European Train the Trainer Programme for Responders

Lecture 2
Properties of hydrogen relevant to safety
LEVEL I
Firefighter

The information contained in this lecture is targeted at the level of Firefighter and above.

This topic is also available at level IV (Specialist Officer).

This lecture is part of a training material package with materials at levels I – IV : Firefighter, crew commander, incident commander and specialist officer. Please see the lecture introduction regarding competence and learning expectations

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Acknowledgements

Summary

This lecture outlines the properties of hydrogen relevant to safety. The advantages of hydrogen over traditional hydrocarbon-based fuels are very clear:

- it does not produce any CO_2 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.

The HyResponse project is acknowledged as the materials presented here are extended based on the original HyResponse lectures (http://www.hyresponse.eu).

Keywords

Buoyancy, ignition, combustion, flammability limit, detonation

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1. Target audience

The information contained in this lecture is targeted at LEVEL 1: Firefighter. Lectures are also available at levels II, III and IV: crew commander, incident commander and specialist officer.

The role description, competence level and learning expectations assumed at crew commander level are described below.

1.1 Roll description: Firefighter

A firefighter is responsible and expected to be capable of carrying out operations safely in personnel protective equipment including breathing apparatus using equipment provided, like vehicles, ladders, hose, extinguishers, communication and rescue tools, under any climatic conditions in areas and to emergency situations which can be reasonably anticipated as requiring a response.

1.2 Competence level: Firefighter

Trained in the safe and correct use of PPE, BA and other equipment which it is expected they will operate first responders must be supported by appropriate knowledge and practice. Behaviours that will keep them and other colleagues safe should be described by Standard Operating Procedures (SOP). Practiced ability to dynamically assess risk to self and others safety is required.

1.3 Prior learning: Firefighter

EQF 2 Basic factual knowledge of a field of work or study. Basic cognitive and practical skills required to use relevant information in order to carry out tasks and to solve routine problems using simple rules and tools. Work or study under supervision with some autonomy.

2. Introduction and objectives

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 Fuel Cell and Hydrogen (FCH) technologies by 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 are aware of all specific hazards related to handling and use of FCH systems. Interestingly, most of hydrogen's 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 responders.

The purpose of this lecture is to provide responders with a critical understanding of hydrogen properties relevant to safety. 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 hydrocarbon fuels. 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 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. as used with 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 with further detail in Lecture 5 – Liquefied Hydrogen.

The main hydrogen safety asset is its buoyancy which is the highest on the Earth. 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. 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 fuels currently used [2].

By the end of this lecture 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.

3. Different forms of hydrogen

3.1 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].

3.2 Gaseous, liquefied and slush forms of hydrogen

At standard temperature and pressure (STP[1]) 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* (GH$_2$) 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.

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

Liquid hydrogen (LH$_2$) is a colourless, odourless, non-corrosive, and not a very reactive liquid. It is a cryogenic fluid (please note: fluids with temperatures below -73 ℃ 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. LH$_2$ will rapidly boil or flash to a gas if exposed to or spilled into an environment with normal temperature. Warming LH$_2$ 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 LH$_2$ to GH$_2$ is 1:848. LH$_2$ expands approximately 850 times upon conversion to a gas at normal temperature and pressure (NTP[2]), thus it is stored at relatively low pressures in double-walled, vacuum insulated containers equipped with burst disks, vents, and pressure relief devices (PRDs). It has the lowest density of any liquefied gas. Unlike for propane, the compression of gaseous hydrogen does not liquefy it. Therefore, LH$_2$ 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]. GH$_2$ storage vessels are also equipped with PRDs to allow a controlled venting of hydrogen gas. This will be discussed in more detail in the lecture on safety of hydrogen storage.

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].

