Hydrogen properties relevant to safety

European Hydrogen Train the Trainer Programme for Responders

Hydrogen properties relevant to safety

Content

Hydrogen properties relevant to safety

Objectives of the lecture (1/2)

1. Understand the effect of atomic and molecular structure on safety considerations for hydrogen storage and handling;
2. Interpret the phase diagram of hydrogen and identify its three aggregate states;
3. Recognise physiological hazards associated with GH_2 (asphyxiation) and LH_2 (cryogenic burns, frostbite, hypothermia, lung damage from inhalation of cold vapours);
4. Relate the low vapour density of GH_2 to the buoyancy as a main safety asset;
5. Explain hydrogen combustion process and its main attributes;
6. Indicate stoichiometric concentrations and flammability range for hydrogen-air and hydrogen-oxygen mixtures;
7. Explain the effect of different factors (temperature, pressure, direction of flame propagation, diluents and inhibitors, etc.) on flammability of hydrogen;

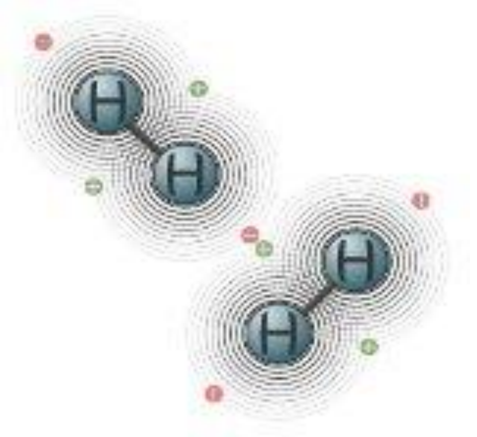
Hydrogen properties relevant to safety

Objectives of the lecture (2/2)

8. Define the main ignition properties: minimum ignition energy, auto-ignition temperature, adiabatic flame temperature, flash point, minimum experimental safety gap, laminar burning velocity;
9. Compare the detonability limits of hydrogen to those of common fuels and to hydrogen flammability range;
10. Describe hydrogen microflames and hydrogen flames quenching parameters (quenching distance; quenching gap; quenching limits; blow-off limits)
11. Relate physical, chemical, ignition and combustion properties to hydrogen hazards/hazardous phenomena (leaks, fires, explosions);
12. Explain the differences (and similarities) in physical properties/combustion characteristics/ignition parameters between hydrogen and common fuels.

Hydrogen properties relevant to safety

Atomic and molecular hydrogen

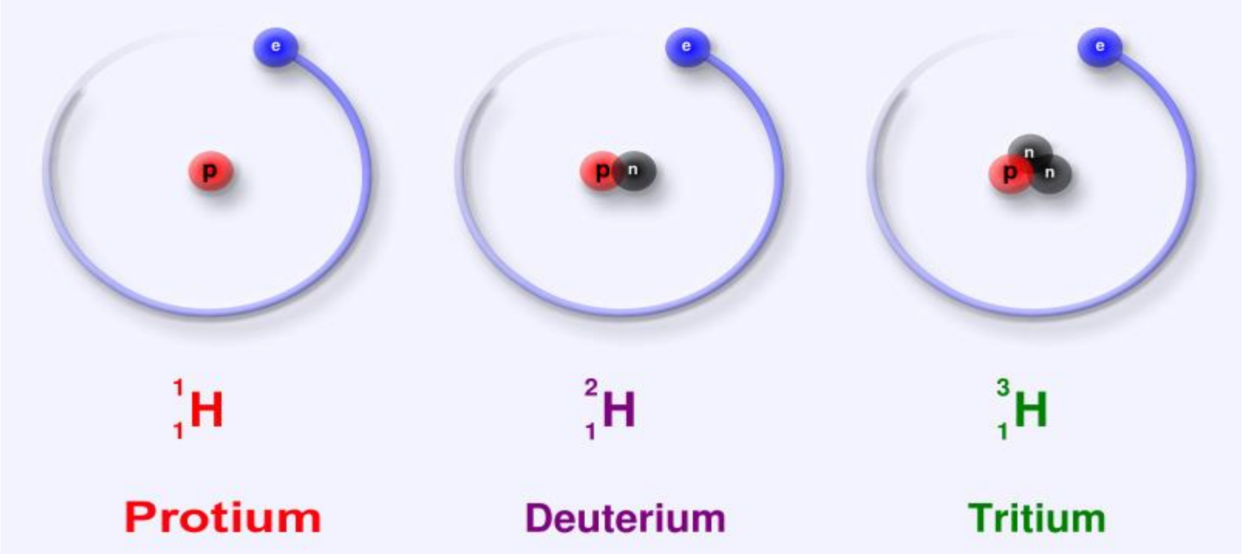


- The most abundant isotope (more than 99.98%) is protium $^{1}_{1}H$
- Hydrogen atom consists of 1 proton and 1 electron
- Hydrogen is **the lightest known element**
- It is not present in a free state in the atmosphere of the Earth; it is present in a free state in the sun and stars
- Hydrogen gas: stable **molecules made of two hydrogen atoms 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.
- A video on Youtube https://www.youtube.com/watch?v=6rdmpx39PRk

Google: free images

Hydrogen properties relevant to safety

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: 2015).

Hydrogen properties relevant to safety

Ortho-para hydrogen conversion

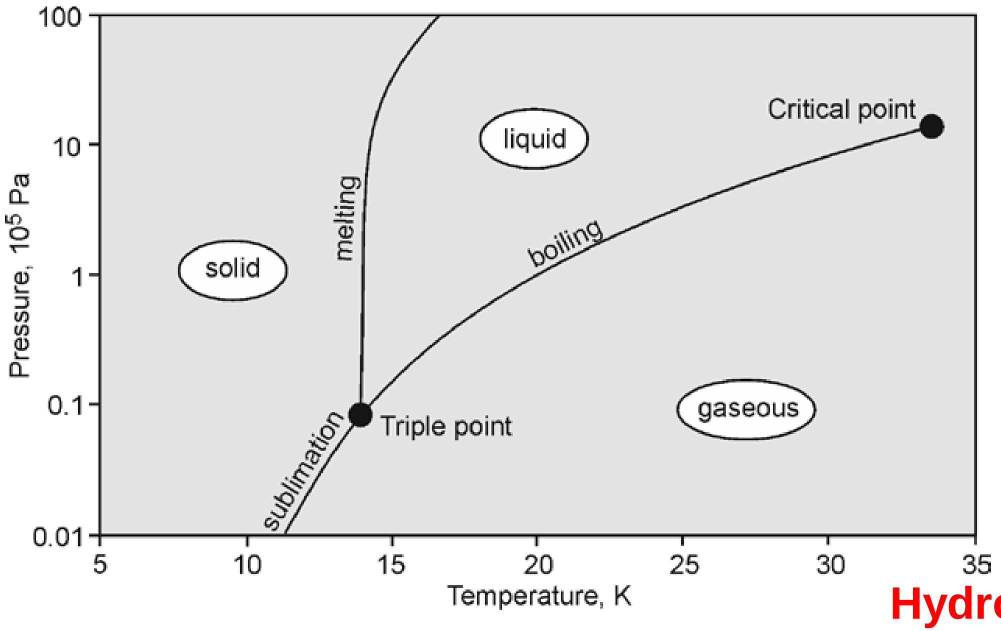
- The ortho-para hydrogen conversion is accompanied by a **release of heat**, 703 kJ/kg at 20 K for ortho- to para-hydrogen conversion, or 527 kJ/kg for normal to para-hydrogen conversion (NASA, 1997).
- The process of hydrogen liquefaction includes the removal of the energy released by the ortho-para state conversion. The heat of conversion is 715.8 kJ/kg, which is1.5 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.

Hydrogen properties relevant to safety

Phase diagram of hydrogen

Hydrogen, slush

- A mixture of solid and liquid hydrogen at the triple point temperature.
- Melting point : -259.2 °C



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

Note: absolute zero temperature of 0 K (-273.15 ^{o}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 K (-240^{o}C) and p=1.3 MPa. The highest temperature, at which a hydrogen gas can be liquefied.

No liquid phase in storage vessels containing compressed hydrogen gas

Hydrogen, gas

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

Hydrogen properties relevant to safety

Liquid hydrogen (LH_2)

- 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_2 (at NBP) has a density of 70.78 kg/m^3.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_2, at NBP is 23 times that of water for ambient conditions. Upon heating LH_2 expands significantly.
- Every cubic meter of water (H_2O) 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 properties relevant to safety

Hydrogen expansion ratio

- Volumetric ratio of **LH_2 to GH_2** is **1:848**. Need for LH_2 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 ($LH_2 \rightarrow GH_2$) 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.

https://www.iso.org/standard/56546.html

Hydrogen properties relevant to safety

LH_2 : safety issues (1/3)

- LH_2 will rapidly boil or flash to a gas if exposed to or spilled into environment with normal temperature. Warming LH_2 to ambient temperature can lead to very high pressures in confined spaces.
- All gases, except helium, will be condensed and solidified at -250 ^{o}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_2 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.

