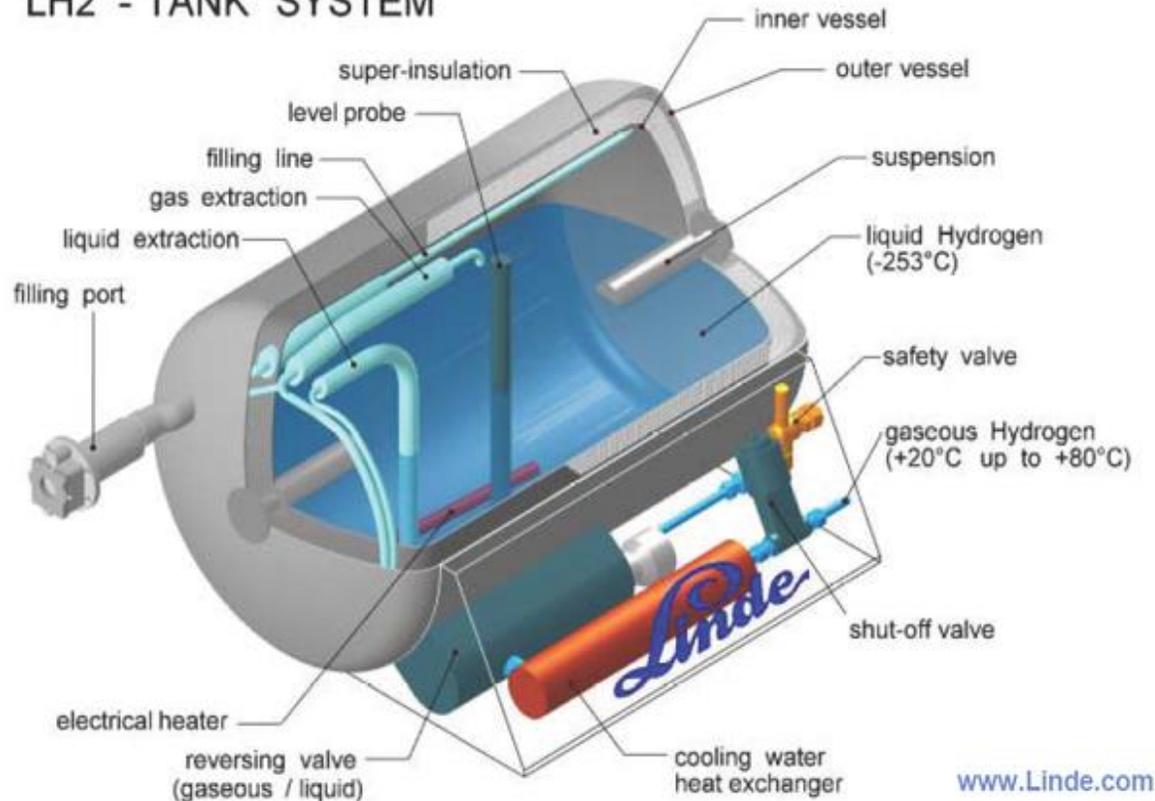
Liquefaction unit = 10 t/d), AL operates four horizontal tanks of 250 m<sup>3</sup> each (in/ex diameter = 4.02 / 5.1 m - perlite thickness = 500 mm).

Source: Deliverable 6.1 – Handbook of hydrogen safety: Chapter on LH<sub>2</sub> safety. Pre-normative PRES-LHY.

## Liquefied hydrogen (LH<sub>2</sub>)

### Cryostat for mobile applications

#### LH<sub>2</sub> - TANK SYSTEM



- ✓ Internal volume of about 100 L
- ✓ Heat absorption about 1 W
- ✓ Boil-off loss of 1.5%/day
- ✓ 7 kg LH<sub>2</sub> will be lost in two months

The boil-off management to reduce boil-off release:

- cold combustion with air in catalytic recombiners
- storing the boil-off gases in metal hydride storages
- re-cycling in a re-liquefaction
- direct energetic use, in a fuel cell for instance.

