

HyResponse

## BASICS OF HYDROGEN SAFETY FOR FIRST RESPONDERS

Lecture. Hydrogen properties relevant to safety



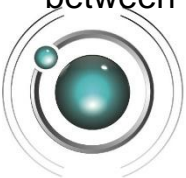
# Content

- Atomic and molecular hydrogen
- Gaseous, liquefied and slush forms of hydrogen
- Physical properties of hydrogen (buoyancy as a main safety asset)
- Combustion characteristics of hydrogen
  - Stoichiometric concentration of hydrogen
  - Lower and upper flammability limits (LFL and UFL)
  - Impact of different factors on LFL and UFL
  - Ignition properties
  - Detonability limits
  - Hydrogen flames quenching
  - Micro-flames
  - Quenching and blow-off limits
  - Leaky fittings
- Comparison of hydrogen with other fuels

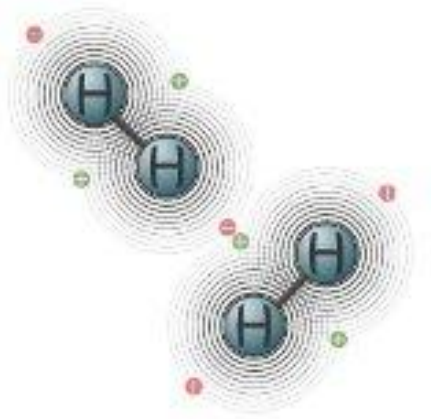


# Objectives of the lecture

- Understand the effect of atomic and molecular structure on safety considerations for hydrogen storage and handling;
- Interpret the phase diagram of hydrogen and identify its three aggregate states;
- Recognise physiological hazards associated with  $\text{GH}_2$  (asphyxiation) and  $\text{LH}_2$  (cryogenic burns, frostbite, hypothermia, lung damage from inhalation of cold vapours);
- Relate the low vapour density of  $\text{GH}_2$  to the buoyancy as a main safety asset;
- Explain hydrogen combustion process and its main attributes;
- Indicate stoichiometric concentrations and flammability range for hydrogen-air and hydrogen-oxygen mixtures;
- Explain the effect of different factors (temperature, pressure, direction of flame propagation, diluents and inhibitors, etc.) on flammability of hydrogen;
- Define the main ignition properties: minimum ignition energy, auto-ignition temperature, adiabatic flame temperature, flash point, minimum experimental safety gap, laminar burning velocity;
- Compare the detonability limits of hydrogen to those of common fuels and to hydrogen flammability range;
- Describe hydrogen microflames and hydrogen flames quenching parameters (quenching distance; quenching gap; quenching limits; blow-off limits)
- Relate physical, chemical, ignition and combustion properties to hydrogen hazards/hazardous phenomena (leaks, fires, explosions);
- Explain the differences (and similarities) in physical properties/combustion characteristics/ignition parameters between hydrogen and common fuels.



# Atomic and molecular hydrogen



- The most abundant isotope (more than 99.98%) is protium  $^1_1\text{H}$
- [Hydrogen atom](#) consists of 1 proton and 1 electron
- Hydrogen is **the lightest known element**
- It is not present in a free state in the atmosphere of the Earth; it is present in a free state in the sun and stars
- Hydrogen gas: stable **molecules made of two hydrogen atoms**  $\text{H}_2$
- The **lightest gas**, it is about **14** times lighter than air: the vapour density of hydrogen is 1; the vapour density of air is 14.
- Please watch [the video about hydrogen characteristics](#).

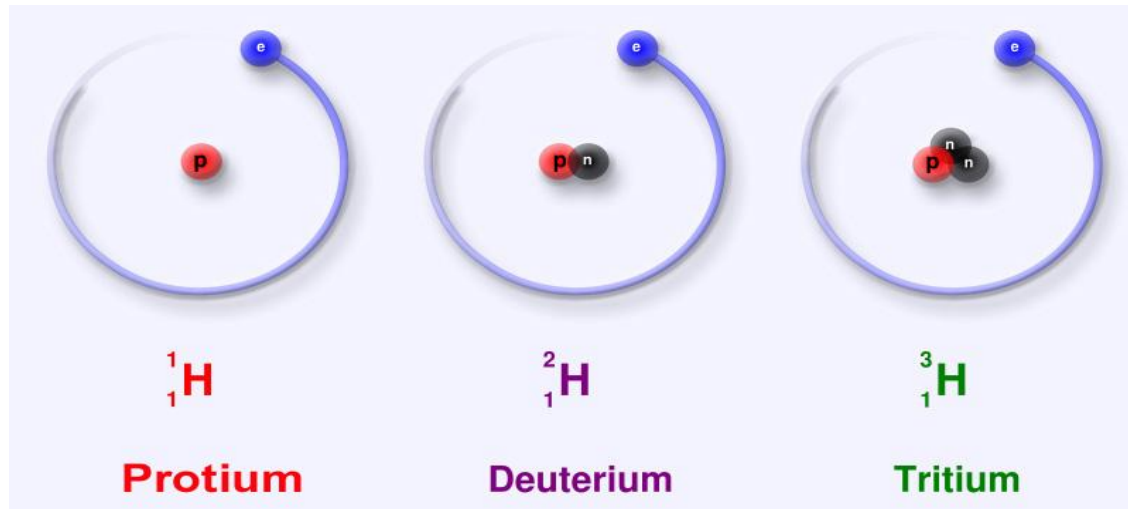


Google: free images



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# Hydrogen isotopes and molecular forms



- **Ortho-hydrogen** (parallel arrangement of the nuclear spin of the two atoms).
- **Para-hydrogen** (anti-parallel arrangement of the nuclear spin).
- Hydrogen gas is a mixture of ortho- and para-forms at normal temperature and pressure (NTP).
- **Normal hydrogen:** 25% para-hydrogen and 75% ortho-hydrogen.
- At lower temperatures, equilibrium favours the existence of para-hydrogen. **Liquid hydrogen** at 20 K composed of 99.8 % para-hydrogen (ISO/TR 15916 (2004)).



# Ortho-para hydrogen conversion

- The ortho-para hydrogen conversion is accompanied by a **release of heat**, 703 kJ/kg at 20 K for ortho- to para-hydrogen conversion, or 527 kJ/kg for normal to para-hydrogen conversion (NASA, 1997).
- The process of hydrogen liquefaction includes the removal of the energy released by the ortho-para state conversion. The heat of conversion is 715.8 kJ/kg, which is 1.5 times of the heat of vaporization (ISO/TR 15916:2004).
- The **liquefaction is a very slow exothermic process** that can take several days to complete, unless it is accelerated with the use of a paramagnetic catalyst.



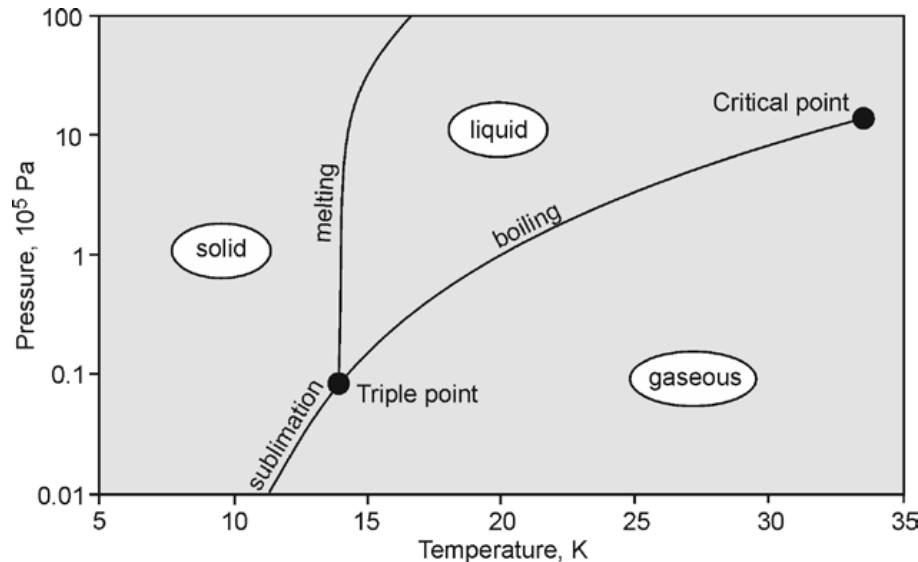
# Phase diagram of hydrogen

## Hydrogen, slush

- A mixture of solid and liquid hydrogen at the triple point temperature.
- Melting point :  $-259.2\text{ }^{\circ}\text{C}$

## Hydrogen, liquid

- Clear liquid with a light blue tint and non-corrosive
- Cold burns possible from a very short contact!



**Critical point:**  $T = 33.2\text{ K}$  ( $-240^{\circ}\text{C}$ ) and  $p = 1.3\text{ MPa}$ . The highest temperature, at which a hydrogen gas can be liquefied.

No liquid phase in storage vessels containing compressed hydrogen gas

**Triple point:** all 3 phases co-exist,  $T = 13.8\text{ K}$  ( $-259^{\circ}\text{C}$ ) and  $p = 7.2\text{ kPa}$ .

## Hydrogen, gas

- Colourless, odourless and tasteless gas
- Hydrogen gas is **non-toxic** and **non-corrosive**; does not support life (**i.e. asphyxiant**).



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

- **Cryogenic fluid**, stored at relatively low pressures in double-walled, vacuum insulated tanks equipped with burst disks, vents, and PRDs.
- The **normal boiling point** (NBP, boiling temperature at absolute pressure of 101.325 kPa) of hydrogen is **20.3 K**. Any liquid hydrogen splashed on the skin or in the eyes can cause serious burns by frostbite or hypothermia.
- LH<sub>2</sub> (at NBP) has a density of 70.78 kg/m<sup>3</sup>. The corresponding specific gravity is 0.071 (specific gravity of water is 1). **14 times less dense than water**.
- Coefficient of thermal expansion of LH<sub>2</sub>, at NBP is 23 times that of water for ambient conditions. Upon heating LH<sub>2</sub> expands significantly.
- Every cubic meter of water (H<sub>2</sub>O) contains 111 kg of hydrogen whereas a cubic meter of liquid hydrogen contains only 70.78 kg of hydrogen (College of the Desert, 2001).
- 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.