Hydrogen properties relevant to safety

LH_2 : safety issues (2/3)

Video of LH_2 spill

https://www.youtube.com/watch?v=nZ7Aga7tt2A&list=PLlphoM9ggM3Rf-Npmdq0S3WrCSpx0U4SL&index=10

Effect of wind on LH_2 spill

https://www.youtube.com/watch?v=pD_OrWVJaW4&list=PLlphoM9ggM3Rf-Npmdq0S3WrCSpx0U4SL&index=11

Hydrogen properties relevant to safety

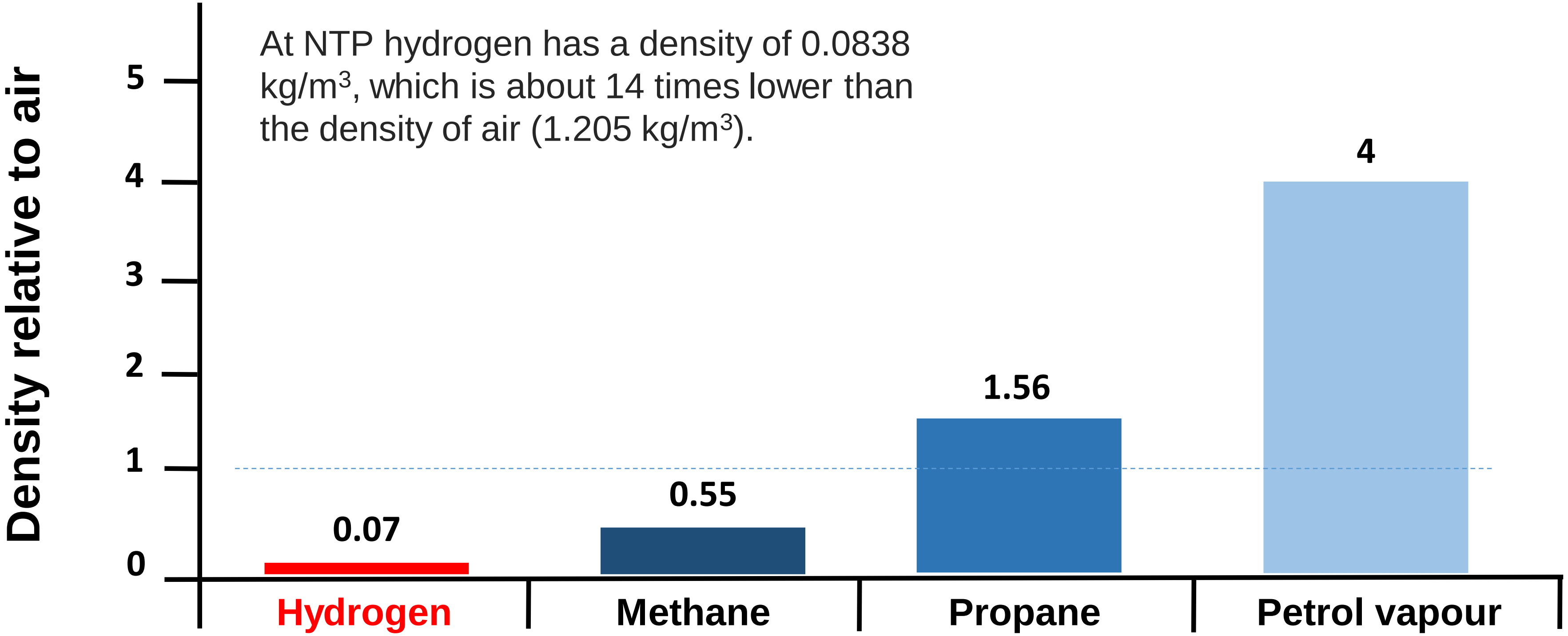
LH_2 : safety issues (3/3)

- Outside of the LH_2 system, insufficiently insulated pipes and vessels containing LH_2 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_2 have to be periodically warmed and purged to keep the accumulated oxygen content in the vessel to less than 2% (ISO/TR 15916: 2015).
- Caution should be exercised if carbon dioxide (CO_2) is used as a purge gas. It may be difficult to remove all CO_2 from the system low points where it can accumulate.

Hydrogen properties relevant to safety

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.**



At NTP hydrogen has a density of 0.0838 kg/m^3, which is about 14 times lower than the density of air (1.205 kg/m^3).

Hydrogen properties relevant to safety

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 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.

Hydrogen properties relevant to safety

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.

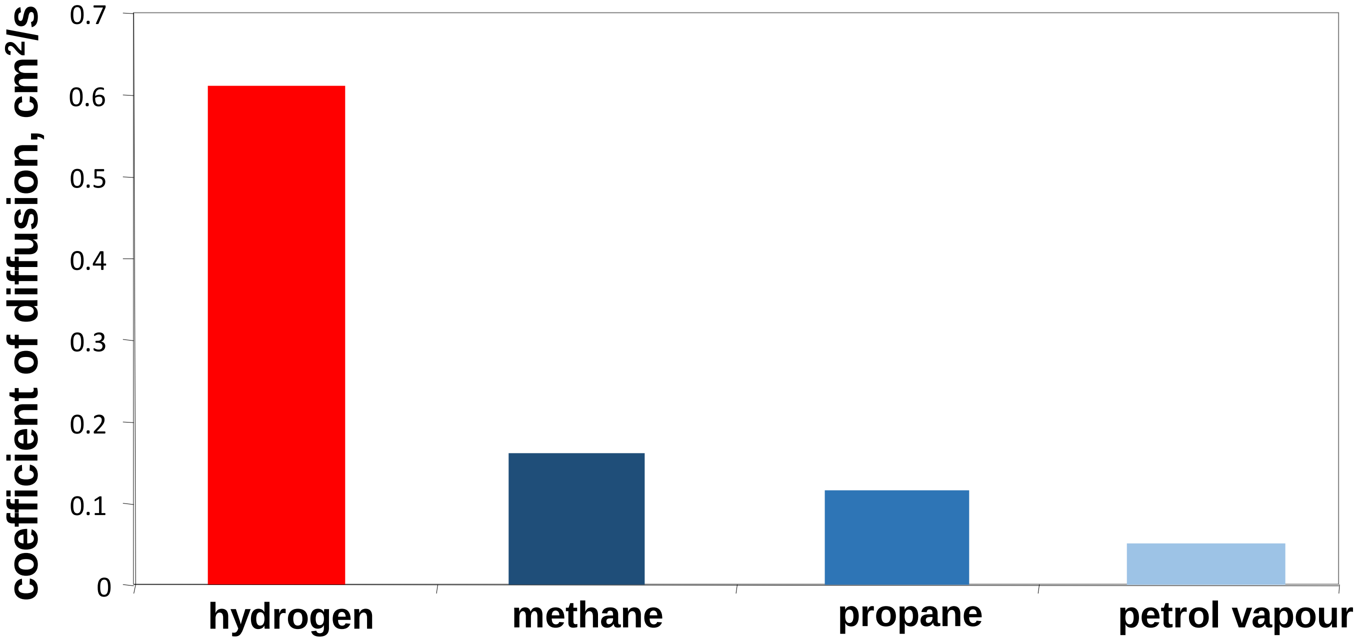
Buncefiled fire: Google images

Source: [1] Health and Safety Executive (1975) The Flixborough Disaster: Report of the Court of Inquiry, HMSO, ISBN 0113610750,1975.
[2] Buncefield Investigation (2010) The Buncefield Major Incident Investigation Board. Available from: http://www.hse.gov.uk/comah/buncefield/miib-final-volume1.pdf.

Hydrogen properties relevant to safety

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. GH_2 also readily diffuses through solids. For example, effective diffusion coefficient of hydrogen through gypsum panels is 1.4E-05 m^2/s at room temperature (Molkov, 2012).



Hydrogen properties relevant to safety

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_2: 89.48 μPoise (NTP) and 11.28 (NBP)

LH_2: 132.0 μPoise (NBP)

- **Specific heat and specific heat ratio**

The heat capacity of GH_2 is similar to that of other diatomic gases despite its low molecular mass.

Specific heat at constant pressure ($c_{p,}$ J/kg/K):

GH_2:14.85 (NTP), 14.304 (STP), 12.15 (NBP).

LH_2: 9.66 (NBP)

Specific heat ratio (γ):

GH_2: γ=1.39 (NTP) and γ=1.405 (STP)

- **Thermal conductivity**

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

GH_2: 0.187 W/m/K (NTP) and 0.0169 W/m/K (NBP).

LH_2: 0.09892 W/m/K (NBP).

- **Speed of sound**:

GH_2: 1,294 m/s (NTP) and 355 m/s (NBP)

LH_2:1,093 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

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

Hydrogen properties relevant to safety

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.

Hydrogen properties relevant to safety

Combustion of hydrogen

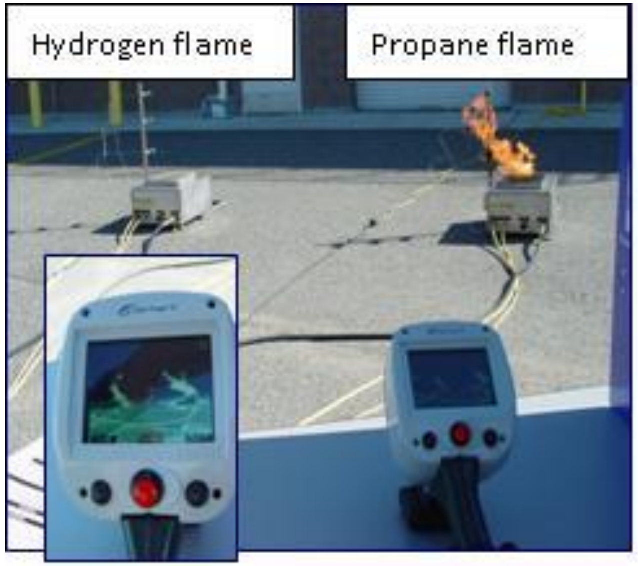
- At NTP hydrogen is a **not very reactive substance**, unless it has been activated with a catalyst.
- **Reaction of hydrogen with oxygen** (forming water) at ambient temperature is extraordinarily slow. However, if the reaction is accelerated by a catalyst or a spark, it proceeds with high rate.

