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LECTURE – Hydrogen properties relevant to safety

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Introduction

Hydrogen as a new energy vector has many advantages over traditional hydrocarbon-based fuels. It is energy-efficient, environmentally-friendly and can be obtained from renewable sources. Potentially, in the future, it can resolve many ecological and energy security issues. For more than a century hydrogen has been produced and used with a high safety record for commercial and industrial purposes [1]. However, the wider use of FCH technologies by the members of general public (not only by trained professionals) will require a new safety culture, innovative safety strategies, and breakthrough engineering solutions. To achieve this, first responders, engineers, designers, operational personnel, etc. should be aware of all specific hazards related to handling and use of FCH systems. Interestingly, most of hydrogen hazards are directly linked to its properties. Therefore, the knowledge of the general physical and chemical properties, as well as flammability and ignition characteristics of hydrogen must be available to first responders.

The purpose of this lecture is to provide first responders with critical understanding of hydrogen properties relevant to safety. First responders should realise that hydrogen has a specific set of properties and characteristics, which makes it different from fossil fuel energy carriers such as Liquefied Petroleum Gas (LPG), Compressed Natural Gas (CNG), and petrol. This lecture considers the effect of hydrogen atomic and molecular structure on safety aspects of its storage (e.g. thermal effects of the ortho-para hydrogen conversion). This lecture also discusses the safety considerations related to three different aggregate states of hydrogen: gas, liquid and slush. It is important for first responders to recognise the fact that hydrogen gas is odourless, colourless, and tasteless, and thus the potential leaks cannot be detected by human senses. The use of special odorants (e.g. mercaptans that are usually added to detect leaks of natural gas) is not acceptable for hydrogen systems as they can contaminate fuel cells [1]. The hazards associated with the liquefaction process and with the storage/distribution/handling of liquid hydrogen are covered in this lecture as well.

The main hydrogen safety asset is its highest on the Earth buoyancy. Also in this lecture, the hydrogen vapour density, diffusivity, viscosity, thermal conductivity, specific heat and specific heat ratio, and other parameters are compared to those for traditional fuels. The first responders, during this lecture, will learn the main flammability characteristics, ignition parameters, detonability limits of hydrogen-air and hydrogen-oxygen mixtures. The above mentioned properties are presented as a comparison to other known fuels. Knowledge of some characteristics such as flame visibility, auto-ignition temperature, effects of diluents and inhibitors on flammability range, adiabatic flame temperature, thermal radiation from flames, quenching and blow-off limits will be very useful to those, who will directly deal with/extinguish hydrogen fires. Physiological (health) hazards of hydrogen, although being mentioned in the current lecture, will be discussed in detail in the subsequent lectures. It is concluded that the safety concerns for hydrogen systems, are not more severe, but different than those for currently used fuels [2].

Objectives of lecture

By the end of this lecture first responders will be able to:

- 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 GH_2 (asphyxiation) and LH_2 (cryogenic burns, frostbite, hypothermia, lung damage from inhalation of cold vapours);
- Relate the low vapour density of 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

An atomic number of hydrogen (H) in the periodic table is 1, and its atomic mass is 1.008 (approximated by four digits) [3]. Hydrogen atom consists of a nucleus with one unit of positive charge (proton) and one electron. The electron carries a negative charge and is usually described as occupying a “probability cloud”, which surrounds the nucleus somewhat like a fuzzy, spherical shell [3]. The size of hydrogen nucleus in its ground state is 10^{-10} m (1 angstrom). The radius of the electron’s orbit, which defines the size of the atom, is approximately 100,000 times as large as the radius of the nucleus. The charges of the proton and the electron of each hydrogen atom cancel each other out, thus the hydrogen atom is electrically neutral [3].

The mass of a hydrogen atom is concentrated in its nucleus. Indeed, the proton is more than 1,800 times heavier than the electron. A neutron, which has almost the same mass as the proton and does not carry any charge, can also be present in the nucleus. Depending on the number of neutrons in the nucleus, hydrogen can have three isotopes: protium ^1_1H (only a proton in the nucleus), deuterium ^2_1H (a proton and a neutron in the nucleus), and tritium ^3_1H (a proton and two neutrons in the nucleus) with atomic mass 1, 2 and 3 respectively (approximated by one digit). The most abundant isotope (more than 99.985%) is protium; deuterium is found in nature in approximately 0.015%; and tritium appears in small quantities in nature, but can be artificially produced by various nuclear reactions. Tritium is unstable and radioactive (generates β -rays, i.e. fast moving electrons as a result of the neutron conversion into a proton, 12.3 years half-decay time) [3].

In normal conditions hydrogen is a gas formed by diatomic molecules (i.e. made of two hydrogen atoms) with a formula H_2 (molecular mass 2.016 g/mol). Two hydrogen atoms form a single covalent bond. Due to the hydrogen atomic arrangement a single electron, orbiting around a nucleus, is highly reactive. For this reason, hydrogen atoms can easily combine into pairs [3]. Hydrogen is the lightest and the most abundant element in the universe representing 75% (per mass) or 90% (per volume) of all matter [4]. Hydrogen practically does not exist as a free element in the Earth’s atmosphere (less than 1 ppm by volume). It is present in a free state in the sun and stars.

Ortho- and para-hydrogen

The hydrogen molecule exists in two forms distinguished by the relative rotation of the nuclear spin of the individual atoms in the molecule. Molecules with spins oriented in the same direction (parallel) are called *ortho-hydrogen*; and those with spins in the opposite direction (anti-parallel), *para-hydrogen* [5]. The chemistry of hydrogen, and in particular the combustion chemistry, is slightly altered by the different atomic and molecular forms.

The equilibrium mixture of ortho- and para-hydrogen at any temperature is referred to as equilibrium hydrogen. The equilibrium ortho-para-hydrogen mixture with a content of 75% ortho-hydrogen and 25% para-hydrogen at room temperature is called *normal hydrogen*. At lower temperatures, equilibrium favours the existence of the less energetic para-hydrogen (liquid hydrogen at 20 K is composed of 99.8% of para-hydrogen). The ortho- to para-hydrogen conversion is accompanied by a release of heat: 703 kJ/kg at 20 K for ortho-para-hydrogen conversion, or 527 kJ/kg for normal to para-hydrogen conversion [5]. This feature of hydrogen underpins inherently safer storage of hydrogen as cryo-compressed rather than liquefied form in automotive applications due to the essential reduction, if not complete exclusion, of the hydrogen *boil-off* phenomenon (the vapours created due to the ambient heat input) at day-to-day normal driving. In fact, due to the

conversion of para- to ortho-hydrogen during “consumption” of external heat the release of hydrogen from storage tank as a result of “boil-off” phenomenon is practically excluded for cryo-compressed storage with clear safety implications [3].

The process of hydrogen liquefaction includes the removal of the energy released by the ortho-para state conversion. The heat of conversion is 703 kJ/kg. This is 1.5 times of the heat of vaporization [6]. 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.

Gaseous, liquefied and slush forms of hydrogen

At standard temperature and pressure (STP¹) hydrogen is a colourless, odourless, tasteless gas. For this reason its leaks are difficult to detect by human senses. Unfortunately, compounds such as mercaptans (normally used as the odorants to detect leaks of natural gas) cannot be added to hydrogen systems as they will contaminate (‘poison’) the fuel cells. In addition, due to the smaller size of hydrogen molecules compared to those of known odorants, hydrogen can migrate/leak through openings, the size of which is not sufficient for the odorants to pass through. Hydrogen tends to move away from the source of leak faster than the odorants due to its buoyancy/high dispersion coefficient. Hydrogen is a non-toxic, non-corrosive, and a flammable compound. However, hydrogen can cause asphyxiation by diluting oxygen in the air below the concentration levels necessary to support life. It is the lightest of all known gases. *Gaseous hydrogen* (GH₂) is 14 times lighter than air (the vapour density of hydrogen is 1; the vapour density of air is 14), which means it will rise and diffuse rapidly upon a release in the air. Hydrogen is widely used as a reducing agent in a range of chemical processes. Although hydrogen is non-corrosive and non-reactive at standard conditions, it is capable to reduce mechanical strength of some materials through a variety of interaction processes commonly referred to as hydrogen embrittlement.

Liquid hydrogen (LH₂) is a colourless, odourless, non-corrosive, and not a very reactive liquid. It is a cryogenic fluid (please note: fluids with temperatures below -73 °C are known as cryogenic) [3]. Any liquid hydrogen splashed on to the skin or in the eyes can cause serious burns by frostbite or hypothermia. LH₂ will rapidly boil or flash to a gas if exposed to or spilled into an environment with normal temperature. Warming LH₂ to ambient temperature can lead to very high pressures in confined spaces. Please note that inhaling cold vapours may lead to respiratory discomfort, and asphyxiation in the end.

The volumetric ratio of LH₂ to GH₂ is 1:848. LH₂ expands approximately 850 times upon conversion to a gas at normal temperature and pressure (NTP²), thus it is stored at relatively low pressures in double-walled, vacuum insulated containers equipped with burst disks, vents, and PRDs. It has the lowest density of any liquefied gas. Unlike for propane, the compression of gaseous hydrogen does not liquefy it. Therefore, LH₂ phase is absent in gaseous hydrogen storage vessels, and in the case of fire the risk of Boiling Liquid Expanding Vapour Explosion (BLEVE) is absent [7]. GH₂ storage vessels are also equipped with pressure relief devices (PRDs) to allow a controlled venting of hydrogen gas. This will be discussed in more detail in the lecture on safety of hydrogen storage.

¹ Standard Temperature and Pressure (STP): 273.15 K (0°C) and 101,325 Pa.

² Normal Temperature and Pressure (NTP): 293.15 K (20°C) and 101,325 Pa.

The phase diagram of hydrogen is presented in Figure 1. There are three curves on the phase diagram of hydrogen. One curve shows the change of boiling (or condensation for the opposite phase transition) temperature with pressure; another curve gives the change of melting (or freezing) temperature with pressure, and the third one indicates pressures and temperatures for sublimation process. The process of condensation is also known as *liquefaction* [3].