# Hydrogen expansion ratio

- Volumetric ratio of **LH<sub>2</sub> to GH<sub>2</sub>** is **1:848**. Need for LH<sub>2</sub> storage to have burst disks and PRDs.
- Volume increases when gaseous hydrogen warmed from the NBP to NTP.
- For vessels with a fixed volume the phase change (LH<sub>2</sub>→GH<sub>2</sub>) and associated temperature rise (from NBP to NTP) will result in a pressure increase of **177 MPa** (ISO/TR 15916:2004). This can lead to an over-pressurisation of the vessel or penetration of the liquid hydrogen into transfer and vent lines (should be accounted for during design of storage tanks).
- Safety valves are needed.



# LH<sub>2</sub>: safety issues (1/2)

- LH<sub>2</sub> will rapidly boil or flash to a gas if exposed to or spilled into environment with normal temperature. Warming LH<sub>2</sub> to ambient temperature can lead to very high pressures in confined spaces.
- [Video of LH<sub>2</sub> spill](#)
- [Effect of the wind on LH<sub>2</sub> spill.](#)
- All gases, except helium, will be condensed and solidified at -250 °C. They can plug pipes and orifices and jam valves. In a process known as **cryo-pumping** the reduction in volume of the condensing gases may create a vacuum that can draw in yet more gas, e.g. oxidiser like air.
- Large quantities of solids can accumulate displacing the LH<sub>2</sub> if the leak persists for long periods. At some point, when the system is warmed for maintenance, these frozen materials will vaporise, possibly resulting in high pressures or forming explosive mixtures. These other gases might also carry heat into the liquid hydrogen and cause enhanced evaporation losses or “unexpected” pressure rise.

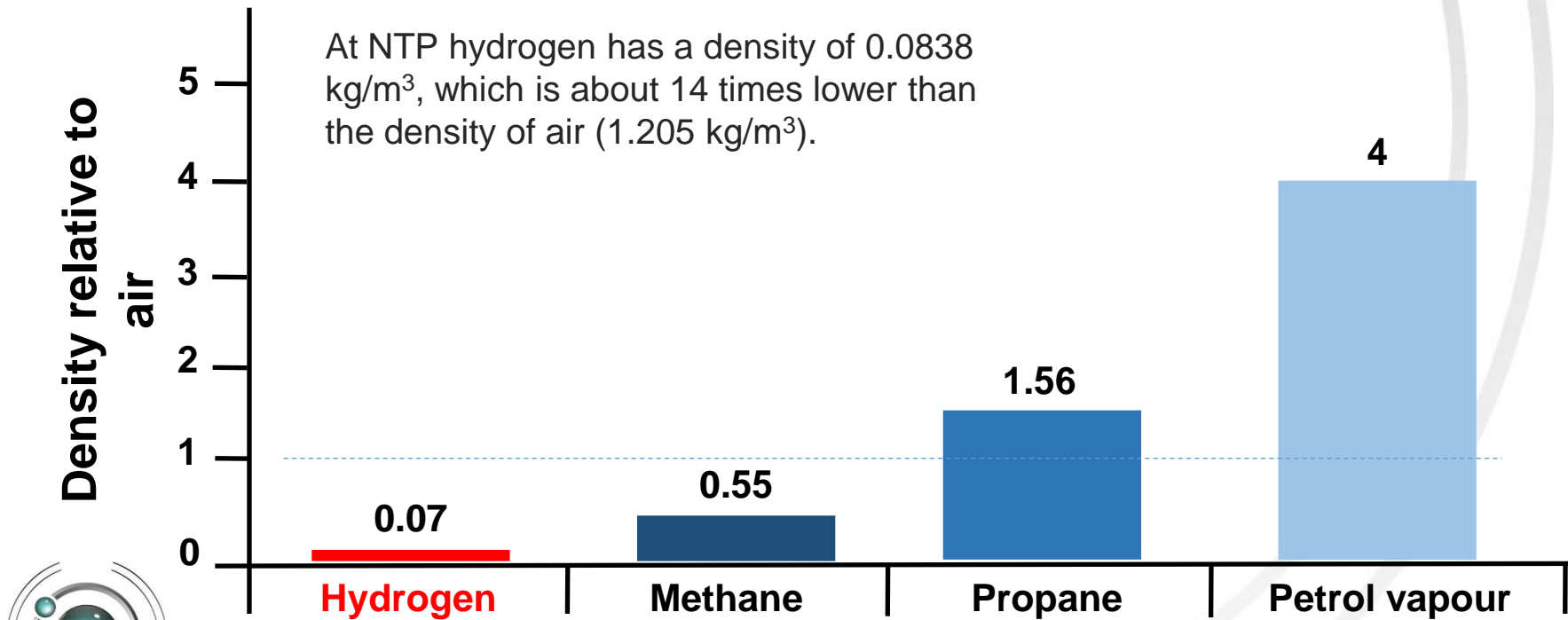


# LH<sub>2</sub>: safety issues (2/2)

- Outside of the LH<sub>2</sub> system, insufficiently insulated pipes and vessels containing LH<sub>2</sub> can condense gases such as air into liquid forms on their outer surfaces. The liquid condensate flows and looks like a liquid water. This oxygen-enriched condensate increases the flammability of materials and/or makes materials combustible that normally are not. This includes for example bituminous road covers. This is of particular concern when transferring large quantities of hydrogen.
- If a piece of equipment cannot be properly insulated, the area underneath should be free of any organic material.
- **Oxygen enrichment** can increase the flammability and even lead to the formation of shock-sensitive compounds. Oxygen particulate in cryogenic hydrogen gas may even detonate. Vessels with LH<sub>2</sub> have to be periodically warmed and purged to keep the accumulated oxygen content in the vessel to less than 2% (ISO/TR 15916: 2004).
- Caution should be exercised if carbon dioxide (CO<sub>2</sub>) is used as a purge gas. It may be difficult to remove all CO<sub>2</sub> from the system low points where it can accumulate.

# Density of hydrogen

- Low vapour density results in the gas being very **buoyant** compared to other compounds.
- Hydrogen has the highest on the Earth buoyancy. This is **the main hydrogen safety asset**, i.e. in case of unwanted releases it is able to **rise and disperse rapidly**.



# Buoyancy as a safety asset

- The unwanted consequences of hydrogen releases into the open or in partially confined spaces (with no accumulation of hydrogen), are **drastically reduced by buoyancy**. Hydrogen will flow out of an incident scene, and mix with the ambient air to a safe concentration level, i.e. below the lower flammability limit LFL (4 vol. % in air).
- Pure hydrogen is positively buoyant above  $T=22\text{ K}$ , within the entire temperature range of its gaseous state (BRHS, 2009).
- Buoyancy provides **comparatively fast dilution of released hydrogen by surrounding air** below the LFL.
- In unconfined conditions only small fraction of released hydrogen would be able to deflagrate. Indeed, a hydrogen-air cloud evolving from the inadvertent release upon the failure of a storage tank or pipeline liberates only a small fraction of its thermal energy in case of a deflagration, which is in the range 0.1-10% and in most cases below 1% of the total energy of released hydrogen (BRHS, 2009). This makes safety consideration of hydrogen accident with a large inventory in the open quite different from that of other flammable gases with often less or no harmful consequences at all.

# Hydrocarbons combustible clouds

- Heavier hydrocarbons are capable to form rather large combustible clouds, as in the cases of disastrous explosions at [Flixborough in 1974](#) [1] and [Buncefield in 2005](#) [2] (England) .
- In many practical situations, **hydrocarbons may pose stronger fire and explosion hazards than hydrogen**. Hydrogen high buoyancy affects its dispersion considerably more than its high diffusivity.

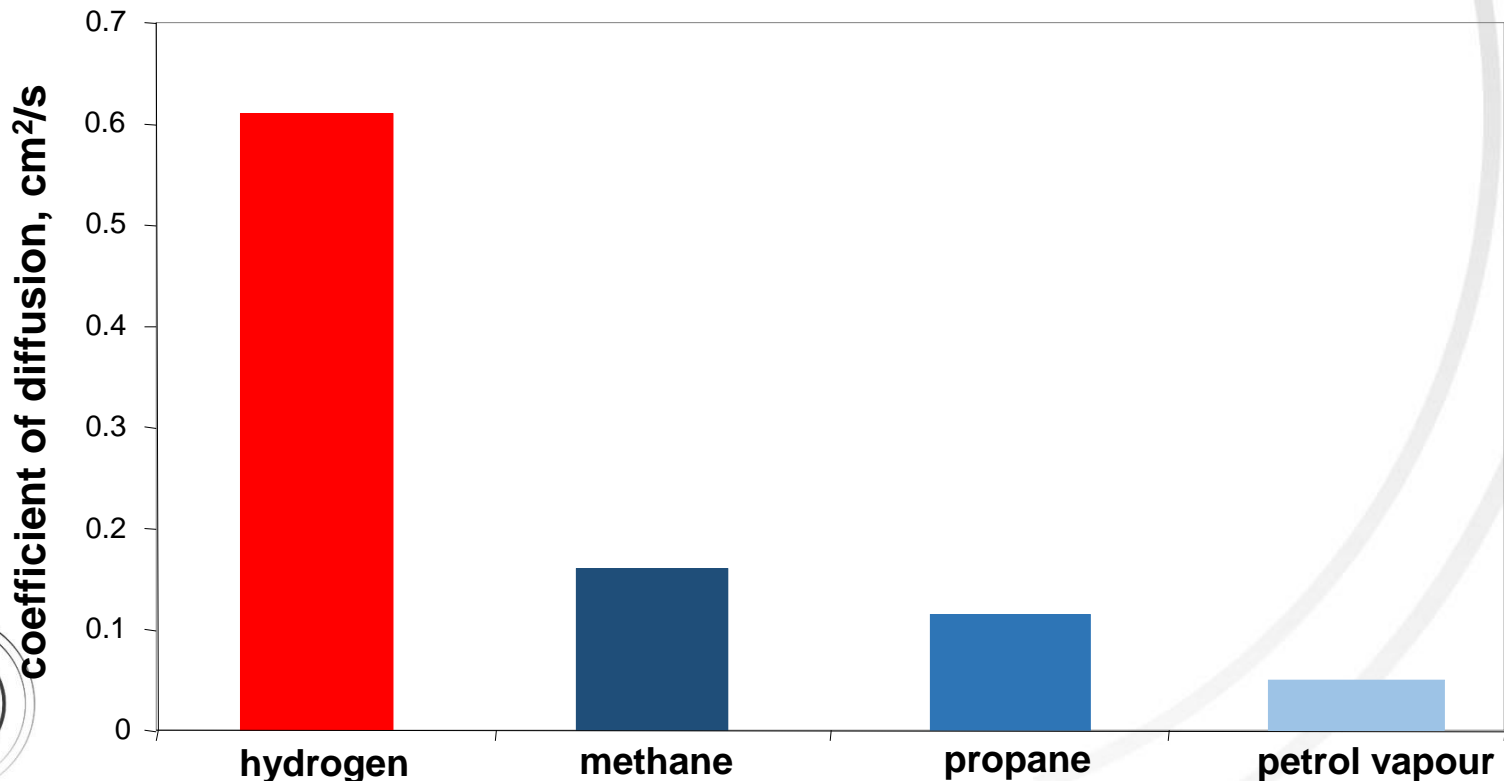


*Buncefield fire: Google images*



# Diffusivity of hydrogen

- Diffusivity of hydrogen is **higher compared to other gases** due to the small size of its molecules.
- Hydrogen diffusivity greater than that of helium and approximately 3 times that of nitrogen in air at ambient conditions.  $\text{GH}_2$  also readily diffuses through solids. For example, effective diffusion coefficient of hydrogen through gypsum panels is  $1.4\text{E-}05 \text{ m}^2/\text{s}$  at room temperature (Molkov, 2012).