hydrogen + oxygen → water + *energy*

$$H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2O + E$$

- Hydrogen is a combustible gas

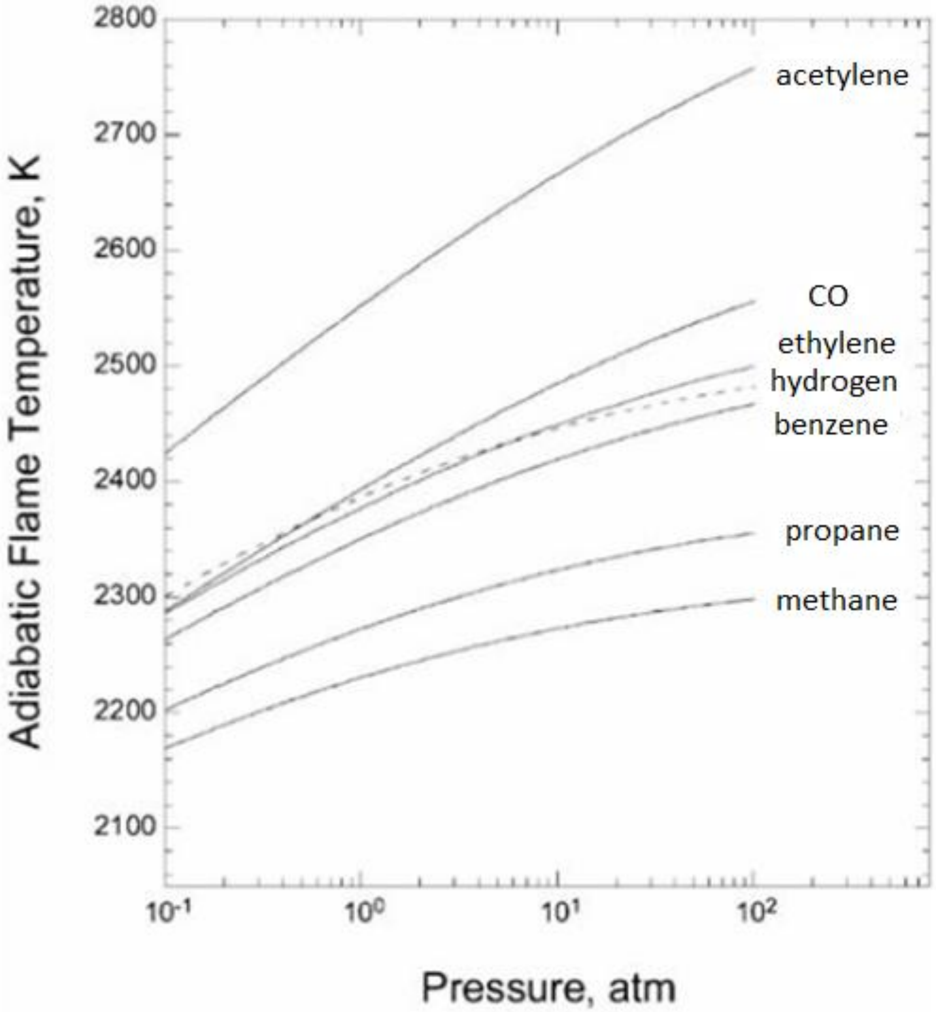
- Pure hydrogen burns with a pale-blue flame invisible in a daylight. On burning with air it forms water.
- Hydrogen produces low radiant heat upon combustion.



Source: H2BestPractices.

Hydrogen properties relevant to safety

Adiabatic flame temperature



Hydrogen properties relevant to safety

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_2) and 79 vol. % nitrogen (N_2):

$$2H_2 + (O_2 + 3.76N_2) = 2H_2O + 3.76N_2$$

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

$$2H_2 + O_2 = 2H_2O$$

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

Hydrogen properties relevant to safety

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**
Higher Heating Value (25 ^{o}C, 0.101 MPa), kJ/g	141.86	55.53	50.36	47.5
Lower Heating Value (25 ^{o}C, 0.101 MPa), kJ/g	119.93	50.02	45.6	44.5

Sources:
BRHS, Biennial Report on Hydrogen Safety (2009). The European network of excellence "Safety of hydrogen as an energy carrier" (NoE HySafe). Available from: www.hysafe.org
CoD, College of the Desert (2001). Hydrogen Fuel Cell Engines and Related Technologies, Module 1: Hydrogen Properties. Energy Technology Training Center, College of the Desert. Available from: http://www.hydrogensafety.info/resources/courseManual.asp.

Hydrogen properties relevant to safety

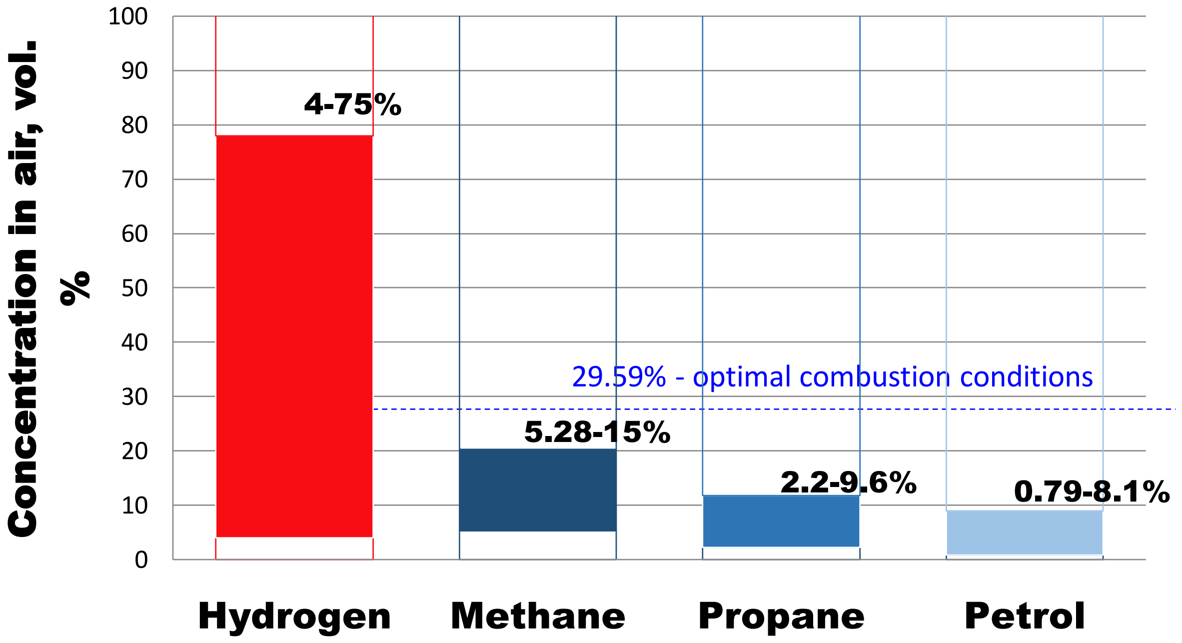
Limiting Oxygen Index

- 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). **$LOI_{H2} = 5$**

Hydrogen properties relevant to safety

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.

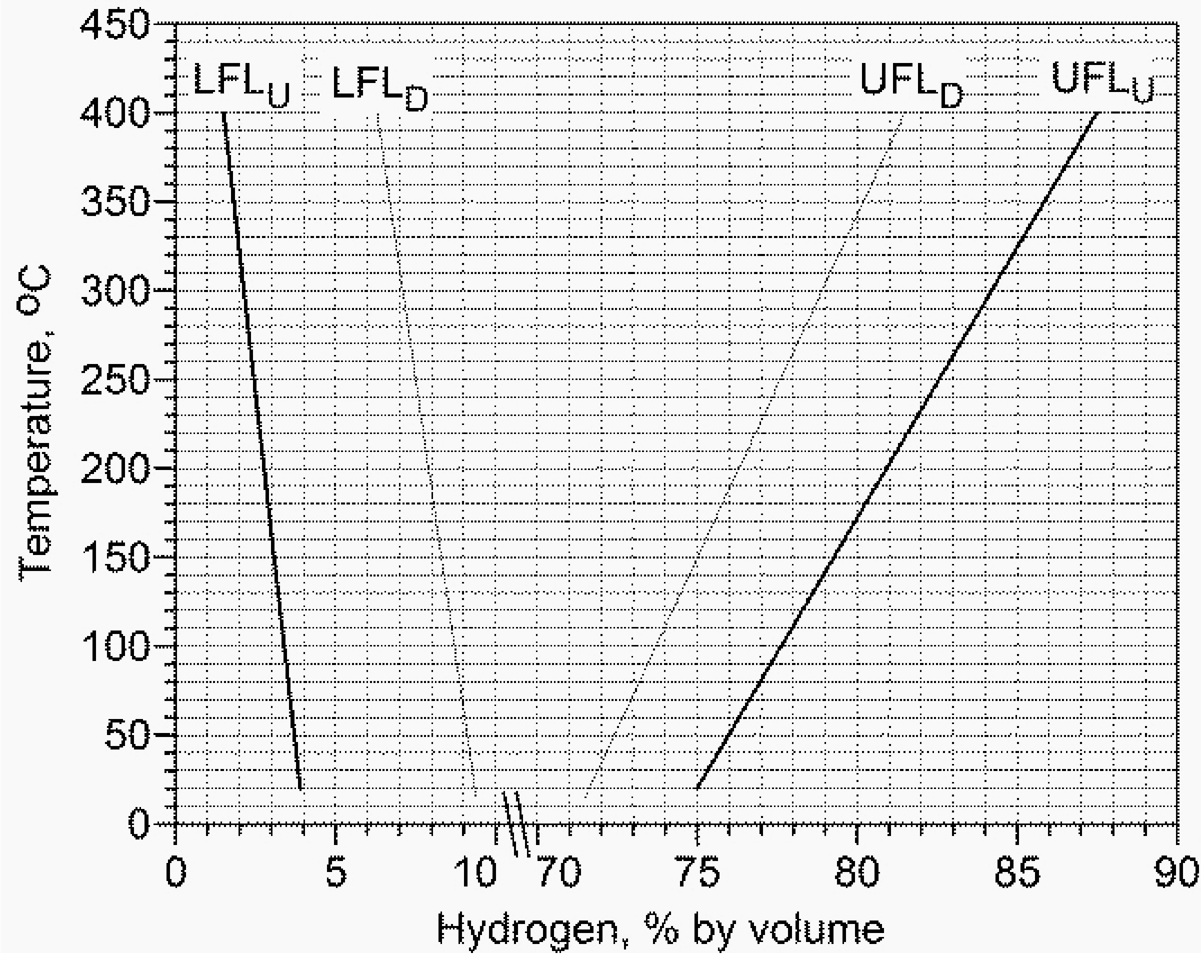


Source: Molkov, V (2012). Fundamentals of hydrogen safety engineering, Part I and Part II.

- 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.

Hydrogen properties relevant to safety

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^{o}C to 400^{o}C, whilst **UFL increases** more significantly - by about 12.5 vol. % for the same change of mixture temperature.