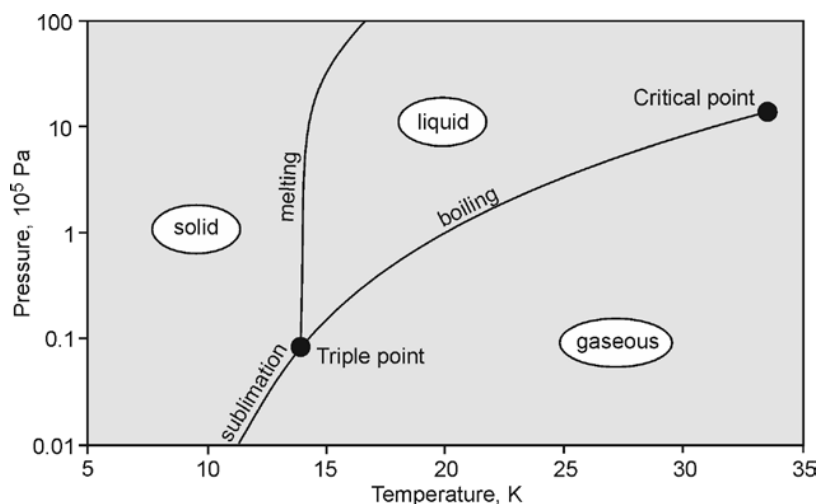


Figure 1. Phase diagram of hydrogen [3].

Hydrogen can exist in gaseous, liquid, or slush forms. LH₂ is a clear liquid with a light-blue tint. The *slush* hydrogen is a mixture of solid and liquid hydrogen at the triple point temperature. The transition between gas, liquid, and solid phases of hydrogen is dominated by the low temperatures. The *triple point* (i.e. the temperature of 13.8 K and the pressure of 7.2 kPa) is the condition, under which all three phases co-exist. The vapour pressure of slush hydrogen can be as low as 7.04 kPa [5] and safety measures must be taken during operations to prevent air leakage into the system that could create a flammable mixture [3]. The heat leakage into slush hydrogen system without ullage present requires the continuous addition of solid fraction of slush hydrogen and the removal of LH₂ because slush fraction expands as it degrades. Significant increases in volume can occur when the solid phase of slush hydrogen melts [8].

The highest temperature, at which hydrogen vapours can be liquefied, is the critical temperature of 33.145 K (*critical point* on the phase diagram). The corresponding critical pressure is 1.3 MPa (density at critical point is 31.263 kg/m³). Above the critical temperature it is impossible to condense hydrogen into a liquid simply by increasing the pressure (i.e. by compression). Above this point only cryo-compressed gas can be obtained because hydrogen molecules have too much energy for the intermolecular forces to hold them together as a liquid [3].

The normal boiling point (NBP, at the absolute pressure of 101.325 kPa) of hydrogen is 20.3 K. The normal melting point is 14.1 K (at 101.325 kPa). Among all the substances hydrogen has the second lowest boiling and melting points (only helium has lower values: boiling temperature of 4.2 K and melting temperature of 0.95 K). All these temperatures are extremely low and below the freezing point of air. It is worth reminding that at the absolute zero temperature of 0 K (-273.15 °C), which is the lowest temperature in the universe, all molecular motion stops [3]. Due to such low temperatures vents and valves on LH₂ storage vessels may be blocked with the accumulations of ice formed from the moisture contained in the air. The excessive pressure may then rupture the container and release hydrogen.

The continuous evaporation of LH_2 in a vessel generates GH_2 , which must be vented to a safe location or temporarily confined safely. When gaseous hydrogen is warmed from the NBP to NTP its volume increases. For storage vessels with a fixed volume the phase change $\text{LH}_2 \rightarrow \text{GH}_2$ and associated temperature rise (from NBP to NTP) will result in a pressure increase from 0.1 MPa to 177 MPa [6]. 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). That is why safety valves needed to be installed on the storage vessels.

Liquid hydrogen (NBP) has a density of 70.78 kg/m^3 . Liquid hydrogen is approximately 14 times less dense than water: the *specific gravity* of LH_2 is 0.071 as opposed to 1 for water. The higher density of the saturated hydrogen vapour at low temperatures may cause the hydrogen cloud to flow horizontally or even downward immediately upon release if an LH_2 spill or leak occurs, or gas at a temperature below 193 K is vented [8]. These facts have to be accounted for by first responders during intervention at an accident scene [3].

An important safety concern of LH_2 use is that all the gases, with the exception of helium, will be condensed and solidified at such low temperature (should they be exposed to it). The leaks of air or other gases directly exposed to liquid hydrogen can lead to several hazards [6]. The solidified gases can plug pipes, orifices and jam valves due to the ice formation. In a process known as cryo-pumping the reduction in volume of condensing gases may create vacuum that can draw in yet even more gas, e.g. oxidant like air. Large quantities of condensed or solidified materials can accumulate displacing LH_2 if the leak persists for long periods of time. At some point, should the system be warmed for maintenance, these solidified 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 [3].

Liquid hydrogen is usually transferred in the vacuum insulated lines. However, when cold hydrogen flows in tubes with insufficient thermal insulation, this can easily cool the system below 90 K so that the condensed air with oxygen content of up to 52% may be present (NBP of nitrogen is 77.36 K, NBP of oxygen is 90.15 K, NBP of carbon dioxide is 216.6 K). The liquid condensate looks and behaves like water. This oxygen-enriched condensate increases the flammability of materials and makes the materials, which normally are not flammable, to combust. This includes, for example, bituminous road covers. This is of a 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 materials [3]. Oxygen enrichment can increase the flammability and even lead to the formation of shock-sensitive compounds. If an oxygen-enriched particulate contaminates cryogenic hydrogen gas this mixture may even detonate. The vessels with LH_2 have to be periodically warmed and purged to keep the accumulated oxygen content in the vessel below 2% [6]. Caution should be exercised if carbon dioxide is used as a purge gas. It may be difficult to remove all carbon dioxide from the system low points where the gas can accumulate [3].

Although an electric current can be passed through LH_2 , this current can be explained in terms of charge carriers formed by background radiation. Thus, the current carrying capacity is small and more or less independent of the imposed voltage. Investigation has shown that the electric charge accumulation in flowing high-purity LH_2 is not a great concern [8].

Physical properties of hydrogen

Hydrogen buoyancy as a safety asset

Gaseous hydrogen has a density of 0.0838 kg/m^3 (at NTP), which is more than 14 times lower than that of air (1.205 kg/m^3) at the same conditions. The specific gravities of hydrogen and air at NTP are 0.07 and 1.0, respectively (Figure 2). Therefore, hydrogen gas is lighter than air, and in ambient conditions it will rise and disperse in an open environment [7]. As for other fuels, propane and petrol vapour are heavier than air, whilst methane, i.e. natural gas, is 2 times lighter than air but almost 8 times heavier than hydrogen gas.

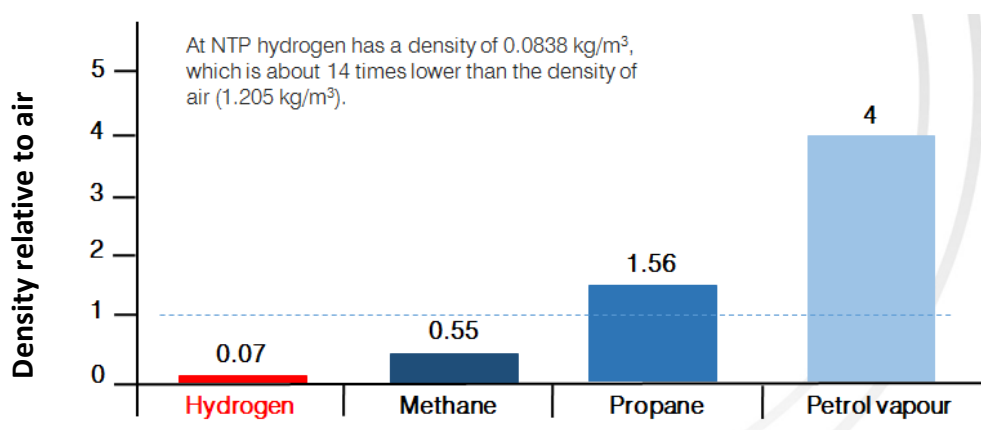


Figure 2. Densities relative to air for hydrogen and other common fuels.

Thus, the low vapour density of hydrogen results in the gas being very *buoyant* compared to other compounds. In fact, hydrogen has the highest on the Earth buoyancy. This is the main hydrogen safety asset, i.e. in case of hydrogen releases it will rise and disperse rapidly. The unwanted consequences of hydrogen releases into the open atmosphere and in partially confined spaces (with no accumulation of hydrogen) are drastically reduced by buoyancy [3]. The heavier hydrocarbon-based fuels are capable to form rather large combustible clouds, as in the cases of disastrous explosions at Flixborough, 1974 [9] and Buncefield, 2005 [10]. In many real-life situations hydrocarbons may pose more severe fire and explosion hazards than hydrogen.

Pure hydrogen is positively buoyant above the temperature of 22 K, i.e. over almost the whole temperature range of its gaseous state [4]. The buoyancy provides comparatively fast dilution of released hydrogen by surrounding air below the lower flammability level. 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 [4, 11]. This makes safety considerations of an accident with a large hydrogen inventory in the open quite different from that for other flammable gases with often less or no harmful consequences at all. Hydrogen high buoyancy affects its dispersion considerably more than its high diffusivity [3].

However, we should be careful in applying gaseous hydrogen buoyancy observations to the releases of hydrogen vapours at cryogenic temperatures [3]. Saturated hydrogen vapour is heavier than air and will remain close to the ground until the temperature rises [8]. Usually the condensation of atmospheric humidity will also add water to the mixture cloud, firstly making it visible, and secondly

increasing the molecular mass of the mixture even more [3]. Buoyant velocities are related to the difference in air and hydrogen densities; therefore, the cold, dense hydrogen gases produced by LH₂ spills will not rise. The buoyant velocity of hydrogen in NTP air reaches 1.2 to 9 m/s [12].

Diffusivity of hydrogen

The diffusivity of hydrogen is higher compared to other fuels due to the small size of its molecules (Figure 3). The literature data on the diffusion coefficient of hydrogen in air are ranging from $6.1 \cdot 10^{-5}$ m²/s [13] to $6.8 \cdot 10^{-5}$ m²/s [14].

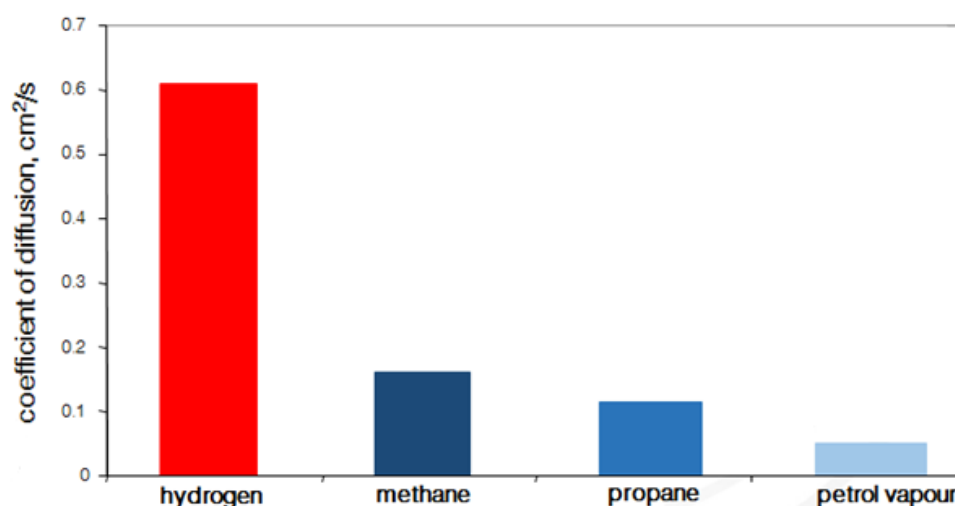


Figure 3. Coefficients of diffusion for hydrogen and hydrocarbon-based fuels.