# Other physical properties

## ● Viscosity

The **low viscosity** of hydrogen and the small size of the molecule cause a comparatively high flow rate if the gas leaks through fittings, seals, porous materials, etc.

GH<sub>2</sub>: 89.48 µPoise (NTP) and 11.28 (NBP)

LH<sub>2</sub>: 132.0 µPoise (NBP)

## ● Specific heat and specific heat ratio

The heat capacity of GH<sub>2</sub> is **similar** to that of **other diatomic gases** despite its low molecular mass.

*Specific heat at constant pressure ( $c_p$ , J/kg/K):*

GH<sub>2</sub>: 14.85 (NTP), 14.304 (STP), 12.15 (NBP).

LH<sub>2</sub>: 9.66 (NBP)

*Specific heat ratio ( $\gamma$ ):*

GH<sub>2</sub>:  $\gamma=1.39$  (NTP) and  $\gamma=1.405$  (STP)

## ● Thermal conductivity

**Thermal conductivity** of hydrogen is **significantly higher** than that of other gases.

GH<sub>2</sub>: 0.187 W/m/K (NTP) and 0.0169 W/m/K (NBP).

LH<sub>2</sub>: 0.09892 W/m/K (NBP).

## ● Speed of sound:

GH<sub>2</sub>: 1,294 m/s (NTP) and 355 m/s (NBP)

LH<sub>2</sub>: 1,093 m/s (NBP).

Stoichiometric hydrogen-air mixture:  
404 m/s (BRHS, 2009).

**Please note:**

**NTP - 293.15 K and 101.325 kPa**

**STP - 273.15 K and 101.325 kPa**

**NBP - 20 K and 101.325 kPa**



# Joule-Thompson effect

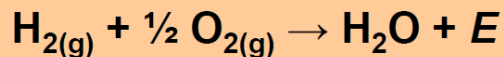
- When gases are expanded from high to low pressure they usually cool down.
- In a Joule-Thomson process starting at ambient temperature, the temperature of hydrogen will increase.
- This temperature rise, however, is not sufficient to cause ignition of hydrogen-air mixture.

Source: Molkov, V (2012). Fundamentals of hydrogen safety engineering, Part I and Part II.

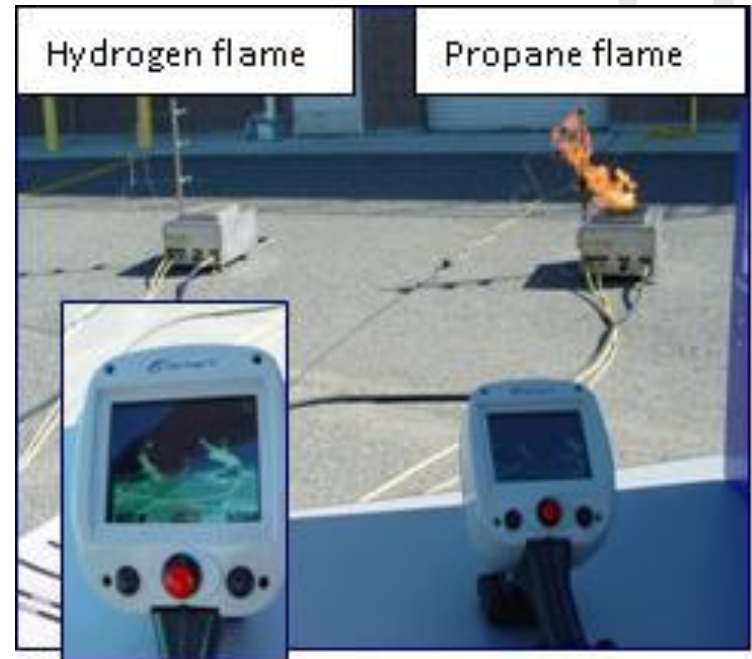
# Combustion of hydrogen

- At NTP hydrogen is a **not very reactive substance**, unless it has been activated with a catalyst.
- **Reaction of hydrogen with oxygen** (forming water) at ambient temperature is extraordinarily slow. However, if the reaction is accelerated by a catalyst or a spark, it proceeds with high rate.
- Pure hydrogen burns with a pale-blue flame invisible in a daylight. On burning with air it forms water.
- Hydrogen produces low radiant heat upon combustion.

hydrogen + oxygen → water + energy

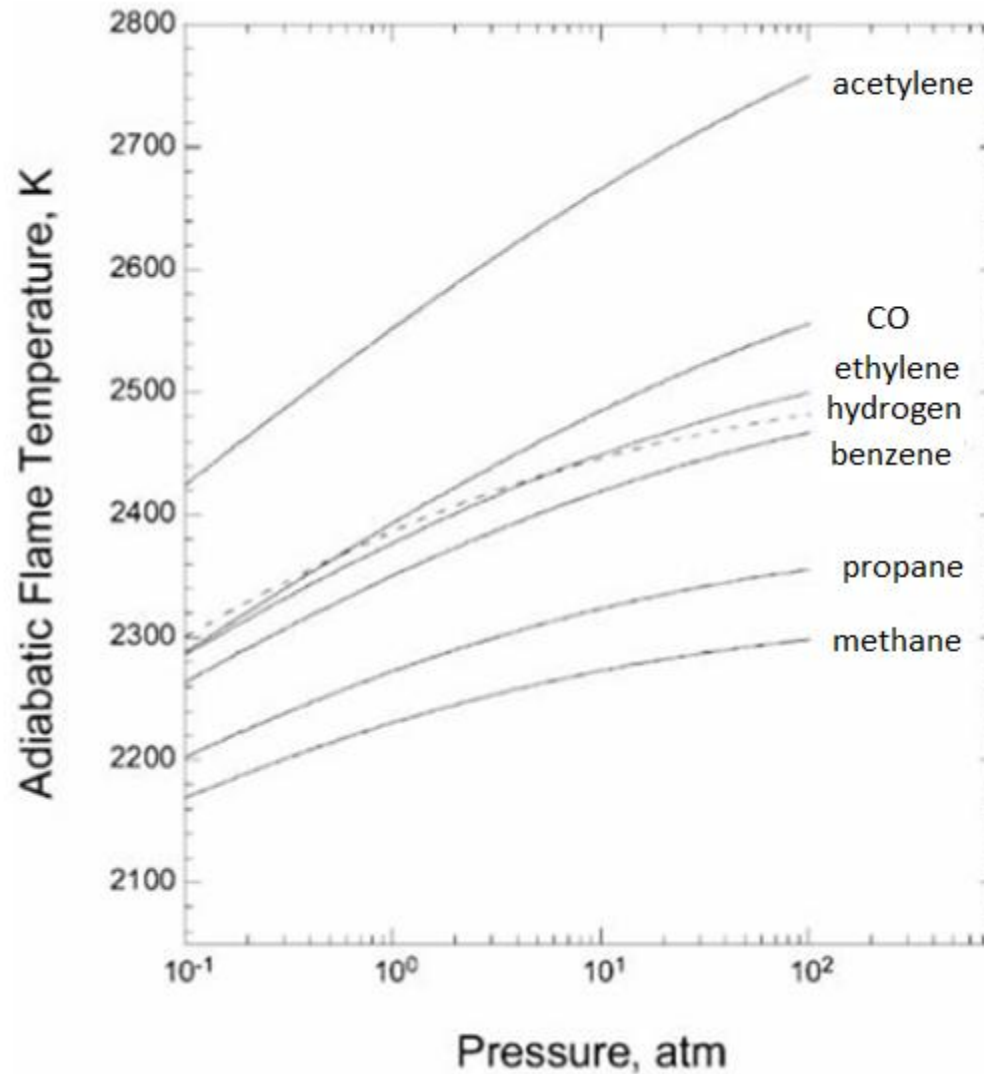


- Hydrogen is a combustible gas



Source: H2BestPractices.

# Adiabatic flame temperature



# Stoichiometric mixture

- **Stoichiometric mixture** is a mixture in which both fuel and oxidiser are fully consumed (i.e. complete combustion) to form combustion product(s).
- Stoichiometric concentration of hydrogen-air mixture: **29.59 vol. %**

Assuming air consists of 21 vol. % of oxygen (O<sub>2</sub>) and 79 vol. % nitrogen (N<sub>2</sub>):



- Stoichiometric concentration of hydrogen-oxygen mixture: **66.66 vol. %**



# Heat of combustion

- The **lower heating value** (heat of combustion) of hydrogen is 241.7 kJ/mol and the **higher heating value** is 286.1 kJ/mol (College of the Desert, 2001; BRHS, 2009).
- The difference of about 16% is due to the heat of condensation of water vapour, and this value is larger compared to other gases.