*LH<sub>2</sub> tank for automotive application (BMW 750h)* Source: Linde

## Liquefied hydrogen (LH<sub>2</sub>)

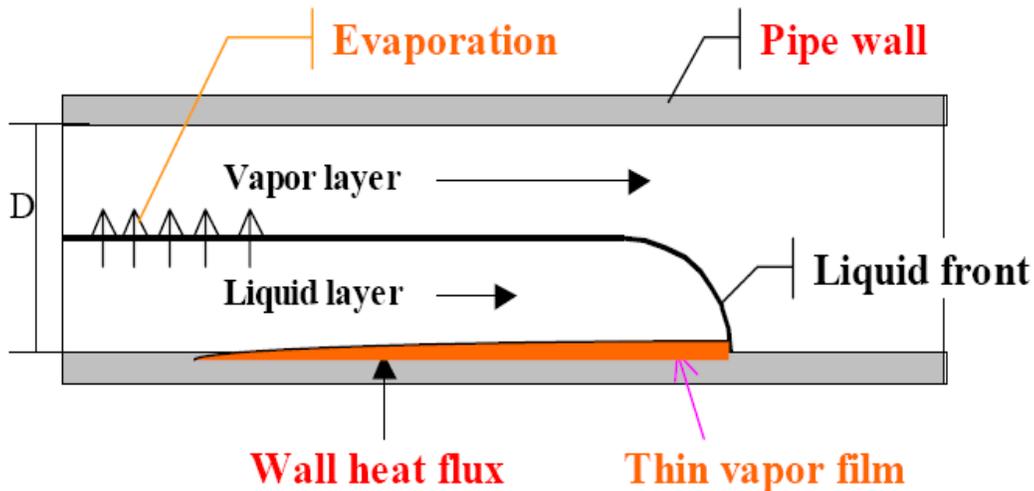
### Liquid hydrogen transport – Road

- Cryogenic liquid hydrogen trailers can carry up to 5000 kg of hydrogen and operate up to 1.2 MPa.
- Hydrogen boil-off can occur during transport despite the super-insulated design of tankers, potentially 0.5%/d.
- Hydrogen boil-off up to roughly 5% also occurs when unloading the liquid hydrogen on delivery.
- The LH<sub>2</sub> tanks on the trailers are insulated using a vacuum super insulation.



Source: Zittel W., Wurster R., Bölkow L., Hydrogen in the energy sector. TÜV SÜD Industrie Service GmbH (1996).

- Pipeline transportation of liquid hydrogen is existing at a small scale only.
- Pipes for transferring cryogenic LH<sub>2</sub> must comply with the extreme low temperature of LH<sub>2</sub> and the associated insulation requirements.
- Similar to LH<sub>2</sub> storage tanks, pipelines are of double-wall design and vacuum-jacketed.
- Stainless steel is taken for the inner line with low heat conduction spacers as a support in the vacuum jacket.
- Cryogenic pipes must be sufficiently flexible which can be done by appropriate pipe routing and expansion joints.



- During the period of chill-down of an LH<sub>2</sub> line, a **two-phase flow** develops which is stratified for horizontal flows.
- This phenomenon is encountered particularly in refuelling lines where **chill-down is required** before the fuelling process itself begins to avoid the gaseous phase to enter the tank.

Two methods of transferring LH<sub>2</sub> via pipeline from one storage to another, e. g from stationary storage to a truck:

- **pressure build-up** (natural pressure build up or voluntary vaporization of LH<sub>2</sub> via a small external heat exchanger). Hence, the pressure in the “mother storage” becomes higher than the pressure in the “daughter storage”. 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 Net Positive Suction Head (NPSH): difference between liquid pressure and saturation vapour pressure of the considered compound - due to low density of LH<sub>2</sub>).