The hydrogen diffusivity is greater than that of helium and approximately 3 times that of nitrogen in air at ambient conditions. GH₂ also readily diffuses through solids. For example, effective diffusion coefficient of hydrogen through gypsum panels is $1.4 \cdot 10^{-5}$ m²/s at room temperature [3]. Helium and hydrogen effective diffusion coefficients through gypsum panels were measured by Yang et al. [15]. The estimated average diffusion coefficients are found to be $D_e = 1.3\text{--}1.4 \cdot 10^{-5}$ m²/s for helium ($3.3 \cdot 10^{-6}$ m²/s for painted gypsum panel), and $D_e = 1.4 \cdot 10^{-5}$ m²/s for hydrogen at room temperature 22 °C. The authors underlined that since the interior of most garages in the US have large surface areas covered with gypsum panels together with the fact that hydrogen can readily diffuse through gypsum panels, this diffusion process should not be overlooked in the hazard assessment of accidental release of hydrogen in garages or enclosures lined with gypsum panels [3].

Other physical properties

The low viscosity of hydrogen and the small size of the molecule explain a comparatively high flow rate if the gas leaks through fittings, seals, porous materials, etc. This negative effect is, to a certain extent, offset by the low energy density (volumetric) of hydrogen in comparison with e.g. methane or other hydrocarbon gases. The viscosity (in μPoise) of GH₂: 89.48 (NTP) and 11.28 (NBP), whilst the viscosity of LH₂ at NBP is 132.0 [4].

The heat capacity of hydrogen is similar to that of other diatomic gases despite its low molecular mass [6]. The specific heat of GH₂ at constant pressure c_p (in kJ/kg/K): 14.85 (NTP), 14.304 (STP), 12.15 (NBP). The specific heat of LH₂ at boiling point is 9.66 kJ/kg/K [4]. The specific heat at constant pressure of liquid para-hydrogen is $c_p = 9.688$ kJ/kg/K. This is more than double than that of liquid

water and 5 times greater than that of liquid oxygen at its NBP. The gas constant of hydrogen is 4.1243 kJ/kg/K (i.e. the universal gas constant divided by the molecular weight). The specific heats ratio (γ) of hydrogen at NTP is 1.39 and at STP conditions γ is 1.405 [3].

Thermal conductivity of hydrogen is significantly higher than that of other gases: for GH₂ it is 0.187 W/m/K (NTP), 0.01694 W/m/K (NBP); for LH₂: 0.09892 W/m/K (NBP). Speed of sound in gaseous hydrogen is 1,294 m/s at NTP and 355 m/s at NBP [3]. Speed of sound in liquid hydrogen is 1,093 m/s (boiling point). Speed of sound in stoichiometric hydrogen-air mixture is 404 m/s [4].

Joule-Thompson (J-T) process or *throttling process* refers to a change in temperature of a real gas when it is forced through a valve or a porous plug while kept well insulated so there is no heat exchange with the surrounding. The majority of gases, when expanded from high to low pressure through a porous plug, a small aperture or a nozzle, usually are cooled due to so called *throttled expansion* [1]. However, the temperature of hydrogen increases when it is expanded at a temperature and pressure beyond the temperature and pressure conditions that define the J-T inversion curve for hydrogen [1]. The maximum inversion temperature for hydrogen is 202 K (-71 °C) at an absolute pressure of zero [16]. Consequently, at any temperature and pressure higher than these values, the temperature of hydrogen will increase upon expansion. The temperature increase as a result of the J-T expansion is not normally sufficient to be the source of ignition for a combustible hydrogen/oxidizer mixture. An example of the extent of the temperature rise is that the temperature of hydrogen initially at 300 K increases to 346 K when expanded from an absolute pressure of 100 MPa to an absolute pressure of 0.1 MPa. A temperature rise of 46 K does not raise hydrogen to its ignition temperature unless it is already near the ignition temperature after mixing with surrounding gas [8].

Combustion of hydrogen: main characteristics

At normal temperature hydrogen is a not very reactive substance, unless it has been activated somehow, e.g. by an appropriate catalyst. Hydrogen reaction with oxygen to form water at ambient temperature is extraordinarily slow. However, if the reaction is accelerated by a catalyst or a spark, it proceeds at a high rate and with an 'explosive' violence:

hydrogen + oxygen → water + energy



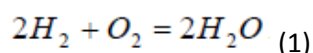
Molecular hydrogen dissociates into free atoms at high temperatures. Atomic hydrogen is a powerful reductive agent, even at ambient temperature e.g. when it diffuses from a high temperature zone of a flame front into its pre-heating low temperature zone. The heat released when the hydrogen atoms recombine to the hydrogen molecule is used for example to obtain high temperatures in the atomic hydrogen welding [3].

Hydrogen burns in a clean atmosphere with an invisible flame. It has a somewhat higher *adiabatic premixed flame temperature* for a stoichiometric mixture in air of 2,403 K compared to other fuels [4]. This temperature can be a reason for serious injury at an accident scene, especially in a clean laboratory environment where hydrogen flame is practically invisible. However, hydrogen combustion and hot currents will cause changes in the surroundings that can be used to detect the flame. Although the non-luminous hydrogen flame makes visual detection difficult, there is a strong

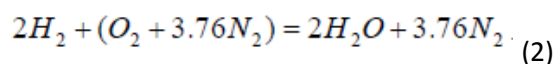
effect of heat and turbulence on the surrounding atmosphere and raising plume of hot combustion products. These changes are called the signature of the fire [3].

Stoichiometric concentration of hydrogen

The stoichiometric mixture is a mixture, in which both fuel and oxidiser are fully consumed (i.e. complete combustion) to form combustion product(s). For example, the two diatomic gases, hydrogen (H_2) and oxygen (O_2) can combine to form water as the only product of an exothermic reaction between them, as described by the equation (1):



Thus, the *stoichiometric hydrogen-oxygen mixture* is composed of 66.66 vol. % of hydrogen and 33.33 vol. % of oxygen. The *stoichiometric concentration of hydrogen in air* (assuming air is made of 21% of oxygen and 79% of nitrogen) is 29.59 vol. % with the air content of 70.41 vol. % as per equation (2):



The *lean mixtures* are the hydrogen-air mixtures, in which concentration of hydrogen is below the stoichiometric value. In the *rich mixtures* the concentration of hydrogen is higher than the stoichiometric [3].

Heat of combustion and limiting oxygen index

The lower heating value (i.e. heat of combustion) of hydrogen is 241.7 kJ/mol and the higher heating value is 286.1 kJ/mol [4]. The difference of about 16% is explained by the heat of condensation of water vapour, and this value is larger compared to other gases. This energy will be released either during combustion or in a fuel cell reaction between hydrogen and oxidiser (air or oxygen). Table 1 compares higher and lower heating values for different fuels³.

Table 1. The heating values for hydrogen and other common fuels.

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

The limiting oxygen index is the minimum concentration of oxygen that will support flame propagation in a mixture of fuel, air, and nitrogen. The mixture of hydrogen, air, and nitrogen at NTP conditions will not propagate the flame if it contains less than 5 vol. % of oxygen [5].

Lower and upper flammability limits (LFL and UFL)

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*

³ To convert the heating value from kJ/mol to kJ/g divide first value by the molecular weight of hydrogen - 2 g/mol.

(UFL) is the highest concentration of a combustible substance in a gaseous oxidizer that will propagate a flame.

Hydrogen ignites if its content in the air is below the UFL and above the LFL, and if an ignition source is present. The flammability range of hydrogen is significantly wider compared to other hydrocarbons, i.e. 4 to 75 vol. % in air at NTP (Figure 4).

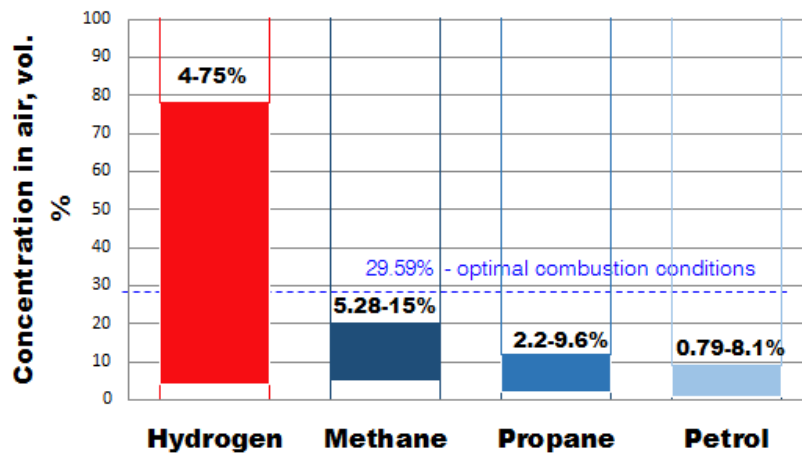


Figure 4. Flammability limits for hydrogen and other common fuels based on the data taken from [3].

Impact of different factors on LFL and UFL

The flammability range expands linearly as *temperature* rises (Figure 5). The LFL decreases by about 2.5 vol. % (from 4 to 1.5 vol. %) with the increase of temperature from 20°C to 400°C, whilst the UFL increases more significantly - by about 12.5 vol. % for the same change of mixture temperature.

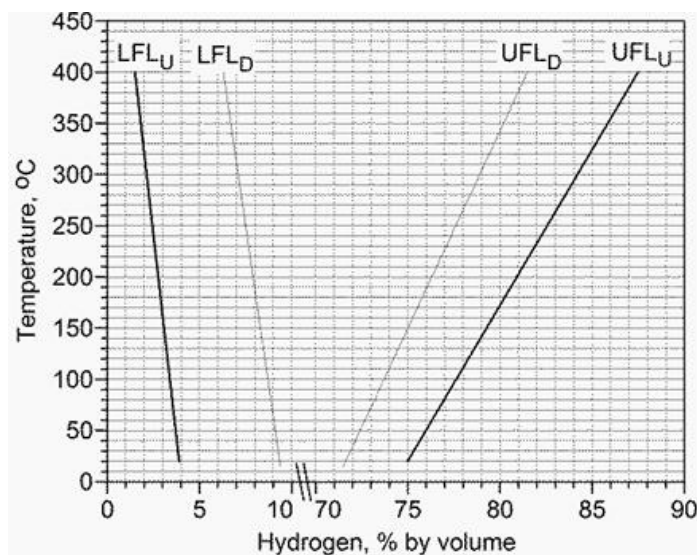


Figure 5. The effect of temperature on LFL and UFL: thick lines U - upward flame propagation; thin lines D - downward flame propagation [3].