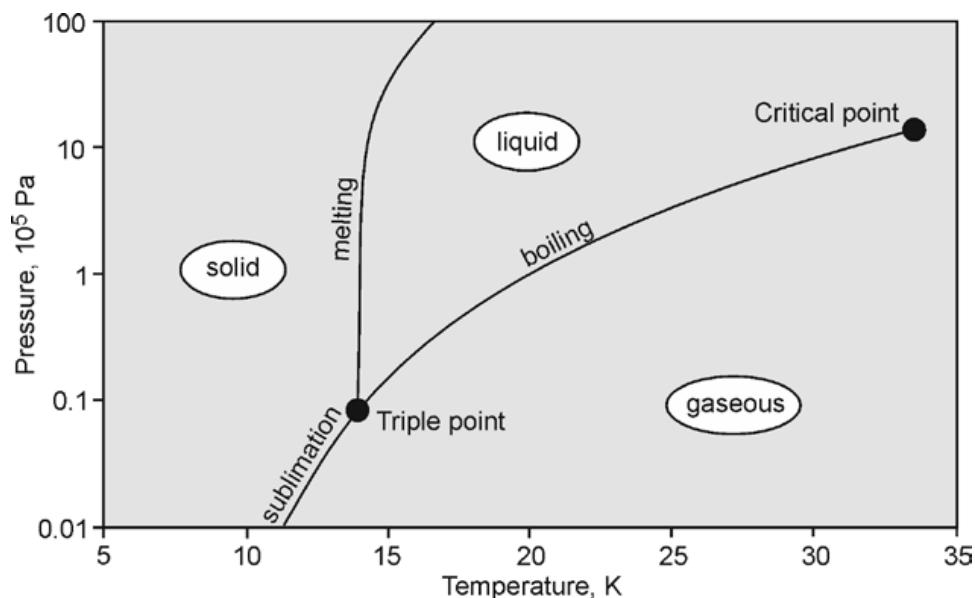Figure 1. Phase diagram of hydrogen [3]

Hydrogen can exist in gaseous, liquid, or slush forms. LH$_2$ is a clear liquid with a light-blue tint. The s*lush* hydrogen is a mixture of solid and liquid hydrogen at the triple point

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[2] Normal Temperature and Pressure (NTP): 293.15 K (20℃) and 101,325 Pa.

temperature. The transition between gas, liquid, and solid phases of hydrogen is dominated by the low temperatures.

LH_2 has a density of 70.78 kg/m^3, which 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].

4. Physical properties of hydrogen

4.1 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.
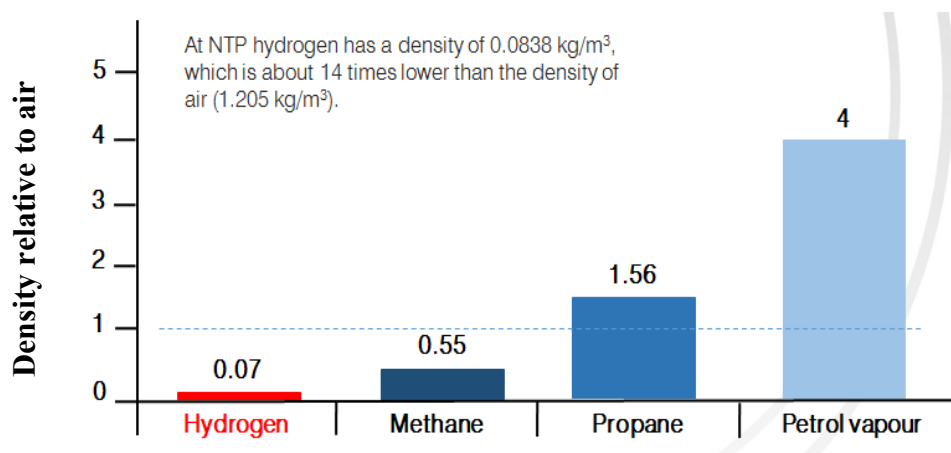

Figure 2. Densities relative to air for hydrogen and other common fuels

Thus, the low vapour density of hydrogen results in the gas being very *buoyant* compared to other compounds. In fact, hydrogen has the highest buoyancy on Earth. 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 of forming 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].