## Liquefied hydrogen (LH<sub>2</sub>)

### Liquid hydrogen transport – Ship



NASA liquid hydrogen barge fleet  
From Louisiana to Florida  
5 t/d capacity since 1990



The world's first LH<sub>2</sub> carrier ship SUISEI FRONTIER  
launched in December 2019 in Kobe, Japan (HySTRA project)  
Ship length 116 m, width 19 m, tonnage 8000 t, speed ~24 km/h  
LH<sub>2</sub> tank with a capacity of 1250 m<sup>3</sup>

## Liquefied hydrogen (LH<sub>2</sub>)

### Liquid hydrogen transport – Rail

- Liquid hydrogen transports in rail cars began in the 1960s by the Linde company using a 107 m<sup>3</sup> tank.
- The US company Praxair is operating a fleet of 16 hydrogen rail cars. The quantities of LH<sub>2</sub> transported in rail cars over long distances (> 1000 km) are about 70 tons.



The design of a rail car for liquid hydrogen (and other cryogenic commodities) transports manufactured by the Chinese company CRRC Xi'an Co.,Ltd., a traditional enterprise in railway transportation equipment. The thermally insulated tank with a total volume of 85 m<sup>3</sup> to carry a payload of 5 t can be used for direct loading, unloading, or transfer filling.

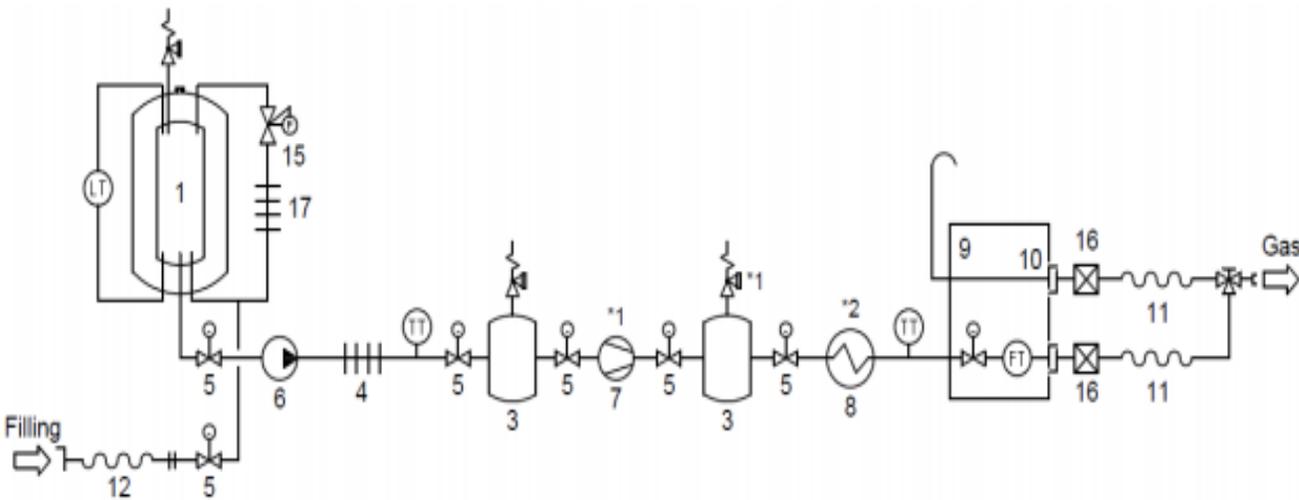
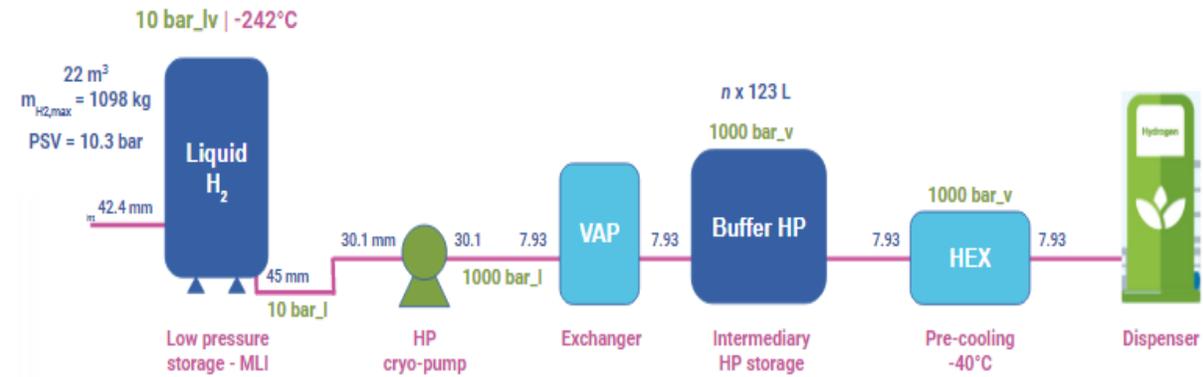
Source: CRRCGC, T85 Type Liquefied Hydrogen Tank Car. (2016)