In addition, the flammability limits of hydrogen depend on a *direction of flame propagation*. The ranges of the flammability limits for different direction of flame propagation referenced in [17] are presented in Table 2.

Table 2. Flammability limits of hydrogen-air for upward, horizontal, and downward (spherical) propagation in hydrogen concentration by volume [17].

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%

For example, in an initially quiescent mixture a conservative value of LFL changes from 3.9 vol. % for upward propagation, through 6 vol. % for horizontally propagating flames, to 8.5 vol. % for downward propagating flames [3].

The flammability range depends on the *pressure* as well (Figure 6). 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 monotonously. 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 [18].

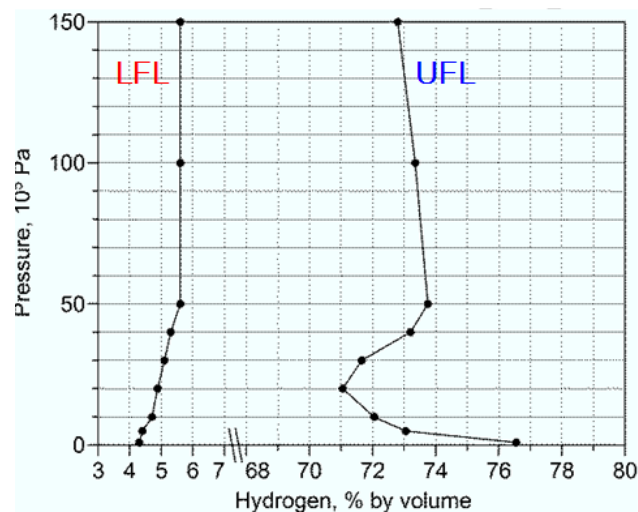


Figure 6. LFL and UFL of hydrogen-air mixture as a function of pressure [18].

A hydrogen-oxidiser mixture can propagate a flame only within the flammability limits, which are in essence the limits of premixed flame propagation out of the ignition source location without the quenching effect of testing vessel (tube, bomb, etc.). The flammability limits depend on the *apparatus and the standard applied* to determine them. Table 3 shows the scattering of the flammability limits values (in vol. %) determined by different standard apparatuses and procedures applied [18]. DIN 51649 is a German standard that used a vertical glass tube (inner diameter 60 mm, height 300 mm) at atmospheric pressure with ignition source being a high voltage spark of 0.5 s in duration. In the standard EN 1839 (T) a vertical glass tube (80 mm in diameter and 300 mm height) was employed with a high voltage spark (0.2 s in duration) as the ignition source. The EN 1839 (B)

standard used a closed spherical steel vessel (bomb), 14 dm³ in volume, and the ignition source is a fusing wire. ASTM E 681 (USA) utilised a glass flask with a volume of 5 dm³, with a pressure ranging from 0.133 bar to atmospheric, and with ignition source a high voltage spark 0.4 s in duration [18].

Table 3. The dependence LFL and UFL of hydrogen-air mixtures at NTP on the standard used [18].

Limit	DIN 51649	EN 1839 (T)	EN 1839 (B)	ASTM E 681
LFL	3.8%	3.6%	4.2%	3.75%
UFL	75.8%	76.6%	77.0%	75.1%

Coward and Jones provided the following description of the initial stages of flame propagation after ignition of hydrogen-air mixture (4 vol. %). 'A vortex ring of flame was seen just above the spark gap; it rose, expanded for about 40 cm, then broke and disappeared. Upward flame propagation at concentrations close to LFL of 4 vol. % is in a form of a collection of small balls of flame, which travel steadily to the top of the vessel' [17]. For hydrogen concentrations in the range 4.4-5.6 vol. % similarly a vortex ring rose about 40 cm, then broke into segments each subdivided into balls of flame that travel to the top [17]. There is an unburnt mixture in between of these small ball flames. An increasing fraction of the hydrogen present was burned as the amount of it was increased. The mixture with 5.6 vol. % of hydrogen showed about 50% combustion. This observation explains why burning of a quiescent hydrogen-air mixture near LFL of 4 vol. % in a closed vessel can generate negligible in a practical sense overpressure. It is worth noting that a quiescent hydrogen-air mixture in the range of concentration 4-6% could burn practically without overpressure for a number of scenarios, e.g. if ignited at the top of an enclosure, as in such conditions it cannot propagate flame in any direction and thus no heat is released accompanied by pressure build up can be observed. Please note this is relevant to the initially quiescent mixtures only.

For the systems such as electrolyzers or fuel cells incidents or accidents may lead to the formation of a flammable hydrogen-oxygen mixture and therefore it is important for first responders to know its flammability range. The flammability range for hydrogen-oxygen mixtures at NTP is from 4 to 95 vol. %. The flammability limits of hydrogen-oxygen mixtures also depend on the pressure as shown in Table 4. The limits were determined by the European standard EN 1839(B) in the range of pressures 1-20 bar. Smaller vessel of 2.8 dm³ was used instead of standard 6 dm³ vessel at pressures above 20 bar. As it is shown in Table 4 the flammability range of hydrogen-oxygen mixtures narrows for the pressures in the range of 1-20 bar; at pressures higher than 20 bar both LFL and UFL increase.

Table 4. The effect of pressure on flammability limits (at 20 and 80 °C) of hydrogen-oxygen mixtures.

Pressure, bar	LFL at 20°C, vol. %	UFL at 20°C, vol. %	LFL at 80°C, vol. %	UFL at 80°C, vol. %
1	4.0	95.2	3.8	95.4
5	4.6	94.6	4.4	95.0
10	5.0	94.2	4.8	94.6
20	5.4	94.2	5.2	94.6
50	5.5	94.6	5.3	95.0
100	5.7	94.9	5.7	95.3
150	5.7	95.1	5.3	95.5
200	5.9	95.1	5.7	95.5

The *diluents* and *inhibitors* also affect the flammability range. The flammability limits for hydrogen-air-diluent systems are presented as a ternary plot in Figure 7. This diagram is very useful to determine the most suitable diluting agent. For examples, the mixture composed of 45 vol. % of hydrogen, 30 vol. % of air and 25 vol. % of diluents is indicated by the green dot on this diagram. For the chosen composition, diluents such as helium, carbon dioxide and nitrogen will still be within the flammability range, whilst the use of water as a diluent will lead to a formation of a non-flammable mixture. Water was the most effective in reducing the flammability range, and helium was the least effective [8].

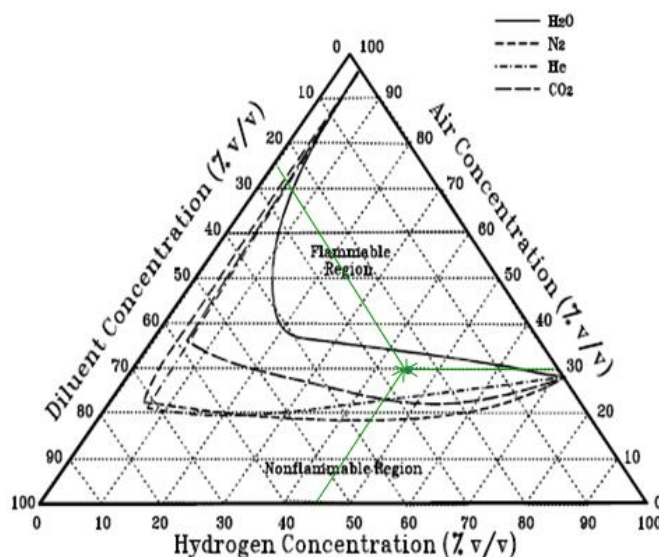


Figure 7. Flammability limits for hydrogen-air-diluent mixtures [5].

Table 5 (adapted from [8]) shows the qualitative effect of helium He, carbon dioxide CO₂, nitrogen N₂, and Argon Ar diluents for various tube sizes. Argon was the least effective in reducing the flammable range for hydrogen in air.

Table 5. Effect of diluents on the flammability range of hydrogen-air mixtures

Tube diameter, cm	Rating of diluents in reducing the flammability range
Wide tubes	CO ₂ > N ₂ > He > Ar
2.2	CO ₂ > He > N ₂ > Ar
1.6	He > CO ₂ > N ₂ > Ar

Table 6 compares the effect of nitrogen N₂ and halocarbon inhibitors (bromomethane CH₃Br and bromotrifluoromethane BrCF₃) required for the extinguishment of hydrogen diffusion flames in air. The halogen-containing inhibitors were more effective when added to the air stream; nitrogen was more effective when added to the fuel stream [8].

Table 6. Effect of nitrogen and halocarbon inhibitors on the extinction of hydrogen flames.

Inhibitor	Concentration at flame extinction vol%
Added to air:	
Nitrogen	94.1
CH ₃ Br	11.7
CBrF ₃	17.7
Added to fuel:	
Nitrogen	52.4
CH ₃ Br	58.1
BrCF ₃	56.6

Turbulence can also significantly affect the overpressure generated by the flame propagation through the lean mixtures in a closed vessel. Indeed, flame propagation through the initially quiescent mixture with hydrogen concentration in air below 8 vol. % creates no overpressure. This can be explained by the incomplete combustion as the flame cannot propagate downwards. However, when the mixture is turbulent the mixture even at LFL, i.e. at 4 vol. % of hydrogen can generate pressure up to 2.5 bar in a closed vessel.

Ignition properties

Hydrogen is very easily ignited [5]. The ignition sources include mechanical sparks from rapidly closing valves, electrostatic discharges in ungrounded particulate filters, sparks from electrical equipment, catalyst particles, heating equipment, lightning strikes near the vent stack, etc. Therefore, the ignition sources must be eliminated or isolated in appropriate way and any operations should be conducted as if unforeseen ignition sources could occur [3].

The 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. The standard auto-ignition temperature of hydrogen in air is above 510 °C [14]. It is relatively high compared to hydrocarbons having long molecules. However, it can be lowered by catalytic surfaces. Objects at temperatures from 500 to 580 °C can ignite hydrogen-air or hydrogen-oxygen mixtures at atmospheric pressure. Substantially cooler objects of about 320°C can cause ignition under prolonged contact at less than atmospheric pressure [5]. Hot air jet ignition temperature is 670 °C [4]. The reported temperature strongly depends on the system, and the values selected for comparison should be applied only to similar systems. As shown in Figure 8 hydrogen, propane, and natural gas (i.e. methane) have almost similar values of auto-ignition temperatures. All three fuels have the auto-ignition temperatures that are at least twice as high as the auto-ignition temperature of gasoline vapour [7].

