European Train the Trainer Programme for Responders

# Lecture 8

# Ignition sources and prevention of ignition

## LEVEL I

## Firefighter

The information contained in this lecture is targeted at the level of firefighter.

This topic is also available at levels III & IV.

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

Note: these materials are the property of the HyResponder Consortium and should be acknowledged accordingly, the outputs of HyResponse have been used as a basis

## Disclaimer

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## Summary

Hydrogen is easily ignited due to having the lowest minimum ignition energy (MIE) amongst known fuels. It is often difficult to establish the exact source of hydrogen ignition and to determine its specific mechanism. This lecture gives an overview of hydrogen ignition incidents and mechanisms.

## Keywords

Minimum ignition energy (MIE), auto-ignition temperature, ignition sources, ignition mechanisms

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# 1. Target audience

The information contained in this lecture is targeted at LEVEL 1: Firefighter.

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

This lecture will provide Responders with information on the possible sources of hydrogen ignition and the related mechanisms, including the diffusion mechanism of spontaneous ignition during a sudden release of hydrogen. It covers the main characteristics related to the ignition of hydrogen-oxygen mixture: minimum ignition energy, its dependence on hydrogen concentration in the mixture, auto-ignition temperature, and effect of triboelectricity. This lecture also describes the methods used for the prevention of hydrogen ignition through careful evaluation of the possibility of ignition and elimination of ignition sources.

By the end of this lecture a Responder/a trainee will be able to:

- Recognise different types of ignition sources;
- Identify mechanisms of hydrogen ignition depending on the ignition source;
- Compare the values of minimum ignition energy (MIE) and auto-ignition temperature of hydrogen with those for other common fuels;
- Explain the minimum ignition energy as a function of hydrogen content in the mixture;
- Evaluate stages of spontaneous ignition of a sudden hydrogen release;
- Recognise the means to control hydrogen ignition sources;
- State the main prevention measures for hydrogen ignition.

# 3. Ignition sources

It is difficult to define the exact source of hydrogen ignition due to the low minimum ignition energy (MIE) of hydrogen. Thus, it is often difficult to distinguish what exactly causes hydrogen to ignite and what was the mechanism of ignition. The list of possible ignition sources is shown below.

**Electrical sources**:

- Electric sparks (e.g. from electrical equipment)
- Static discharges (e.g. in ungrounded particulate filters)
- Electric arc (switches, electric motors, portable phones, pagers and radios).
- Lightning discharge (e.g. lightning strikes near the vent stack)
- Electrical charge generated by equipment operation (compressors, generators, vehicles, and other construction equipment)
- Electrical short circuits or other electrical equipment
- Electrified particles

**Mechanical sources**:

- Mechanical sparks (from rapidly closing valves)
- Mechanical impact and/or friction
- Metal fracture
- Mechanical vibration and repeated flexing

**Thermal sources:**

- Hot surfaces (e.g. heating equipment)
- Open flames
- Hot jets
- Exhausts (e.g. combustion engines and exhaust stacks)
- Explosive charges (e.g. charges used in construction, fireworks or pyrotechnic devices)
- Catalysts, explosives and reactive chemical materials
- Shock waves and/or fragments
- Reflected or repeated acoustic and shock waves

**Other sources:**

- Ionizing radiation (radioactivity)

- Electromagnetic radiation
- Ultrasonic radiation
- Light (laser/flash)
- Adiabatic compression (pressure increase)

It is generally recognised that pure gases do not become electrostatically charged under normal conditions [3], but this refers generally to low velocities and pressures. When gases are released at very high pressures, the flow becomes sonic and the propensity of electrostatic charging occurring is not known. It is known that pure gases tend not to charge, but particles within the gas stream are known to become electrostatically charged [3].

The discharge path in many practical cases would probably be convoluted and not in a straight line. This would require the hydrogen to discharge through bends, which would potentially allow materials on the surface of the discharge path, e.g. piping, to be eroded and form particles which could become electrostatically charged [3].

## 3.1 Electrostatic discharge ignition

There are three main types of electrostatic discharge: spark, brush, and corona [1]. A *spark discharge* is a single plasma channel between a high potential conductor and an earthed conductor. A *brush discharge* is a discharge between a charged insulator and a conducting earthed point. A *corona discharge* is a silent, usually continuous, discharge with a current but without a plasma channel.