# Liquefied hydrogen (LH<sub>2</sub>)

## Liquid hydrogen refuelling stations

A LH<sub>2</sub>-based refueling station basically consists of:

- a LH<sub>2</sub> tank (around 20 m<sup>3</sup>) with a maximal operating pressure of 10.3 bar;
- an insulated process line driving LH<sub>2</sub> from the storage tank to a vaporizer;
- a heater to heat up hydrogen at 1000 bar;
- 1000 bar gaseous buffers (few m<sup>3</sup>).

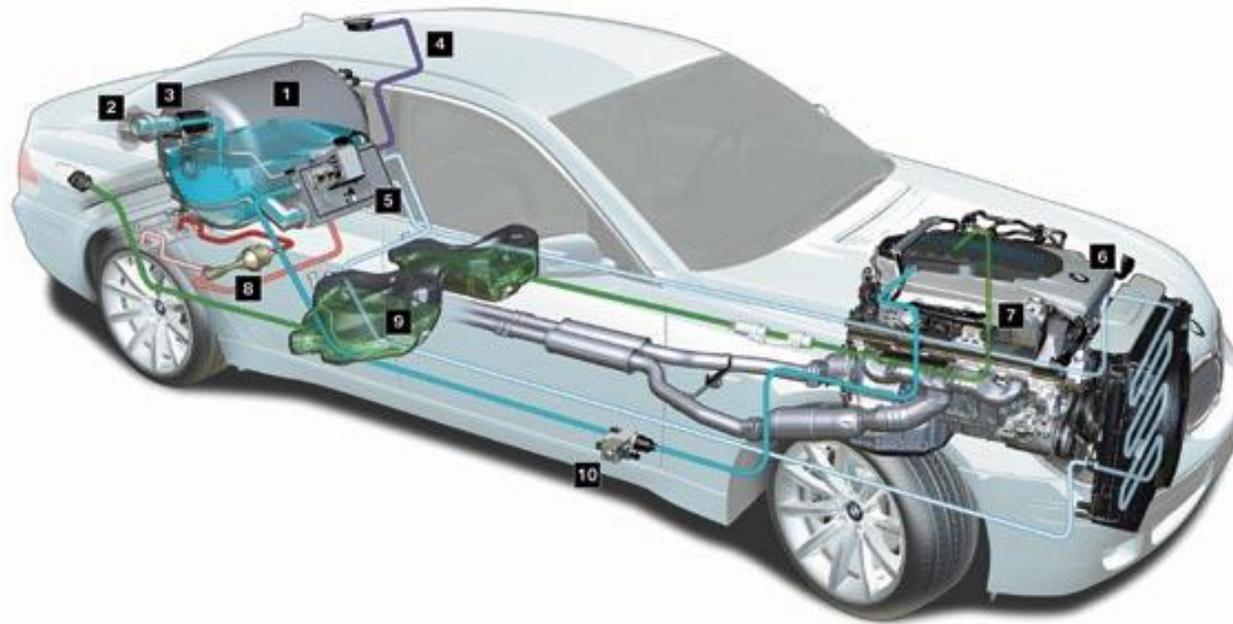


1. liquid hydrogen storage unit	8. chiller	15. pressure regulator
2. gaseous hydrogen storage unit	9. dispenser	16. breakaway coupling
3. intermediate gas storage	10. safety valve	17. pressure build-up evaporator
4. evaporator	11. delivery hose	
5. emergency shutdown system	12. off-loading hose	
6. pump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