	Hydrogen	Methane	Propane	Petrol
<b>Higher Heating Value (25 °C, 0.101 MPa), kJ/g</b>	141.86	55.53	50.36	47.5
<b>Lower Heating Value (25 °C, 0.101 MPa), kJ/g</b>	119.93	50.02	45.6	44.5

# Limiting Oxygen Index

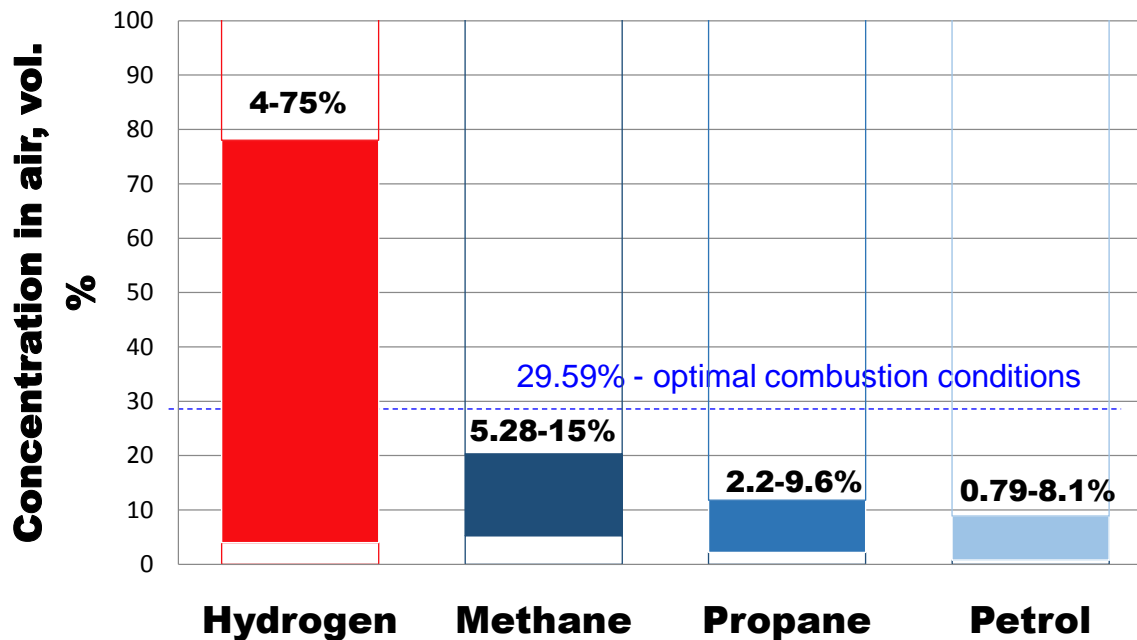
- The **limiting oxygen index (LOI)** is the minimum concentration of oxygen that will support flame propagation in a mixture of fuel, air, and nitrogen. No mixture of hydrogen, air, and nitrogen at NTP conditions will propagate flame if the mixture contains less than 5% by volume oxygen (NASA, 1997).  **$LOI_{H_2} = 5$**





# LFL and UFL in air: hydrogen vs. other fuels

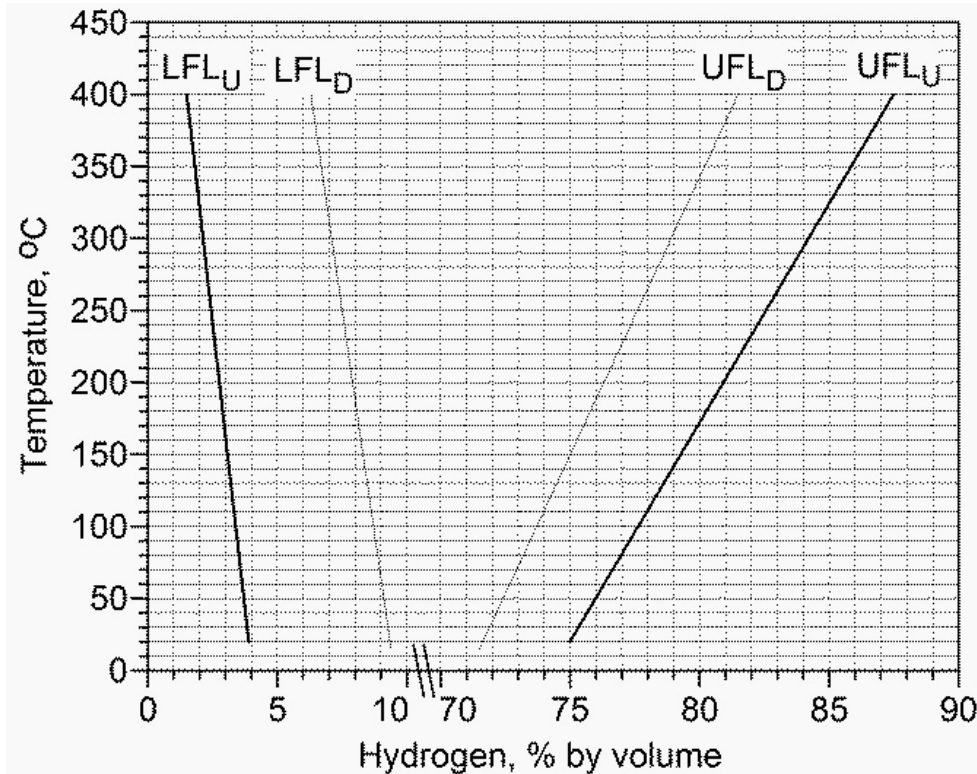
**Flammability range** is the range of concentrations between the lower and the upper flammability limits. **The lower flammability limit (LFL)** is the lowest concentration and **the upper flammability limit (UFL)** is the highest concentration of a combustible substance in a gaseous oxidizer that will propagate a flame.



- Hydrogen ignites if its content in air below the UFL and above the LFL, and if an ignition source is present.
- The flammability range of hydrogen is wider compared to most hydrocarbons: **from 4 to 75 vol. %** at NTP.

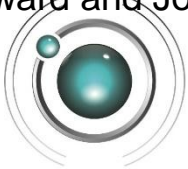
Source: Molkov, V (2012). Fundamentals of hydrogen safety engineering, Part I and Part II.

# Effect of temperature on LFL and UFL



LFL and UFL of hydrogen-air mixture as a function of temperature: thick lines - upward flame propagation (Molkov, 2012); thin lines - downward flame propagation (Coward and Jones, 1952).

- The **flammability range expands** linearly as temperature rises.
- **LFL decreases** by about 2.5 vol. % (from 4 to 1.5 vol. %) **with increase of temperature** from 20°C to 400°C, whilst **UFL increases** more significantly - by about 12.5 vol. % for the same change of mixture temperature.



Sources:

Molkov, V (2012). Fundamentals of hydrogen safety engineering, Part I and Part II.

Coward, HF and Jones, GW (1952). Limits of flammability of gases and vapors, Bulletin 503, Bureau of Mines, p. 155.

# Flammability limits: function of flame propagation direction

- The flammability limits of hydrogen depend on a direction of flame propagation.

Flammability limits of hydrogen-air for upward, horizontal, and downward (spherical) propagation in hydrogen concentration by volume (Molkov (2012); Coward and Jones (1952)).

Upward propagation		Horizontal propagation		Downward propagation	
LFL	UFL	LFL	UFL	LFL	UFL
3.9-5.1%	67.9-75%	6.0-7.15%	65.7-71.4%	8.5-9.45%	68-74.5%

Sources:

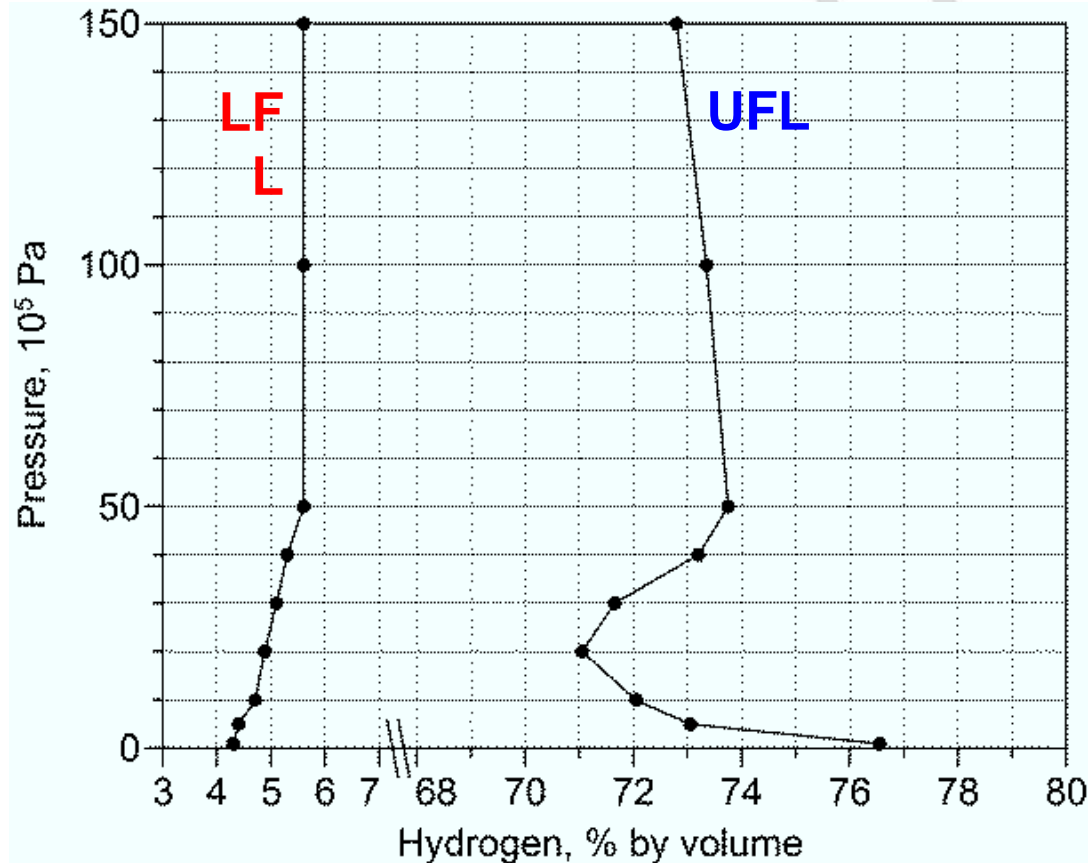
Molkov, V (2012). Fundamentals of hydrogen safety engineering, Part I and Part II.

Coward, HF and Jones, GW (1952). Limits of flammability of gases and vapors, Bulletin 503, Bureau of Mines, p. 155.