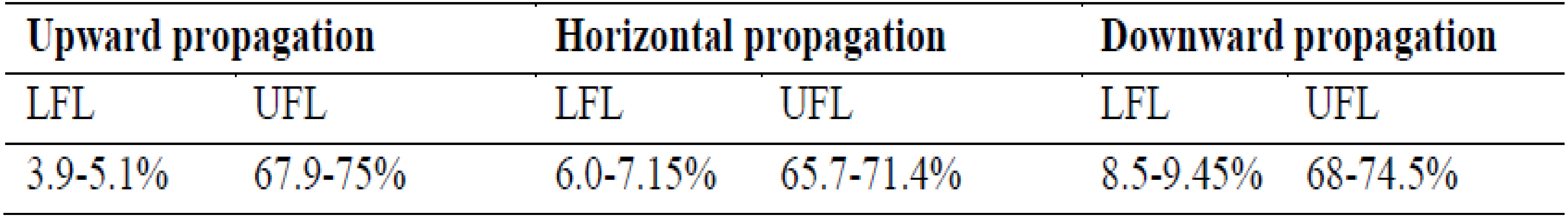
Sources:
Molkov, V (2012). Fundamentals of hydrogen safety engineering, Part I and Part II.
Coward, HF and Jones, GW (1952). Limits of flammability of gases and vapors, Bulletin 503, Bureau of Mines, p. 155.

Hydrogen properties relevant to safety

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)).



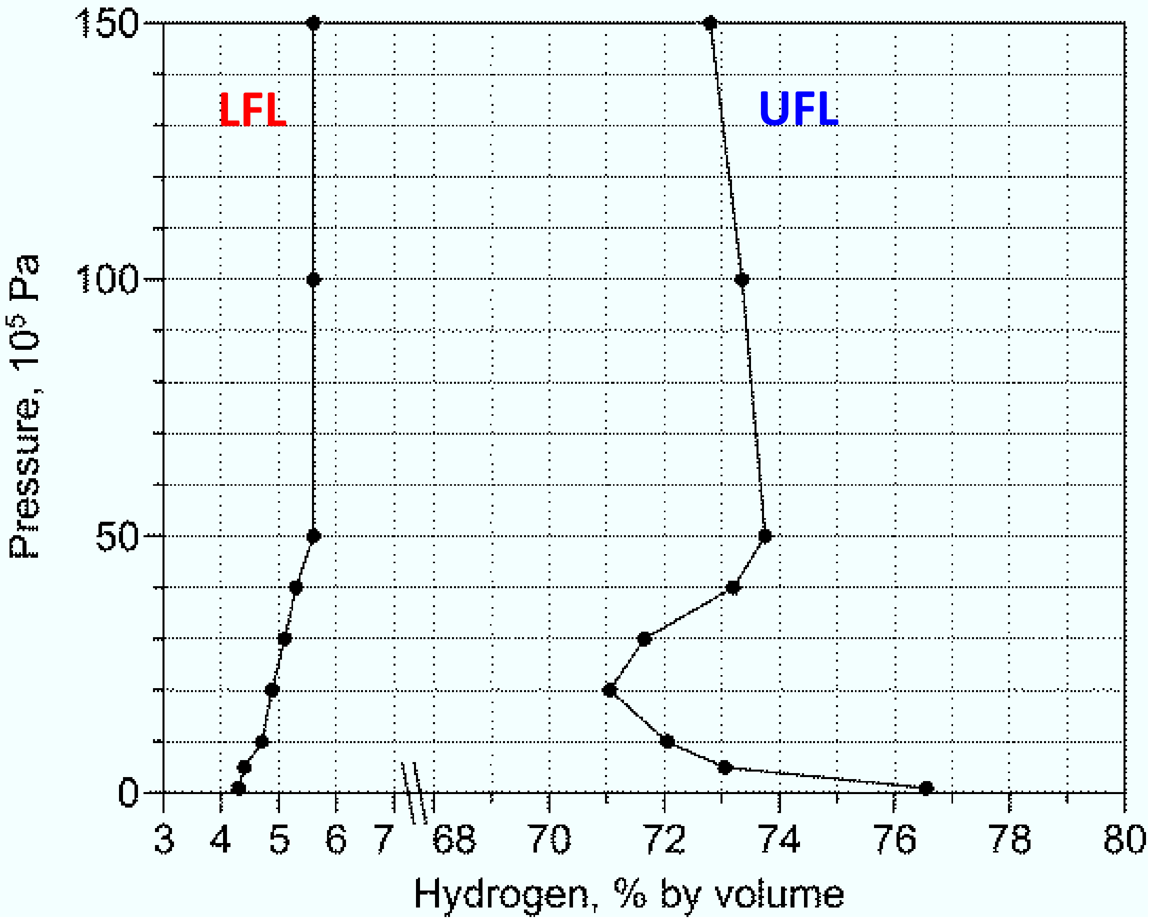
Upward propagation		Horizontal propagation		Downward propagation	
LFL	UFL	LFL	UFL	LFL	UFL
3.9-5.1%	67.9-75%	6.0-7.15%	65.7-71.4%	8.5-9.45%	68-74.5%

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.

Hydrogen properties relevant to safety

Effect of pressure on flammability range

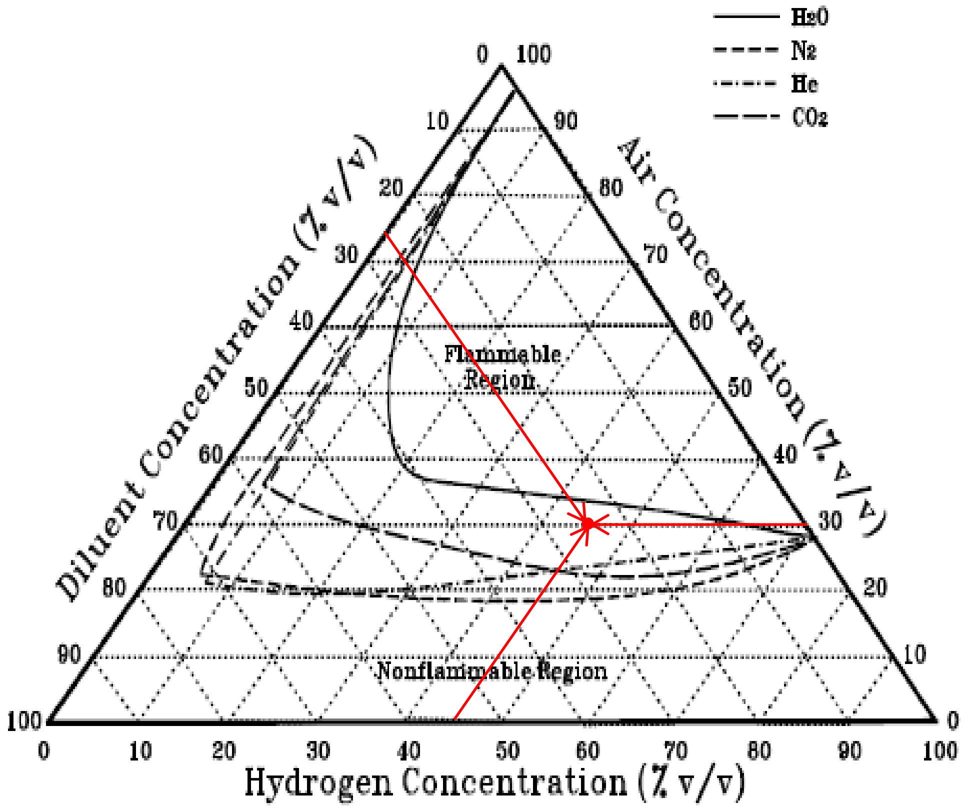
- **LFL increases** to 5.6 vol. % if pressure rises from 0.1 to 5.0 MPa and then it remains constant up to pressure of 15 MPa.
- **UFL changes not monotonically**. It decreases from 76.6 to 71 vol. % as pressure rises from 0.1 to 2.0 MPa; then UFL increases from 71 to 73.8 vol. % with pressure increase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

Hydrogen properties relevant to safety

Effect of diluents on flammability range



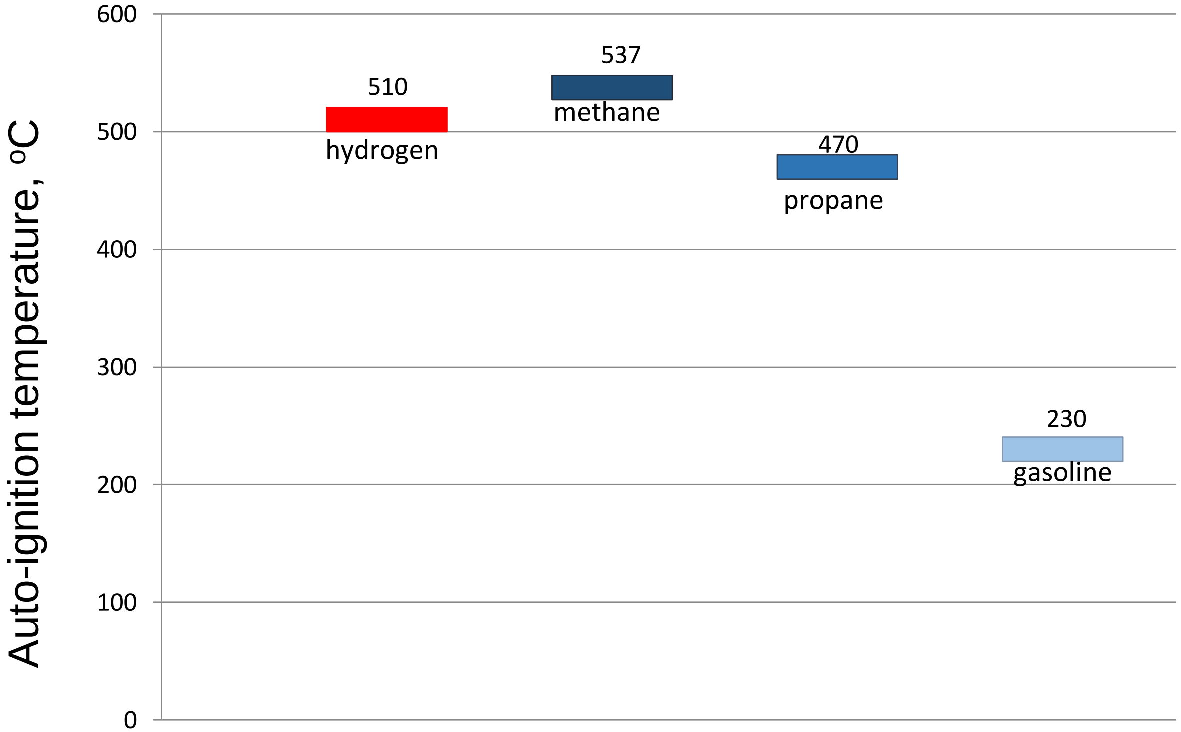
Effects of N_2, He, CO_2, and H_2O diluents on flammability limits of hydrogen in air at 101.3 kPa (NASA, 1997).