# Liquefied hydrogen (LH<sub>2</sub>)

## Liquid hydrogen systems for mobility - cars



- |   |  |  |
|---|--|--|
| <p><b>1</b> LH<sub>2</sub>-Kraftstoffbehälter<br/>LH<sub>2</sub> fuel tank</p> <p><b>2</b> LH<sub>2</sub>-Tankklappe<br/>LH<sub>2</sub> tank cover</p> <p><b>3</b> LH<sub>2</sub>-Tankkupplung<br/>LH<sub>2</sub> tank coupling</p> <p><b>4</b> Sicherheitsabblaseleitung<br/>Safety line to blow valve</p> <p><b>5</b> Nebensystemkapsel (NSK) beinhaltet Kühlwasserwärmetauscher für LH<sub>2</sub> (KWWT) + Steuereinheit des Tanks<br/>Auxiliary units capsule containing heat exchanger for H<sub>2</sub> and control unit of the tank</p> | <p><b>6</b> Bivalent Verbrennungsmotor (H<sub>2</sub> / Benzin)<br/>Bivalent internal combustion engine (H<sub>2</sub> / Gasoline)</p> <p><b>7</b> Sauganlage mit H<sub>2</sub>-Rail<br/>Intake manifold with H<sub>2</sub>-Rail</p> <p><b>8</b> Boil-Off-Management-System (BMS)<br/>Boil-Off-Management-System (BMS)</p> <p><b>9</b> Benzintank<br/>Gasoline tank</p> <p><b>10</b> Druckregelventil<br/>Pressure control valve</p> | <p><b>GH<sub>2</sub>-Vorlaufleitung</b><br/>GH<sub>2</sub> feed line</p> <p><b>Boil-Off-Leitung</b><br/>Boil-Off pipe</p> <p><b>Sicherheitsabblaseleitung (re. + li.)</b><br/>Safety Blow-Valve feed line</p> <p><b>Abgasrohr BMS</b><br/>Exhaust pipe BMS</p> <p><b>Luftansaugung BMS</b><br/>Air inlet BMS</p> <p><b>Kühlwasserkreislauf</b><br/>Water Cooling Cycle</p> <p><b>Benzinkreislauf</b><br/>Gasoline pipe</p> |
|---|--|--|



*Refuelling station for both GH<sub>2</sub> and LH<sub>2</sub> in Berlin*

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*BMW 7 series with LH<sub>2</sub> storage tank and dual fuel (H<sub>2</sub> and gasoline) internal combustion engine*

Source: BMW



- Three super insulated elliptical cryo-tanks with 200 L geometrical volume each;
- A total of 570 L of LH<sub>2</sub> in an underfloor arrangement;
- A cruising range of 250 km

*MAN hydrogen-driven fuel cell bus of 1996 with LH<sub>2</sub> storage tanks*

Source: Euro Quebec Hydro Hydrogen Project, 1995-1997.

## Liquefied hydrogen (LH<sub>2</sub>)

### Liquid hydrogen systems for mobility - trucks



*Musashi-9 LH<sub>2</sub> truck Musashi Institute of Technology (Japan)*

Hydrogen-powered engine with a 150L LH<sub>2</sub> tank.  
A high pressure LH<sub>2</sub> pump delivers fuel to engine.

Source: Yamane K., et al., Int J Hydrogen Energy 21(9) (1996) 807–811.



*Mercedes FC truck GenH<sub>2</sub> concept with LH<sub>2</sub> storage*

Operated with two fuel cell stacks each comprising 200 cells.  
Total power output of 300 kW.  
Cruising range to be 1000 km on a single tank filling.

## Liquefied hydrogen (LH<sub>2</sub>)

### Liquid hydrogen systems for mobility - ships

#### SF-BREEZE

- A zero-emission, hydrogen fuel cell, high-speed passenger ferry, conducted by Sandia National Laboratory.
- Designed for 150 passengers to travel ~93 km round-trip routes each day at a top speed of 35 knots (~65 km/h).
- A total of 1200 kg (or 17 m<sup>3</sup>) of LH<sub>2</sub> are stored in a single tank installed on the roof.
- Power is provided by 41 PEMFC racks, each rack composed of four 30 kW FC stacks amounting to a total of 4.92 MW.