4.2 Ignition properties

Hydrogen is very easily ignited [5]. Potential 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 the 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 ºC [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 ºC can ignite hydrogen-air or hydrogen-oxygen mixtures at atmospheric pressure. Substantially cooler objects of about 320 ºC can cause ignition under prolonged contact at less than atmospheric pressure [5]. Hot air jet ignition temperature is 670 ºC [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 3 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].
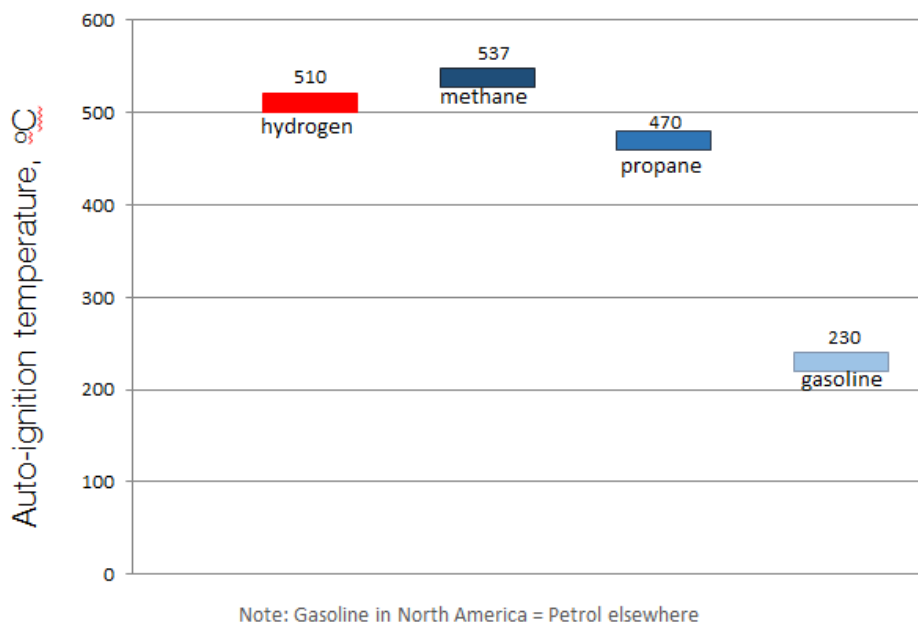

Figure 3. The auto-ignition temperatures, based on the data published in [3], of hydrogen and other fuels.

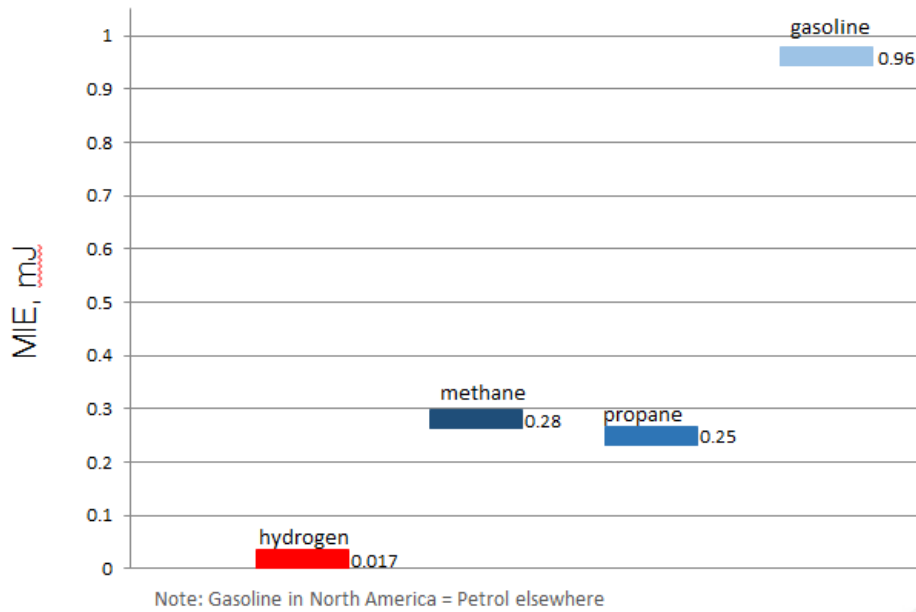Note: Gasoline in North America = Petrol elsewhere