- Mixture: 45% of hydrogen, 30% of air and 25% of diluent
- For CO_2, He and N_2 mixture flammable
- For H_2O mixture is non-flammable

Hydrogen properties relevant to safety

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.



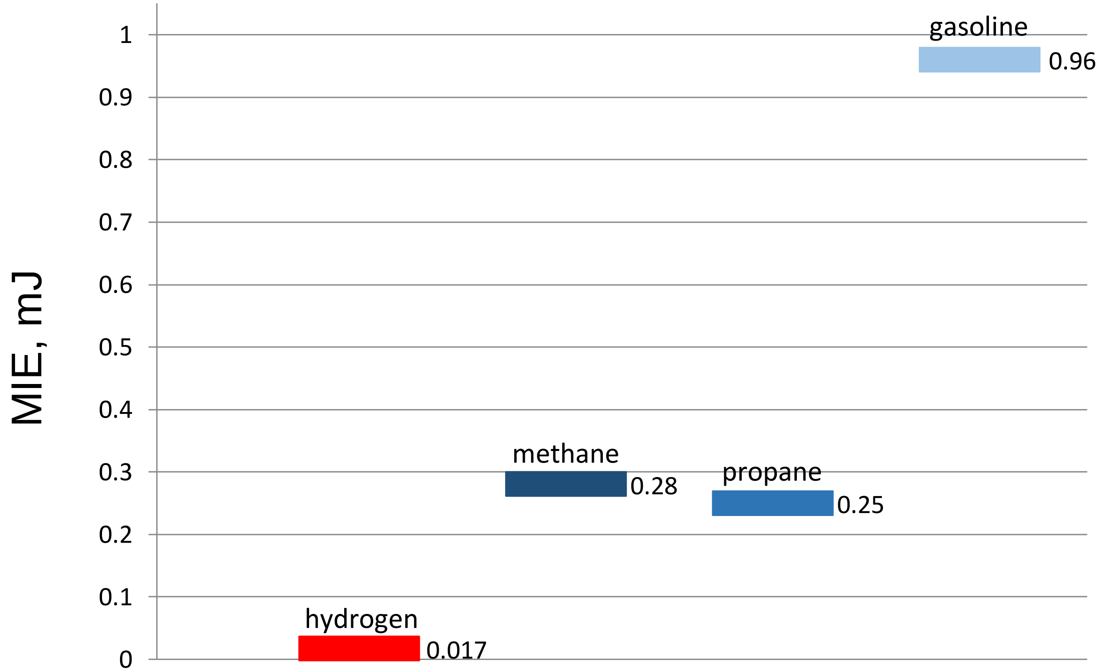
Note: Gasoline in North America = Petrol elsewhere

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

Hydrogen properties relevant to safety

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.

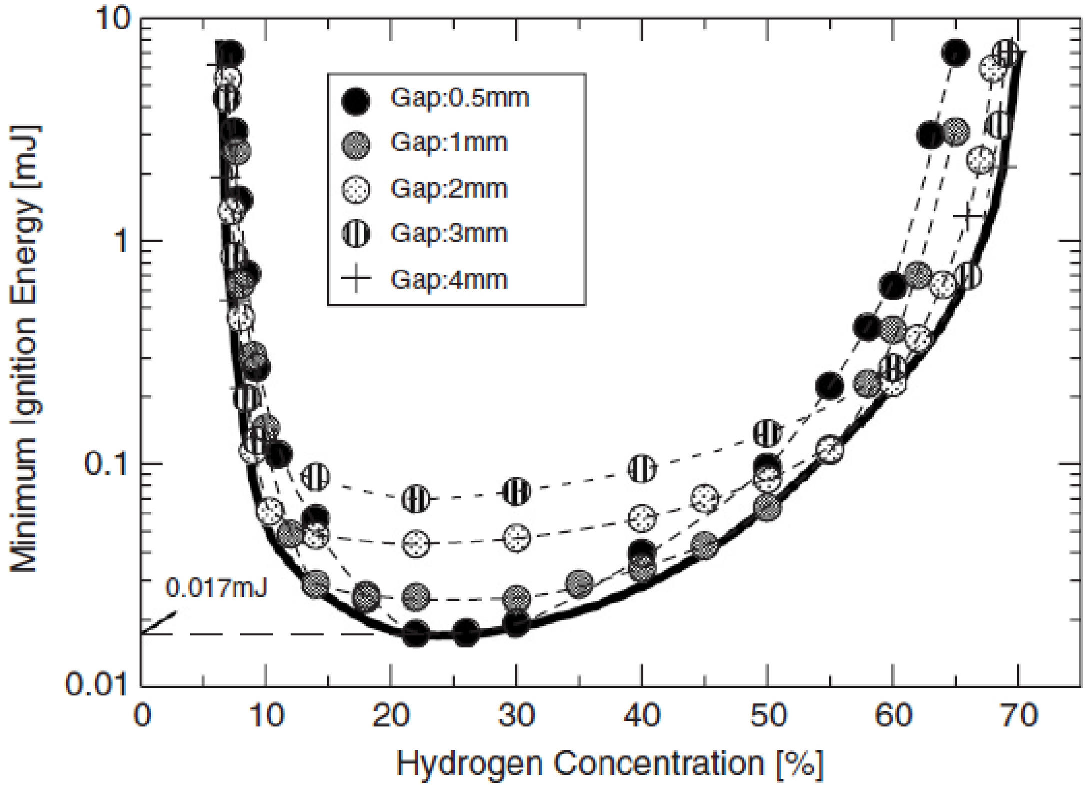


Note: Gasoline in North America = Petrol elsewhere

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

Hydrogen properties relevant to safety

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.

Hydrogen properties relevant to safety

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.

Hydrogen properties relevant to safety

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 properties relevant to safety

Hydrogen flame emissivity

- The max temperature hydrogen flame is ~ 2130 °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 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.

Videos: 1. Hydrogen explosion in slow motion 2. Hydrogen bubbles

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

Hydrogen properties relevant to safety

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.

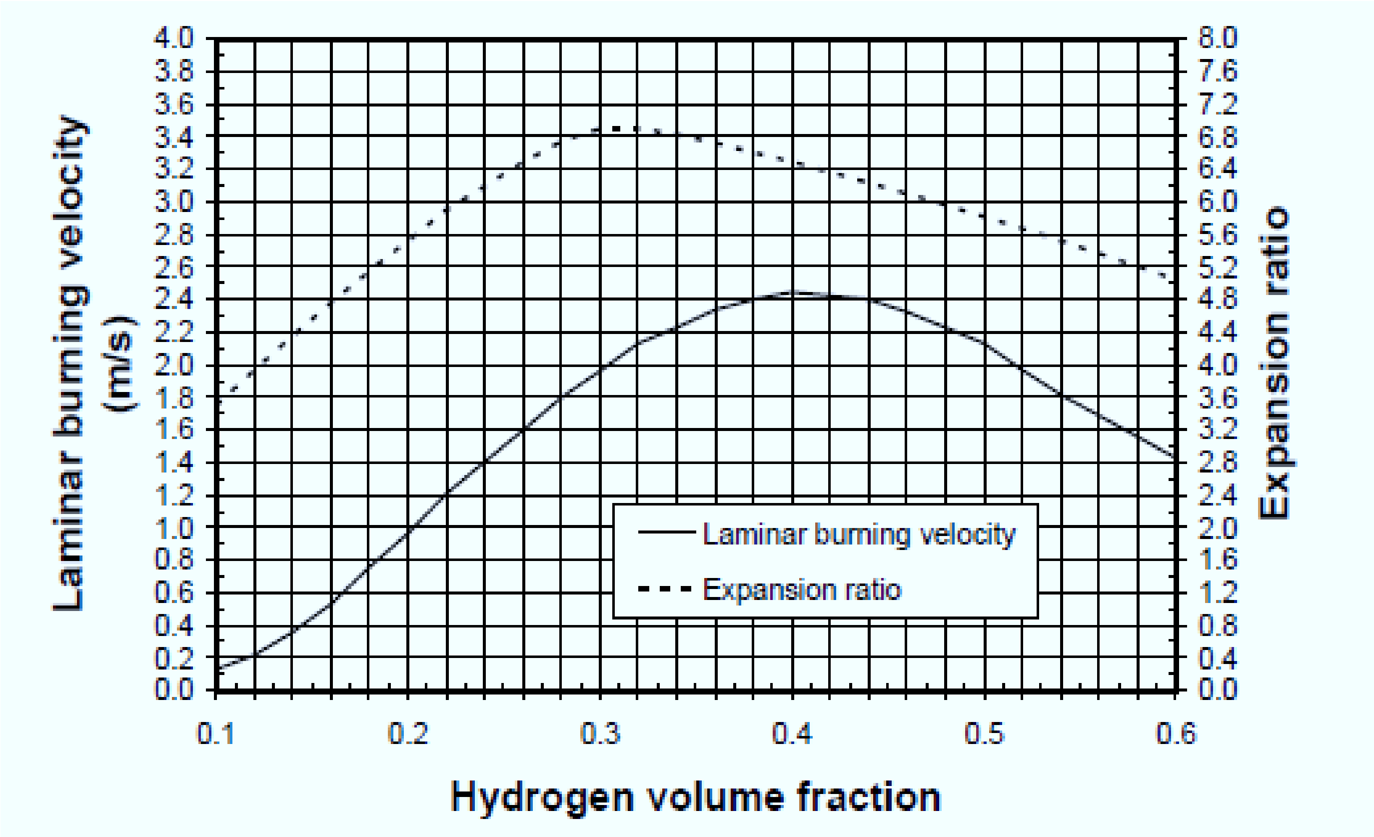
- E_i is the **expansion coefficient** (ratio) equal to the ratio of the unburnt mixture density to the density of combustion products at the same pressure. $E_i=7.2$ for stoichiometric hydrogen-air mixture.