#### NORLED ferry

- Two options for the storage of the hydrogen fuel, as liquid or as compressed gas.
- Power is provided by two 200-kW fuel cell modules.
- The LH<sub>2</sub> tank will be installed on the roof.

#### TOPEKA prototype FC ship

- Starting in 2021 the EU project HySHIP with 14 partners and led by the Norwegian shipping operator Wilhelmsen.
- equipped with a 3 MW PEM fuel cell stack and supported by a 1 MWh battery pack.
- On-board storage of hydrogen will be a single LH<sub>2</sub> tank installed on the roof.



Source: NORLED, World's first ship driven by LH<sub>2</sub>. Presentation at GCE Ocean Technology workshop, Florø, Norway (2019).

## Liquefied hydrogen (LH<sub>2</sub>)

### Liquid hydrogen systems for mobility - aircrafts

#### **B-57B twin-engine aircraft (USA)**

- The first successful in-flight test of an experimental hydrogen-propelled aircraft.
- LH<sub>2</sub> stainless-steel tank on the left-wing tip (6.2 m long, volume of 1.7 m<sup>3</sup> and a 50 mm plastic foam insulation).
- Start with the conventional JP-4 fuel, switched to H<sub>2</sub> fuel at an altitude of ~ 16,400 m.
- The H<sub>2</sub> engine operated for about 20 min at a speed of Mach 0.72.

#### **Tu-155 (ANTK-Tupolev, Russian)**

- A hybrid version of the Tu-154 airplane.
- Fuelled with either hydrogen or natural gas in a 17.5 m<sup>3</sup> tank.
- Total operating experience with LH<sub>2</sub> accumulated to 10 h.



#### **Zeroe aircraft (Airbus, France)**

- The world's first zero-emission commercial aircraft enters service by 2035.
- Rely on hydrogen as a primary power source.
- Liquid hydrogen storage and distribution system located behind the rear pressure bulkhead.