Studies undertaken many years ago on hydrogen vents showed that ignition was rare during fine weather, but was more frequent during thunderstorms, sleet, falling snow, and on cold frosty nights [1].

## 3.2 Mechanical ignition

The key properties of burning metal particles or sparks that are relevant to their ability to cause ignition of a flammable mixtures include:

- Size
- Material
- Velocity
- Temperature
- Number
- Combustion rate and time

There are metal-to-metal contact pressure and relative velocity threshold for spark production during impact, rubbing or grinding. Above the threshold metal particles are lost from the weakest of two materials. Generally, the particles are only produced when the relative velocity between the two surfaces exceeds 1 m/s [4].

## 3.3 Ignition by a hot surface

This phenomenon, common for the most flammable gas/vapour-air mixtures, is that the surroundings are providing a high enough temperature, the combustion heat cannot be lost to the surrounding surfaces so this is allowing the oxidation chain-reaction to progress [3].

# 4. Hydrogen ignition mechanisms

In 2007, Astbury and Hawksworth published a paper analysing the statistics of hydrogen ignition incidents and the associated mechanisms [1]. The authors discovered that there have been reports of high-pressure hydrogen leaks igniting for no obvious reasons, and several ignition mechanisms have been proposed. It was underlined that although many leaks have been ignited, there are also reported leaks where no ignition has occurred. For the cases where ignitions occurred without any obvious ignition sources the mechanisms suggested are rather speculative, lacking a rigorous scientific analysis. This work identified the knowledge gaps of the exact ignition mechanism for a hydrogen release. The mechanisms, which have been considered by Astbury and Hawksworth [1] include electrostatic charge generation, mechanical ignition, reverse Joule-Thompson effect, diffusion ignition, sudden adiabatic compression, and hot surface ignition. These mechanisms will be discussed below in the present lecture.

By analysing the Major Hazard Incident Database Service of the Health and Safety Executive[1] (UK), Astbury and Hawksworth [1] revealed 81 incidents involving releases of hydrogen. Of those, a delay between a release and ignition was reported only for 4 cases. The authors assumed that in other cases hydrogen was ignited immediately. In 11 cases, the source of ignition was identified, but in the remaining, i.e. in 86.3% of incidents, the source of ignition was not clear. As for non-hydrogen releases, 1.5% of them did not ignite, and 65.5% of ignition sources were not identified. This does prove the suggestion that there is a difference in propensity for ignition between hydrogen and non-hydrogen gases when released. The following incidents/accidents have been reviewed by Astbury and Hawksworth [1] among the others. From work undertaken by Nusselt in Germany several spontaneous ignitions of hydrogen at 2.1 MPa being discharged to atmosphere had been reported. The storage cylinders had been noted for having quantities of iron oxide (i.e. rust) in them even though they were apparently dry, and it was thought first that there was potential for electrostatic charging to occur. However, the experiments on discharging hydrogen into an open funnel fitted with a long pipe showed no ignitions, except when the funnel was obstructed by an iron cap. The mechanism was not understood, so further trials were undertaken. Only when the tests were carried out in the dark a corona discharge was observed. When hydrogen leaked out of a flange and the pipe was tapped to stir up dust the corona discharge increased. An ignition occurred after the tapping. Further work showed that when sharpened copper wires were used to promote corona discharges, the ignition happened when the point was bent away from the gas direction, whereas no ignition occurred when the wire was pointing in the direction of flow [1].

Another incident reported by Astbury and Hawksworth [1] refers to a cylinder of hydrogen being connected to a piece of laboratory apparatus. A laboratory technician forced open

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[1] In this database hydrogen releases, which simply dispersed and did not involve fire, explosion, or other major hazard, are not recorded. Thus, the non-ignition being reported as zero is not necessarily an indication that all hydrogen releases were ignited.