- 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.

Hydrogen properties relevant to safety

Laminar burning velocity: effect of hydrogen concentration

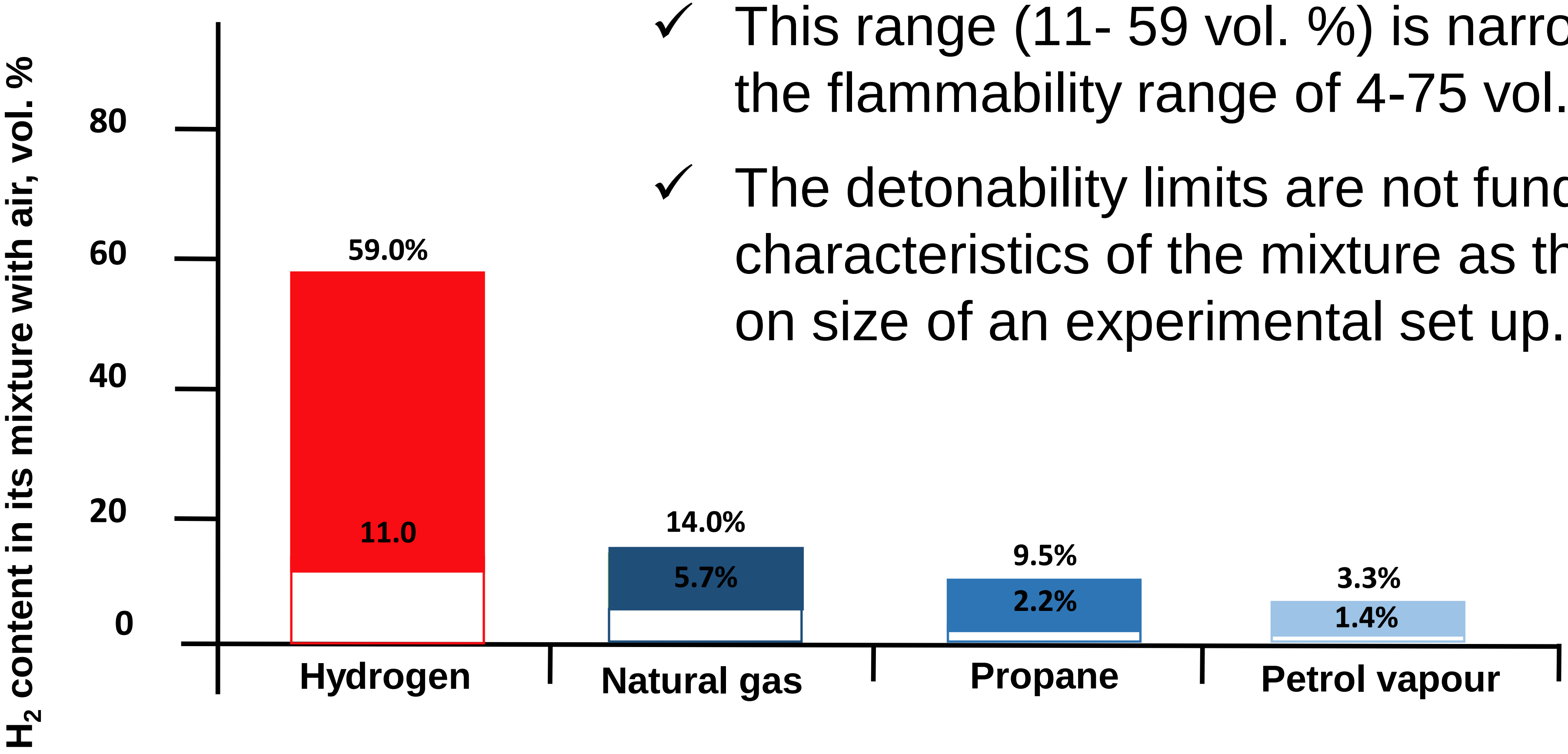


Sources:
Lamoureux, N et al (2003). Experimental Thermal and Fluid Science. Vol. 27, pp. 385-393.
Molkov, V (2012). Fundamentals of hydrogen safety engineering, Part I and Part II.

- **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 reach 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 6.1E-05 m^2/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.

Hydrogen properties relevant to safety

Detonability range: hydrogen vs. conventional fuels



- ✓ 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 properties relevant to safety

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 properties relevant to safety

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.

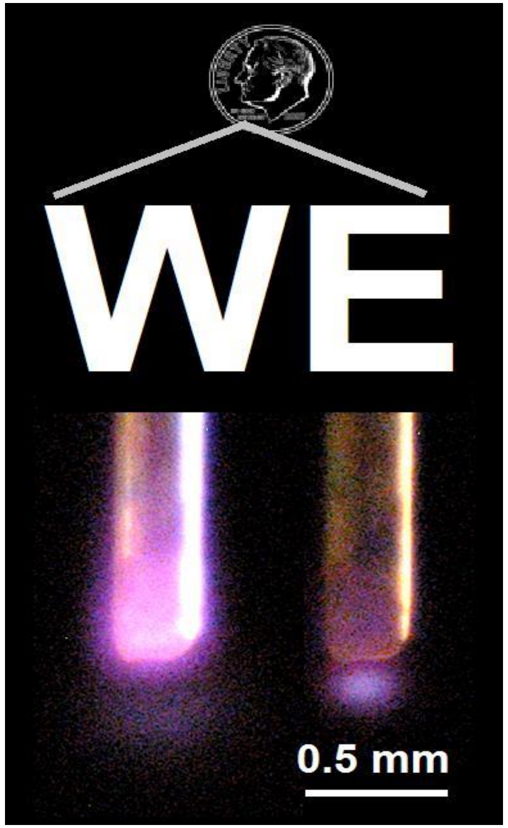
Source:
ISO/TR 15916 (2004). Basic considerations for the safety of hydrogen systems. ISO Technical Committee 197 Hydrogen Technologies.

Hydrogen properties relevant to safety

Micro-flames: typical flow rates

- A mass flow rate: **~ 10^{-9} kg/s** (1 μg/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 μg/s.
- The lowest leak which may sustain a flame from a miniature burner configuration is 5 μg/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

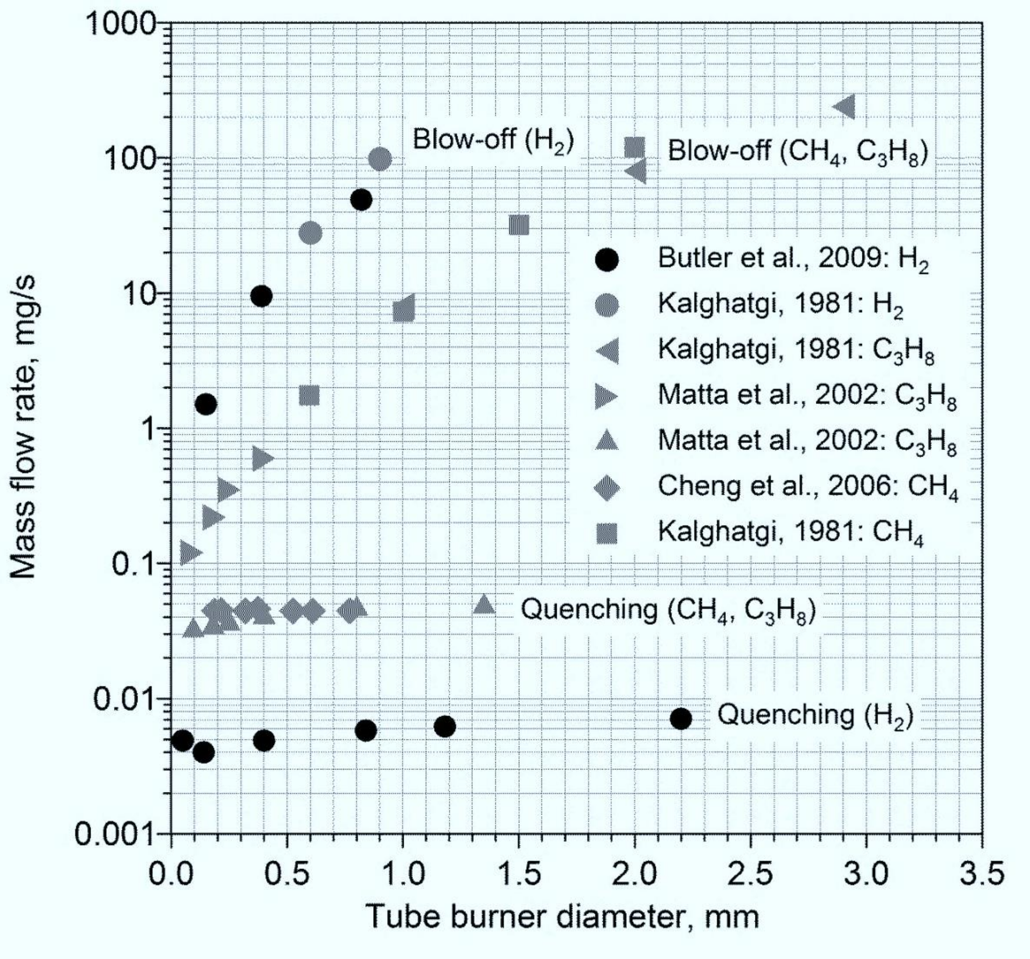


In air (flow rate: 3.9 μg/s) **In oxygen**

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.