Figure 4. MIE values, based on data published in [3], for 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 4.

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, from [3, 14] are summarised in Table 1.

Table 1. The flashpoints for hydrogen and other common fuels

	Hydrogen	Methane	Propane	Petrol	Diesel
Flashpoint, ºC	-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].

4.3 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.

4.4 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 5). The diagram shows the upper and lower detonation limits for four fuels [6].
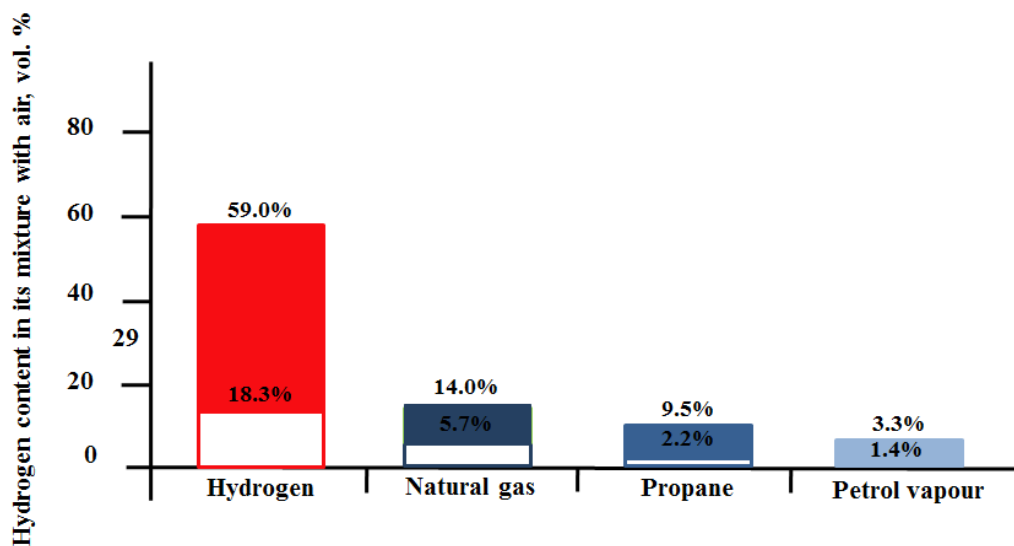
Figure 5. Detonability range as per data published in [6] for hydrogen and other common fuels

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].

5. 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. And 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 2. Properties of hydrogen compared to other fuels [7]

	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

A comparison of key flammability and explosion indices for hydrogen and other fuels is presented in Table 3.

Table 3. Comparison of flammability and explosive indices for hydrogen and other fuels [6, 7]

	Hydrogen	Natural gas	Petrol vapour
Flammability in air (LFL – UFL), vol.%	4.1 - 75	5.3 - 15	0.8 - 8.1
Detonability 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 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 ºC, 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 [38] published results on the extinction of diffusion flames on a burner placed in a Pyrex jacket for six different fuels. 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 (N_2), methyl bromide (CH_3Br), trifluoromethyl bromide (CF_3Br) for various fuels burning in air is shown in Table 4 (in percentage by volume).

Table 4. 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_3Br	CF_3Br	N_2	CH_3Br	CF_3Br	CH_3Br	CF_3Br	CH_3Br	CF_3Br
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 [38] 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 [38] 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 [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 [38] 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].

References

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.

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.

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.