(cracked the valve open) to clear any dirt out of the connection, and when he did so, the escaping gas ignited immediately. Bond [5] attributed this ignition to the phenomenon of *diffusion ignition* in 1991. Whilst no pressure of gas is quoted in this incident, it can be assumed that the pressure would have been the typical full cylinder pressure of 23 MPa. Reider et al. [16] tested a release of a large quantity of hydrogen to determine the sound pressure levels. Gaseous hydrogen was released at an initial pressure of 23.6 MPa and an initial rate of 54.4 kg/s, for a period of 10 s. The gas was transferred through a 200 mm nominal bore pipe and a 150 mm bore ball valve to a cylindrical vessel fitted with a convergent–divergent nozzle venting to atmosphere. In the test run where the gas was not deliberately ignited, after 10 s, the 150 mm diameter valve was closed, and 3 s after starting to close the valve, ignition occurred. The three potential ignition mechanisms examined were: electrification of the gas, electrification of particles in the gas, and metal particles abrading a metal bar welded across the mouth of the nozzle. Of these, the first was discounted as pure gases are known to have negligible electrostatic charging. The second mechanism was considered, but the system had been thoroughly cleaned and blown down prior to the test. Yet, the velocity of the gas being discharged, at 1216 m/s, was far higher during the run than had been used before, so this potential mechanism could not be discounted. The third mechanism was considered as a possibility as the discharge velocity was high thus possibly dislodging particles and impacting them on the bar. This mechanism must also be counted. However, after the ignition it was found that the bar had been torn loose at one end, and this may have presented a possible ignition source, which had not been foreseen. In addition, the “unexpected” spontaneous ignition of hydrogen release in large-scale experiments was reported as well by Chaineaux et al. (1991) [6], Groethe et al. (2005) [7].

## 4.1 Minimum Ignition Energy (MIE)

Minimum Ignition Energy (MIE) of flammable gases and vapours is the minimum value of the electric energy, stored in the discharge circuit with a loss in the leads as small as possible, which (upon discharge across a spark gap) just ignites the quiescent (calm/still) mixture in the most ignitable composition. A weak spark caused by the discharge of a static electricity from a human body may be sufficient to ignite any of the fuels [3]. For a given mixture composition the following parameters of the discharge circuit must be varied to get the optimum conditions: capacitance, inductivity, charging voltage, shape and dimensions of the electrodes as well as the distance between the electrodes [4]. In addition to the mixture composition MIE depends 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 the 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.

As shown in Figure 1, compared to other fuels, hydrogen has the lowest MIE, which is 0.017 mJ for hydrogen-air mixtures and 0.0012 mJ for hydrogen-oxygen mixture, respectively.

(please see lecture on 'Properties of hydrogen relevant to safety'). As mentioned earlier MIE is a function of hydrogen concentration in the flammable mixture (either with air or with any other oxidizer). For a given combustible mixture and an ignition type, there is a concentration dependent minimum energy below which ignition does not occur. The MIE becomes infinite at the flammability limits (Figure 2). Over the flammable range of hydrogen-air mixtures, the ignition energy varies by almost three orders of magnitude.

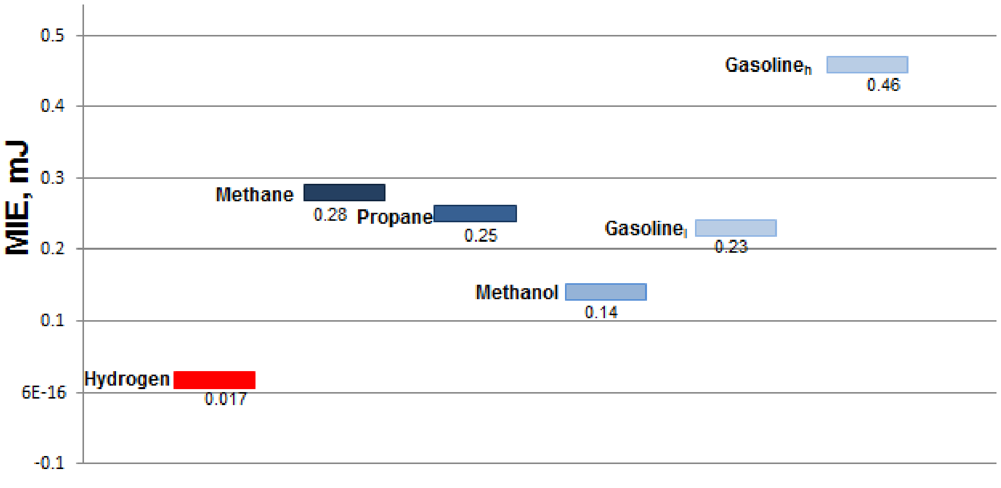

Figure 1. The values of MIE of hydrogen and other fuels.