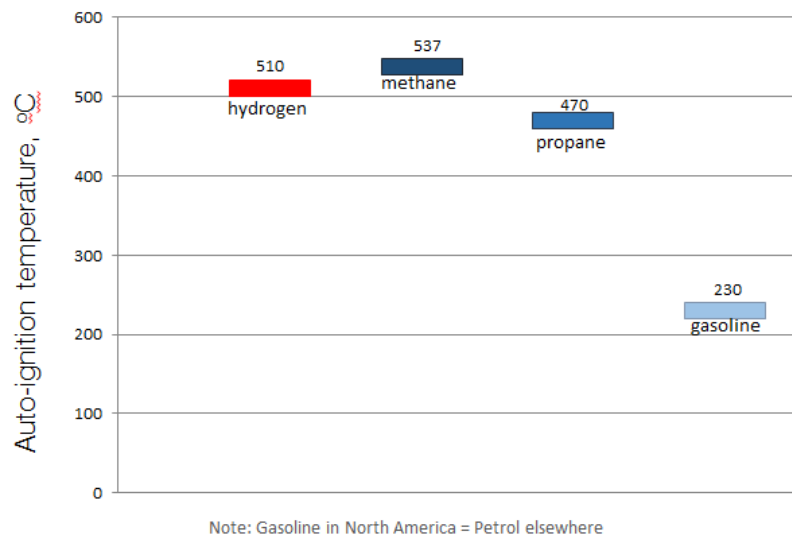


Figure 8. The auto-ignition temperatures, based on the data published in [3], of hydrogen and other fuels.

The *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 [3]. 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 on Figure 9.

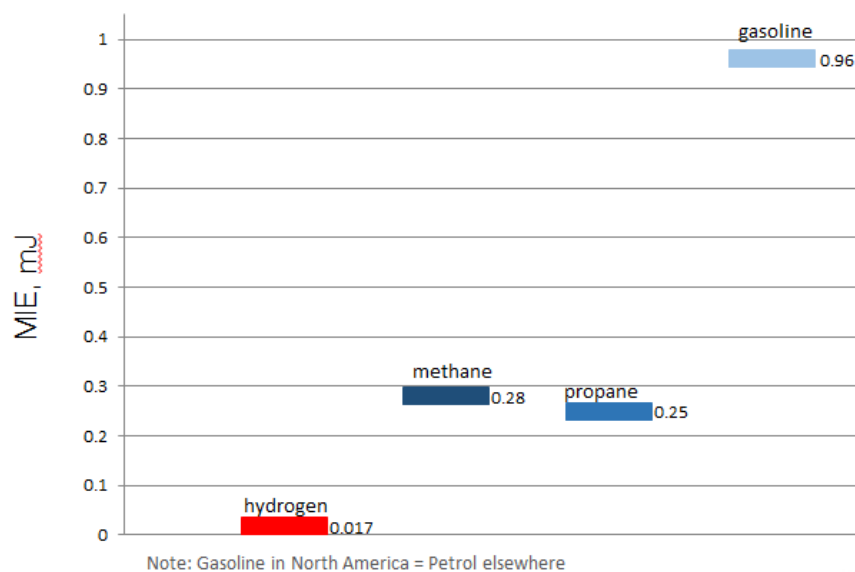


Figure 9. MIE values, based on data published in [3], for hydrogen and other fuels.

The MIE of hydrogen-air mixture varies with its composition, and becomes infinite at the flammability limits as indicated on Figure 10. The MIE values of hydrogen-dry air mixture are shown as a solid line, and MIE at fixed gap distances of 0.5, 1, 2, 3, and 4 mm are on the corresponding broken lines.

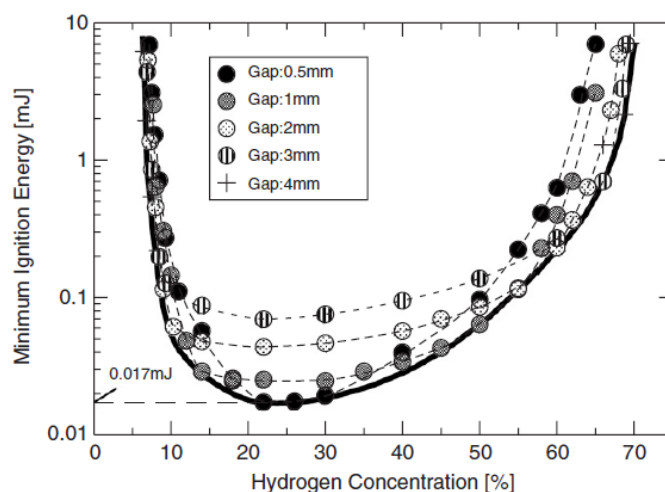


Figure 10. MIE as a function of hydrogen concentration: [19]

Less energy is needed to ignite a mixture that is closer to its stoichiometric composition. Over the flammable range of hydrogen-air mixtures, the ignition energy varies by almost three orders of magnitude [3]. The MIE for the most ignitable hydrogen-air mixture is 0.017 mJ [14]. The ignition energy depends, in addition to the mixture composition, on other factors such as the initial pressure and temperature. Since most ignition sources generate more than 10 mJ, practically all common fuels would be ignited in mixture with air if their concentration exceeds the lower flammability limit (LFL). The ignition sources capable of forming shocks, for example high-energy spark discharges and high explosives, can directly initiate detonation [3].

The energy stored as a static electricity on an object varies, depending on the size of the object and its capacitance, the voltage to which it is charged, and the dielectric constant of the surrounding medium [31]. For modelling the effect of static discharge, a human being is represented as a capacitor of 100 picofarads, charged to a voltage of 4,000 to 35,000 volts. The total energy is of the order of millijoules. Larger objects will store more energy. This energy is typically discharged in less than a microsecond and is sufficient to ignite not only near stoichiometric mixtures but also mixtures close to the flammability limits [3]. Insulation materials such as wood, paper, and some fabrics will typically form a conductive layer that can prevent static build-up by absorbing water from the air in environments where the relative humidity is greater than 50% [6].

The *flashpoint* is the lowest temperature, at which the fuel produces enough vapours at its surface to form a flammable mixture with air [3]. The flashpoint temperatures for hydrogen and other common fuels are summarised in Table 7.

Table 7. The flashpoints for hydrogen and other common fuels [3, 14].

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

The *Maximum Experimental Safe Gap* 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 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 [3].

The *flame temperature* for 19.6 vol. % of hydrogen in air has been measured as 2,318 K [20]. An obvious hazard resulting from this property is severe burns of persons directly exposed to hydrogen flames. The maximum hydrogen flame temperature is 2,400 K [8].

The flame radiation

Hydrogen burns with very pale-blue flames and emits neither visible light in day time (because the sun radiation can overpower the hydrogen flame visibility) nor smoke (it produces only water when it burns in air) unless sodium-containing or dust particles are entrained and burned along with the combustible mixture. Compared to hydrocarbon combustion, hydrogen flames radiate significantly less heat. Thus, a human physical feel of this heat does not occur until direct contact is made with the flame. A hydrogen fire may remain undetected and will propagate in spite of any direct monitoring by people in the areas where hydrogen can leak, spill or accumulate and form potentially combustible mixtures. Therefore, convective and radiative heat fluxes are important parameters and must be assessed for the protection of life, property and the environment.

Thermal radiation depends on the water vapour content in the atmosphere. The atmospheric moisture absorbs thermal energy radiated from a fire and can reduce its values. This effect is significant for hydrogen fires. The *intensity of radiation from a hydrogen flame* (I) at a specific distance (r) depends strongly on the amount of water (w) vapour present in the atmosphere and is expressed as:

$$I = I_0 \cdot e^{-0.0046wr} \quad (3),$$

where I_0 is the initial intensity (energy/time (area))

w - water vapour contents (% by weight)

r - distance (meters) [8].

The variation in a distance from a hydrogen fire for thermal radiation intensity of 2 cal/cm² for an exposure duration of 10 s is shown in Figure 11 [21]. The intensity of 2 cal/cm² is roughly the radiant flux required to produce flesh burns and ignite certain combustible materials in short exposure times. 2 cal/cm² = 8.4 J/cm² (0.051 Btu/in²) [8].

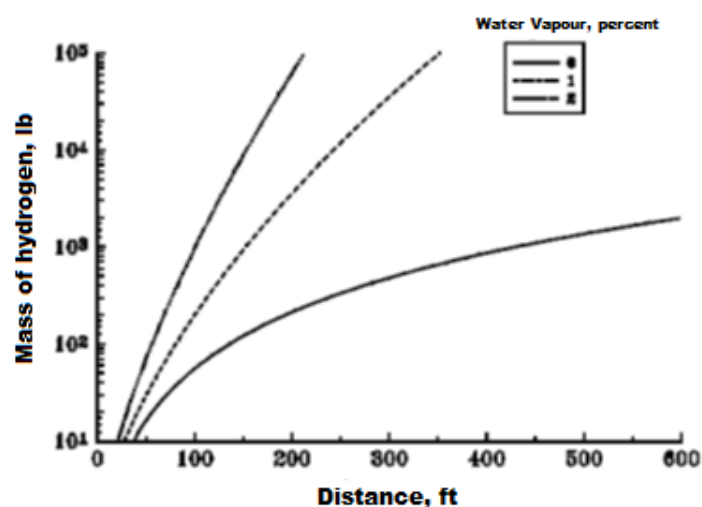


Figure 11. The effect of the moisture content on the distance from burning different masses of hydrogen [21].

Hydrogen flames are almost invisible in a daylight irradiating mostly in the infrared and ultraviolet region. The main regions of the flame are indicated in Figure 12. Any visibility of a hydrogen flame is caused by impurities such as moisture or particles in the air. Yet, hydrogen fires are readily visible in the dark and large hydrogen fires are detectable in daylight by the “heat ripples” and the thermal radiation felt on the skin [22]. Thermal energy radiated from flame to surroundings ranges from 17 to 25% [8].

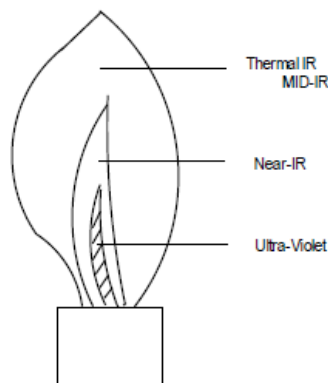


Figure 12. The regions of the flame [8].