Hydrogen properties relevant to safety

Quenching and blow-off limits

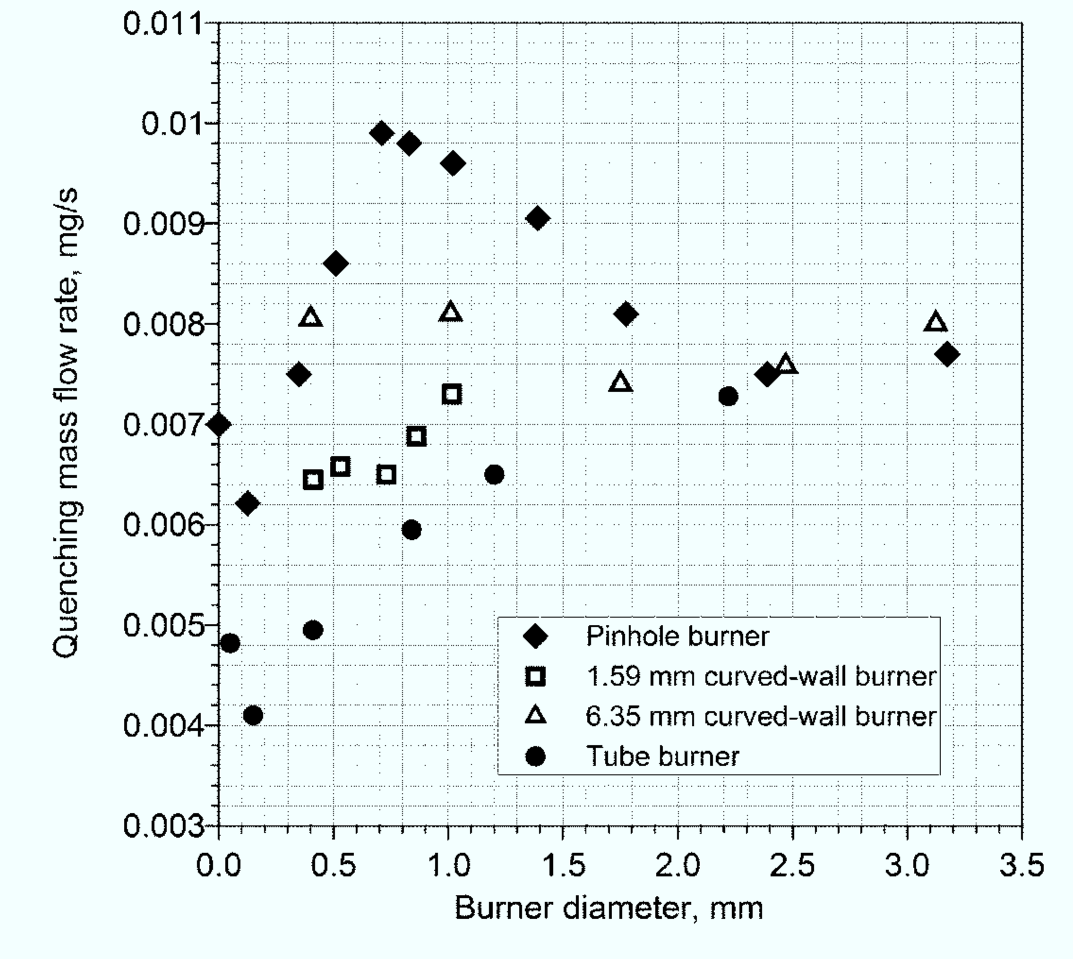


- A limited range of flow rates for, which a flame can be established on the present burners.
- Below this range, the flow is said to be below **the quenching limit**.
- Quenching occurs when there is too much heat loss for combustion to be sustained.
- On the other extreme, **blow-off limit** occurs 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".

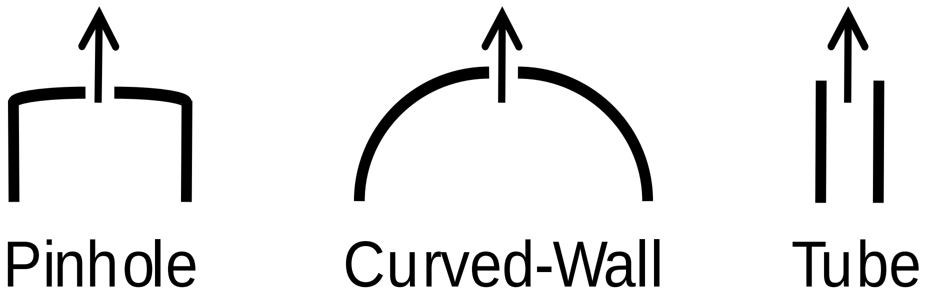
Hydrogen properties relevant to safety

Round burners and quenching limit



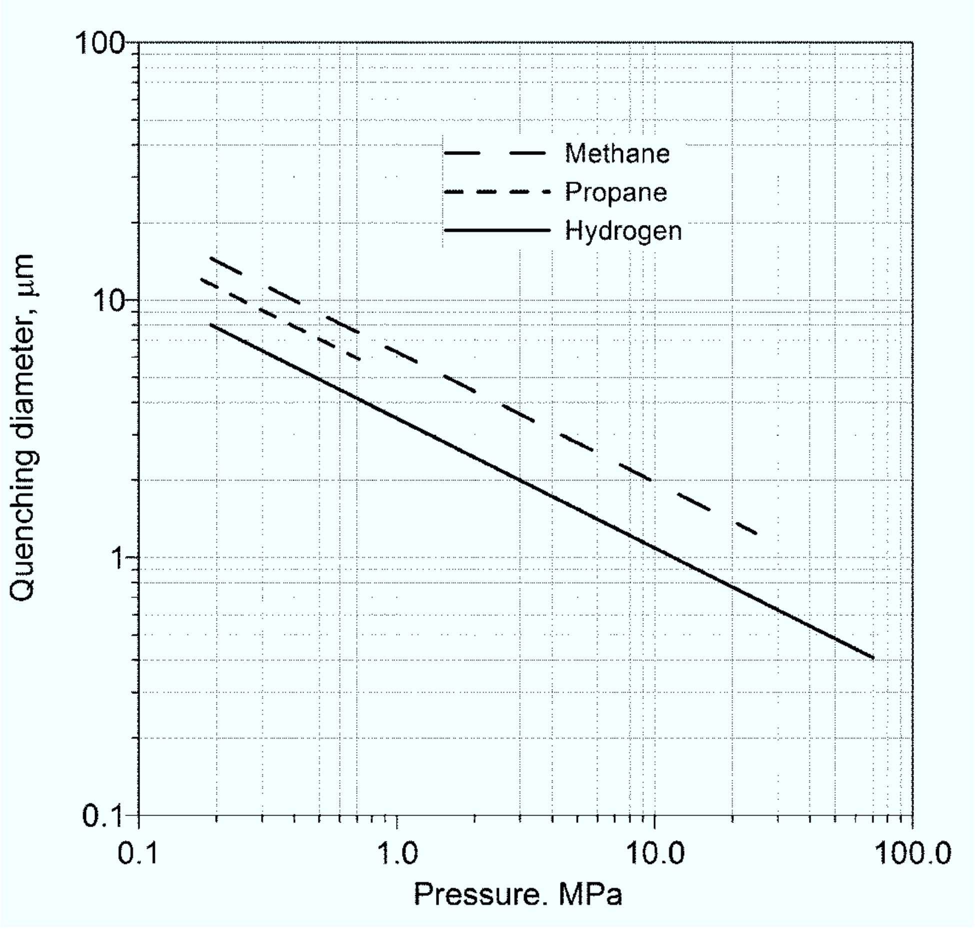
Source: Molkov, V (2012). Fundamentals of hydrogen safety engineering, Part I and Part II.

- Dependence on the diameters of a burner.



Hydrogen properties relevant to safety

Quenching diameter as a function of pressure



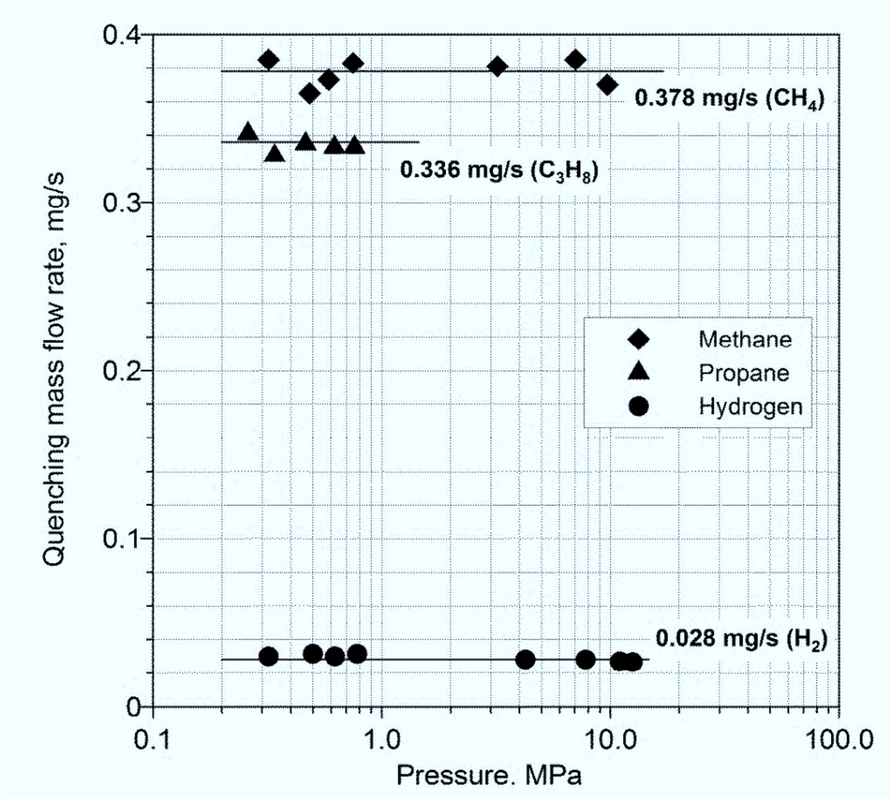
Source: Molkov, V (2012). Fundamentals of hydrogen safety engineering, Part I and Part II.

- At storage pressure of **69 MPa** a hole diameter of just **0.4 µm** is predicted to support a flame.