As shown in Figure 2, a source with ignition energy of 0.24 mJ will not ignite methane or propane but it will ignite a mixture of hydrogen and air within the concentration range of 6.5 to 58 vol. % of hydrogen. A source with energy of 1 mJ will ignite hydrogen-air mixture with hydrogen content ranging from 6 to 64 vol. %. Please note that at the limits of flammability the ignition energy is somewhat similar for three fuels. Its value is relatively high compared to the MIE, and many ignition sources would be able to provide this level of energy. Less energy is needed to ignite a mixture that is closer to its stoichiometric composition.

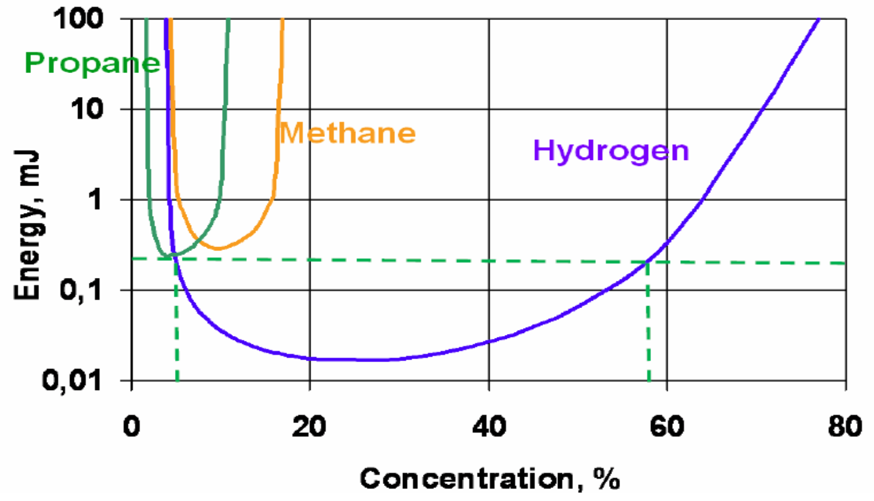

Figure 2. The dependence of the ignition energy on the concentration of a fuel (hydrogen, propane or methane) in the air [8].

The energy stored as static electricity on an object varies, depending on its size and its capacitance, on the voltage to which it is charged, and on the dielectric constant of the surrounding medium [3]. For modelling the effect of static discharge, a human being is considered as a capacitor of 100 picofarads (pF), charged to a voltage of 4,000 to 35,000 volts. The total energy is of the order of millijoules (mJ). The 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 the mixtures close to the flammability limits. Some 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% [9].

## 4.2 Auto-ignition temperature

The auto-ignition temperature is the minimum temperature required to initiate a combustion reaction of a fuel-oxygen mixture in the absence of any external source of ignition [3]. The standard auto-ignition temperature of hydrogen in air is above 510 ºC [10]. It is relatively high compared to hydrocarbons with long molecules. However, this auto-ignition temperature can be reduced by catalytic surfaces such as platinum. The objects at temperatures ranging from 500 to 580 ºC can ignite either hydrogen-air or hydrogen-oxygen mixtures at atmospheric pressure. The substantially cooler objects at about 320 ºC can cause hydrogen ignition under prolonged contact at less than atmospheric pressure [11]. Hot air jet ignition temperature is 670 ºC [12].

## 4.3 Diffusion ignition

The phenomenon of diffusion ignition has been calculated by Wolanski and Wojcicki [13], who demonstrated that ignition occurred when high pressure hydrogen was admitted to a shock tube filled with air or oxygen. They found that ignition could be achieved even if the temperature was below the auto-ignition temperature of the hydrogen.