# Effect of pressure on flammability range

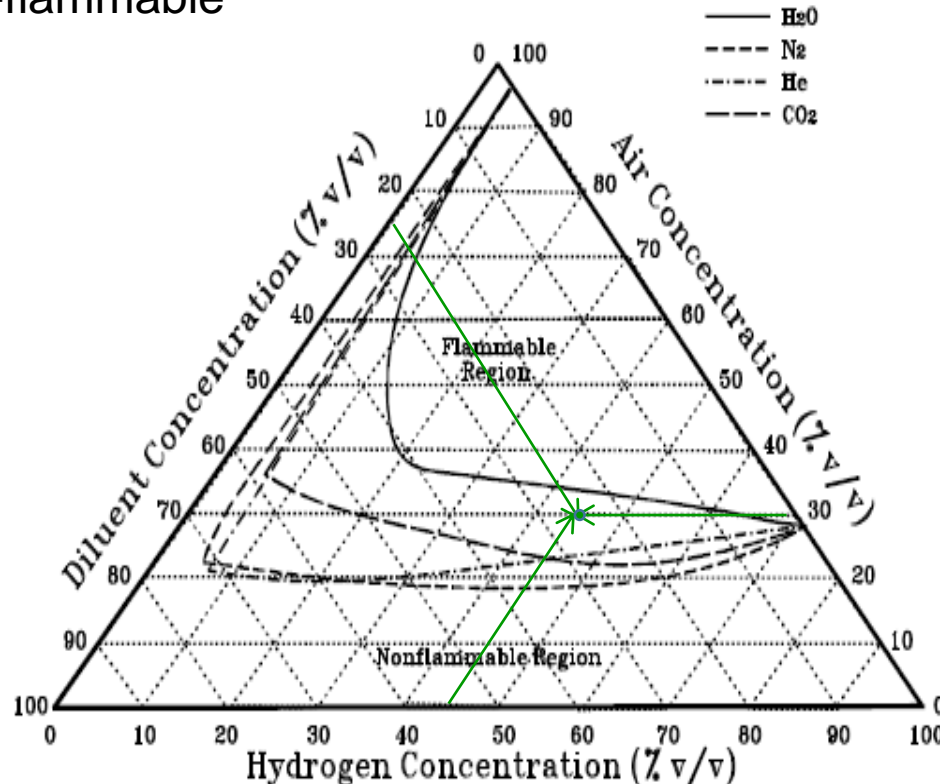
- **LFL increases to 5.6 vol. %** if pressure rises from 0.1 to 5.0 MPa and then it remains constant up to pressure of 15 MPa.
- **UFL changes not monotonically.** It decreases from 76.6 to 71 vol. % as pressure rises from 0.1 to 2.0 MPa; then UFL increases from 71 to 73.8 vol. % with pressure increase from 2.0 to 5.0 MPa; and it decreases again slightly from 73.8 to 72.8% with pressure rising from 5.0 to 15.0 MPa.



LFL and UFL of hydrogen-air mixture as a function of pressure (Schroeder, V and Holtappels, K (2005))

# Effect of diluents on the flammability range

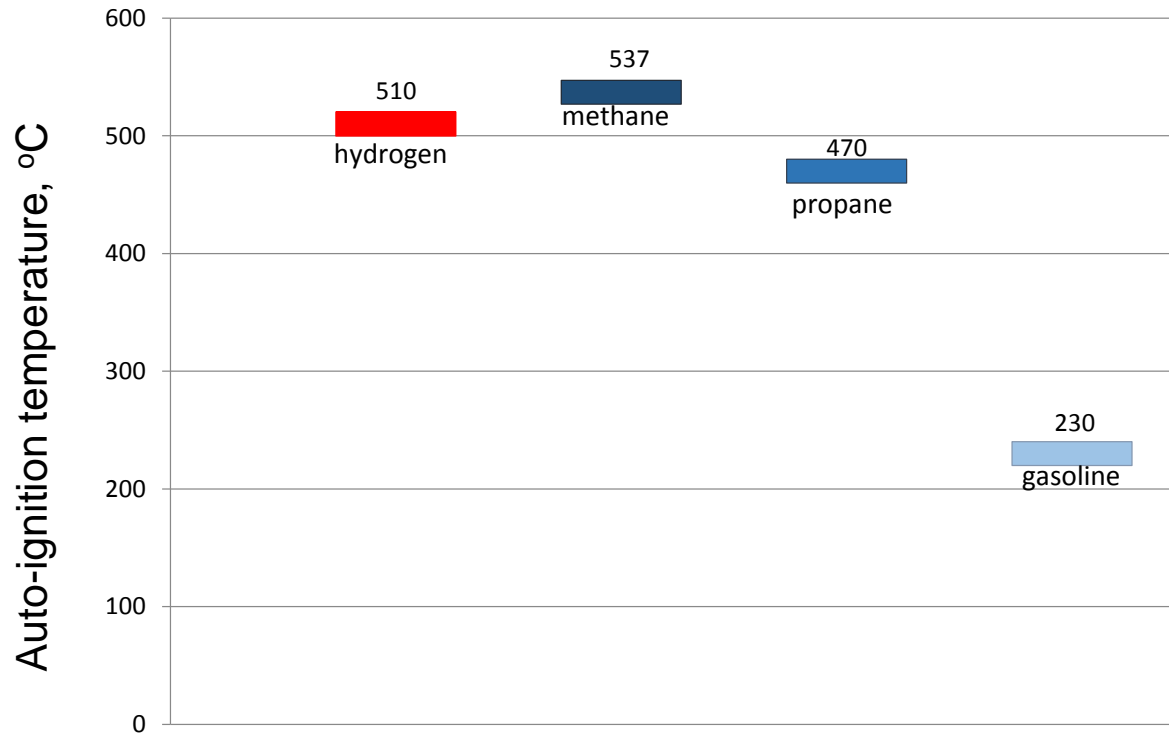
- Mixture: 45% of hydrogen, 30% of air and 25% of diluent
- For CO<sub>2</sub>, He and N<sub>2</sub> mixture flammable
- For H<sub>2</sub>O mixture is non-flammable



Effects of N<sub>2</sub>, He, CO<sub>2</sub>, and H<sub>2</sub>O diluents on flammability limits of hydrogen in air at 101.3 kPa (NASA, 1997).

# Auto-ignition temperature

**Auto-ignition temperature** is the minimum temperature required to initiate combustion reaction of fuel-oxidiser mixture in the absence of an external source of ignition.

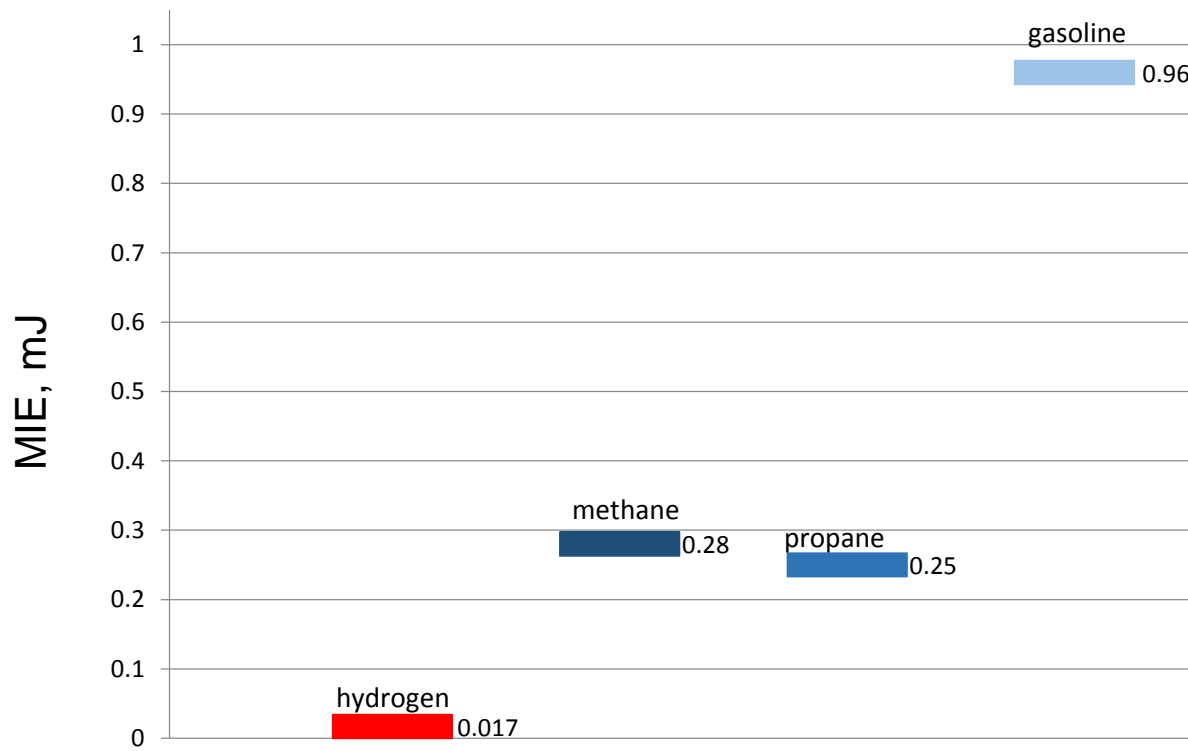


Note: Gasoline in North America = Petrol elsewhere

Source: Molkov, V (2012). Fundamentals of hydrogen safety engineering, Part I and Part II.

# Minimum ignition energy (1/2)

**Minimum ignition energy (MIE)** of flammable gases and vapours is the minimum value of the electric energy, stored in the discharge circuit with as small a loss in the leads as possible, which (upon discharge across a spark gap) just ignites the quiescent mixture in the most ignitable composition. A weak spark caused by the discharge of a static electricity from a human body may be sufficient to ignite any of the fuels shown below.