(Note: A larger portion of the flame emits in the thermal infrared than in the ultraviolet. This means that a fire looks bigger with a thermal imager than it does with a near-infrared imager)

The *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 the stated conditions of composition, temperature, and (both spherical flame curvature and strain) of a stoichiometric hydrogen-air mixture can be calculated as an experimental propagation velocity S_v of a spherical flame, e.g. observed by schlieren photography⁴, divided by the expansion coefficient of combustion products E_i :

$$S_u = S_v / E_i \quad (4)$$

The *expansion coefficient* (E_i) is the ratio of the unburnt mixture density to the density of combustion products at the same pressure. E_i is equal 7.2 for the stoichiometric hydrogen-air mixture [3]. The laminar burning velocity of a stoichiometric hydrogen-air mixture is 1.91 m/s. This value is one order of magnitude higher compared to the values of most hydrocarbons (velocities are in the range 0.30-0.45 m/s). The burning velocity of a stoichiometric hydrogen-oxygen mixture is above 10 m/s at NTP. It is more than 5 times higher than the burning velocity of stoichiometric hydrogen-air mixture [3].

The dependence of laminar burning velocity and expansion coefficient on hydrogen concentration in air for the entire flammability range is shown in Figure 13. Maximum expansion ratio E_i was obtained for the 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 [3]. This effect of shifting to the higher laminar burning velocity value is due to the high molecular diffusivity of hydrogen in air. The maximum possible flame propagation speed, i.e. deflagration front velocity relative to a fixed observer, is given by the speed of sound in

⁴ The schlieren photography is a method to register the flow of fluids of varying density (see for instance Wikipedia)

the combustion products, which is 975 m/s for a stoichiometric hydrogen-air mixture [4]. These high values indicate high explosive potential of hydrogen and the difficulty of confining or arresting hydrogen flames and explosions [8].

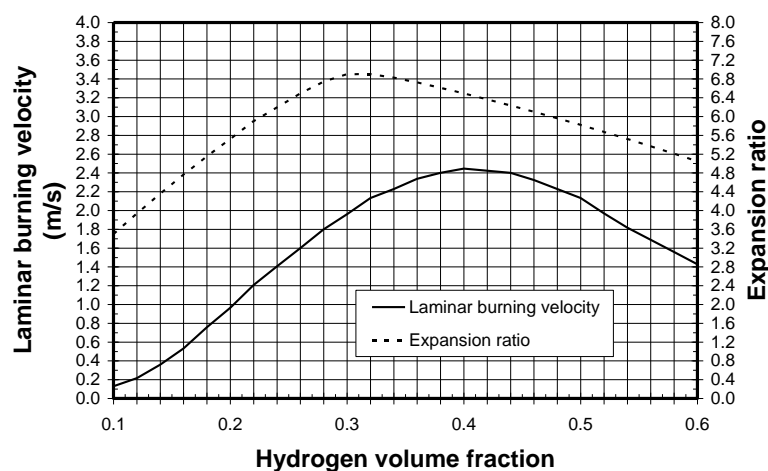


Figure 13. Laminar burning velocity and expansion coefficient of combustion products E_i as functions of hydrogen mole fraction in air [3].

Detonability limits

Detonation is the worst case scenario for an accident, which involves hydrogen. Hydrogen has a wider detonability range compared to other fuels (Figure 14). The diagram shows the upper and lower detonation limits for four fuels.

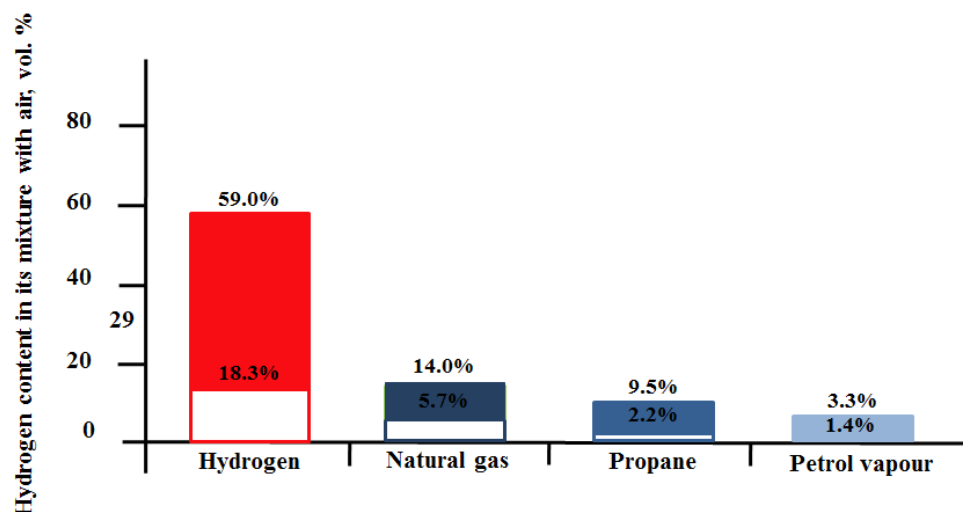


Figure 14. Detonability range as per data published in [6] for hydrogen and other common fuels [6].

The detonability range mentioned in the technical report [6] is between 18 and 59 vol. % of hydrogen in air. This range is narrower than and within the flammability range of 4-75 vol. %. The detonation range of 13-70 vol. % is reported for hydrogen-air mixtures in a 43 cm diameter tube [23]. A lower detonability limit of 12.5% by volume was observed in the Russian large-scale detonation test facility RUT [3]. The widest detonability range of hydrogen in air 11-59 vol. % is recommended by Alcock et al. [13].

The detonability limits are not fundamental characteristics of the mixture as they strongly depend on the size of the experimental set up where they are measured. In more detail the detonation parameters will be discussed in a dedicated lecture. The LFL is a critical parameter for first responders. The flammable gas monitors will trigger when the hydrogen concentration reaches 25% of the LFL (i.e., 1 vol. %), and that's all firefighters should be concerned with [7]. First responders should know that hydrogen in air is flammable from 4 to 75 vol. %, and that if it accumulates in a confined space, an explosion could occur [7]. First response is based on the potential for explosions to occur within the entire flammability range and therefore first responders will be acting conservatively and responding in a safe manner.

Hydrogen flames quenching

Hydrogen flames are difficult to quench. For example, premixed hydrogen-air combustion can be aggravated by heavy sprays of water due to induced turbulence and ability of mixture to burn around the droplets. Hydrogen has the lowest quenching distance compared to other flammable gases. Quenching of any flame occurs when the heat losses from flame are comparable with the heat generated through combustion, and thus the chemical reactions cannot be sustained. The published data are quite scattered and terminology used can complicate the problem further.

The *quenching distance* is the maximum distance between two parallel plates that will extinguish a flame passing between them [3]. Sometimes quenching distance is reported as the minimum pipe diameter through which a premixed flame can pass [3]. The *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 a passage gap dimension requirement to prevent propagation of an open flame through a flammable fuel-air mixture that fills the passage [3]. The quenching distance decreases with the increase of pressure and temperature. It also depends on the mixture composition. This is why the published data is scattered. Faster burning gases generally have smaller quenching gaps. Indeed, hydrogen-air mixture with higher burning rate has a shorter quenching gap, and thus the flame arrester should have smaller apertures [3]. The quenching gap is a function of ignition energy. Lower ignition energy of 0.001 mJ, corresponds to a smaller gap of 0.01 cm, whilst high ignition energy, 10 mJ, requires a larger gap of 1 cm [24].

Hydrogen has the narrowest MESG of 0.08 mm [4], which prevents premixed flame propagation out of a shell composed of two hemispherical parts, through the gap between flanges of these hemispheres. Due to the difference in the experimental set up (high deflagration pressures between hemispheres in MESG testing); the MESG is always shorter than the quenching gap. The lowest reported quenching distance for hydrogen is 0.076 mm [25].

Sometimes quenching distance is reported as the minimum pipe diameter through which a premixed flame can pass. The quenching distance for hydrogen, methane, and propane are 0.51 mm, 2.3 mm, and 1.78 mm, respectively [26]. Technical report of ISO/TR 15916 states that the quenching gap in air (NTP) for hydrogen is 0.64 mm [6]. There is another limit for "quenching" of hydrogen flames. This is a blow-off limit corresponding to the flow rate reached, beyond which the flame blows off the nozzle [3].

Microflames

The microflames have a mass flow rate of the order $\gamma 10^{-9}$ kg/s (1 μ g/s). They are associated with small flow rates of subsonic laminar flows from cracks [3]. The scenario of concern is a small leak in a

hydrogen system, which could ignite and burn undetected for a long period of time. This can potentially: degrade the surrounding materials, damage the containment system, provide an ignition source or ignite any hydrogen release that may occur nearby [27]. The technical information report SAE J2579 (2009) states that a localised hydrogen leak from a typical compression fitting cannot sustain a flame when mass flow rate is below $28 \mu\text{g/s}$ [28]. The lowest leak possible sustain a flame from a miniature burner configuration is $5 \mu\text{g/s}$ [31].

The images of hydrogen diffusion microflames near their quenching limits are shown in Figure 15 (left image - in air and right image - in oxygen) [29]. The hydrogen flow was directed downward. To give an impression about the real flame size the word “WE” from a US dime is shown at the same scale as the flames. The burner was a stainless steel hypodermic tube with an internal diameter of 0.15 mm and an outside diameter of 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. A shutter time for a camera used to make the images was 30 s. Buoyancy was found to be insignificant for hydrogen microflames [30].



Figure 15. The images of hydrogen diffusion microflames near their quenching limits [29].

Near their quenching limits these flames had hydrogen flow rates of $3.9 \mu\text{g/s}$ in air and $2.1 \mu\text{g/s}$ in oxygen [29]. Assuming a complete combustion and based on the hydrogen lower heating value of 119.9 kJ/g , the associated heat release rates were 0.46 W (in air) and 0.25 W (in oxygen). These are the weakest self-sustaining steady flames ever observed. Hydrogen leaks support combustion at flow rates much lower than leaks of other gaseous fuels [3].

Quenching and blow-off limits

There is generally a limited range of flow rates, for which a flame can be established on the present burners [31]. Below this range, the flow is said to be below a *quenching limit*. Quenching occurs when the heat loss is too high to sustain combustion. On the other hand, a *blow-off limit* refers to the moment when the flow rate reached the level, beyond which the flame blows off the burner. Quenching and blow-off limits bound the leak flow rates that can support combustion [3].