# 5. Spontaneous ignition of a sudden releases

## 5.1 Diffusion ignition mechanism

Many attempts have been made to explain spontaneous ignition of a sudden release over the last decades, starting from the pioneering study by Wolanski and Wojcicki [13] on the so-called “diffusion ignition mechanism” as discussed in Section 3.5. The experimental data gave critical conditions of this phenomenon. Unfortunately, they cannot provide a detailed insight into the dynamics of the process. For example, the exact location of the initial ignition spots and a chemical reaction progression within tubing downstream a rupture disk or valve can hardly be identified by experimental means at high pressures [3].

It is an agreed opinion that the probability of hydrogen spontaneous ignition at a sudden release from high-pressure equipment is relatively high if mitigation measures are not in place. However, there are no references in codes and standards with regards to a spontaneous ignition problem or on a specific engineering design to avoid or promote it for piping, storage and use of high-pressure systems handling compressed hydrogen [3]. Control of spontaneous ignition of high-pressure hydrogen release is one of the challenges in hydrogen safety, for which a little fundamental explanation exists.

## 6. Prevention of hydrogen ignition

The ignition sources must be eliminated or isolated in an appropriate way and the operations on FCH facilities should be conducted as if unforeseen ignition sources could occur. Grounding (earthing) methods should be in place to minimize the risk of static discharge and the potential for lightning strikes in outdoor environments. Materials selected for the use in hydrogen environments should be evaluated for their ability to discharge static electricity. 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%. Recommended practices for grounding methods to prevent static discharges can be found in various national and international standards that cover the installation of electrical equipment in hazardous environments. Electrical equipment selected for use in hydrogen environments can also be a source of sparks or heat generation, and care should be taken to follow the appropriate national and International Electrical Standards for installation.

There are several ways to eliminate or at least to reduce the risk of ignition. Health and Safety Executive (UK) compiled the list of the following preventive measures [14]:

- Use of adequate electrical equipment (i.e. the equipment classified for the zone in which it is located). Mechanical equipment should be selected in a similar manner.
- Earthing all the equipment with a facility.
- Elimination of the surfaces with temperature above the auto-ignition temperature of flammable materials being stored/used.
- Provision of lightning protection.
- Correct selection of vehicles/internal combustion engines that can work in zoned areas.
- Correct selection of equipment to avoid high intensity electromagnetic radiation sources, e.g. limitations of the power input to fibre-optic systems, avoidance of high intensity lasers or sources of infrared radiation.
- Prohibition of smoking/use of matches or lighters.
- Control over the use of regular vehicles.
- Control over the activities that create the intermittent hazardous areas, e.g. tanker loading/ unloading.
- Control of maintenance activities that may cause sparks/hot surfaces/naked flames through a permit to work scheme.
- Precautions to control the risk from pyrophoric scale, usually associated with the formation of iron sulphide inside the process equipment.

## 6.1 Control of thermal and mechanical sources of ignition

Ignition of hydrogen-air mixture can be caused by a hot surface. For hydrogen, the temperature of hot surfaces or hot spots shall not exceed 585 °C even for a few $mm^2$ according to the experiments conducted within the European project MECHEX (please note that hydrogen auto-ignition temperature, 510 °C, is still lower than specified above).

Physical separation of ignition sources, such as welding, flames or hot working is preferable.

Mechanical ignition is generally the result of mechanical distress under abnormal or fault conditions (i.e. rubbing, grinding and impact or a combination of these factors) and consists usually of three steps: generation of heat, transfer of heat to the surrounding explosive atmosphere and finally the ignition itself [15]. The control of mechanical ignition requires a careful design of equipment by one of the following means:

- Limiting rotating speed,
- Provide a sufficient distance between fixed and rotating parts,
- Setting up temperature sensors.

The energy produced by the impact can be as little as a couple of Joules and is sufficient to ignite hydrogen-air mixture. To avoid the ignition caused by impact it is necessary to [15]:

- Use appropriate spark-free tools,
- Purge hydrogen before any intervention
- Avoid contact between aluminium and steel.

Hot works have similarities with the mechanical ignition, but they are not generated by a process mechanical failure but by a human activity. It is necessary to prevent any accident/incident arising from this by [15]:

- Delivering 'Hot Work Permit',
- Appropriate training of relevant staff,
- Providing an adequate fire-fighting equipment,
- Switching off gas supply during intervention,
- Purging equipment prior to intervention.

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