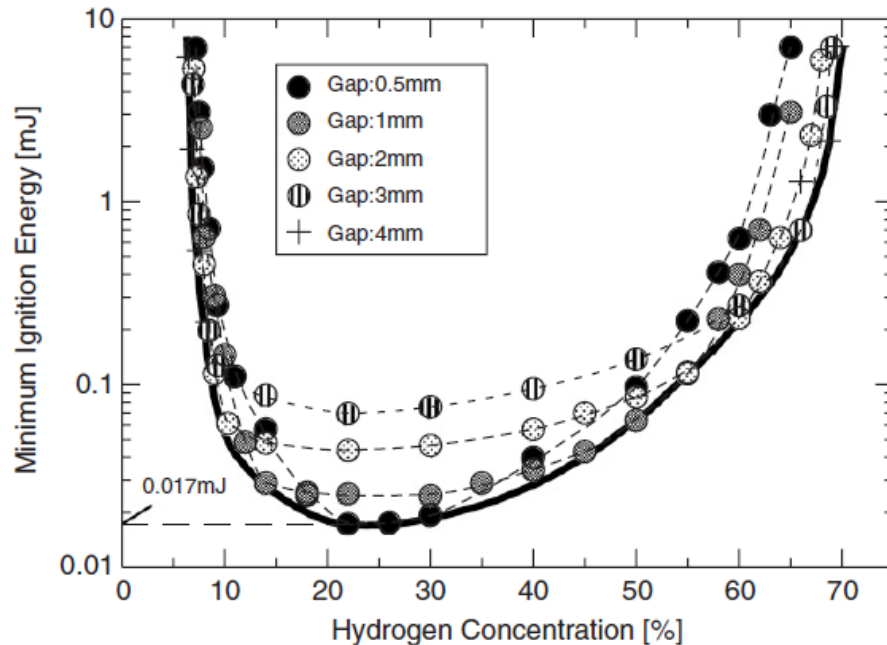


Note: Gasoline in North America = Petrol elsewhere

Source: Molkov, V (2012). Fundamentals of hydrogen safety engineering, Part I and Part II.



# Minimum ignition energy (2/2)



MIE of hydrogen–dry air mixture (solid line) and that at fixed gap distances of 0.5, 1, 2, 3, and 4 mm (broken line).

Source: Ono, R et al. (2007). Journal of Electrostatics. Vol. 65, p. 87-93.

- MIE depends on hydrogen concentration in the mixture with air, on pressure, and temperature.
- MIE becomes infinite at the flammability limits.
- Over the flammable range of hydrogen-air mixtures, the ignition energy varies by almost three orders of magnitude
- Ignition sources capable of forming shocks, for example high-energy spark discharges and high explosives, can directly initiate detonation.



# Flashpoint

- **Flashpoint** is the lowest temperature at which the fuel produces enough vapours to form a flammable mixture with air at its surface (Baratov et al., 2009; Molkov, 2012).

	Hydrogen	Methane	Propane	Petrol	Diesel
Flashpoint, °C	-253	-188	-96	-(11-45)	37-110

Sources:

Baratov, AN, Korolchenko, AY and Kravchuk, GN (Eds.) (1990). Fire and explosion hazards of substances and materials. Moscow: Khimia. 496 p., ISBN 5-7245-0603-3 part 1, ISBN 5-7245-0408-1 part 2 (in Russian).

Molkov, V (2012). Fundamentals of hydrogen safety engineering, Part I and Part II.

# Maximum experimental safety gap

- **Maximum experimental safe gap** (MESG) of flammable gases and vapours is the lowest value of the safe gap measured according to IEC 60079-1-1 (2002) by varying the composition of the mixture. The safe gap is the gap width (determined with a gap length of 25 mm) at which in the case of a given mixture composition, a flashback just fails to occur.
- For hydrogen: the narrowest **MESG of 0.08 mm** to prevent flame propagation out of a shell, composed of two parts, through the gap between two flanges.
- Compare: MESG for **propane 0.92 mm**; for **petrol 0.96-1.02**.

Source: Molkov, V (2012). Fundamentals of hydrogen safety engineering, Part I and Part II.



# Hydrogen flame emissivity

- The max temperature hydrogen flame is  $\sim 2130^{\circ}\text{C}$ , but low radiant heat is produced. Firemen may not feel heat until almost in the flame.
- Petrol can produce carbon when it burns, so radiant heat can be felt from a great distance.
- Due to  $\text{CO}_2$  released when burning, ethanol produces twice the radiant heat as the same volume of petrol.
- Real hydrogen jet flame can be visible due to combustion of entrained particulates
- Radiation emitted from hydrogen flames is very low. The emissivity  $<0.1$  (ADL, 1960). Sandia National Laboratory (US) research: emissivity  $<0.3$ .
- Hydrocarbon flames have emissivity around 1.



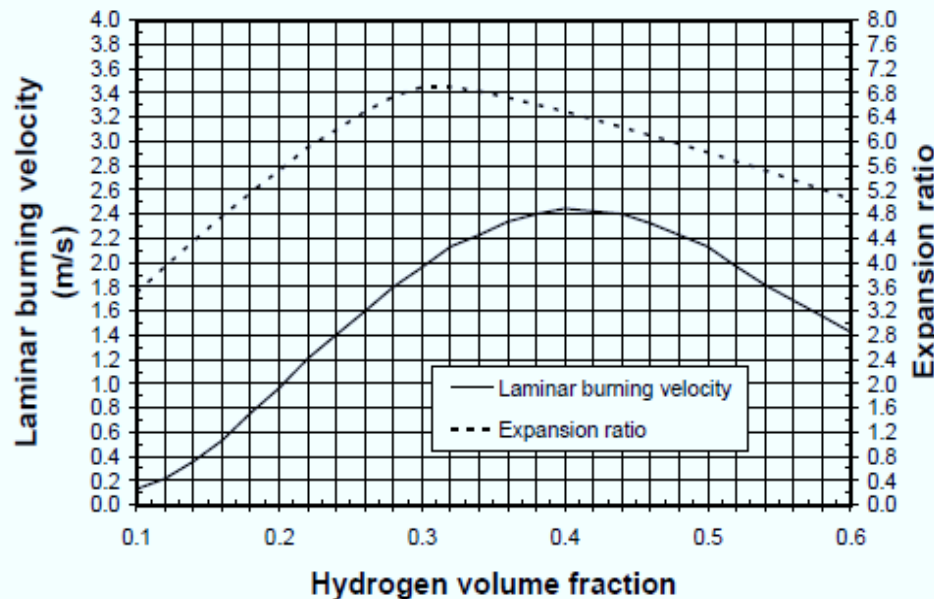
# Laminar burning velocity

- **Laminar burning velocity**  $S_u$  is the rate of flame propagation relative to the velocity of the unburnt gas that is ahead of it, under stated conditions of composition, temperature, and pressure of the unburnt gas.
- $E_i$  is the **expansion coefficient** (ratio) equal to the ratio of the unburnt mixture density to the density of combustion products at the same pressure.  $E_i=7.2$  for stoichiometric hydrogen-air mixture.
- The **laminar burning velocity** of a **stoichiometric** hydrogen-air mixture is **1.91 m/s**. This value is far greater compared to most of hydrocarbons when velocities are in the range 0.30-0.45 m/s.

Source: Molkov, V (2012). Fundamentals of hydrogen safety engineering, Part I and Part II.



# Laminar burning velocity: effect of hydrogen concentration



Sources:

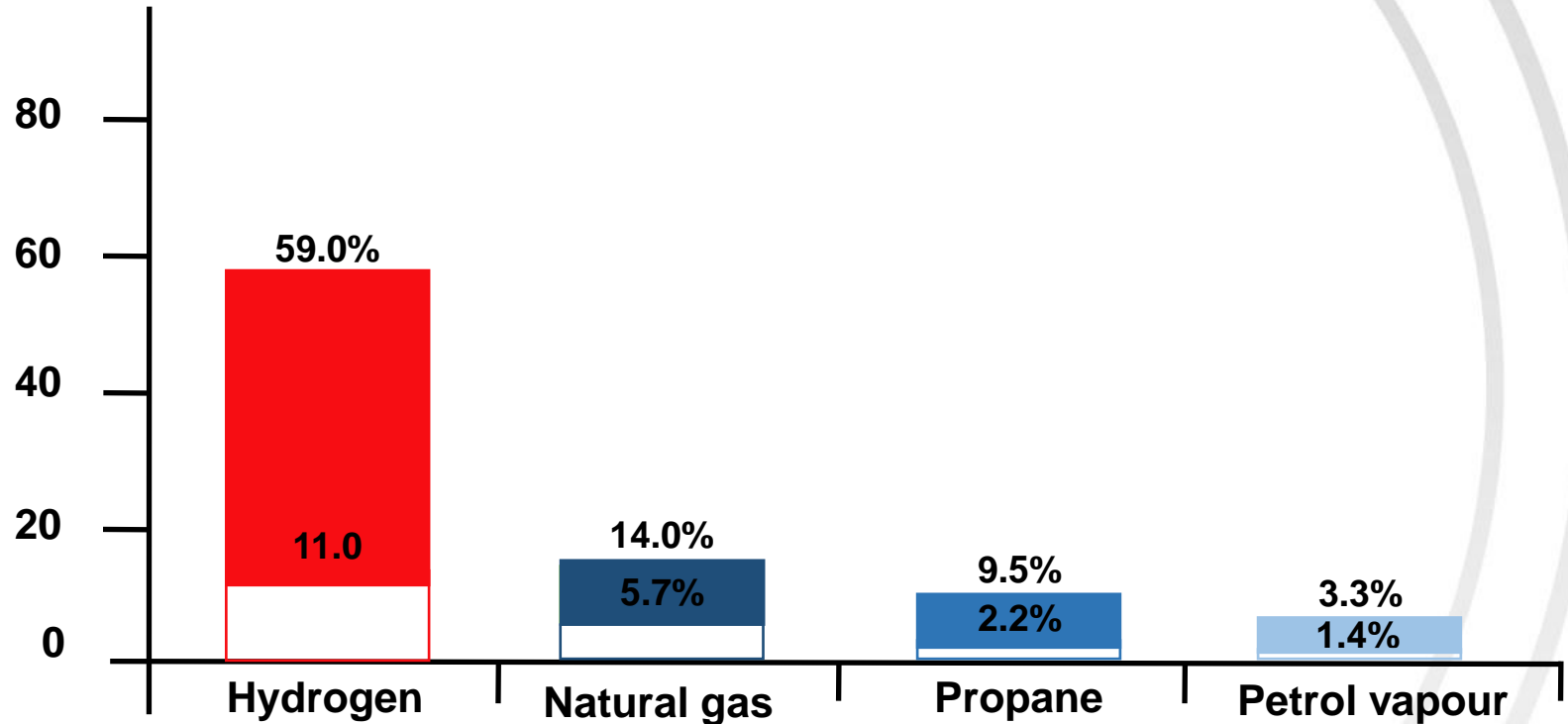
Lamoureux, N et al (2003). Experimental Thermal and Fluid Science. Vol. 27, pp. 385-393.