The quenching and blow-off limits of different gases including propane, methane and hydrogen on tube burners were measured by Kalghatgi [32], Matta et al. [33], Butler et al. [27], Cheng et al. [34] (measurement results are given in Figure 16). A flame cannot exist when its predicted length is less than the measured stand-off distance (i.e. the distance between the solid surface and the position of the peak flame temperature at a fixed value) [33]. The stand-off distance can be approximated as one half of the quenching distance of a stoichiometric premixed flame. The above mentioned experiments verified this method of finding the quenching flow rate by establishing a flame over a hypodermic stainless steel tube and decreasing the fuel flow rate until extinction. These studies showed that hydrogen blow-off limits are higher than those for methane and propane. For a given leak size, there is a range of mass flow rates where hydrogen is able to support a stable flame but methane and propane would be blown off [3]. As it follows from Figure 16 the blow-off limits increase with the increase of a tube internal diameter, and the quenching flow rates are practically independent of the diameter. The combustion limits are much wider for hydrogen than for methane and propane. Quenching and blow-off limits for methane and propane are very similar.

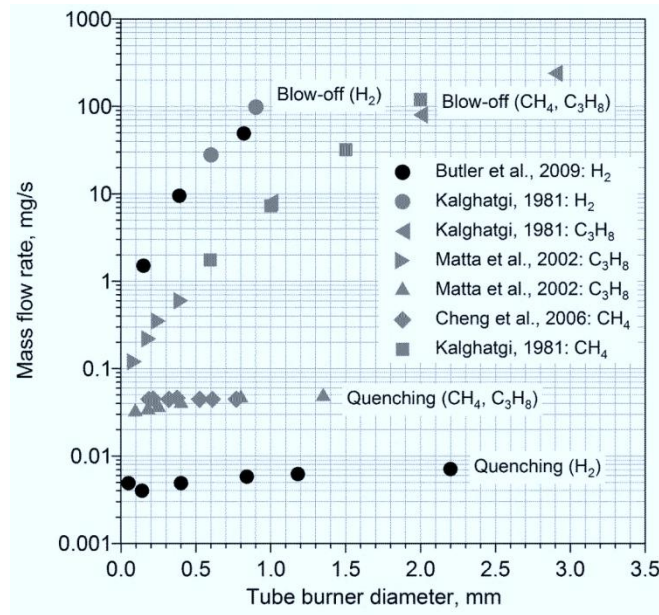


Figure 16. The quenching and blow-off limits on tube burners for hydrogen, methane and propane [3].

Three different types of round burners were considered by Butler et al. [27]: pinhole, curved-wall pinhole, and tube burners, as depicted in Figure 17.

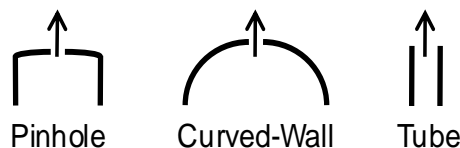


Figure 17. The scheme of round burners used for quenching limits measurements [27] (the arrows indicate the direction of hydrogen flow).

The pinholes diameters ranged from 0.008 to 3.18 mm. The *pinhole burners* were stainless steel nozzles that are manufactured for solid-stream spray generation, the top of each burner (except the two smallest ones) is a slightly curved surface with a hole passing through its axis, the two smallest burners had holes in planar, not curved, surfaces. The *curved-wall pinhole burners* were constructed

of stainless steel tubes with two outside diameters, i.e. 1.59 mm (holes 0.41-1.02 mm) and 6.35 mm (holes 0.41-3.12 mm), in which a radial hole was drilled. The *tube burners* were made from stainless steel hypodermic tubes of inside diameters ranged from 0.051 to 2.21 mm. These burners resemble micro-injectors that may be used in future small-scale microelectro-mechanical power generators [35].

The small flow rates required special flow measurement procedures [31]. For the tests with round burners a glass soap-bubble meter was installed upstream of the burners. Quenching flow rates were measured by first establishing a small flame, decreasing the flow rate until the flame extinguished, and then introducing a soap bubble in the meter for flow rate measurement. Tests performed at different burner temperatures, from room temperature and up to about 200 °C, found the quenching flow rate to be largely independent of the burner temperature provided condensation was avoided [27]. Tests were also conducted with varying ambient humidity, and quenching limits were found to be generally independent of the relative humidity of the air in the range of 46-90% [27, 31].

Hydrogen flow rate at the blow-off limit was measured with a soap bubble meter [27]. A stable flame was established and then the flow rate was increased until the flame first lifted and then extinguished. For the blow-off tests the flames were detected visually. Hearing protection was required for the blow-off tests for the larger burners [3].

Figure 18 shows the hydrogen quenching limits for three types of burners [27]. The simple theory predicts that the quenching flow rate is independent of burner diameter at 0.008 mg/s. Figure 18 shows that the analysis performed by Butler et al. [27] approximately predicts the average quenching flow rate for hydrogen, especially at burner diameters greater than 1.5 mm. Clearly, for smaller burners, there are other mechanisms that are affecting quenching limits that are not accounted for in the simple model [27].

Heat loss contributes to the differences in the quenching limits for different round-hole burners. For burners with small diameters such as pinhole burners, the quenching flow rates are the highest, while the tube burners have the lowest values. The 6.35 mm curved-wall burners act similar to pinhole burners, whereas the 1.59 mm curved wall burners act more like tube burners, and thus the 6.35 mm curved-wall burners have higher average quenching flow rates than the 1.59 mm curved-wall burners [3].

Butler et al. (2009) in [27] investigated the effect of burner orientation (vertical, horizontal, inverted) on the quenching limits. The results revealed that the quenching flow rate for pinhole and tube burners is nearly independent of orientation. The weakest was an inverted flame with a hydrogen flow rate of 3.9 $\mu\text{g/s}$. With no mechanism other than radiative heat losses, and this being low for hydrogen flames, it is the weakest ever observed flame [27]. During these experiments, the burner was found to be warmer during non-vertical tests. If burner does not affect temperature and the quenching limit is independent of orientation, then the flow field must also be constant with varying orientation [3].

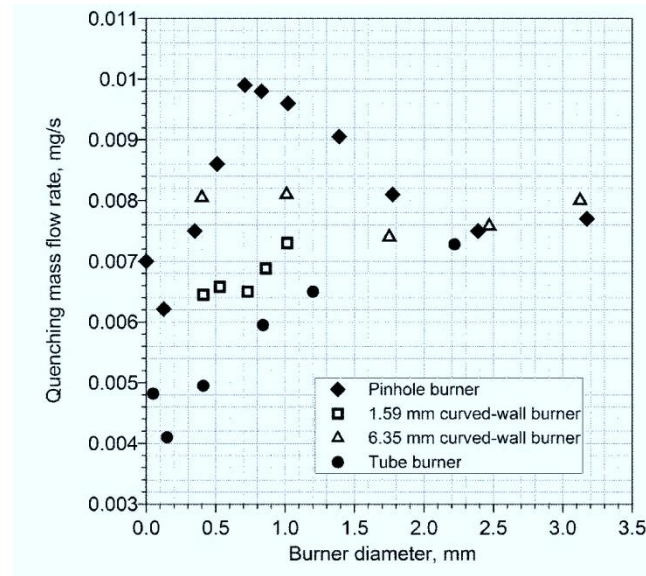


Figure 18. Quenching limits as a function of burner internal diameter and round burner type [27].

The quenching also depends on the pressure (Figure 19). Each line in Figure 19 starts at the minimum upstream pressure for choked flow and ends at the maximum pressure anticipated in FC vehicles. This plot predicts that for a given storage pressure, hydrogen is susceptible to leak flames for hole diameters that are smaller than those for methane or propane. Furthermore, at storage pressure of 69 MPa a hole diameter of just 0.4 μm is predicted to support a flame.

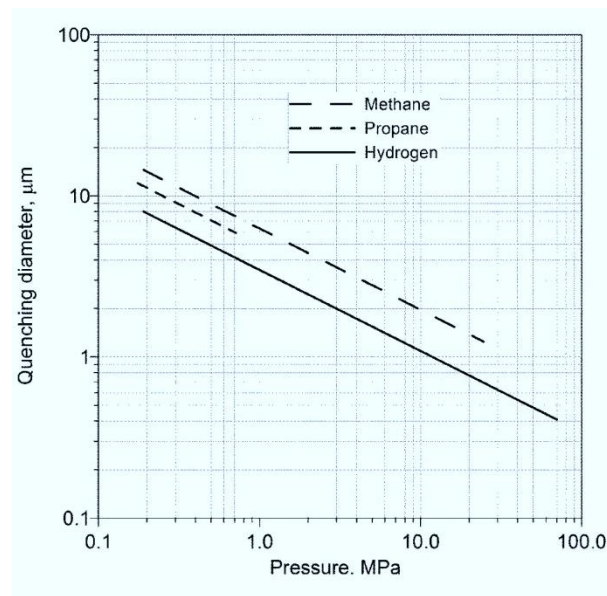


Figure 19. Quenching diameter as a function of upstream absolute pressure assuming isentropic choked flow [27].

Leaky fittings

The compression fittings are often used for gases stored at high pressure [31]. These fittings are a reliable method that allows for them to be taken apart and attached with ease. A benefit of using compression fittings over pipe thread fittings is the lack of Teflon tape that is necessary to prevent

any leakage. Any time a pipe thread fitting is taken apart, it must be cleaned and rewrapped before it can be used again.

Figure 20 (left plot) shows the measured ignition flow rates for hydrogen, methane, and propane for a leaky fitting in the vertical orientation [27]. The minimum flow rate necessary for sustained ignition is plotted versus pressure. For each fuel, the measurements at increased pressures are associated with an increase in torque on the fitting. The upper limit on pressure for propane is lower than that of the other gases because the vapour pressure of propane at 21 °C is 0.76 MPa. Butler et al. (2009) converted the measured ignition mass flow rates of Figure 20 (left) to volumetric flow rates using the measured current temperature and pressure of the laboratory. The resulting volumetric flow rates are plotted in Figure 20 (right plot) with respect to upstream pressure. Within experimental uncertainties, the minimum fuel mass and volumetric flow rates are independent of pressure. Propane requires the lowest volumetric flow rate for ignition while methane requires the highest. The volumetric flow rates for hydrogen, methane and propane are 0.337, 0.581, and 0.187 mL/s, respectively. Although 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 [3].