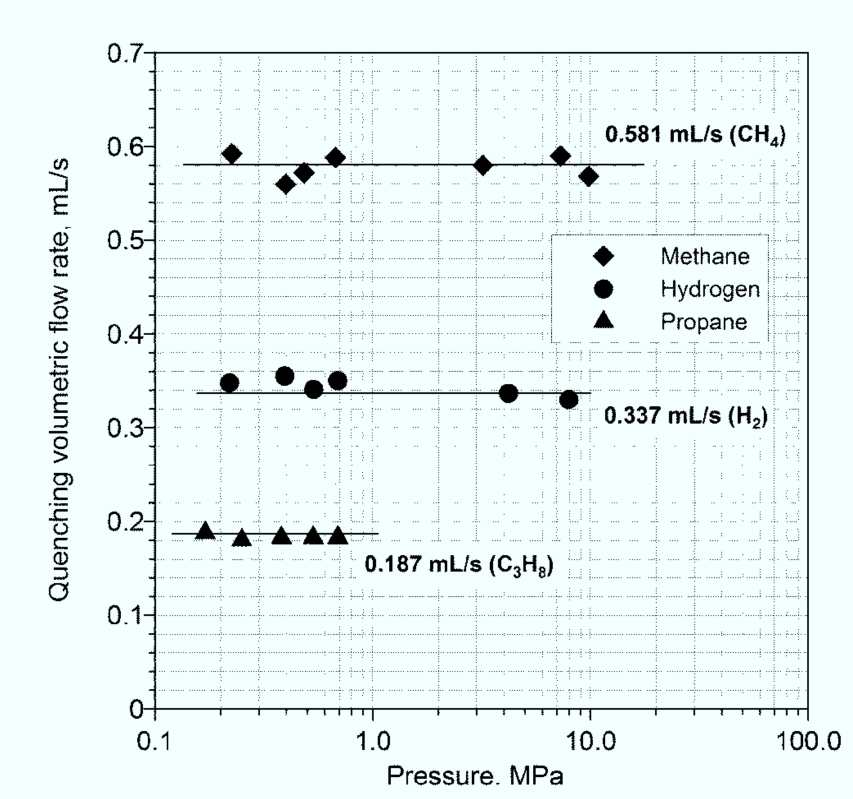
Hydrogen properties relevant to safety

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.

Sources: Butler, MS et al (2009). International Journal of Hydrogen Energy. Vol. 34, pp. 5174-5182. Sunderland, PB (2010). Proceedings of the 8th International Short Course and Advanced Research Workshop in the series “Progress in Hydrogen Safety”.

Hydrogen properties relevant to safety

Hydrogen vs. 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

Source: California Fuel Cell Partnership

* - not always

Hydrogen properties relevant to safety

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

Hydrogen properties relevant to safety

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.

Hydrogen properties relevant to safety

Reference (1/3)

1. Rigas, F and Amyotte, P (2013). Hydrogen safety. Boca Raton: CRC press. Taylor and Francis Group.
2. Rigas, F and Amyotte, P (2013). Myths and facts about hydrogen hazards. Chemical Engineering Transactions. Vol. 31.
3. Molkov, V (2012). Fundamentals of hydrogen safety engineering, Part I and Part II. Available from: www.bookboon.com, free download e-book.
4. BRHS, Biennial Report on Hydrogen Safety (2009). The European network of excellence “Safety of hydrogen as an energy carrier” (NoE HySafe). Available from: www.hysafe.org [accessed on 06.11.20].
5. NASA (1997). Safety standard for hydrogen and hydrogen systems. Guidelines for hydrogen system design, materials selection, operations, storage, and transportation. Technical report NSS 1740.16, Office of safety and mission assurance, Washington. Available from: http://www.hq.nasa.gov/office/codeq/doctree/canceled/871916.pdf was cancelled on July 25 2005 [accessed 06.11.20].
6. ISO/TR 15916 (2004). Basic considerations for the safety of hydrogen systems. International Organization for Standardization. ISO Technical Committee 197 Hydrogen Technologies. International Organization for Standardization, Geneva.
7. US DoE, US Department of Energy (2008). Hydrogen safety training for first responders. Available from: http://hydrogen.pnl.gov/FirstResponders/ [accessed on 06.1.20].
8. AIAA standard G-095-2004 (2004). Guide to safety of hydrogen and hydrogen systems. American Institute of Aeronautics and Astronautics, Reston, VA, USA.
9. Health and Safety Executive (1975).The Flixborough disaster: report of the court of inquiry, HMSO, ISBN 0113610750, 1975.
10. Buncefield Investigation (2010). The Buncefield major incident investigation board. Available from: https://www.hse.gov.uk/comah/buncefield/policyproceduresreport.pdf [Accessed 06.11.20].
11. Lind, CD (1975). What causes unconfined vapour cloud explosions? *Loss Prevention*, 9. pp. 101–105.
12. McCarty, RD, Hord, J, and Roder, HM (1981). Selected Properties of Hydrogen. NBS Monograph 168, National Bureau of Standards, Boulder, CO, February 1981.
13. Alcock, JL, Shirvill, LC and Cracknell, RF (2001). Comparison of existing safety data on hydrogen and comparative fuels. Deliverable report of European FP5 project EIHP2, May 2001. Available from: http://www.eihp.org/public/documents/CompilationExistingSafetyData_on_H2_and_ComparativeFuels_S..pdf [accessed on 06.11.20].
14. 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).
15. Yang, JC, Pitts, WM, Fernandez, M and Kuldeep, P (2011). Measurements of effective diffusion coefficients of helium and hydrogen through gypsum. Proceedings of the Fourth International Conference on Hydrogen Safety, paper ID 144, 12-14 September 2011, San Francisco, USA.
16. Walker, G (1983). Cryocoolers, Part 1: Fundamentals. New York: Plenum Press.

Hydrogen properties relevant to safety

Reference (2/3)

17. Coward, HF and Jones, GW (1952). Limits of flammability of gases and vapors, Bulletin 503, Bureau of Mines, p. 155.
18. Schroeder, V and Holtappels, K (2005). Explosion characteristics of hydrogen-air and hydrogen-oxygen mixtures at elevated pressures. 1st International Conference on Hydrogen Safety, Pisa, Italy.
19. Ono, R, Nifuku, M, Fujiwara, S, Horiguchi, S, Oda, T (2007). Minimum ignition energy of hydrogen-air mixture: Effect of humidity and spark duration. *Journal of Electrostatics*, 65. pp. 87-93.
20. Zuettel, A, Borgschulte, A, Schlapbach, L, Eds. (2008). Hydrogen as a Future Energy Carrier, Wiley-VCH Verlag, Berlin, Germany, Chap. 4, p. 90-93.
21. Zabetakis, MG and Burgess, DS (1961). Research on the hazards associated with the production and handling of liquid hydrogen. Bureau of Mines Report of Investigation RI 5707, US Department of Interior.
22. Hord, J (1978). Is hydrogen a safe fuel? *International Journal of Hydrogen Energy*, 3, p. 157.
23. Tieszen, SR, Sherman, MP, Benedick, WB, Shepherd, JE, Knystautas, R and Lee, JHS (1986). Detonation cell size measurements in hydrogen-air-steam mixtures. Progress in Astronautics Aeronautics. Vol. 106, pp. 205–219.
24. Van Dolah, RW, et al. (1963). Review of Fire and Explosion Hazards of Flight Vehicle Combustibles. BM-IC-8137, Bureau of Mines, Pittsburgh, PA.
25. Wionsky, SG (1972). Predicting Flammable Material Classifications. *Chemical Engineering*, 79 (26). pp. 81-86.
26. Kanury, AM (1975). Introduction to combustion phenomena: (for fire, incineration, pollution and energy applications). New York; London: Gordon and Breach.
27. Butler, MS, Moran, CW, Sunderland, PB and Axelbaum, RL (2009). Limits for hydrogen leaks that can support stable flames. *International Journal of Hydrogen Energy*, 34. pp. 5174-5182.
28. SAE J2579 (2009). Technical information report for fuel systems in fuel cell and other hydrogen vehicles, SAE International, Detroit, Michigan, USA, January, 2009.
29. Lecoustre, VR, Sunderland, PB, Chao, BH and Axelbaum, RL (2010). Extremely weak hydrogen flames, *Combustion and Flame*. Vol. 157, pp. 2209-2210.
30. Cheng, TS, Chao, Y-C, Wu, C-Y, Li, Y-H, Nakamura, Y, Lee, K-Y et al. (2005). Experimental and numerical investigation of microscale hydrogen diffusion flames. *Proceedings of Combustion Institute*, 30, pp. 2489-2497.
31. Sunderland, PB (2010). Hydrogen microflame hazards, Proceedings of the 8th International Short Course and Advanced Research Workshop in the series “Progress in Hydrogen Safety”, Hydrogen and Fuel Cell Early Market Applications, 11 - 15 October 2010, University of Ulster, Belfast.
32. Kalghatgi, GT (1981). Blow-out stability of gaseous jet diffusion flames. Part I: in still air. *Combustion Science and Technology*, 26(5), pp. 233-239.
33. Matta, LM, Neumeier, Y, Lemon, B and Zinn, BT (2002). Characteristics of microscale diffusion flames. *Proceedings of the Combustion Institute*, vol. 29, pp. 933-938.

Hydrogen properties relevant to safety

Reference (3/3)

34. Cheng, TS, Chen, CP, Chen, CS, Li, YH, Wu, CY and Chao, YC (2006). Characteristics of microjet methane diffusion flames. *Combustion Theory and Modelling*, 10, pp. 861-881.
35. Lee, ID, Smith, OI and Karagozian, AR (2003) Hydrogen and helium leak rates from micromachined orifices. *AIAA Journal*, vol. 41, pp. 457-463.
36. Swain, MR and Swain, MN (1992). A comparison of H_2, CH_4, and C_3H_8 fuel leakage in residential settings. International Journal of Hydrogen Energy. Vol. 17, pp. 807-815.
37. Dryer, FL, Chaos, M, Zhao, Z, Stein, JN, Alpert JY and Homer, CJ (2007). Spontaneous ignition of pressurized releases of hydrogen and natural gas into air. Combustion Science and Technology. Vol. 179, pp. 663-694.
38. Creitz, EC (1961). Inhibition of diffusion flames by methyl bromide and trifluoromethyl-bromide applied to the fuel and oxygen sides of the reaction zone. Journal of Research for Applied Physics and Chemistry. Vol. 65A, pp. 389-396.

HyResponder

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (JU) under grant agreement No 875089. The JU receives support from the European Union's Horizon 2020 research and innovation programme and United Kingdom, France, Austria, Belgium, Spain, Germany, Italy, Czechia, Switzerland, Norway