Molkov, V (2012). Fundamentals of hydrogen safety engineering, Part I and Part II.

- **Maximum expansion ratio  $E_i$**  at stoichiometric mixture (29.5 vol. %)
- **Maximum burning velocity  $S_u$**  for hydrogen-air mixture is reached not at stoichiometric mixture but in a rich mixture with **concentration of hydrogen 40.1 vol. %**, when it is **2.44 m/s**.
- This is due to the high molecular diffusivity of hydrogen, with the **diffusion coefficient** equal to  $6.1 \text{E-}05 \text{ m}^2/\text{s}$ .
- The maximum burning velocity for a hydrogen-air premixed flame occurs at an **equivalence ratio 1.6** while for hydrocarbon-air flames it occurs at around 1.1.

# Detonability range: hydrogen vs. conventional fuels

Hydrogen content in its mixture with air, vol. %



- ✓ This range (11- 59 vol. %) is narrower than and within the flammability range of 4-75 vol. %.
- ✓ The detonability limits are not fundamental characteristics of the mixture as they strongly depend on size of an experimental set up.





# Hydrogen flames quenching (1/2)

- **Quenching distance** is the maximum distance between two parallel plates that will extinguish a flame passing between the plates.
- **Quenching gap** is the spark gap between two flat parallel-plate electrodes, at which the ignition of combustible fuel-air mixtures is suppressed. The quenching gap is the passage gap dimension requirement to prevent propagation of an open flame through a flammable fuel-air mixture that fills the passage.

Source: Molkov, V (2012). Fundamentals of hydrogen safety engineering, Part I and Part II.

# Hydrogen flames quenching (2/2)

- Hydrogen flames are **difficult to quench**. For example, premixed hydrogen-air combustion can be made more severe by applying heavy sprays of water. This is due to an induced turbulence and an ability of the mixture to burn around the droplets.
- Hydrogen has the lowest **quenching distance** compared to other flammable gases.
- Usually quenching distance is reported as the minimum pipe diameter through which a premixed flame can pass. For example, technical report of ISO (ISO/TR 15916:2004) states that the quenching gap in air (NTP) for hydrogen is **0.64 mm**.
- The quenching distance decreases with increase of pressure and temperature, depends of mixture composition, etc.



Source:

ISO/TR 15916 (2004). Basic considerations for the safety of hydrogen systems. ISO Technical Committee 197  
Hydrogen Technologies.

# Micro-flames: typical flow rates

- ✓ A mass flow rate:  $\sim 10^{-9}$  kg/s (1  $\mu$ g/s).
- ✓ **Scenario:** a small leak burns undetected for a long period, damaging the containment system and providing an ignition source.
- ✓ SAE J2579 (2009): a localised hydrogen leak from a typical compression fitting cannot sustain a flame when mass flow rate is below 28  $\mu$ g/s.
- ✓ The lowest leak which may sustain a flame from a miniature burner configuration is 5  $\mu$ g/s.
- ✓ Hydrogen flows downward. The burner: stainless steel hypodermic tube; internal diameter 0.15 mm; outside diameter 0.30 mm. The flames and any glowing of the burner tip were not visible even in a darkened laboratory and hence were detected with a thermocouple (Lecoustre et al, 2010).
- ✓ These are the weakest self-sustaining steady flames ever observed (HRR 0.46 W)

Hydrogen diffusion micro-flames near their quenching limits



In air (flow  
rate: 3.9  $\mu$ g/s)

In oxygen



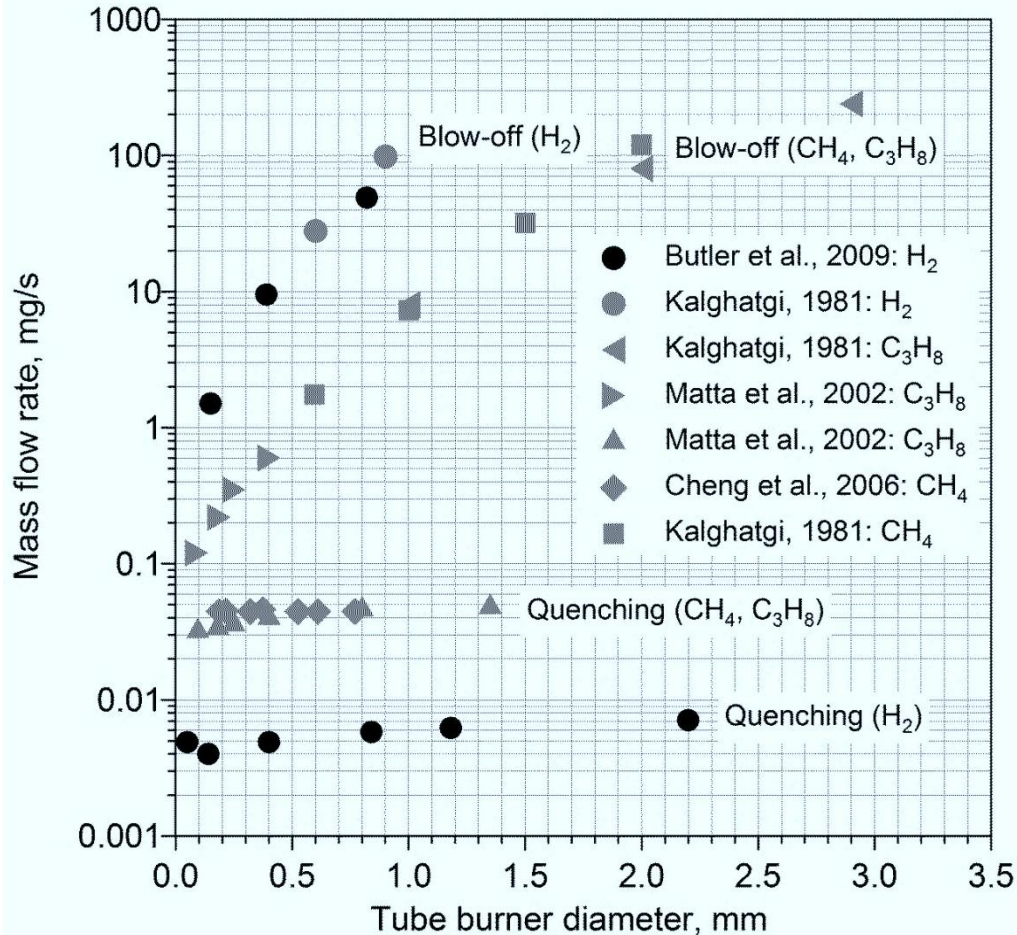
HyResponse

Sources:

SAE J2579 (2009). Technical information report for fuel systems in fuel cell and other hydrogen vehicles.

Lecoustre, VR et al (2010). Combustion and Flame. Vol. 157, pp. 2209-2210.

# Quenching and blow-off limits

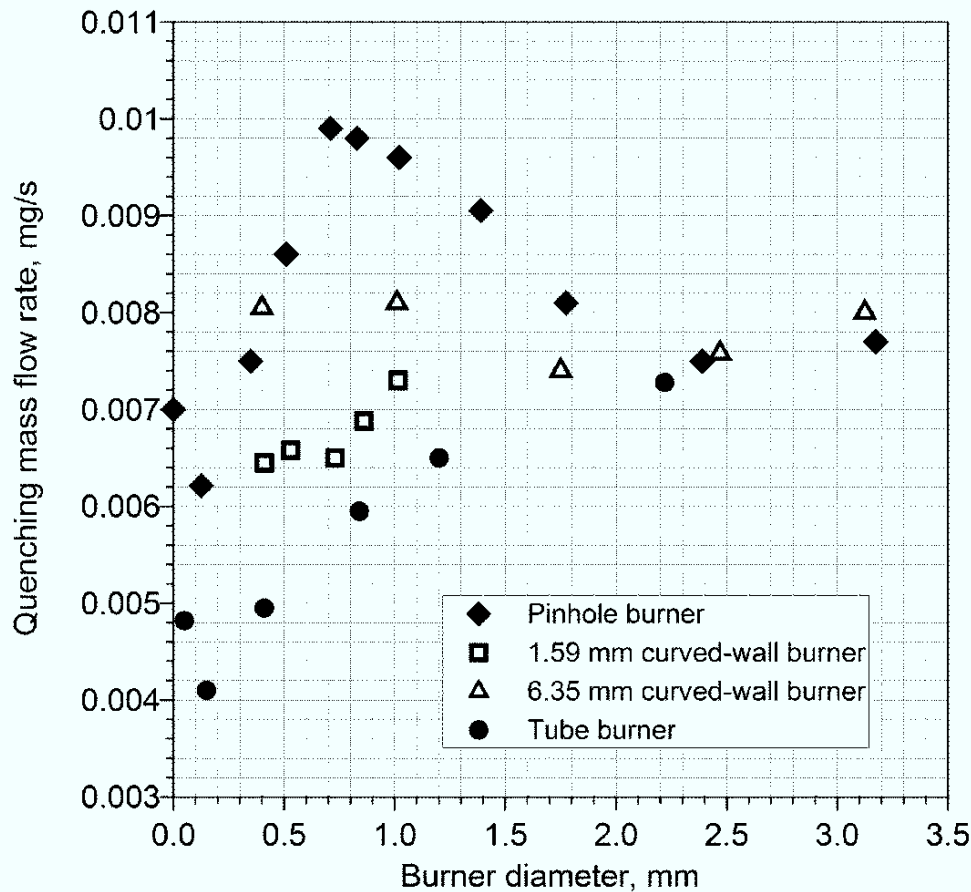


- A limited range of flow rates for, which a flame can be established on the present burners.
- Below this range, the flow is said to be below **the quenching limit**.
- Quenching occurs when there is too much heat loss for combustion to be sustained.
- On the other extreme, **blow-off limit** occurs when the flow rate is reached, beyond which the flame blows off the burner.
- Quenching and blow-off limits bound the leak flow rates that can support combustion.
- Depend on the tube diameters.