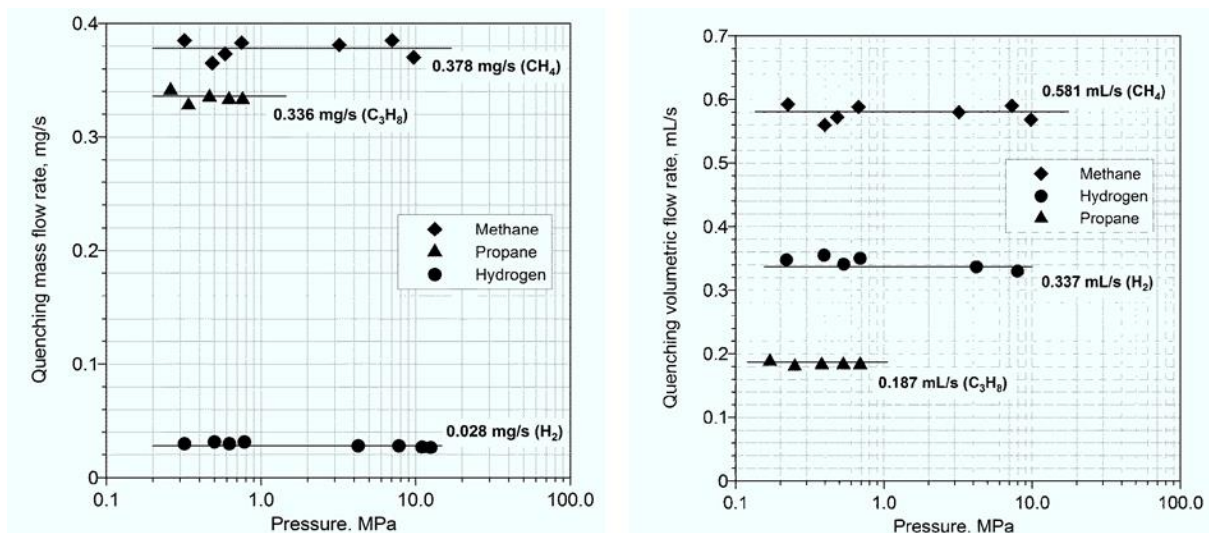


Figure 20. Quenching mass flow rate limit (left [27]) and quenching volumetric flow rate (right [31]) as functions of upstream pressure in the vertical orientation of fittings.

Comparison of hydrogen with other fuels

Hydrogen is not more or less dangerous than any other conventional fuel. Hydrogen is an unusual fuel. It has a unique set of characteristics that differ from other well-known fuels. As it follows from the materials discussed earlier in this lecture hydrogen leaks support combustion at flow rates much lower than leaks of other fuels [27]. Hydrogen flames are the dimmest of any fuel, and its mass flow rate blow-off limits are higher than those for methane and propane. Hydrogen flames cause much faster corrosion than methane flames, when they impinge on samples made of aluminium, stainless steel, and silicon carbide fibres [31]. The volumetric flow rate of hydrogen through the same leak path, at the same supply pressure, was found to be significantly higher than for methane and propane [36]. Hydrogen has the lowest values of molecular mass, density, and viscosity. The thermal conductivity of hydrogen is significantly higher than that of other gases. The diffusion coefficient in

air is the highest among all gases. The unwanted consequences of hydrogen releases into the open or in partially confined spaces (with no accumulation of hydrogen), are drastically reduced by its buoyancy, its safety asset. Hydrogen will flow out of an incident scene, and mix with the ambient air to a safe concentration level, i.e. below the LFL (4 vol. % in air).

Hydrogen has the highest heating value per unit of mass and lowest per unit volume. To provide a competitive driving range hydrogen has to be stored as a gas under pressure or should be liquefied. This has obvious safety implications. The summary of the main physical parameters is presented in Table 8.

The LFL of hydrogen is high compared to most hydrocarbons. The near-stoichiometric concentration of hydrogen in air (29.5 vol. %) is much higher than that of hydrocarbons (usually only a few percent). At the LFL the ignition energy requirement of hydrogen is similar to that of methane, and weak ignition sources such as electrical equipment sparks, electrostatic sparks or sparks from striking objects typically involve more energy than is required to ignite these flammable mixtures [37].

Table 8. Properties of hydrogen compared to other fuels [7].

	Hydrogen	Natural gas	Petrol
Colour	No	No	Yes
Toxicity	None	Some	High
Odour	Odourless	<u>Mercaptan</u>	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

The comparison of key flammability and explosion indices for hydrogen and other fuels is presented in Table 9.

Table 9. Comparison of flammability and explosive indices for hydrogen and other fuels [6, 7].

	Hydrogen	Natural gas	<u>Petrol vapour</u>
Flammability in air (LFL – UFL), vol. %	4.1 - 75	5.3 - 15	0.8 - 8.1
<u>Detonability</u> in air (LDL – UDL), vol. %	18.3 - 59	5.7 - 14	1.4 - 3.3
Stoichiometric mixture in air, vol. %	29.59	9	2
Flame temperature (°C)	2130	1961	1977

This laminar burning velocity of stoichiometric hydrogen-air mixture of about 2 m/s is far greater compared to most of hydrocarbons, the velocities of which are in the range 0.30-0.45 m/s. Hydrogen is more prone to deflagration-to-detonation transition (DDT) compared to most other flammable gases [3].

Compared to other fuels hydrogen is the most prone to spontaneous ignition during sudden releases to air by the so-called diffusion mechanism, when high temperature air, heated by a shock, mixes with cold hydrogen at the contact surface between these two gases and chemical reactions can be initiated, when critical conditions are reached. Indeed, sudden hydrogen releases into a piping filled with air, after a safety burst disk ruptures, can be spontaneously ignited at pressures as low as about 2 MPa [37]. On the other hand, the standard auto-ignition temperature of hydrogen in air is above 520°C, which is higher than for hydrocarbons. Interestingly, the hot air jet ignition temperature is lower for hydrogen compared to all hydrocarbons, decreasing further with the increase in jet diameter [37].

The performance of octane (i.e. hydrocarbon) is used as a standard to measure resistance to knock in internal combustion engines, and is assigned a relative octane rating of 100. Fuels with an octane number over 100 have more resistance to auto-ignition than octane itself. Hydrogen has a very high research octane number, and therefore is resistant to knock (combustion under lean conditions), i.e. 130+ (lean combustion) compared to other fuels: methane (125), propane (105), gasoline (87), diesel (30). The octane number has no relevance for use of hydrogen with fuel cells [1]. The quenching distance (i.e. the minimum pipe diameter through which a premixed flame can propagate) for hydrogen, methane, and propane are 0.51 mm, 2.3 mm, and 1.78 mm, respectively [26]. Thus, hydrogen has the lowest quenching distance [3].

Hydrogen fires normally are not extinguished until the supply of hydrogen has been shut off because of the danger of re-ignition and “explosion”. Creitz (1961) published results on the extinction of diffusion flames on a burner placed in a Pyrex jacket for six different fuels [38]. The difference in extinguishing effectiveness of an inhibitor introduced on the two sides of the reaction zone of diffusion flames has been measured as a function of oxygen concentration in the oxygen-nitrogen mixture supplied to the flames. Comparison of extinguishment characteristics of nitrogen (N₂), methyl bromide (CH₃Br), trifluoromethyl bromide (CF₃Br) for various fuels burning in air is shown in Table 10 (in percentage by volume).

Table 10. Comparison of extinguishment characteristics of nitrogen, methyl bromide, and trifluoromethyl bromide [38].

Fuel	Percentage of inhibitor in air or fuel at extinction						Efficiency relative to nitrogen			
	When added to air			When added to fuel			Added to air		Added to fuel	
	N ₂	CH ₃ Br	CF ₃ Br	N ₂	CH ₃ Br	CF ₃ Br	CH ₃ Br	CF ₃ Br	CH ₃ Br	CF ₃ Br
Hydrogen	94.1	11.7	17.7	52.4	58.1	52.6	8.0	5.3	0.9	1.0
Methane	83.1	2.5	1.5	51.0	28.1	22.9	33.2	55.4	1.8	2.2
Ethane	85.6	4.0	3.0	57.3	36.6	35.1	21.4	28.5	1.6	1.6
Propane	83.7	3.1	2.7	58.3	34.0	37.6	27.0	31.0	1.7	1.6
Butane	83.7	2.8	2.4	56.8	40.0	37.9	29.9	34.9	1.4	1.5
Carbon monoxide	90.0	7.2	0.8	42.8	19.9	-	12.5	112	2.2	-

It was found that when the inhibitor was added to the fuel, the volume percentage required for extinguishment was much greater than when added to the oxygen side of the reaction zone, with the single exception of CO flames inhibited by trifluoromethyl bromide. This result of Creitz (1961) can be explained by the entrainment law, stating that a mass flow rate of the entrained into a plume surrounding gas grows with the distance from the source of fuel and with the momentum flux of the plume. It is well known from fire safety science that the amount of air entrained into fire at flame height is about two orders of magnitude greater than amount of released fuel [3]. Above oxygen concentrations of the order of 25% by volume, methyl bromide was completely ineffective when added to the oxygen side of the reaction zone, and above about 32% oxygen it was ineffective when added to the fuel, since at this oxygen concentration it burns without additional fuel.

Extinction of a diffusion flame may be affected by a number of factors, among them being the rate at which the fuel is supplied to the burner and the velocity of the secondary air past the flame [38]. The latter effect was found to be important at rather low or very high flow rates. When the rate of fuel supply was too low, for a given burner size, the flame would not burn, and conversely, when the rate was too high, lifting occurred and the flame tended to float off and be extinguished. The latter observation of Creitz (1961) could be due to shielding effect of Pyrex jacket that limits oxidiser entrainment to the flame. This particular test condition limits the importance of conclusions of such experiments [3].

In the test carried out by Creitz (1961) [38] conditions for the extinction of hydrogen are the most difficult among the fuels tested and require more inhibitor. Methyl bromide is more efficient to extinguish hydrogen diffusion flame in air compared to trifluoromethyl bromide. Work of Creitz (1961) can be considered as a comparative study of extinction efficiency of selected inhibitors for different fuels rather than quantitative recommendation on inhibitor concentrations for extinction of real flames, especially non-premixed turbulent flames, which are characteristic for hydrogen technologies [3].

Summary

The advantages of hydrogen over traditional hydrocarbon-based fuels are very clear:

- it does not produce any CO₂ emissions during combustion;
- hydrogen is capable to produce more energy per unit mass;
- it can be generated from a range of renewable sources such as wind, sun, tidal and hydro-power.

From a safety point of view, hydrogen is not more or less dangerous than other fuels, but it is different. This difference is in its specific physical properties and combustion characteristics. Not only first responders but the members of general public should be aware of these properties as they are directly linked to hazardous behaviour of hydrogen. For example, hydrogen leaks are difficult to detect by human senses because it is colourless, odourless and tasteless. Hydrogen has an invisible flame when it burns in a clean atmosphere. It is prone to leakage, and hydrogen fires can escalate to explosions. Nevertheless, the main safety asset of hydrogen is its highest among other gases buoyancy, which allows it to flow out of an incident/accident scene and to mix with air to a safe concentration levels.

This lecture relates hydrogen structural, physical, chemical, ignition, combustion and other characteristics to a range of safety considerations. It also compares the main parameters of hydrogen against those for traditional fuels, which are currently in use.

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