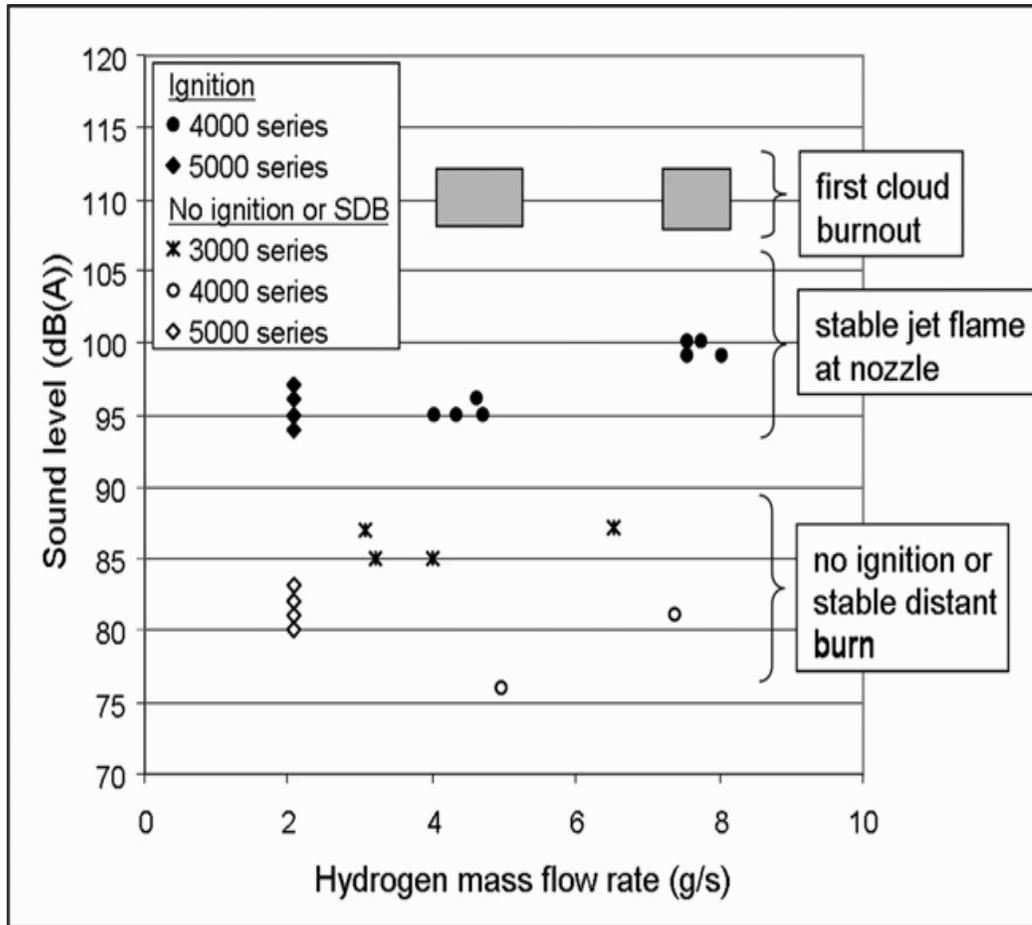


Source: Tupolev. Development of cryogenic fuel aircraft. (2008). Airbus, Airbus reveals new zero-emission concept aircraft. (2020).

## Liquefied hydrogen (LH<sub>2</sub>)

### Liquid hydrogen hazards and risks for Responders

- **Frostbite or hypothermia:** contact with LH<sub>2</sub> or its splashes on the skin or in the eyes can cause serious cold burns.
- **Cryogenic burns:** contact of unprotected parts of human body with either cold fluids or cold surfaces.
- Inhalation of cold hydrogen vapours may cause **respiratory discomfort** and can result in **asphyxiation**.
- Direct physical contact with LH<sub>2</sub>, cold vapours or cold equipment can cause serious **tissue damage**. Momentary contact with a small amount of the liquid may not pose as great a danger of a burn because a protective film of evaporating gaseous hydrogen may form. Danger of freezing occurs when large amounts are spilled, and exposure is extensive.
- Personnel should not touch cold metal parts and they should wear **protective clothing**. They also need to protect the affected area with a loose cover.
- **Cardiac malfunctions** are likely when the internal body temperature drops to 27°C or lower, and death may result when the internal body temperature drops lower than 15°C.
- **Asphyxiation** is also possible if liquefied hydrogen released and vaporised indoors.



- The ignited jets generated about 10 dB (A) higher sound levels compared to unignited jets.
- A weak increase of the sound level with increasing hydrogen mass flow rate.
- The sound levels ( $\leq 112$  dB(A)) are considered hazardous only in case of permanent or long-time exposures.
- An ear damage from short sound waves becomes possible for 120 dB(A) and above.
- Sound levels from unignited and ignited cryogenic hydrogen jets measured in this study pose no health hazards, even at the close distances investigated (1.2 - 4.5 m).
- The measured sound levels are loud enough to allow an early identification and location of flame.

## Liquefied hydrogen (LH<sub>2</sub>)

### Safety measures and engineering solutions

The safety issues of hydrogen transportation are:

- Ability to embrittle materials;
- Easy to escape from containment;
- Wide flammability range;
- Low ignition energy;
- Formation of dense flammable cloud;
- Delayed ignition and explosion of large cloud;
- Jet fires due to leakages in pipelines under pressure.

**Artificial barriers** may be inserted to decrease the safety distances from the possible release point to the receptor.

- A major problem when producing and handling LH<sub>2</sub> is the potential contamination of the hydrogen with air or other impurities which might freeze and block pipes, filters or armatures.
- On the exterior of poorly insulated containers or pipes the cryogenic temperatures may condense air with serious enrichment of oxygen. Liquefied or frozen solid oxygen promotes ignition and oxidizes easily materials which are usually non-flammable.
- The extreme low temperatures require careful selection of materials. Conventional carbon steels will suffer from a transition to nil ductility (NDTT). Aluminium or stainless steels are typically suitable structural materials for cryogenic hydrogen and welded connections are preferred to screwed connections.

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