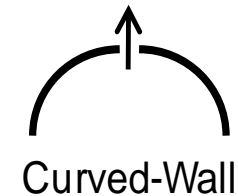


Source: Sunderland, PB (2010). Proceedings of the 8th International Short Course and Advanced Research Workshop in the series "Progress in Hydrogen Safety".

# Round burners and quenching limit

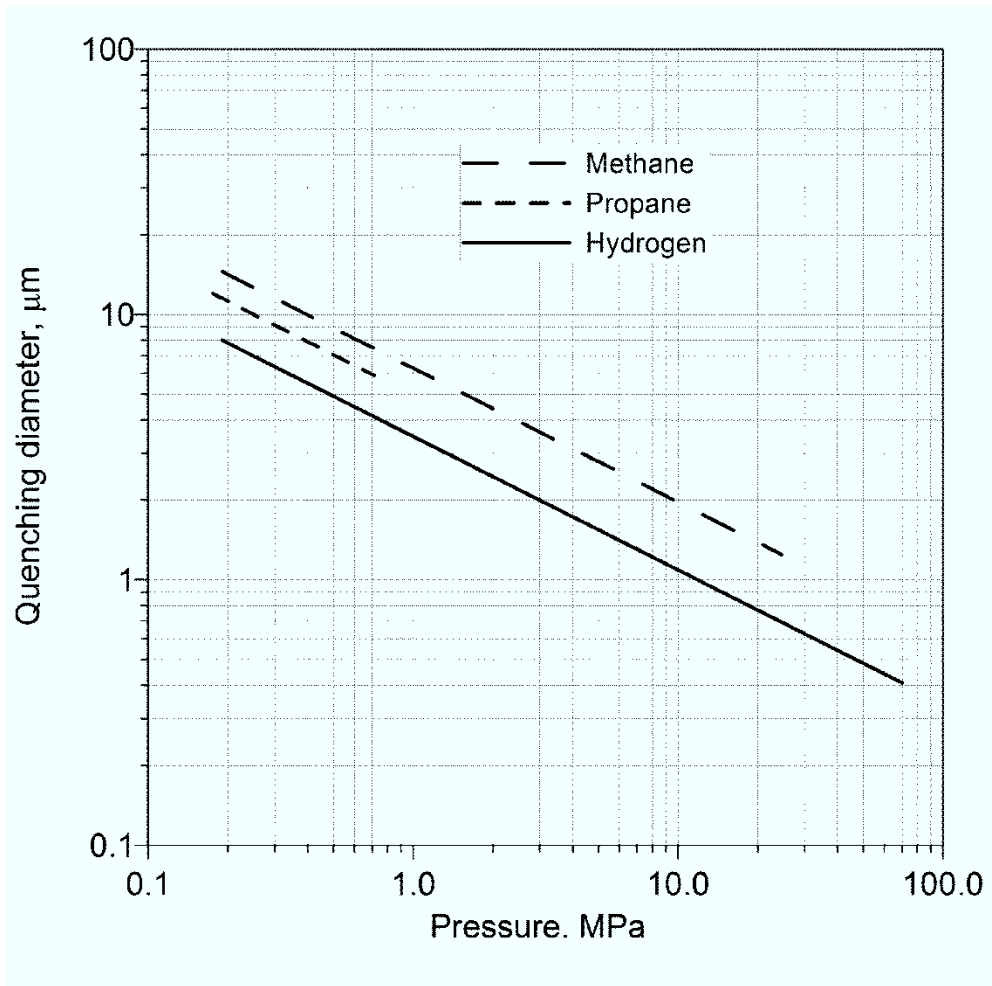


● Dependence on the diameters of a burner.





# Quenching diameter as a function of pressure

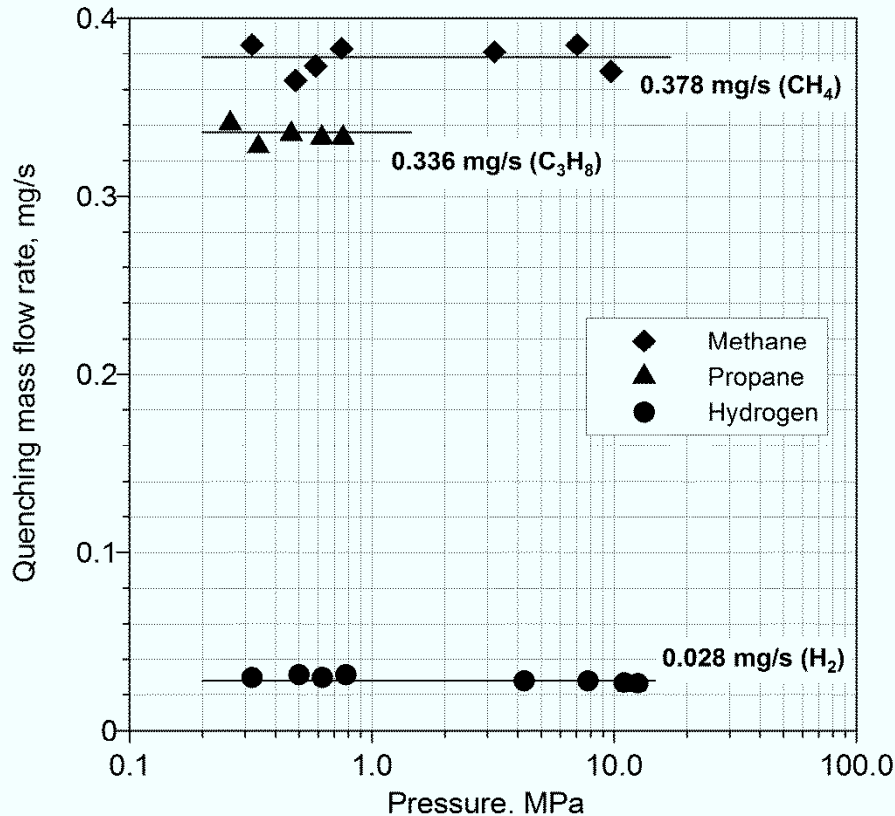


- At storage pressure of **69 MPa** a hole diameter of just **0.4  $\mu\text{m}$**  is predicted to support a flame.

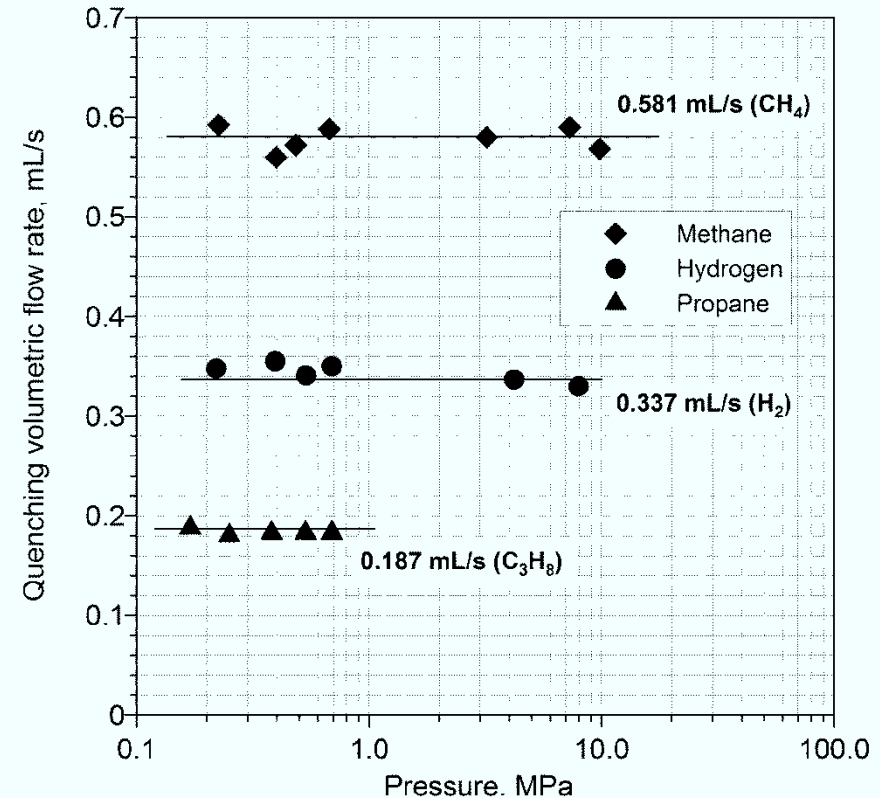


# Leaky fittings

## Quenching mass flow rate limit (Butler et al, 2009)

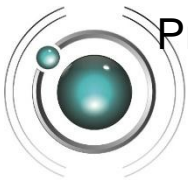


## Quenching volumetric flow rate (Sunderland, 2010)



Hydrogen has the lowest mass flow rate necessary to sustain fittings micro-flames.

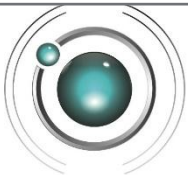
Propane has the lowest volumetric flow rate to sustain fittings micro-flames.





# Hydrogen *versus* conventional fuels

	Hydrogen	Natural gas	Petrol
Colour	No	No	Yes
Toxicity	None	Some	High
Odour	Odourless	Mercaptan*	Yes
Buoyancy relative to air	14 times lighter	2 times lighter	3.75 times heavier
Energy by weight	2.8 times more than petrol	~1.2 times more than petrol	43 MJ/kg
Energy by volume	4 times less than petrol	1.5 times less than petrol	120 MJ/Gallon



# Comparison of hydrogen with traditional fuels

	Hydrogen	Natural gas	Petrol vapour
Flammability range in air (LFL – UFL), vol. %	4.1 - 75	5.3 - 15	0.8 - 8.1
Detonability range in air (LDL – UDL), vol. %	11 - 59	5.7 - 14	1.4 - 3.3
Stoichiometric mixture in air, vol. %	29.6	9	2
Flame temperature (°C)	2,130	1,961	1,977

# Conclusions

- Hydrogen is not more (or less) dangerous than any other conventional fuel.
- Hydrogen has a unique set of properties and characteristics.
- Hydrogen safety fully depends on **how professionally it is handled** at the designed stage and afterwards.
- Hydrogen is getting out of hands of trained professionals in industry and become everyday activity for public (700 bar). This implies **a new safety culture**, innovative safety strategies, and breakthrough engineering solutions.
- It is expected that the level of safety at the consumer interface with hydrogen must be similar or exceeds that present with fossil fuel usage.



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